UTILISING PLANTATION-GROWN ACACIA AND EUCALYPT WOOD FOR THE MANUFACTURE OF CEMENT-BONDED COMPOSITES

By K. E. Semple

A Thesis submitted for the degree of DOCTOR OF PHILOSOPHY of THE AUSTRALIAN NATIONAL UNIVERSITY

June 2003
STATEMENT OF ORIGINALITY

I hereby declare that this submission is my own original work and that it contains no unacknowledged material previously published or written by another person, nor any material which has been accepted for the award of any other degree or diploma of a university or other institute of higher learning.

K. Semple

Kate Semple
June 2003.
ACKNOWLEDGEMENTS

There are numerous people who provided academic and valuable in-kind support for the conduct of my research project. Thanks very much to all the following people and organisations:

Supervisory Panel:
Prof. Philip Evans (Chair, formerly of ANU Forestry now at the University of British Columbia,), for generating and introducing me to two funded projects which enabled the sampling of tropical acacia and eucalypt trees in North Queensland and mallee eucalypts in Western Australia. Prof. Evans provided an excellent level of supervision, interest and support throughout the project, encouraged and facilitated the publication of papers, and enabled me to spend two months in the Centre for Advanced Wood Processing, UBC in late 2002 in the latter stage of my PhD.
Dr Roger Heady from the ANU Electron Microscopy Unit, who provided expert and friendly guidance in the use of the Scanning Electron Microscopy facilities at ANU.
Mr Ross Cunningham and later Dr Anne Cowling (Statistical Consulting Unit, ANU), who provided professional consultancy with experimental design and experimental analysis.

Financial support at various stages of the project work was provided by the following organisations: Australian Centre for International Agricultural Research (ACIAR), Western Australian Department of Conservation and Land Management (CALM) and the Rural Industries Research and Development Corporation (RIRDC).

Valuable material support for the project was provided by the following people and companies: Mr John Woolley and staff (Woodtex Pty Ltd, Bendigo, Victoria), Mr Wayne Maher and staff (Carter Holt Harvey Panels, Oberon NSW), Messrs. John Bartle, Steve Davis, Graham Siemons and Andrew Macarthy (Western Australian Department of Conservation and Land Management), Bob Parkin and staff (Blue Circle Southern Cement Australasia Pty Ltd) and Alan Davies (ACT Forests).

Thank very much also to the following people for valuable advice at various stages of the project: Prof. Alan Sargenson (RSC, ANU), Dr Chris Harwood (Australian Tree Seed Centre, CSIRO), Dr Garth Nickles (QFRI), Dr Zbigniew Stachurski and Darius Krivanek (Engineering, ANU), Messrs. Peter Beutel (ACT Forests), Nicholas Wellham and Lee Welling, (RSPysE, ANU), Rico Cabangon (FPRDI, Philippines), Tony Cooke (ANUTECH).

Proof reading and editorial support at various times for report and paper publication and thesis write-up was kindly provided by Mr Noel Semple, and Dr Anne Gibson, Dr Sue Holznecht and Dr Ryde James of SRES, ANU.

Administrative support was provided by Dr Ryde James, Mr Mark Lewis and Ms Zosha Smith (SRES, ANU).

Last, but not least, thanks very much to my Father, Mr Noel Semple and Mr Paul Oboohov for their love and support throughout the duration of my PhD.
ABSTRACT

This thesis aims to improve the suitability of plantation acacia and eucalypt wood for the manufacture low cost portland cement-bonded building panels, including wood wool-cement board (WWCB), cement-bonded particleboards (CBP) and cement-bonded flakeboard. In many countries where acacia and eucalypt species have been introduced in the last several decades to supply wood and pulp needs there is the urgent need for the development of low-cost housing. Cement-bonded composite panels are among the most suitable materials for such purposes. They can be made using smaller, less capital-intensive facilities from simple, locally available constituents; wood fibre, cement and water, with the cement binder giving the panels good resistance to weathering, fire and biodeterioration.

Despite the widespread presence of acacia and eucalypt species in plantations, mainly in developing countries, little is known of their suitability for wood-cement composites. A small number of species have been subjects of wood-cement compatibility tests of various types, however, the results of such tests often do not correlate well with the performance of woods in wood-cement composites in practice, possibly because the wood is tested in a finely ground form that is dissimilar to the strands and particles used to manufacture composites such as WWCB and CBP. This problem was addressed in the early part of this study by developing a compatibility test method that more accurately predicts the effects of wood wool and flakes on cement hydration. A wide range of tropical and temperate species of acacias and eucalypts, sourced from controlled growth trials, were tested for potential suitability for WWCB or flakeboard using this testing method. Acacia species were less compatible with cement than most eucalypt species due to higher quantities of hot-water-soluble extractives in the wood.

Waste stem residues from short-rotation mallee eucalypt trees grown on farms to ameliorate soil degradation and to service the leaf oil industry were examined as a potential wood source for CBPs and flakeboards. Such wood is thought to have little use other than for low-value fuelwood, however, alternative markets for the wood are necessary for the commercial viability of mallee plantations. The compatibility with cement of five commercially important species of mallee and three of melaleuca was assessed first, followed by the manufacture of cement-bonded boards with emphasis on appropriate conversion techniques for flakes from small diameter stems with a high volume of bark. The performance of mallee eucalypt wood in cement boards was compared with that of commercial timber species including blue gum, radiata pine and maritime pine. Large flakes imparted better strength properties to boards than particles. The strength of boards made from mallee flakes was compromised somewhat by the production of thicker flakes from the small-diameter, higher density stems, whereas boards made from pine and fast-grown blue gum wood were of good quality.
Readily available wood from planted acacias, both tropical and temperate species, is often not immediately suitable for cement-bonded composites because of the presence of soluble wood extractives including sugars and heartwood tannins that affect the bonding between wood and its cement binder. As a result, many previous attempts to use acacias (particularly tropical species) in wood-cement composites have not been successful. Even when wood has been pre-soaked to remove extractives and/or cement-setting accelerators used to strengthen the consolidation of the composite, the mechanical properties of boards made from species such as *Acacia mangium* were found to be below standard in some studies. Reasons for these poor results were investigated in detail in this thesis since a principle objective was to manufacture good quality wood-cement composites (in this case low-cement content WWCB) from the wood of *A. mangium*, which is easily machined into good quality wood wool. Questions including the efficacy or necessity of cold-water extraction, and strong variation in the efficacy of cement setting accelerators for this species were addressed.

It is demonstrated that the use of carefully selected chemical additives, either singly or in combination, can eliminate the need to pre-soak the wood, thus addressing problems relating to the extra time, space and water required for this process and the disposal of extract. When used in small quantities cement-setting accelerators were only effective in neutralising the strong inhibitory effect of the heartwood of *A. mangium* on cement if they chemically interacted with heartwood polyphenols and strongly accelerated cement hydration. Paradoxically, the most effective additives were also those with the most potential to cause problems with corrosion of nails or any adjacent metal framing if boards were exposed to moisture, and therefore accelerator addition needs to be kept to a minimum.

The study was designed to provide more comprehensive information on the suitability of acacia and eucalypt wood for wood-cement composites and demonstrate that the problems hampering the use of selected species can be overcome using relatively simple manufacturing techniques. Further research is needed, however, to further improve flake quality from higher density eucalypt woods and to determine whether the board manufacturing techniques developed for *Acacia mangium* can be applied in the case of other tropical and temperate acacia species.
# TABLE OF CONTENTS

Declaration........................................................................................................................................ i
Acknowledgments.......................................................................................................................... ii
Abstract ........................................................................................................................................ iii
Table of Contents ........................................................................................................................ v
List of Tables .................................................................................................................................. xi
List of Figures ................................................................................................................................ xiii
List of Plates ................................................................................................................................... xvii

## Chapter 1 General introduction

1.1 Background to the study............................................................................................................. 1
   1.1.1 Wood-cement composites for building applications in tropical countries ................. 1
   1.1.2 The utilisation of acacias and eucalypts for wood-cement composites ..................... 2

1.2 Aims and structure of the thesis ............................................................................................... 4
   1.2.1 Assessment of literature and problem definition ......................................................... 4
   1.2.2 Compatibility of acacia and eucalypt species with cement .......................................... 6
   1.2.3 Improvement of wood-cement composites made from mallee .................................... 7
   1.2.4 Improvement of the compatibility of *A. mangium* with cement and its suitability for the manufacture of wood-cement composites ................................................................. 7

## Chapter 2 Literature Review

2.1 Portland cement components and hydration reactions .......................................................... 9
   2.1.1 Origin and components ................................................................................................. 9
   2.1.2 Hydration .................................................................................................................... 10
   2.1.3 The action of accelerators .......................................................................................... 11

2.2 Historical development of cement-bonded wood composites ............................................. 11
   2.2.1 Wood-wool cement board (WWCB) ............................................................................ 11
   2.2.2 Cement-bonded particleboard (CBP), flakeboard and aggregates ............................. 12

2.3 Properties and utilisation of cement-bonded wood composites .......................................... 14
   2.3.1 General features ......................................................................................................... 14
   2.3.2 Mechanical properties of wood-cement composites .................................................... 15
   2.3.3 Fire resistance of wood-cement composites ............................................................... 18
   2.3.4 Resistance to weathering and bio-deterioration............................................................ 20

2.4 Wood-wool cement board (WWCB): applications, manufacture and properties ................. 22
   2.4.1 WWCB as an ideal building material in developing countries .................................. 22
   2.4.2 Manufacturing WWCBs ............................................................................................. 24
   2.4.3 Properties of WWCBs ............................................................................................... 27

2.5 Cement-bonded particleboard (CBP): applications, manufacture and properties ................. 30
   2.5.1 Applications of CBPs .................................................................................................. 30
   2.5.2 Manufacturing CBPs ................................................................................................ 31
   2.5.3 Properties of CBPs .................................................................................................... 33

2.6 Challenges associated with the use of wood-cement composites ......................................... 34
   2.6.1 Creep and deterioration ............................................................................................... 34
   2.6.2 Dimensional stability .................................................................................................. 37
   2.6.3 Corrosion .................................................................................................................... 39
   2.6.4 Wood-cement interactions and species specificity ...................................................... 40
   2.6.5 Production and utilisation economics ....................................................................... 40

2.7 Improving the mechanical properties of wood-cement composites ..................................... 41
   2.7.1 Wood pre-storage ........................................................................................................ 42
   2.7.2 Adjustment of wood-cement ratio ............................................................................... 43
   2.7.3 Adjustment of curing time and temperature ............................................................... 44
   2.7.4 Chemical additives ..................................................................................................... 45
   2.7.4 Adjustment of cement type and substitution ............................................................... 48
Chapter 3 Developing an appropriate methodology for testing the potential suitability of species of *Acacia* and *Eucalyptus* for cement-bonded wood composites

3.1 Introduction ................................................................. 69
3.2 The suitability of wood-flour for assessing suitability of acacias and eucalypts for wood wool or flake based cement composites ........................................... 70
  3.2.1 Aims and objectives .................................................. 70
  3.2.2 Materials and methods ............................................. 71
    3.2.2.1 Source of samples ............................................ 71
    3.2.2.2 Preparation of wood wool ................................... 71
    3.2.2.3 Preparation of wood flour ................................... 71
    3.2.2.4 Hydration sample preparation and testing ............... 73
    3.2.2.5 Experimental design and statistical analysis .......... 75
    3.2.2.6 Cold-water-soluble extractive content and determination of sugar content of leachate from the sapwood .......... 75
  3.2.3 Results and Discussion ............................................ 76
    3.2.3.1 Main effects and interactions between factors .......... 76
    3.2.3.2 Confounding effects of wood extractive content .......... 79
  3.2.4 Conclusions .......................................................... 82
3.3 Testing and selection of an appropriate wood form for assessing potential suitability of acacia and eucalypt wood for wood wool or flake based cement composites ........................................... 84
  3.3.1 Aims and objectives ................................................. 84
  3.3.2 Materials and methods ............................................. 84
    3.3.2.1 Species and sample collection ............................ 84
    3.3.2.2 Preparation of wood in different forms ................. 85
    3.3.2.3 Aqueous extraction of samples ........................... 88
    3.3.2.4 Hydration sample preparation and testing ............... 88
    3.3.2.5 Experimental design and statistical analysis .......... 89
  3.3.3 Results and Discussion ............................................ 90
    3.3.3.1 Unextracted samples ....................................... 90
    3.3.3.2 The effect of pre-soaking .................................. 94
  3.3.4 Conclusions .......................................................... 96
3.4 General discussion of findings ..................................... 96

Chapter 4 Species and intra-species variation in wood-cement compatibility among commercially important tropical species of *Acacia* and *Eucalyptus*

4.1 Introduction .................................................................. 98
4.2 Aims and objectives ................................................... 99
4.3 Materials and methods ............................................... 99
  4.3.1 Collection of wood core samples ............................. 99
  4.3.2 Measurement of wood properties and wood-cement compatibility ........................................... 102
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3.3 Hot-water-extractive content of selected samples</td>
<td>104</td>
</tr>
<tr>
<td>4.3.4 Experimental design and statistical analysis</td>
<td>104</td>
</tr>
<tr>
<td>4.3.5 Scanning Electron Microscopy (SEM) assessment of wood-cement</td>
<td>105</td>
</tr>
<tr>
<td>interface</td>
<td></td>
</tr>
<tr>
<td>4.4 Results and discussion</td>
<td>107</td>
</tr>
<tr>
<td>4.4.1 Species differences in wood-cement compatibility--unextracted</td>
<td>107</td>
</tr>
<tr>
<td>samples</td>
<td></td>
</tr>
<tr>
<td>4.4.2 Effects of cold-water-extractive removal by soaking</td>
<td>109</td>
</tr>
<tr>
<td>4.4.3 Provenance variation in wood-cement compatibility</td>
<td>111</td>
</tr>
<tr>
<td>4.4.4 Relationship between % heartwood and wood-cement compatibility</td>
<td>111</td>
</tr>
<tr>
<td>4.4.5 Ranking and identification of compatible families of <em>A. mangium</em></td>
<td>114</td>
</tr>
<tr>
<td>4.4.6 Practical limitations to the use of CA-factor</td>
<td>117</td>
</tr>
<tr>
<td>4.4.7 SEM analysis of wood-cement samples</td>
<td>119</td>
</tr>
<tr>
<td>4.5 Conclusions</td>
<td>124</td>
</tr>
</tbody>
</table>

Chapter 5 The compatibility of temperate acacias and eucalypts with Portland cement

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Introduction</td>
<td>126</td>
</tr>
<tr>
<td>5.2 Aims and objectives</td>
<td>127</td>
</tr>
<tr>
<td>5.3 Materials and methods</td>
<td>127</td>
</tr>
<tr>
<td>5.3.1 Wood sample collection</td>
<td>127</td>
</tr>
<tr>
<td>5.3.2 Measurement of % heartwood, basic density and wood-cement</td>
<td>129</td>
</tr>
<tr>
<td>compatibility</td>
<td></td>
</tr>
<tr>
<td>5.3.3 Experimental design and statistical analyses</td>
<td>130</td>
</tr>
<tr>
<td>5.3.4 Determination of hot-water-soluble extractive content</td>
<td>131</td>
</tr>
<tr>
<td>5.4 Results and discussion</td>
<td>131</td>
</tr>
<tr>
<td>5.4.1 Wood-cement compatibility: main effects</td>
<td>131</td>
</tr>
<tr>
<td>5.4.2 Wood-cement compatibility of temperate acacias</td>
<td>133</td>
</tr>
<tr>
<td>5.4.3 Wood-cement compatibility of temperate eucalypts</td>
<td>135</td>
</tr>
<tr>
<td>5.4.4 The effects of wood properties including heartwood content</td>
<td>138</td>
</tr>
<tr>
<td>and hot water extractive content</td>
<td></td>
</tr>
<tr>
<td>5.4.5 Comparison with tropical acacias and eucalypts</td>
<td>143</td>
</tr>
<tr>
<td>5.5 Conclusions</td>
<td>144</td>
</tr>
</tbody>
</table>

Chapter 6 The compatibility of Western Australian species of mallee eucalypt and melaleuca with Portland cement

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1 Introduction</td>
<td>146</td>
</tr>
<tr>
<td>6.2 Aims and objectives</td>
<td>148</td>
</tr>
<tr>
<td>6.3 Materials and methods</td>
<td>148</td>
</tr>
<tr>
<td>6.3.1 Wood sample collection and preparation</td>
<td>148</td>
</tr>
<tr>
<td>6.3.2 Removal of extractives and measurement of wood-cement compatibility</td>
<td>150</td>
</tr>
<tr>
<td>6.3.3 Manufacture of cement-bonded particleboards from mallee in the laboratory</td>
<td>151</td>
</tr>
<tr>
<td>6.3.4 Determination of mechanical properties of CBPs</td>
<td>152</td>
</tr>
<tr>
<td>6.3.5 Experimental design and statistical analysis</td>
<td>152</td>
</tr>
<tr>
<td>6.4 Results and discussion</td>
<td>154</td>
</tr>
<tr>
<td>6.4.1 Effect of mallee wood and bark residues on cement hydration</td>
<td>154</td>
</tr>
<tr>
<td>6.4.1.1 Species differences and the effect of bark</td>
<td>155</td>
</tr>
<tr>
<td>6.4.1.2 Site and age effects</td>
<td>157</td>
</tr>
<tr>
<td>6.4.2 Effect of melaleuca and tagasaste wood and bark residues on cement hydration</td>
<td>157</td>
</tr>
<tr>
<td>6.4.3 Mechanical properties of CBPs made from mallee residues</td>
<td>160</td>
</tr>
<tr>
<td>6.5 Conclusions</td>
<td>165</td>
</tr>
</tbody>
</table>
## Chapter 7 The manufacture of cement bonded particle, flake and wood-wool boards from Western Australian mallee, bluegum and commercial pine species

### 7.1 Introduction

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>167</td>
</tr>
</tbody>
</table>

### 7.2 Aims and objectives

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>168</td>
</tr>
</tbody>
</table>

### 7.3 Materials and methods

<table>
<thead>
<tr>
<th>Sub-section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3.1 Log harvesting</td>
<td>169</td>
</tr>
<tr>
<td>7.3.2 Preparation of wood flakes and particles</td>
<td>170</td>
</tr>
<tr>
<td>7.3.3 Manufacture and testing of cement bonded flakeboards, CBPs and WWCBs</td>
<td>172</td>
</tr>
<tr>
<td>7.3.3.1 Experiment 1: Species and pre-treatment (flakeboards)</td>
<td>172</td>
</tr>
<tr>
<td>7.3.3.2 Experiment 2: Flake size and curing temperature (flakeboards and CBPs)</td>
<td>174</td>
</tr>
<tr>
<td>7.3.3.3 Experiment 3: Commercial WWCBs</td>
<td>176</td>
</tr>
<tr>
<td>7.3.4 Experimental designs and statistical analyses</td>
<td>179</td>
</tr>
</tbody>
</table>

### 7.4 Results and discussion

<table>
<thead>
<tr>
<th>Sub-section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.4.1 Experiment 1: Species and pre-treatment (flakeboards)</td>
<td>180</td>
</tr>
<tr>
<td>7.4.1.1 Mechanical properties</td>
<td>181</td>
</tr>
<tr>
<td>7.4.1.2 Board dimensional stability and resistance to water</td>
<td>184</td>
</tr>
<tr>
<td>7.4.1.3 The effects of wood density, flake parameters and mat structure</td>
<td>185</td>
</tr>
<tr>
<td>7.4.2 Experiment 2: Flake size and curing temperature (flakeboards and CBPs)</td>
<td>190</td>
</tr>
<tr>
<td>7.4.2.1 Mechanical properties</td>
<td>190</td>
</tr>
<tr>
<td>7.4.2.2 Board dimensional stability and resistance to water</td>
<td>196</td>
</tr>
<tr>
<td>7.4.3 Experiment 3: Commercial WWCBs</td>
<td>197</td>
</tr>
<tr>
<td>7.4.3.1 Physical properties and static bending tests</td>
<td>197</td>
</tr>
<tr>
<td>7.4.3.2 Impact resistance of WWCBs</td>
<td>200</td>
</tr>
<tr>
<td>7.4.4 Current interest in, and further potential for, cement-bonded flakeboards</td>
<td>201</td>
</tr>
</tbody>
</table>

### 7.5 Conclusions

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>204</td>
</tr>
</tbody>
</table>

## Chapter 8 The pre-treatment of Acacia mangium heartwood to improve its compatibility with portland cement

### 8.1 Introduction

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>206</td>
</tr>
</tbody>
</table>

### 8.2 Aims and objectives

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>208</td>
</tr>
</tbody>
</table>

### 8.3 Materials and methods

<table>
<thead>
<tr>
<th>Sub-section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.3.1 Wood sample collection and preparation</td>
<td>208</td>
</tr>
<tr>
<td>8.3.2 Pre-treatments for heartwood wood wool samples</td>
<td>209</td>
</tr>
<tr>
<td>8.3.2.1 Chemical dip</td>
<td>209</td>
</tr>
<tr>
<td>8.3.2.2 Application of water repellents</td>
<td>210</td>
</tr>
<tr>
<td>8.3.2.3 Removal of extractives</td>
<td>210</td>
</tr>
<tr>
<td>8.3.2.4 Exposure to pre-heating, sunlight or plasma</td>
<td>211</td>
</tr>
<tr>
<td>8.3.3 Preparation of hydration test samples</td>
<td>212</td>
</tr>
<tr>
<td>8.3.4 Experimental design and statistical analysis</td>
<td>212</td>
</tr>
</tbody>
</table>

### 8.4 Results and discussion

<table>
<thead>
<tr>
<th>Sub-section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.4.1 Treatment class</td>
<td>212</td>
</tr>
<tr>
<td>8.4.2 Extractive removal pre-treatments</td>
<td>213</td>
</tr>
<tr>
<td>8.4.3 Non-extractive removal pre-treatments</td>
<td>219</td>
</tr>
</tbody>
</table>

### 8.5 Conclusions

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>220</td>
</tr>
</tbody>
</table>

## Chapter 9 Addition of admixtures to improve the compatibility of A. mangium heartwood with portland cement

### 9.1 Introduction

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>222</td>
</tr>
</tbody>
</table>

### 9.2 Aims and objectives

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>223</td>
</tr>
</tbody>
</table>
9.3 Materials and methods
9.3.1 Preparation of compounds
9.3.2 Addition of compounds to cement hydration samples
9.3.3 Experimental design and statistical analysis
9.3.4 Determination of polyphenol-metallic complexes

9.4 Results and discussion
9.4.1 Compound ranking
9.4.2 Effects of cations and anions on cement hydration
9.4.3 Factors affecting compound efficacy
9.4.4 Effect of accelerators on the wood-cement interface
9.4.5 Interaction with heartwood polyphenols

9.5 Conclusions

Chapter 10 Manufacture of WWCBs from A. mangium using simple inorganic additives

10.1 Introduction
10.2 Aims and objectives
10.3 Materials and methods
10.3.1 Preparation of wood wool from billets
10.3.2 Additives used and their preparation
10.3.3 Manufacture of WWCBs
10.3.4 Determination of board mechanical properties
10.3.5 Experimental design and statistical analysis
10.3.6 Effect of accelerators on wood wool strength
10.3.7 Assessment of nail corrosion

10.4 Results and discussion
10.4.1 Density and strength properties of boards containing unsaturated wood wool and single compounds
10.4.2 The effect of using pre-soaked wood wool and single compounds on board properties
10.4.3 Dimensional stability of WWCBs
10.4.4 Strength loss upon wetting
10.4.5 The effects of additive combinations
10.4.6 Further enhancement of board properties
10.4.7 Effect of accelerators on strand strength
10.4.8 Relating cement hydration data to WWCB strength properties
10.4.9 Effects of WWCBs containing accelerators on deterioration of nail fastenings

10.5 Conclusions

Chapter 11 General summary, conclusions and suggestions for further research

11.1 Summary and conclusions of this thesis
11.1.1 Background to the research
11.1.2 Establishment of methodology for wood-cement compatibility testing
11.1.3 Compatibility of acacias and eucalypts with Portland cement
11.1.4 Improving the quality of wood-cement composites made from mallee eucalypt wood
11.1.5 Improving the compatibility of A. mangium with cement and its suitability for the manufacture of wood-cement composites

11.2 Specific and general suggestions for further research
11.2.1 Extensions of findings from this research
11.2.2 General suggestions for improving acacia and eucalypt wood suitability for wood-cement composites

References

ix
Appendix 1 Published Papers


Semple, K.E., Cunningham, R.B. and Evans, P.D. (2002). Screening inorganic additives for ameliorating the inhibition of hydration of portland cement by the heartwood of Acacia mangium. In Wood-Cement Composites in the Asia-Pacific Region, ed P.D. Evans, ACIAR Proceedings No. 107, Australian Centre for International Agricultural Research, Canberra, pp. 29-39. 376

Symposium papers


Appendix 2 Supplementary information for Chapter 2

1. Portland cement components and hydration reactions 407
2. Wood-cement chemical interactions 416
3. Cement supplements and alternative mineral binders to portland cement type I 432
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1</td>
<td>The principle phases and their approximate proportions in Portland cement clinker.</td>
<td>10</td>
</tr>
<tr>
<td>Table 2.2</td>
<td>Selected mechanical properties of different types of reconstituted wood panels including WWC, cement-bonded fibre and particleboards.</td>
<td>16</td>
</tr>
<tr>
<td>Table 2.3</td>
<td>Log requirements and capital costs of different types of wood processing plants.</td>
<td>24</td>
</tr>
<tr>
<td>Table 2.4</td>
<td>WWC minimum mechanical properties PNS/CTP 07 (1990).</td>
<td>29</td>
</tr>
<tr>
<td>Table 2.5</td>
<td>Physical and mechanical properties of WWC manufactured at Zamboanga Enterprises, Zamboanga, Philippines.</td>
<td>29</td>
</tr>
<tr>
<td>Table 2.6</td>
<td>Amounts of wood, cement and water used in hydration samples by various authors.</td>
<td>52</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>F-probabilities (p-values) for significance of main effects and interactions between factors on the compatibility indices $T_{\text{max}}$ and $C_A$-factor.</td>
<td>77</td>
</tr>
<tr>
<td>Table 3.2</td>
<td>Average $T_{\text{max}}$ for wood flour and wood-wool of <em>E. pellita</em>, <em>A. mangium</em> and <em>P. euramerica</em>.</td>
<td>80</td>
</tr>
<tr>
<td>Table 3.3</td>
<td>Average $C_A$-factor for wood flour and wood-wool of <em>E. pellita</em>, <em>A. mangium</em> and <em>P. euramerica</em>. by % heartwood content and wood level.</td>
<td>81</td>
</tr>
<tr>
<td>Table 3.4</td>
<td>Heartwood and sapwood wood wool extractive contents and sapwood sugar content for <em>A. mangium</em>, <em>E. pellita</em> and <em>P. euramerica</em>.</td>
<td>81</td>
</tr>
<tr>
<td>Table 3.5</td>
<td>F-probability (p-values) for effects of and interactions between species, heartwood content and wood form for unsoaked samples.</td>
<td>90</td>
</tr>
<tr>
<td>Table 3.6</td>
<td>F-probability (p-values) for effects of soaking and interactions between soaking and other factors.</td>
<td>94</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>Summary of species, provenances, sites and planting dates of sampled trees.</td>
<td>102</td>
</tr>
<tr>
<td>Table 4.2</td>
<td>Significance levels for species effects on for Extracted and unextracted acacia and eucalypt wood samples.</td>
<td>107</td>
</tr>
<tr>
<td>Table 4.3</td>
<td>Average wood-cement compatibility indices for un-extracted (us) and extracted (s) samples of <em>A. alula</em>carpa, <em>A. crassicaarpa</em>, <em>A. mangium</em>, <em>E. pellita</em> and <em>E. urophylla</em>.</td>
<td>107</td>
</tr>
<tr>
<td>Table 4.4</td>
<td>Ranking of the ten most compatible and ten least compatible families of <em>A. mangium</em> (unsoaked samples) by hydration rate.</td>
<td>115</td>
</tr>
<tr>
<td>Table 5.1</td>
<td>Location, climate and soil types for field trial sites at Kowen and Uriarra, ACT.</td>
<td>129</td>
</tr>
<tr>
<td>Table 5.2</td>
<td>Experimental block structure for compatibility testing of temperate acacia and eucalypt species.</td>
<td>130</td>
</tr>
<tr>
<td>Table 5.3</td>
<td>Levels of significance from the accumulated ANOVA for main factors (site, genus, soaking) and interactions between factors.</td>
<td>131</td>
</tr>
<tr>
<td>Table 5.4</td>
<td>F-probabilities (p-values) for main effects and interactions between factors on hydration rate for unsoaked and soaked wood samples.</td>
<td>132</td>
</tr>
<tr>
<td>Table 5.5</td>
<td>Ranking of <em>Acacia</em> species by hydration rate for unsoaked and soaked samples across both sites.</td>
<td>134</td>
</tr>
<tr>
<td>Table 5.6</td>
<td>Ranking of <em>Eucalyptus</em> species by hydration rate for unsoaked samples averaged across sites.</td>
<td>136</td>
</tr>
<tr>
<td>Table 5.7</td>
<td>Average % heartwood content in <em>Eucalyptus</em> species grown at Kowen and Uriarra.</td>
<td>139</td>
</tr>
<tr>
<td>Table 5.8</td>
<td>Average content of hot-water-soluble extractives in species of <em>Acacia</em> and <em>Eucalyptus</em>.</td>
<td>140</td>
</tr>
<tr>
<td>Table 6.1</td>
<td>F-probabilities (p-values) for main effects and interactions between factors on cement hydration reaction indices.</td>
<td>154</td>
</tr>
<tr>
<td>Table 6.2</td>
<td>Cement compatibility indices of mallee eucalypt wood species (with and without bark) and radiata pine (RP).</td>
<td>155</td>
</tr>
<tr>
<td>Table 6.3</td>
<td>F-probabilities (p-values) for effects of main factors, species, extraction and bark content, and interactions between factors on compatibility indices of melaleuca species.</td>
<td>158</td>
</tr>
<tr>
<td>Table 6.4</td>
<td>F-probabilities (p-values) for main effects and interactions between factors influencing mechanical properties of CBPs made from mallee and radiata pine wood species.</td>
<td>161</td>
</tr>
<tr>
<td>Table 6.5</td>
<td>Average strength and mechanical properties for CBPs made from mallee with and without bark and radiata pine particles without bark.</td>
<td>161</td>
</tr>
</tbody>
</table>
Table 7.1 Summary of species, planting dates and sites for wood species used to manufacture flakeboards ..................................................................................................................................... 170
Table 7.2 Chi-squared probabilities for the significance of effects of species, flake pre-treatment and interactions. N.S. = not significant at the 5% probability level. ........................................................................................................ 181
Table 7.3 Average basic density (kg/m³) of flakeboards as influenced by species and flake treatment. .......... 181
Table 7.4 Chi-squared probabilities (p-values) for effects of species, wood pre-treatment and test condition (wet or dry) on strength properties MOR and MOE of flakeboards. ................................................................................ 181
Table 7.5 Average dry MOR (MPa) of flakeboards as influenced by species and flake treatment. ...... 183
Table 7.6 Average dry MOE (MPa) of flakeboards as influenced by species and flake treatment. .......... 183
Table 7.7 Average wet MOR (MPa) of flakeboards as influenced by species and flake treatment........ 184
Table 7.8 Average thickness swelling (%) of flakeboards as influenced by species and flake treatment; water absorption, %, in parentheses .................................................................................................................................. 185
Table 7.9 Average wood density and flake thickness as affected by species ........................................... 188
Table 7.10 Chi-squared probabilities (p-values) for effects of species, flake size, flake pre-treatment, curing temperature and interactions on board properties. N.S. = not significant at the 5% probability level. .................................................................................................................................. 190
Table 7.11 Average MOE of flakeboards and CBPs made from radiata pine, blue gum and mallee eucalypt according to wood pre-treatment and board curing temperature. Shading denotes boards that did not meet ISO 8335. ........................................................................................................ 195
Table 7.12 Average wet MOR of flakeboards and CBPs made from radiata pine, blue gum and mallee eucalypt according to wood pre-treatment and board curing temperature. Shading denotes boards that did not meet the ISO 8335 requirement of 5.5 MPa. ................................................................................................. 196
Table 7.13 Average thickness swelling of flakeboards and CBPs made from radiata pine, blue gum and mallee eucalypt according to wood pre-treatment and board curing temperature. Shading denotes boards that did not meet the ISO 8335 limit of 2%. ................................................................................................. 197
Table 7.14 Average density, thickness and flexural properties for factory-made WWCBs of blue gum, maritime pine, radiata pine and commercial 'WoodTex' boards (standard deviation in parentheses). .................................................................................................................................. 197
Table 7.15 Percentage of wood wool boards that failed after dropping different weights from different heights. Shading highlights the limit of the majority of boards of each species ............................................................................... 201

Table 8.1 Pre-treatments applied to A. mangium heartwood strands ........................................................................................................ 209

Table 9.1 Top 20 compounds ranked by hydration rate of wood-cement mix, with corresponding maximum hydration temperature and time. .................................................................................................................................. 227
Table 9.2 The average hydration rates (for pure cement and cement + wood) for compounds that accelerated the hydration of pure cement, listed in descending order of their effect on the hydration of pure cement. .................................................................................................................................. 229
Table 9.3 The average hydration rates (for pure cement and cement + wood) for compounds that retarded the hydration of pure cement, listed in descending order of their effect on the hydration of pure cement. .................................................................................................................................. 230

Table 10.1 Compounds used and their molar concentrations .................................................................................................................................. 249
Table 10.2 Chi-square probabilities (p-values) for significance of effects of additive/concentration ('Treatment') and pre-soaking wood wool ('Soaking') on board mechanical properties .................................................................................................................................. 256
Table 10.3 Wet MOR, Thickness Swelling and Water Absorption of boards made from unsoaked and pre-soaked wood wool. .................................................................................................................................. 266
Table 10.4 Chi-square probabilities (p-values) for effects of factors on the accumulation of rust oxides on nails embedded in WWCBs made from A. mangium containing different accelerators. .................................................................................................................................. 273

Appendix 2

Table 1 The principle phases and their approximate proportions in Portland cement clinker. .......... 407
Table 2 Phase composition, fineness and compressive strength characteristics of five common types of portland cement. .................................................................................................................................. 432
LIST OF FIGURES

Figure 2.1 Hydration temperature vs time curve for ordinary portland cement (ASTM Type I) showing influence of accelerating/retarding admixtures (from Thomas 1987) .......................................................... 10

Figure 2.2 Influence of different quantities of CaCl2 on the heat evolution characteristics of hydrating C3S (from Ramachandran 1994) ................................................................................. 11

Figure 2.3 Bending strength of cement-bonded wood composites as a function of density (from Wolfe and Gjinoli 1997) ........................................................................................................ 18

Figure 2.4 Average temperature time curves for different types of wood-based wall linings in a fire chimney using 40 Kg of spruce timber used to supply primary fire load (from Knaublach 1973) .......................................................................................................................... 19

Figure 2.5 Schematic diagram of the WWCB manufacturing process (from Pablo et al. 1998) .......................................................... 27

Figure 2.6 Schematic diagram of process used to produce CBPs (from Anthony and Seymour-Walker 1989) .......................................................................................................................... 32

Figure 2.7 Four different kinds of apparatus for monitoring cement hydration temperature in situ; (a) Sandermann and Kohler (1964), (b) Moslemi et al. (1983), (c) Moslemi and Lim (1984), and (d) Tachi et al. (1989) ........................................................................................................................................ 51

Figure 2.8 Relationships between maximum hydration temperature and time required to reach maximum temperature of wood-cement mixtures (from Lee et al. 1987) .......................................................... 53

Figure 2.9 Schematic diagram for deriving the area ratio compatibility index or CA-factor (from Hasumi et al. 1990) .......................................................................................................................... 56

Figure 2.10 The effect on wood-cement compatibility (I) of decreasing wood particle size used in wood-cement hydration samples at the same mix ratio (from Weatherwax and Tarkow 1964) .......................................................... 58

Figures 3.1 Interaction between heartwood content and wood form for (a) Tmax and (b) CA-factor; data averaged across species and wood level .......................................................................................................................... 77

Figures 3.2 Interaction between species and wood form (a) Tmax and (b) CA-factor; data averaged across heartwood content and wood level .......................................................................................................................... 78

Figures 3.3 Interaction between wood level and wood form (a) Tmax and (b) CA-factor; data averaged across species and heartwood content .......................................................................................................................... 79

Figure 3.4 Interaction between heartwood content and species for (a) Tmax and (b) CA-factor; data averaged across wood form and wood level .......................................................................................................................... 80

Figure 3.5 Effects of species and wood form on the hydration rate of Portland cement containing unsoaked wood, averaged across heartwood content (0%, 50% and 100%) .......................................................................................................................... 91

Figures 3.6 Interactive effect between wood form and % heartwood on compatibility (hydration rate) for (a) A. aulacocarpa, (b) A. mangium, (c) E. pellita and (d) P. deltoides .......................................................................................................................... 93

Figure 3.7 Effect of soaking on compatibility of wood in different for (a) A. aulacocarpa, (b) A. mangium, (c) E. pellita and (d) P. deltoides. *green and dry combined .......................................................................................................................... 95

Figure 4.1 Location of tropical and eucalypt field trials in North Queensland with inset showing sampling sites between Townsville and Cooktown .......................................................................................................................... 100

Figures 4.2 Average hydration rates for (a) acacia species and (b) eucalypt species showing cement control for comparison .......................................................................................................................... 108

Figure 4.3 Average hydration rate for acacia and eucalypt species before and after soaking; means are from different ANOVA models so standard deviations are used for comparison .......................................................................................................................... 110

Figures 4.4 Correlations between hydration rate and % heartwood for (a) A. mangium samples and (b) E. pellita samples ........................................................................................................................................ 112

Figure 4.5 Average hot-water-soluble extractive content of heartwood from the ten most compatible and ten least compatible samples (families) of Acacia mangium ........................................................................................................................................ 113

Figure 4.6 Distribution of hydration rates for A. mangium families (unsoaked samples) by provenance and site group. (11 most compatible families above 0.8°C/h shown by line) .......................................................................................................................... 115

Figure 4.7 Average hydration rate for the ten most and ten least compatible A. mangium families before and after soaking. (LSD unsoaked = 0.17, LSD soaked = 0.18; Standard deviation indicated by bars) .......................................................................................................................... 116
Figures 4.8 Correlations between $C_s$-factor and hydration rate for (a) *A. mangium* unsoaked samples, (b) *A. mangium* soaked samples, (c) *E. pellita* unsoaked samples and (d) *E. pellita* soaked samples..............................................................118

Figure 5.1 Locations of the Uriarra and Kowen field trials of temperate acacias and eucalypts in the ACT, with inset showing the location of the ACT.................................................................128

Figure 5.2 Average compatibility (Hydration rate) for samples from the genera *Acacia* and *Eucalyptus* before and after soaking. (Means are from different ANOVA models, so standard deviation is used for comparison; means from the same models (i.e. ‘soaked’ and ‘unsoaked’) are significantly different at the 0.1% level). ..................................................133

Figures 5.3 Correlation between hydration rates and % heartwood content for individual unsoaked and soaked samples of (a) acacias and (b) eucalypts...............................................................138

Figures 5.4 Correlation between hydration rate and wood extractive content for (a) acacias and (b) eucalypts...............................................................141

Figure 6.1 Sampling locations for mallee and melaleuca trees in Western Australia...............................................................149

Figure 6.2 Typical hydration temperature v time curves for pure cement and cement containing mallee eucalypt wood residue of selected species (all examples shown are for 2.5 y.o. residues from Beverley site). ...............................................................155

Figure 6.3 Effect of species and of bark content in residue on wood-cement compatibility (hydration rate) of mallee eucalypts, averaged across site and age class...............................................................156

Figures 6.4 The effects of melaleuca eucalypt, bark content and extractive removal on (a) time taken to set cement and (b) $C_s$-factor (‘$s$‘ denotes pre-soaked samples) ...............................................................158

Figures 6.5 Flexural properties (a) ln MOR and (b) ln MOE of CBPs manufactured from mallee eucalypt residues as affected by testing condition (wet or dry); results averaged across site, age class and bark content...............................................................161

Figures 6.6 Effect of bark in residue on average (a) water absorption and (b) thickness swelling of CBPs manufactured from mallee eucalypt residues; results averaged across species, site and age class...............................................................162

Figure 7.1 Sampling locations for eucalypt and pine species s in the south-west of Western Australia...............................................................169

Figure 7.2 Average MOR of flakeboards made from different species with no treatment, extractive removal or addition of accelerator. (Bars = Stdev., ISO standard of 9 MPa indicated by line).......................................................................................182

Figure 7.3 MOR vs MOE for cement-bonded flakeboards manufactured from pine and eucalypt wood...............................................................186

Figure 7.4 Variation in average thickness of cement bonded flakeboards manufactured from pine and eucalypt wood...............................................................187

Figures 7.5 The average effects of wood pre-treatment and curing temperature on MOR of (a) flakeboards and (b) CBPs manufactured from eucalypt (blue gum and mallee eucalypt) and pine (radiata) wood...............................................................191

Figures 7.6 Interactions between wood pre-treatment and ‘treatment type’ (size and curing temp.) on MOR for boards made from (a) pine, (b) blue gum, and (c) mallee eucalypt...............................................................192

Figure 7.7 MOR vs MOE for CBPs manufactured from pine and eucalypt wood...............................................................195

Figure 7.8 MOR vs MOE for all WWCBs manufactured at WoodTex Pty Ltd...............................................................198

Figure 7.9 MOR vs basic density of WWCBs manufactured at WoodTex Pty Ltd...............................................................199

Figure 8.1 Average effect on compatibility of *A. mangium* heartwood of different types of wood pre-treatment; bars indicate 95% confidence interval...............................................................213

Figure 8.2 Effect of water temperature, NaOH and ‘Alcohol’ on compatibility of *A. mangium* heartwood; averages are shown for 1 and 6 hour duration treatment groups, i.e 8 samples...............................................................214

Figure 8.3 Effect of extractive removal in different kinds of solvents for different time periods on wood-cement compatibility (hydration rate); 95% confidence interval = 0.169...............................................................216

Figure 8.4 Effect of extraction of *A mangium* heartwood wood wool in water at different temperatures and in 0.01 M NaOH at ambient temperature (20°C) on the amount of extractives removed from the dry weight of wood...............................................................218

Figure 8.5 Effect on wood-cement compatibility of different pre-treatments that do not involve the removal of extractives from *A. mangium* heartwood...............................................................219
Figure 9.1 Average hydration rates of cement containing compounds denoted by their cation (x-axis) and anion (legend) content; hydration rate for cement containing no additive is denoted by line. ........................................................................................................... 231

Figure 9.2 Average hydration rates of cement and wood mixtures containing compounds denoted by their cation (x-axis) and anion (legend) content; hydration rate for cement containing no additive is denoted by line. ........................................................................................................... 231

Figure 9.3 T_{max} for cement containing compound only vs T_{max} for cement containing compound plus wood wool. T_{max} for pure cement (cement control) and for cement containing wood only (wood control) is indicated by lines. ........................................................................................................... 233

Figure 9.4 Hydration rate for cement containing compound only vs hydration rate for cement containing compound plus wood wool. Hydration rate for pure cement (cement control) and for cement containing wood only (wood control) indicated by lines. ........................................................................................................... 233

Figures 9.5 Flavonol structures for the acacia heartwood polyphenols, (a) (+)-mollicacidin (R = OH) and gibourtacidin (R = H); and (b) (--)-teracacidin (R = H) and (--)-melacacidin (R = OH) (From Tindale and Roux 1969). ........................................................................................................... 238

Figure 9.6 Retarding power of aromatics (phenolics) commonly found in heartwood extractives (from Double 1983). ........................................................................................................... 239

Figure 9.7 Schematic diagram of bi-dentate chelation of catechol units by Fe^{3+} proposed by Kennedy and Powell (1985b). ........................................................................................................... 241

Figure 9.8 Schematic diagram of Teracacidin as determined by Clark-Lewis et al. (1961). ........................................................................................................... 241

Figure 10.1 Modulus of Rupture (MOR) v Basic Density for all boards manufactured. Lines show minimum MOR (7 MPa) specified in JIS-A 5908, and corresponding minimum board density (640 kg/m^3), below which no boards met this standard. ........................................................................................................... 257

Figures 10.2 Average basic density of boards manufactured from unsoaked and soaked A. mangium wood wool with accelerators at (a) 0.05 M and (b) 0.1 M strength. ........................................................................................................... 257

Figure 10.3 Average MOR of boards manufactured from unsoaked and soaked A. mangium wood wool with accelerators at (a) 0.05 M and (b) 0.1 M strength. ........................................................................................................... 258

Figure 10.4 Average MOE of boards manufactured from unsoaked and soaked A. mangium wood wool with accelerators at (a) 0.05 M and (b) 0.1 M strength. ........................................................................................................... 259

Figure 10.5 Average thickness swelling of boards manufactured from unsoaked and soaked A. mangium wood wool with accelerators at (a) 0.05 M and (b) 0.1 M strength. ........................................................................................................... 261

Figure 10.6 Average water absorption of boards manufactured from unsoaked and soaked A. mangium wood wool with accelerators at (a) 0.05 M and (b) 0.1 M strength. ........................................................................................................... 262

Figure 10.7 Average wet MOR of boards manufactured from unsoaked and soaked A. mangium wood wool with accelerators at (a) 0.05 M and (b) 0.1 M strength. ........................................................................................................... 263

Figure 10.8 The effect on (a) MOR and (b) MOE of combining selected accelerators with 0.05 M (1%) MgCl_2 compared to adding the accelerators on their own to WWCBs made from unsoaked wood wool. ........................................................................................................... 266

Figure 10.9 The effect on (a) MOR and (b) MOE of combining selected accelerators with 0.05 M (1%) MgCl_2 compared to adding the accelerators on their own to WWCBs made from pre-soaked wood wool. ........................................................................................................... 266

Figure 10.10 Effect of concentration of different accelerators on dry and wet MOR of WWCBs made from unsoaked A. mangium wood wool. ........................................................................................................... 268

Figure 10.11 Effect of different accelerators and concentrations on the tensile strength of wood wool strands. ........................................................................................................... 269

Figure 10.12 Relationship between hydration rate attained in cement hydration test samples containing accelerators at 0.01 M concentration and the strength (MOR) of boards manufactured using the same accelerators and concentration. ........................................................................................................... 271

Figure 10.13 Average accumulation index for each accelerator in the wet and dry environments. Accumulation index derived from summation of visual scores for oxide accumulation on each nail type. ........................................................................................................... 273

Figure 10.14 The effects of different accelerators contained in WWCBs on the accumulation of oxides on four different kinds of nails. ........................................................................................................... 274

Figure 10.15 The effect of corrosion environment (dry or wet) on oxide accumulation on different nail types exposed to cement-setting accelerators in WWCBs. ........................................................................................................... 275
Appendix 2

Figure 1  Hydration temperature vs time curve for Ordinary Portland Cement type I showing the influence of accelerating/retarding admixtures (from Thomas 1987) ........................................... 413
Figure 2  Influence of different quantities of CaCl₂ on the heat evolution characteristics of hydrating C3S (from Ramachandran 1994). ........................................... 414
Figure 3  Effect of different admixtures on cement hydration (from Double 1983) ........................................... 415
Figure 4  Sugars (reducing and non-reducing) listed in order of their capacity for retarding the hydration of portland cement (from Thomas and Birchall 1983) ........................................... 422
Figure 5  Concentrations of soluble silicate in solutions filtered from cement pastes containing EDTA, citric acid and sucrose admixtures, compared with a control sample containing no admixture (from Double 1983) ........................................... 424
Figure 6  X-ray diffraction diagrams for ground samples of (I) dry, unhydrated portland cement powder, (II) hydrated cement with no admixture, (III) retarded cement containing 1% tannin, and (IV) retarded cement containing 1% starch (from Sandermann et al. 1960) ........................................... 425
Figure 7  Partial chemical structures for (a) O-acetyl-4-methylglucuronoxylan from hardwood and (b) arabino-4-O-methylglucuronoxylan from softwood (from Fengel and Wegener 1994) ........................................... 431
Figure 8  Partial chemical structure of arabinogalactan from larch wood (from Fengel and Wegener 1984) ........................................... 431
LIST OF PLATES

Plates 2.1 Housing construction using WWCB panels in the Philippines with inset showing nailing of panels into wooden frame.................................................................23
Plate 2.2 Rendered houses built from WWCB in (a) Brazil and (b) Philippines...........................................23
Plate 2.3 Manufacturing of WWCB in the Philippines showing (a) shredding billets and collecting wood-wool, (b) pre-soaking wood-wool and spreading out to dry; (c) collecting cement coated wood-wool from mixing drum; (d) mat forming by hand using forming boxes; (e) pressing; and (f) outdoor drying and curing for approx. 3 weeks.............................................26
Plate 2.4 Embossed and painted CBP in domestic housing in Japan (from Kuroki et al. 1995)..................30

Plate 3.1 Van Elten wood wool shredding machine at WoodTex, Pty Ltd, Bendigo.................................72
Plates 3.2 Wood sample grinding equipment; (a) rotary mill and (b) Wiley mill.........................................72
Plate 3.3 Cement hydration temperature logging apparatus inside controlled temperature room with schematic diagram of the apparatus below.................................................................74
Plate 3.4 Ultraviolet light spectrophotometer used to determine sugar content of leachates..................76
Plate 3.5 Guilotine used to prepare wood flakes........................................................................................86
Plate 3.6 Wiley toothed crushing mill Model No. 54 used to produce coarse wood particles................86
Plate 3.7 Ball mill used to produce fine wood powder..................................................................................87
Plate 3.8 Different forms of wood produced from A. mangium heartwood..............................................87
Plate 3.9 Tap aspirator used to wash and filter fine wood particles...........................................................88

Plate 4.1 Motorised core extraction drill (from manufacturer P&N Trecor)................................................100
Plate 4.2 A. mangium trees growing at Damper site in North Queensland.............................................101
Plate 4.3 E. pellita trees growing at Damper site in North Queensland....................................................101
Plate 4.4 Examples of cores from A. mangium showing differences in heartwood proportion and colour.................................................................103
Plates 4.5 (a) Conditioning prepared heartwood and sapwood flakes, (b) aqueous extraction of flakes.....106
Plates 4.6 (a) Gold sputter coater, and (b) Cambridge Scanning Electron Microscope located at The Australian National University, Canberra.........................................................106
Plates 4.7 Cement relief of (a) and (b) unsoaked A. mangium heartwood, (c) A. mangium sapwood, and (d) soaked wood sample.................................................................121
Plates 4.8 Cement reliefs of (a) A. crassicaarpa heartwood, (b) A. crassicaarpa sapwood, (c) close-up of plate hydrates (possibly C3A) formed in contact with the sapwood, and (d) soaked wood sample.................................................................122
Plates 4.9 Cement reliefs of (a) and (b) E. pellita heartwood, (c) E. pellita sapwood, and (d) E. urophylla sapwood.................................................................123

Plate 5.1 View of the drier Kowen sampling site.........................................................................................129
Plate 5.2 Distinctive yellow colouring of sapwood in A. dangarensis (top) and A. leucoclada (bottom). Yellow colouring disappeared after soaking (samples on right).........................................................141

Plates 6.1 (a) mallee hedgerows, (b) hedgerow ready for harvest, and (c) stems to be utilised for composites after chipping.................................................................150
Plates 6.2 (a) sieves used to screen chipped mallee particles for desired size, and (b) typical particles produced from mallee residues, with radiata pine core particleboard flake sourced from CSR, Tumut as a comparison.................................................................151
Plates 6.3 Sanded cross-sections of cement bonded boards made from (a) radiata pine particleboard flake, and (b) chipped residues from E. polybractea.................................................................164

Plate 7.1 Disk flaker used to produce flakes and particles from log samples................................................171
Plate 7.2 Sieving flaked mallee eucalypt wood to separate (a) large flakes and (b) small flakes................171
Plates 7.3 Appearance of (a) maritime pine, (b) blue gum 1, and (c) blue gum 2 and mallee flakes Scale bar represents 10 mm.................................................................172
Plates 7.4 (a) to (f) Manufacturing and testing process for cement-bonded flakeboards........................175
Plate 7.5 Three-point testing jig fitted to an Instron 4505 Universal Testing Machine used to determine board flexural properties.................................................................176
Plates 7.6 (a) to (g) Commercial WWCB manufacturing process at WoodTex, Bendigo.........................178
Plates 7.7 (a) 470 mm span 3-point bending test jig for WoodTex panel samples and (b) impact test rig for 600 x 900 mm panels showing the 5 kg load .................................................179
Plates 7.8 Cross sections of flakeboards made from (a) pine, (b) blue gum 1, (c) blue gum 2, and (d) mallee eucalypt .................................................................189
Plates 7.9 Cross-sectional profiles of CBPs made from (a) factory-produced particles of radiata pine, and screened small-sized elements of (b) blue gum and (c) mallee eucalypt. ................................................194
Plates 8.1 (a) Water extraction of A. mangium heartwood strands using a temperature controlled water bath, and (b) Soxhlet apparatus used for solvent extraction of A. mangium heartwood strands ........................................211
Plate 8.2 The apparatus used to expose wood strands to plasma .................................................................211
Plates 9.1 (a) to (c) Appearance of cement at the wood-cement interface produced by adding CaCl2 0.1M, (d) and (e) adding Cr2O3 0.1M to the hydrating wood-cement mix .................................................................235
Plate 9.2 Examples of insoluble complexes formed with A. mangium heartwood polyphenols, showing heavy precipitation by SnCl4, Al2(SO4)3, FeCl3 and CuCl2, very light precipitation by CaCl2 and no precipitation by MgCl2 or water control ................................................237
Plates 10.1 (a) to (e) Laboratory WWCB manufacturing process ........................................................................251
Plates 10.2 (a) Strand thickness micrometer and (b) tensile test jig used to determine the tensile properties of wood wool strands exposed to different kinds of cement set accelerators ........................................254
Plate 10.3 Sealable tub containing water, elevated mesh and corrosion test samples ..........................................255
Plates 10.4 Examples of exposed nails given an accumulation rating of 0 (L) to 5 (R) for (a) ordinary wood nails, (b) cut tacks, (c) zinc-plated nails and (d) galvanised fibre-cement nails ..................276
1.1 Background to the study

1.1.1 Wood-cement composites for building applications in tropical countries

The tropics or 'tropical zone' encompasses about 30% of the earth's surface, and countries in this zone have high rates of population growth and a great need to develop their infrastructure and stock of affordable housing. Challenges to housing development in these regions are posed not only by limited financial and other resources but also by the occurrence of more severe environmental and climatic phenomena than those found in temperate regions of the world; for example, high temperatures and humidity, torrential rainfall, hurricanes and earthquakes. Socio-economic factors throughout much of the tropics, such as widespread poverty and the increasing migration of large numbers of people from rural areas into urban fringes, have created an urgent need for the development of low-cost housing that is suited to tropical regions.

Cement-bonded wood composites such as cement-bonded particleboard (CBP) and wood wool-cement board (WWCB) have long been considered as being among the most suitable building materials for low-cost housing in tropical countries (Simatupang et al. 1977, Hawkes and Robinson 1978a and b). Production of structural CBP and WWCB for low-cost housing projects in developing regions is increasing, particularly in South-East Asia and Central America (Pablo 1989, Buys 1995, Soriano et al. 1997, Ramirez-Coretti et al. 1998, van Elten 1997, 2000). Considerable research and development of cement-bonded composite panels is also taking place in African countries (Badejo 1988 and 1989, Oyagade 1990 and 1994, Fuwape 1995). In addition to their low cost, cement-bonded wood composite panels have a number of attractive attributes, including good resistance to weathering, fire and biodeterioration (including termites, borers and fungi). They also possess good insulation properties and are very suitable for modular or prefabricated structures (Stillinger and Wentworth 1977, Buys 1995, Ramirez-Coretti et al. 1998). The properties of CBP and WWCB and their suitability for use in tropical regions such as in Asia are examined in detail in Chapter 2.

The best example of the use of cement-bonded wood building materials, in particular WWCB, for housing in the tropics can be found in the Philippines. In the Philippines research to develop WWCBs from indigenous wood species and use them in the construction of housing commenced 25 years ago (Pablo 1995). This research and subsequent technology transfer has led to the development of an indigenous industry that manufactures and uses WWCB for building construction, mainly from local tree species. However, it is hoped that exotic plantation species,
particularly Australian acacias and eucalypts, can also be adopted for use as raw materials for wood-cement composite industries.

1.1.2 The utilisation of acacias and eucalypts for wood-cement composites

Over the past 50 years, Australian eucalypt and acacia species have contributed significantly to both reafforestation and wood production in many tropical countries throughout Africa, South and South-East Asia and Latin America (Evans 1992, Brown 1993). They feature commonly in field trials of species and provenances, programs for the amelioration of degraded lands and reafforestation, small-scale farm plantings and in industrial-scale commercial wood lots (Brown 1993, Vercoe 1993). Australian acacias (dominated by black wattle (Acacia mearnsii de Wild.), Acacia saligna (Labill.) H. Wendl., and brown salwood (Acacia mangium Willd.) have been planted in over 70 countries and cover approximately 2 million ha (Turnbull et al. 1998). Tropical acacias such as A. mangium, brush ironbark wattle (Acacia aulacocarpa Cunn. ex Benth.), northern wattle (Acacia crassicarpa Cunn. ex Benth.) and earleaf acacia (Acacia auriculiformis Cunn. ex Benth.), collectively known as ‘salwoods’, are rapidly attaining prominence in tree planting programs in the humid tropics (Pinyopasarerk 1993, Seng 1993, Thompson 1997), with A. mangium covering over 600 000 ha, mainly planted for the pulp and paper industries (Turnbull et al. 1998).

Species such as A. mangium have been widely planted for their adaptability and capacity to colonise and grow rapidly on degraded, low-nutrient and weed-infested sites and to produce large volumes of wood, mainly for use as pulp and fuelwood (Gunn and Midgley 1991, Arcocena-Francisco 1993, Awang and Taylor 1993). However, there is the potential to expand the utilisation of small-diameter wood from such species to include a much wider range of end products, especially wood composites (Abdul-Kader 1993, Abdul-Kader and Sahri 1993a and b, Chew et al. 1991). These include cement-bonded composites, such as WWCB and CBP. Species of sub-tropical and tropical eucalyptus such as red mahogany (Eucalyptus pellita F. Muell.) and Timor mountain gum (Eucalyptus urophylla S.T. Blake) are less well known, but have the potential to be much more widely grown for industrial wood production in the humid and sub-humid tropics (Doran and Turnbull 1997, Harwood 1998).

Soil deterioration in parts of Australia has created an urgent need to find and plant perennial tree crops that not only help ameliorate land degradation but also complement crop/livestock production with wood and non-wood products that generate additional farm income (Shea 1994). The most substantial single project of this type in Australia is the establishment of oil mallee eucalypt and melaleuca tree crops in the wheatbelt of Western Australia (WA) (Shea and Hewett 1997, Shea 1998, Bartle 2001). This has been designed to meet the above-mentioned objectives and provide raw materials for new regional processing industries, namely leaf oils, biomass energy and wood-
based products (Bartle 2001). The planting of oil mallee trees in WA could potentially generate some 13 million m$^3$ of woody waste material annually (Shea 1998, Bartle 2001). Wood-cement composites could be a suitable end use for the waste wood and bark residues left over from the stripping of leaves for the extraction of leaf oils.

Despite plentiful raw materials the major obstacle to the expansion and adoption of mineral-bonded wood composite technology world wide has been the problem of inhibition of cement hydration reactions, or 'cement poisoning', by soluble extractives present in many woods. This results in poor bonding at the wood-cement interface in wood-cement composites (Pazner and Klemarevski 1989). There is extreme variation in the compatibility of wood species and types with cement (Sandermann and Kohler 1964, Hachmi and Campbell 1989), and a lack of information on the compatibility of many species with cement (including most acacias and eucalypts). For example, the compatibility of mallee eucalypts with portland cement is not known. Many wood species with high sugar or tannin contents are unsuitable for the manufacture of wood-cement composites without the removal of extractives or more specialised manufacturing techniques that counteract their effects. Hence, relatively few wood species are used in the manufacture of wood-cement composites commercially.

Nevertheless several attempts have been made to utilise plantation grown tropical acacia and eucalypt species for the manufacture of cement-bonded composites in countries such as the Philippines (Pablo 1989, Soriano et al. 1998, Eusebio et al. 2002a and b) and Indonesia (Kamil and Ginoga 1975, Sulastiningsih et al. 1990), but these attempts have met with only limited success. For example, previous studies (Rahim and Ong 1983, Tachi et al. 1988 and 1989, Jegasethwaran 1989, Sulastiningsih et al. 1990) have shown that, although $A. \textit{mangi}m$ wood is readily machined into wood wool or flakes, its heartwood is highly incompatible with portland cement and hence unsuitable for use in wood-cement composites without prior removal of extractives which inhibit cement setting and/or the use of chemical cement-setting accelerators.

Site- and/or genotype-induced variation in the amount and/or types of soluble extractives in wood that interfere with cement setting may also play an important role in determining the suitability of acacia and eucalypt woods for wood-cement composites. This factor has been shown to significantly affect the suitability of eucalypt, in this case Mindanao gum ($E\text{ucalyptus} \textit{deglupta}$ Blume), wood for the manufacture of WWCB (Kamil and Ginoga 1976, Paribotro and Suwandi-Kliwon 1977). Problems in converting eucalypt wood to particles of the correct geometry for particleboard have also been identified as a barrier to their suitability for the manufacture of CBP (Tachi et al. 1988). The above-mentioned problems have all conspired to hamper the adoption of many fast-growing and readily available acacia and eucalypt species for use in the manufacture of wood-cement composites. There has been insufficient research aimed at expanding knowledge and
experience in the use of acacias and eucalypts in different kinds of wood-cement composites or overcoming problems already identified as barriers to their use.

1.2 Aims and structure of the thesis

The overall aim of this thesis is to examine the suitability of a wide range of Australian acacias and eucalypts for the manufacture of low-cost wood-cement composites, and to overcome impediments to the utilisation of selected acacias and eucalypts for such products. Major objectives of the research were to screen acacia and eucalypt woods for compatibility with cement, develop strategies to overcome the inhibitory effects of *A. mangium* wood on the hydration of cement and use this species for the manufacture of WWCBs, and to utilise wood from small-diameter mallee eucalypt for the manufacture of cement-bonded particulate and flake boards. Each Chapter (apart from the Literature Review in Chapter 2) describes one or more discrete experiments to answer specific questions, and each chapter contains its own Introduction, Aims and objectives, Materials and methods, Results and discussion, and Conclusions. Experiments focus on species that are of commercial importance, and attention is given to identifying the most appropriate types of wood-cement composite to suit selected different woods that are available commercially. Specific objectives covered in the thesis are outlined below.

1.2.1 Assessment of literature and problem definition

Chapter 2 reviews and discusses the comprehensive but highly disparate literature on wood-cement composites. Much valuable information on wood-cement composites is only found in regional journals, unpublished reports and theses. Often these reports are not written in English, making it difficult to completely review all of the relevant literature. However, considerable effort has been made to obtain as much literature as possible written in English on wood-cement composites from Russia, Germany and Eastern Europe, China, Indonesia, Africa and the Americas. The review contains a brief introduction to portland cement and factors that affect its hydration, followed by the evolution of wood-cement composites and their general properties. The review then focuses on the manufacture and use of two important kinds of cement-bonded composite boards, WWCB and CBP, with an emphasis on their use in developing countries. The final aim of the review is to pool existing knowledge and experience in using acacias and eucalypts for wood-cement composites, most of which pertains to South-East Asian countries, including the Philippines, Malaysia and Indonesia. The literature suggests that widely planted species such as *A. mangium* can be readily converted to wood wool or flakes for the manufacture of WWCB and CBP, respectively, but the inhibitory effect of the wood on cement hydration has prevented such species from being used to manufacture wood-cement composites. Large-scale acacia and eucalypt
plantations have been established in many developing countries and wood from such plantations is therefore likely to become increasingly important as a source of raw material for the manufacture of wood-cement composites in the future.

A supplement to Chapter 2 is contained in Appendix 2 (Vol. 2, pp. 1 to 30), which provides further information on the hydration of portland cement and factors influencing it, and the complex chemical interactions between wood and cement. The supplement also briefly covers efforts made to find alternative compositions and mineral supplements for portland cement and replacement mineral binders to offset the problems of wood specificity and long curing times that have historically hampered the production of wood-cement composites. The chemical and physical interactions between wood and cement are often only superficially described in the wood-cement literature because of their complexity. Better information on the chemical interactions between cement and wood constituents (especially carbohydrates) can be found in the cement and concrete literature; however, there is little published information on how certain wood extractives, for example tannins, chemically interfere with cement hydration. The possible interactions of acacia heartwood polyphenols with cement are discussed in Chapter 9.

Another major problem in the field of wood-cement composite materials, which is relevant to the overall aim of this thesis, is the interpretation of available information on the suitability of different wood species for wood-cement composites produced from laboratory tests of wood-cement compatibility. There is no universal standard method for testing woods for their compatibility with portland cement nor for accurately predicting their potential suitability for wood-cement composites. Before discussing the testing and use of acacias and eucalypts for the manufacture of wood-cement composites the methodology used to test wood-cement compatibility is reviewed in detail. The literature indicates considerable variation in experimental methodology used to test wood-cement compatibility. There are often discrepancies between the 'perceived' compatibility of a wood species with cement, generated from cement hydration tests, and how the species performs in wood-cement composites such as WWCB and CBP.

Most of the studies of the compatibility of wood from different species with cement have tested the wood in the form of finely ground wood flour. Thus there is the obvious (and unresolved) question of whether the results from such tests accurately reflect the suitability of the wood for the manufacture of wood-cement composites such as CBP and WWCB that use wood flakes or wood wool. Before such methodology can be adopted for use in this study, this question has to be addressed and the methodology modified if necessary (Chapter 3). In the first part of Chapter 3 wood-cement compatibility data from the use of wood flour and wood wool were generated and compared in order to determine whether the use of wood flour in cement hydration tests can accurately predict the behaviour of wood wool with cement. Alternative methodologies for testing
the potential suitability of acacia and eucalypt wood for cement-bonded composites (particularly WWCB) are investigated and the suitability of each is considered in the second part of Chapter 3.

1.2.2 Compatibility of acacia and eucalypt species with cement

One of the major objectives of this thesis is to assess the suitability of a wide range of acacia and eucalypt species for the manufacture of wood-cement composites. This is achieved by testing a range of tropical and temperate acacia and eucalypt species using a modified wood-cement compatibility test developed as a result of the findings presented in Chapter 3. As discussed in Chapter 2, the results from previous studies using wood-cement hydration tests suggest that there is wide variation in the compatibility of acacias and eucalypts with cement, and trials of the use of acacias and eucalypts for the manufacture of wood-cement composites have also yielded mixed results.

The compatibility of seven important tropical species of acacias and eucalypts with cement is examined in Chapter 4. Possible causes of variation in wood-cement compatibility for two important plantation species, *A. mangium* and *E. pellita*, are also investigated. The influence of factors such as site, tree provenance, heartwood content and heartwood extractive content on wood-cement compatibility is examined. *A. mangium* is most intensively sampled in order to identify any trees or provenances that have a higher natural compatibility with portland cement. This aspect of Chapter 4 forms part of the research aimed at improving the suitability of *A. mangium* for the manufacture of wood-cement composites. The question of whether heartwood content in *A. mangium* strongly affects the compatibility of its wood with cement is also examined.

In Chapter 5 the compatibility of a large range of mostly temperate Australian acacias and eucalypts with portland cement is assessed, thus greatly increasing the available knowledge of the interactions of acacia and eucalypt wood with cement. To avoid the confounding effects of variation in growing site, tree age and wood storage time on the results, species from both genera are obtained from well-designed field trials where these factors are consistent across all trees sampled. The effects of factors such as growing site, heartwood/sapwood proportion in trees, and extractive content on wood-cement compatibility are investigated.

The potential suitability of waste wood and bark residues from mallee eucalypt trees for the manufacture of CBP is examined in Chapter 6. The compatibility of chipped residues (with or without bark) from five oil mallee species with cement is measured and compared with that of chipped wood and bark residues from three salt-tolerant, oil-producing species of *Melaleuca* and radiata pine (*Pinus radiata* D. Don). Stem wood from a salt-tolerant, widely planted fodder tree, tagasaste or tree lucern (*Chamaecytisus proliferus* var. *palmensis* (Christ.) Hansen & Sunding) is also tested for its compatibility with cement as a comparison. The performance of mallee wood and
bark residues that were chipped using relatively simple, farm-based equipment in cement-bonded particleboards is assessed and potential problems identified for further investigation.

1.2.3 Improvement of wood-cement composites made from mallee eucalypts

In Chapter 7 the findings of the CBP manufacturing trial using chipped mallee eucalypt wood (Chapter 6) are followed up with subsequent work on the manufacture of wood-cement flakeboards and particleboards from selected mallee eucalypt species. The experiments are designed to address the problems associated with using chipped mallee wastes for wood-cement composites that were identified in Chapter 6, the aim being to adjust and improve parameters, including flake size, pre-treatment and board curing conditions. The properties of cement-bonded flake and particle boards made from mallee eucalypt wood were compared with those of similar boards made from the wood of three commercial plantation tree species in WA, specifically Tasmanian bluegum (Eucalyptus bicostata Labill.), radiata pine (Pinus radiata D. Don) and maritime pine (Pinus pinaster Ait.).

Mallee and bluegum represent two very different kinds of eucalypt wood as potential source material for wood-cement composites. The mallee is in the form of small-diameter, relatively high density wood that had to be processed with the bark still on, whereas the plantation bluegum is mostly in the form of straight, fast-grown, larger diameter, lower density wood. In Chapter 7 the properties of WWCBs manufactured on a commercial scale for the first time from WA bluegum are compared with those of boards manufactured from radiata pine and maritime pine.

1.2.4 Improvement of the compatibility of A. mangium with cement and its suitability for the manufacture of wood-cement composites

The third major theme of this thesis focuses on overcoming the major obstacle to the utilisation of A. mangium for wood-cement composites, namely the low compatibility of its heartwood with portland cement. As mentioned above, A. mangium is one of the most important tree species for reforestation, rural development and industrial wood production throughout South-East Asia, in particular Indonesia, Malaysia, the Philippines and Thailand (Awang and Taylor 1993). A. mangium can be readily processed to produce high-quality wood wool (Cabangon et al. 1998), but the wood is not suitable for the manufacture of wood-cement composites because soluble polyphenols in the heartwood strongly inhibit cement setting (Tachi et al. 1988, 1989). In Chapter 8 strategies to improve the compatibility of A. mangium wood with portland cement to facilitate the manufacture of WWCBs from this important and readily available species are examined. Pre-treatments for the heartwood of A. mangium include: extractive removal in various media, dipping
wood wool in cement-setting accelerators, and the addition of water repellent barriers to retard the leaching of extractives from wood by cement.

Chapter 9 presents the results of experiments that investigated the use of simple chemical additives designed to increase the compatibility of *A. mangium* heartwood with portland cement. The aim was to identify compounds that could be used to facilitate the manufacture of WWCBs from fresh *A. mangium* wood, eliminating the need to pre-soak the wood prior to the manufacture of WWCBs. This is necessary because continuous supplies of fresh water and the disposal of waste water are important concerns in the wood and composite processing industries (Thompson 1977). The mechanisms by which the most effective chemical additives improve the compatibility of *A. mangium* heartwood are investigated and are discussed.

Following on from the findings of Chapter 9, the manufacture of WWCBs from *A. mangium* wood is reported in Chapter 10. The manufacture of WWCBs involved the use of compounds identified in Chapter 9 as being the most effective at increasing the compatibility of *A. mangium* heartwood with cement. Compounds are tested at different concentrations, and the properties of WWCBs made from untreated *A. mangium* wood wool are compared with those made from wood wool that had been pre-soaked (in order to determine whether pre-soaking is critical to board quality). Properties of WWCBs are benchmarked using international and country-specific standards to ensure that the improvements to board properties arising from the use of selected additives are of practical importance.

Finally, a summary of the findings and conclusions from the experimental chapters of this thesis is given in Chapter 11. Some of the more interesting and unexplained findings arising from the experimental work are highlighted. Suggestions for additional research needed to further improve the potential of Australian acacias and eucalypts for the manufacture of wood-cement composites are discussed.
Chapter 2 Literature Review

This review is designed to draw together a wide range of source materials to provide an overview of the characteristics, manufacture and use of wood-cement composite materials, especially in developing countries. Accordingly the review focuses on wood wool cement board (WWCB) and cement-bonded particleboard (CBP), which are manufactured in many developing countries, rather than the third important class of wood-cement composites, cement-bonded fibreboards. The manufacture of portland cement, its hydration reactions and the influence of accelerators on cement hydration are presented briefly, with more detailed information contained in Appendix 2.1 (pp. 407-416).

Problems associated with manufacture and use of cement-bonded wood composite materials are reviewed, the major obstacle being the incompatibility between many wood species and portland cement which affects the bonding, strength and durability of wood-cement composites. A wide variety of innovative strategies have been tested in attempts to overcome wood-cement compatibility problems.

To determine the potential suitability of wood species for wood-cement composites, laboratory methods have been developed to monitor the effects of different wood species on the hydration and setting of portland cement. However, no standard test methodology has been developed and adopted, which makes it difficult to directly compare information from different wood-cement compatibility studies. Furthermore, very few studies have attempted to relate results from wood-cement compatibility tests to the properties and performance of wood-cement composites.

The final section of this review presents information from scientific studies on the utilisation of Australian acacias and eucalypts for wood-cement composites as background to the research in this thesis. Laboratory wood-cement compatibility studies as well as trials of wood-cement composites are covered, concentrating on the use of the important plantation species brown salwood (Acacia mangium Willd.) in wood-cement composites. More detailed information on related subjects, including cement hydration reactions, cement supplements, and wood-cement chemical interactions, can be found in Appendix 2 (pp. 407-436).

2.1 Portland cement components and hydration

2.1.1 Origin and components

Modern portland cements are produced by a clinkering process involving a mix of calcium oxide (CaO) from limestone and coral deposits, silica (SiO₂) from sands and shales, aluminium oxide (Al₂O₃) and ferric oxide (Fe₂O₃) from ores (Brunauer and Copeland 1964, Lea 1971). These raw materials are crushed, mixed and pre-heated to ≈800°C and then passed through a large rotary kiln
where they are cooked at 1300-1500°C for 1-2 minutes. The clinker is then refined with a small amount (3-6%) of gypsum (CaSO₄) in a large water-cooled ball-mill. The resulting portland cement is a hydraulic inorganic binder whose principal phases are tricalcium silicate (C₃S, Alite), β-dicalcium silicate (C₂S, Belite), tricalcium aluminate (C₃A) and tetracalcium alumino-ferrite (C₄AF). The approximate proportions of these components in portland cement ASTM Type I are shown in Table 2.1 (figures from Ramachandran and Feldman 1994).

Table 2.1 The principle phases and their approximate proportions in portland cement clinker (ASTM Type I).

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviated Formula</th>
<th>Proportion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium silicate (C₃S)</td>
<td>3CaO·SiO₂</td>
<td>50</td>
</tr>
<tr>
<td>β-dicalcium silicate (C₂S)</td>
<td>2CaO·SiO₂</td>
<td>24</td>
</tr>
<tr>
<td>Tricalcium aluminate (C₃A)</td>
<td>3CaO·Al₂O₃</td>
<td>11</td>
</tr>
<tr>
<td>Tetracalcium alumino-ferrite (C₄AF)</td>
<td>4CaO·Al₂O₃·Fe₂O₃</td>
<td>8</td>
</tr>
<tr>
<td>Pentacalcium trialuminate (C₄A)</td>
<td>5CaO·3Al₂O₃</td>
<td>1-2</td>
</tr>
<tr>
<td>Minor constituents</td>
<td></td>
<td>5-8</td>
</tr>
</tbody>
</table>

2.1.2 Hydration

When mixed with water portland cement undergoes 'hydration' as it hardens and sets, the characteristic hydration curve for which is shown in Figure 2.1. An initial short period of exothermic reaction, from heat of wetting and rapid hydration of C₃A, is followed by a dormant period prior to the main phase of hydration of the silicate (alite and belite) phases. After initial setting, hydration reactions continue to contribute to the hardening of the cement matrix for months and years after (Brunauer and Copeland 1964).

Figure 2.1 Hydration temperature vs time curve for ordinary portland cement (ASTM Type I) showing the influence of accelerating/retarding admixtures (from Thomas 1987).
2.1.3 The action of accelerators

Cement-setting accelerators are commonly used during the manufacture of wood-cement composites (See Section 2.7.4). The most common and readily available accelerator is calcium chloride (CaCl₂) (Lea 1971, Skalny and Maycock 1975, Ramachandran 1994, Taylor 1997). The addition of an accelerating admixture such as CaCl₂ to portland cement decreases the dormant period of hydration caused by the early formation of ettringite and increases heat evolution during renewed hydration as shown in Figure 2.2 (Ramachandran 1994).

![Figure 2.2 Influence of different quantities of CaCl₂ on the heat evolution characteristics of hydrating C3S (from Ramachandran 1994).](image)

2.2 Historical development of cement-bonded wood composites

2.2.1 Wood wool cement board (WWCB)

Industrial scale production of modern inorganic-bonded wood composites first took place in Europe in 1900 when magnesite-bonded wood particleboards were manufactured in Germany. Gypsum-bonded Excelsior (wood wool) boards were first manufactured in 1905 (Kossatz et al. 1983). Magnesite-bonded wood wool boards were later produced on an industrial scale at Radenthein in Austria in 1914 (Kollmann 1963a). Although portland cement had been available in Germany since 1856 (Lea 1971), early inorganic-bonded wood composites used magnesite mainly because of its rapid setting properties and the scarcity and expense of portland cement.

Portland cement-bonded wood wool boards were first manufactured in the early 1920s in Germany and had become widely available in the market by the late 1920s because of the product’s excellent thermal insulation properties, high production capacity and low cost (Kollmann 1963a).
Prior to World War II wood wool boards manufactured in Germany were bonded using a mixture of 39% portland cement, 35% magnesite and 26% gypsum. Increasing post-war availability of portland cement resulted in the adoption of pure portland cement to replace the cement, magnesite and gypsum binder mix, and in increased sophistication and scale of wood wool cement board manufacturing (Kollman 1963b). The development and adoption of cement-bonded wood wool board also effectively overcame the problems of composite quality and durability caused by the high sensitivity of magnesite and gypsum binders to moisture (Kossatz et al. 1983).

Although wood wool cement board manufacture for end uses requiring the thermal and sound insulation properties of the boards had become widespread throughout Europe by the 1940s, it was not until the 1960s that full automation of all stages of production—shredding wood, mixing and pressing—was implemented (Anon 1998). Wood wool cement board (termed Cement Excelsior Board (CEB)) did not appear in the USA until the 1940s and has had only a small market share compared to other wood-based composites (Lee 1984). Throughout the 1930s and 1940s, a WWCB plant operated in Washington State, producing acoustic insulation panels for use in many large auditoriums throughout the eastern states (Maloney 1996).

Slow development of the WWCB industry in the USA has largely been attributed to the problem of inhibition of cement-setting by certain wood species (Lee 1984, Moslemi and Pfister 1987). However these problems of low compatibility of wood species with cement did not attract scientific study in the USA until the 1960s. Weatherwax and Tarkow (1964, 1967) and Biblis and Lo (1968) were the first to examine these problems and studied the effects of North American wood species on the hydration of portland cement. Wood wool boards had also been developed and manufactured in the West with an emphasis on acoustic insulation, fire resistance and aesthetics rather than on structural applications (Wolfe and Gjinolli 1997). Demand for wood wool cement insulation boards has suffered a gradual decline in market share in the USA with their replacement by modern synthetic insulating materials (Deppe 1977). Wood wool insulating boards have a minor share of the market in Australia, and are intermittently manufactured to order in one single plant in Victoria (Woolley, J. pers. comm. 1999).

2.2.2 Cement-bonded particleboard (CBP), flakeboards and aggregates

The early 1930s saw the development in Europe of cement-bonded moulded block composites made from waste wood chips and sawdust using the 'Durisol' mould process (Deppe 1977). The use of pressing technology in mineral-bonded composite manufacturing did not take place until the mid-1930s. The development and production of platen-pressed cement-bonded composite boards using engineered particles is even more recent and has followed the evolution of conventional resin-bonded particleboard manufacturing technology, beginning in the USA in the mid-1960s (Moslemi
1989). Surprisingly, CBP was not commercially produced in Europe until about 1972, by the Durisol company in Switzerland (Dinwoodie and Paxton 1991).

Both wool-wool-cement boards and cement-bonded strand (large-flake) boards were manufactured in the USA during the early 1960s (Elmondorf 1963, 1966). Elmondorf's research concentrated on orientating flakes in boards to produce boards with superior strength, beginning with cement-bonded panels. The findings were later transferred to the resin-bonded wood composite industry leading to the development of Orientated Strand Board (OSB) (Elmondorf 1965), which is now the major wood composite panel produced in North America (McNatt et al. 1992, Youngquist 1999).

Waste sawdust and planer shavings have been successfully recycled into wood-cement aggregates such as hollow blocks and building boards. These were widely manufactured and used in the former USSR under the trade name 'Arbolit' (Sandermann 1971). In Britain such products were manufactured under the trade name 'Lignacite' and in Switzerland as 'Durisol' (Chittenden 1972). Keen interest in developing building materials from wood or cane processing wastes has led to considerable research into making hollow blocks, bricks and panels from sawdust (Parker 1947, Elmondorf 1963, Hallak 1972, Prestemon 1976, Rashwan et al. 1992), planer shavings (Huffaker 1961, Olorunmisaola and Adefisan 2002) and chipped construction wastes (Wolfe and Gjinolli 1999). Waste bark-cement composites for internal insulation ('Korolit') were also developed in the USSR and widely utilised as a low-cost, non-structural building product (Miller et al. 1973, Karger et al. 1978, Byzov 1991). Bark-cement composites have also attracted research interest in Japan (Kawamura et al. 1976, Yoshimoto and Minami 1976a), but commercialisation of the technology in industrialised countries has not occurred. Elmondorf (1963) has pointed out that such products are weak and lack the physical properties necessary for building panels, and hence it is unlikely that they would achieve commercial importance.

In recent years, however, wood-cement composites have attracted renewed interest in industrialised countries, including the USA, as a potential outlet for recycling waste wood from milling operations and construction sites (Rashwan et al. 1992, Youngquist 1995, Wolfe and Gjinolli 1999, Ledhem et al. 2000 a and b). Systems that combine wood waste aggregates with portland cement into moulded hollow blocks to assemble permanent wall formwork (‘FASWALL’) have only relatively recently been commercialised in the USA and Canada (Walter and Walter-Gurzeler 1991, Hoene 1993, Walter 1993, Youngquist 1995) and are popular in some developing countries (Manzanares et al. 1992). These ‘new’ products appear to have been inspired by the 60-year-old Swiss 'Durisol' technology. Cement-bonded composites are also being examined as a possible outlet for the recycling and re-use of chromated copper arsenate (CCA) treated wood (Hsu 1995, Plackett et al. 1995, Wolfe and Gjinolli 1999, Huang and Cooper 2000, Zhou and Kamdem 2002). Such
composites are attractive in that they combine materials of very high decay resistance (i.e. cement and CCA-treated wood particles), however, some uncertainty exists as to whether CCA-treated wood is more compatible with cement than untreated wood (Shukla 1977b, Schmidt et al. 1994), and to the extent to which copper, chromium and arsenic can be leached from the composite (Hsu 1995, Cooper et al. 1997, Huang and Cooper 2000). Most studies suggest that the use of CCA-treated wood waste enhances wood-cement composite properties compared with untreated wood. However, work by Hsu (1994) and Huang and Cooper (2000) found that incorporation of CCA-treated wood into wood-cement particleboard increased the leaching of arsenic and led to oxidation of Cr$^{3+}$ to soluble, toxic Cr$^{6+}$, although this problem can be mitigated by employing higher cement and water contents during composite manufacture.

2.3 Properties and utilisation of cement-bonded wood composites

2.3.1 General features

Mineral-bonded wood or other lignocellulosic composites are moulded or compressed blocks or panels containing approximately 30-70% by weight of wood in various forms and 70-30% mineral binder (Simatupang et al. 1977). The most common mineral binders include portland cement, magnesite, gypsum, and a combination of these. They assume considerable importance where technology and materials for manufacturing conventional resin-bonded wood composites are expensive or unavailable (Kavvouras 1987, Badejo 1988, Fuwape and Oyagade 1993, Alberto et al. 2000). They can also be manufactured where available wood or plant waste resources are unsuitable for the production of sawn timber or conventional resin-bonded wood composites (Kelly 1977, Ledhem et al. 2000b). More importantly, they are much better suited to end uses requiring high resistance to fire, weathering and bio-deterioration than solid wood and resin-bonded composites, which are vulnerable to these effects (Stillinger and Wentworth 1977, Chapola 1989, Dinwoodie and Paxton 1991). Cement-bonded composites also employ an inert binder free from the health risks associated with the use of formaldehyde-containing resin binders (Chen and Hwang 1998). The high weight-to-strength ratio of cement-bonded wood panels, however, affects the economics of manufacture, transport and utilisation, which has historically disadvantaged them compared to conventional wood-based composite panels (Moslemi and Pfister 1987).

Chittenden (1972) divided wood-mineral composites into two distinct groups, (1) composites in which wood is incorporated as an aggregate (as fibres, sawdust, shavings or particles) in the mineral matrix, and (2) composites in which the cement (or other mineral) acts purely as a binder, such as in WWCB or flakeboard. Wood can therefore serve simply as a low-cost filler or can act as a reinforcing material, greatly improving the stiffness, fracture toughness, strength to weight ratio, creep deflection, and thermal and acoustic resistance of cement (Goodell et al. 1997).
Although the market share of cement-bonded wood panels such as WWCB has declined in many Western countries, they have increased in popularity in developing countries for many of the reasons outlined above. Cement-bonded wood panels are of particular relevance in warm, humid climates where termites and decay are major concerns (Pablo 1989, Wolfe and Gjinolli 1997, Ramirez-Corretti et al. 1998). More importantly, cement-bonded composites are made from materials that are relatively inexpensive and widely available in many developing countries (i.e. cement, wood fibre, water and simple, low-cost additives such as CaCl₂ or sodium silicate) (Simatupang et al. 1977, Moslemi 1989). The potential for cement-bonded wood composite manufacturing technology in developing countries was comprehensively discussed by Simatupang et al. (1977). Of the various types of cement-bonded composites, including fibreboard, flakeboard, CBP and WWCB, elements of the WWCB production cycle have lent themselves most readily to less capital-intensive processes better suited to developing countries (Van Elten 1997). An example of this is the manual process used to manufacture WWCB in the Philippines (Section 2.4). WWCB is also one of the most cost-effective cement composites due to its lower cement to wood ratio.

CBP, cement-bonded fibreboard and WWCB are the most important cement-bonded wood composite panels in production at present. Only WWCB and CBP are discussed in detail in this review since they are relevant to the subject matter of this thesis.

2.3.2 Mechanical properties of wood-cement composites

Cement-bonded wood composite boards are claimed to be extremely versatile, with wider application than any other types of wood composite board products (Dix 1989). Their relatively low strength, however, limits them largely to non-structural siding and roofing applications (Karam and Gibson 1994, Oyagade et al. 1995, Xiong 1996, Wolfe and Gjinolli 1999). Another problem is that, from a civil engineering point of view, detailed information on mechanical properties of wood-cement composites is often restricted to experimental boards, and there is almost no information on the performance of full-sized boards in building applications over time (Karam and Gibson 1994). The lack of realistic data on the mechanical properties of different commercially available wood-cement composites greatly hampers their use in most structural applications (Karam and Gibson 1994, Wolfe and Gjinolli 1997).

Nevertheless a significant advantage of wood-cement composites for engineering applications is their ability to absorb and dissipate sound and mechanical energy (Wolfe and Gjinolli 1997, 1999). This has led to their widespread adoption as highway sound barriers (Wolf and Gjinolli 1999, Lan and Huang 2000, Boothby et al. 2001). Wood-cement composites can also be manufactured to exhibit a range of energy-dissipating properties advantageous in areas subject to seismic activity and/or heavy wind loads arising from hurricanes (Wolfe and Gjinolli 1997, 1999). For these
reasons, cement-bonded wood panels are used for building construction in Japan, where building codes place strong emphasis on the resistance of building materials to earthquakes and fires. In 1991 cement-bonded panels occupied a 41% share of the Japanese siding market (Kuroki et al. 1993, 1995). Good energy-dissipating properties have made composites such as WWCB well suited for house construction in countries such as the Philippines where hurricanes are frequent (Van Elten 1997). However, these properties do not necessarily translate into high impact strength; CBP is classed as 'fragile' with very low impact strength compared to solid timber boards or composites such as plywood (Aoki 1991). Nevertheless, cement- and other inorganic-bonded composite materials are receiving much attention in countries such as China (Zhang and Wang 1998), with innovative research into solving problems such as long press times and low flexural and impact strength in progress. Research has included examining the partial substitution of portland cement with fine siliceous pozzolanas such as fly ash (Lange et al. 1989, Sun et al. 1997), combining cement with MDI (heat-setting reactive isocyanate) resins (Bach and Kolker 1995, Eusebio et al. 1993, 1996), and even the impregnation of boards during pressing with the heat-activated copolymers styrene and acrylonitrile (Ilter 1997). Other (more practical) methods of improving board strength include simply adjusting the size and arrangement of the wood reinforcing elements in cement-bonded boards (Elmondorf 1963, Kayahara et al. 1979, Stahl et al. 1997, Cabangon et al. 2002a).

The density and flexural properties of a range of different wood-cement composites compared with those of some conventional wood composites are shown in Table 2.2.

<table>
<thead>
<tr>
<th>Panel Type</th>
<th>Density (kg/m³)</th>
<th>MOR (MPa)</th>
<th>MOE (GPa)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>WWCB (non-structural)</td>
<td>375 - 570</td>
<td>1.7 - 5.5</td>
<td>0.6 - 1.3</td>
<td>1</td>
</tr>
<tr>
<td>WWCB (structural)</td>
<td>650 - 750</td>
<td>7 - 15</td>
<td>1.8 - 2.7</td>
<td>2</td>
</tr>
<tr>
<td>WWCB (oriented)</td>
<td>700 - 800</td>
<td>17</td>
<td>4.0</td>
<td>2</td>
</tr>
<tr>
<td>Resin-bonded particleboard</td>
<td>750</td>
<td>11 - 16.5</td>
<td>1.7 - 2.8</td>
<td>3</td>
</tr>
<tr>
<td>Plywood</td>
<td>750</td>
<td>20 - 48</td>
<td>6.9 - 13.1</td>
<td>3</td>
</tr>
<tr>
<td>Oriented strand board (OSB)</td>
<td>750</td>
<td>47</td>
<td>8.3</td>
<td>3</td>
</tr>
<tr>
<td>Cement-bonded OSB</td>
<td>1000 - 1200</td>
<td>23 - 50</td>
<td>6.5 - 8</td>
<td>4, 5</td>
</tr>
<tr>
<td>Medium density fibreboard</td>
<td>640 - 800</td>
<td>24 - 34.5</td>
<td>2.4 - 3.4</td>
<td>3</td>
</tr>
<tr>
<td>Cement-bonded fibreboard</td>
<td>1200 - 1300</td>
<td>25</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>Cement-bonded particleboard</td>
<td>1250 - 1450</td>
<td>9 - 15</td>
<td>4.5</td>
<td>3, 4</td>
</tr>
</tbody>
</table>


It is important to note that the mechanical properties of medium-density WWCB (650-750 kg/m³) can be similar to those of resin-bonded particleboard, and that strand orientation can greatly improve the flexural properties of cement-bonded composite panels. WWCB with oriented wood
wool strands made using a cement:wood ratio of 1:1 can attain similar bending strength (MOR) to CBP which contains about 3.5 times the cement content of WWCB (Cabangon et al. 2002a).

Despite the restricted use of wood-cement composites to non-structural paneling applications, a few studies have sought to extend their application by clever design or artificial reinforcement to structural end uses. Fuji and Miyatake (1996, 1998a and b, 2000) describe a process to produce structural beams from multi-layered wood strands and cement. Small-diameter green stems are sliced using roller-shredders into strips that are aligned paralell, coated with cement and moulded to form beams. These are reportedly between 30 and 50% higher in bending strength and stiffness than the solid parent material, willow (*Salix ssp*) or Japanese cedar (*Cryptomeria japonica*). MOR of such beams is about 1050 kgf/cm² and MOE about 15000 kgf/cm².

Xiong (1996) developed a system for steel strip reinforcement of two-layered roofing components made from high-density 10-mm-thick cement-bonded wood flake board. This two-layer reinforced structure improved the tensile and bending strength of roof components, reduced creep deformation and enabled smaller, shallower components to be manufactured and used for roofing. The long-term load-carrying capacity of the roofing components was assessed over 3 years (Xiong 1998), and it was found that the safe load-bearing capacity of the components was about 50% of that of new roof components. The deterioration of the load-bearing properties of the wood-cement composite was attributed to increased brittleness due to creep and micro-cracking at the wood-cement interface. Long-term durability and strength retention in wood-cement composites is examined later (Section 2.3.4). Another study (Oyagade et al. 1995) found that it was possible to increase the flexural properties of CBP by 2 to 3 times by laminating the surfaces with 0.6-mm-thick wood veneer. Average MOR increased from ≈6 MPa for un laminated boards to ≈15 MPa for laminated boards.

Data compiled for different kinds of cement-bonded wood composite panels by Wolfe and Gjinolli (1997, 1999) indicate that panel stiffness is largely a function of density, as shown in Figure 2.3. Within the groups of low-density WWCBs and medium- to high-density CBPs, there is a good linear relationship between board density and bending strength; however, among high density fibre-reinforced cement boards, the relationship between product density and strength is not as clear. The experimental data from Wolf and Gjinolli (1997) showed that increases in board density did not result in improved strength of experimental laboratory-made CBPs made from wood wastes. This may have been due to the confounding effects of wood-cement compatibility, particle geometry and processing technique used to manufacture boards on the strength properties of the CBPs. Some of these questions are investigated further in Chapters 6 and 7 where laboratory-made CBPs from waste wood are assessed.
2.3.3 Fire resistance of wood-cement composites

Fire resistance is among the most important safety features of building materials, and wood-cement composites, especially the aggregate types, have been commonly referred to as being virtually incombustible (Deppe 1977, Stillinger and Wentworth 1977, Topf 1989a and b, Moslemi 1993, Ramirez-Coretti et al. 1998). The resistance of aggregate-cement composites such as CBP to fire is attributed to their low content of organic matter and the crystal water in the binder. The Combustibility, heat evolution and spread in, and the smoke and flame behaviour of, wood-cement composites is strongly correlated with their wood:cement ratio (Namioka 1976, Topf 1989b). CBP has been rated as being 'semi-noncombustible' (combustibility class 2) according to the Japanese Industrial Standard A 1321 (1970) (Namioka 1976). This classification is only given to composites with a cement:wood ratio above 2:1 and containing cement-setting accelerators (CaCl₂ or MgCl₂), which help reduce the combustibility of boards. CBP was also given a fire propagation index of class 0 (incombustible) in tests by Abdul-Rashid (1987).

Despite general claims of fire resistance of wood-cement composites, very few realistic in-house tests on fire behaviour of panels have been undertaken. One study by Knaublach (1973), who used a simulated 8-m square room lined with CBP found that, unlike resin-bonded wood composites (tested with and without fire retardants), the panels did not contribute to or exacerbate the combustion process or flame spread. The after-glow effects were negligible. Figure 2.4 illustrates the temperature propagation in different lining materials in a fire chimney exposed to fire. Note
that, unlike the resin-bonded particleboards (even when manufactured with a fire retardant), the CBP exhibits a similar temperature rise to that of the unlined fire-brick chimney.

Although these confirm the high resistance of wood-cement composites to flame spread and fire propagation, there are almost no studies which have actually tested the effect of high temperatures experienced in building fires on the subsequent strength of wood-cement composite materials. Work by Firmanti and Subiyanto (1998) exposed cylindrical moulds of wood particle-cement composite with a wood:cement ratio 1:2.75 to temperatures between 600°C and 1000°C for between 30 and 90 minutes. All heat treatments markedly reduced composite strength, the highest residual strength being only 5.3% of original strength after exposure of composites to 600°C for 30 min. Temperature, time of exposure and degree of consolidation of the composites significantly influenced their resistance to thermal degradation.

![Graph showing temperature-time curves](Figure 2.4 Average temperature-time curves for different types of wood-based wall linings in a fire chimney using 40 kg of spruce timber to supply primary fire load (from Knaublach 1973).)

Very little information of this type is available for any kind of WWCB, although manufacturers such as Heraklith GmbH (1963) and Eltoman (Anon 1998) claim the products to be 'fire-proof'. Some information about the inflammability, fire propagation and spread of flame for WWCBs has been provided by Hawkes and Robinson (1978a and b). Here, fire propagation indices calculated from the time-temperature charts generated by exposing materials to controlled sources of heat are listed for different panel types. Despite their relatively high wood content, WWCBs are reported to have very low fire propagation indices (7.9-11.5) compared with wood fibre internal insulating board (66.4), solid softwood (42.5), solid hardwood (34.9) and particleboard (36.3). WWCBs also performed well in ignitability tests where no ignition occurred when boards were subjected to a jet of flame of known flow and calorific value for 10 seconds.
2.3.4 Resistance to weathering and bio-deterioration

Wood-cement composites, including WWCB, are frequently referred to as being highly resistant to various forms of bio-deterioration (principally fungal and termite attack) which affect many other wood-based composites and solid wood (Pablo 1989, Moslemi 1989, 1993, Ramirez-Coretti et al. 1998). Certainly composites that contain a high cement content, such as CBP, have been shown to be 'resistant' or 'highly resistant' to stain, mould and both white and brown rot fungi compared to the solid parent wood materials (Goodell et al. 1997, Okino et al. 2002, Wong and Chee 2002). The long-term durability of WWCB has also been demonstrated in a study by Parameswaran and Broker (1979). They found that a 50-mm-thick WWCB insulating board that had been buried for more than 30 years showed only superficial deterioration by fungi. The surface 2-3 mm of the board showed decay attributable to both soft rot and basidiomycete attack, whereas the internal portion of the board showed no signs of fungal attack and no fungal hyphae penetrating into the board deeper than the first few mm.

Parameswaran et al. (1977) used scanning electron microscopy (SEM) to demonstrate that 'mineralisation' of the woody tissue in a wood-cement composite takes place over time, with the gradual penetration of minerals from the cement into the wood cell wall. Such minerals appear to impart better resistance to both decay and combustion (Cziesielski 1975, Dix 1989). Wood-cement board was rated as 'decay resistant' compared with other types of wood panels after exposure to decay fungi Coniophora puteana and Pleurotus ostreatus by Lea and Bravery (1986). Studies by Goodell et al. (1997), Souza et al. (1997), Wang and Takahashi (1997) and Okino et al. (2002) exposed CBPs for between 12 and 16 weeks in soil-block tests using a variety of species of white rot (Trametes versicolor, Tyromyces palustris and Coriolus versicolor) and brown rot fungi (Gloeophyllum trabeum and Postia placenta). Wood particles exposed on the board surfaces (despite the alkalinity) were degraded by the fungi, particularly white rot, but the interior portions of the boards were unaffected. Goodell et al. (1997) suggested that the high pH of cement in wood-cement composites inhibits decay by fungi, rather than wood mineralisation or the physical encrustation of wood elements by cement.

Although the above-mentioned studies found no visible evidence of internal fungal decay in wood-cement composites, they did not measure the possible effects of the fungi on board strength properties. There appear to be very few studies available on the effects of fungal attack on the strength properties of wood-cement composites, although an early study by Kunzelmann (1961) suggested that WWCB exposed to fungal attack over a long period of time could lose considerable bending strength. Wood-cement composites with lower cement content have been shown to be particularly susceptible to strength losses caused by decay (Lutomski 1985). Lutomski (1985) exposed cubes of WWCB with a cement:wood ratio of 1.25:1 to Serpula lacrymans, Coniophora
puteana or Poria placenta (on malt-agar or soil-peat medium) for 5 months. Maximum compressive strength loss was 29.8% after 5 months exposure to C. puteana on soil-peat media. Wang and Takahashi (1997) measured residual strength of CBP after decay tests. Despite minimal weight loss (<1.5%), CBP lost between 10 and 13% of its internal bond (IB) strength after exposure in a wet environment. This compared with weight losses of between 20 and 26% and IB strength losses of between 65 to 75% for resin-bonded OSB and medium density fiberboard (MDF) products exposed under the same conditions.

One crucial property required of wood and wood-based composites for use in tropical and subtropical regions of the world is resistance to termite attack. Commercially produced CBPs made from Malaysian rubberwood have been shown to be highly resistant to attack by subterranean termites (Coptotermes curvignathus) in a 4-week outdoor burial trial by Wong and Chee (2002), and to Reteticulitermes flavipes in 12-week jar tests (Souza et al. 1997). Factors that increase the risk of termite attack on cement-bonded composites include; high wood content, the presence of exposed wood and interconnected wood elements at board surfaces (Sukartama et al. 2002). WWCB panels fit this description but results of the few scientific studies on the resistance of WWCB to termite attack are contradictory. WWCB is often quoted as having very good resistance to termite attack, making it eminently suitable for use as a building material in tropical regions (Heraklith GmbH 1963, Kollmann 1963b, Pinion 1975, Van Elten 1997, 2000, Ramirez-Coretti et al. 1998). An unpublished study by Pablo (1989) in the Philippines subjected WWCBs made from pre-soaked wood wool to a local termite species (Macrotermes losbañosensis) and found the boards to have good resistance to attack. In contrast, Shukla (1977a) found that WWCBs manufactured from untreated mango (Mangifera indica L.) or Himalayan cedar (Cedrus deodara (D. Don.) G. Don. wood were severely attacked by the termite Odontotermes obesus after 6 months of exposure, and some attack had occurred after 1 month. In a follow-up study, Shukla et al. (1981a) manufactured WWCBs from west Himalayan fır (Abies pindrow Royle), chir pine (Pinus roxburghii Sarg.) and morinda spruce (Picea smithiana (Wallich.) Boiss), which had been treated with CCA or Copper Chrome Boron (CCB) in an attempt to increase the resistance of boards to termite attack. WWCBs containing CCA-treated wood showed good resistance to termite attack after 60 days exposure, while the CCB treatment was only moderately effective in preventing termite attack. Control boards containing untreated wood suffered severe degradation. These studies provide evidence to suggest that lower cement-content composites such as WWCB are not completely resistant to termite attack, and that preservative pre-treatment of the wood component may be required if WWCBs are to be used in termite-infested areas.
2.4 Wood wool cement board (WWCB): applications, manufacture and properties

2.4.1 WWCB as a suitable building material for use in developing countries

Wood in the form of wood wool imparts very good flexural properties to wood-cement composites without requiring a high cement:wood ratio (Kayahara et al. 1979). For example, using thin wood strands as reinforcement in structural WWCB requires less than half the cement content, lower mat compression and less specialised curing techniques compared with most other cement-bonded panels, including CBP and fibre-cement board, to achieve similar mechanical properties (Van Elten 2000).

Over the last 30 years, WWCBs have gained popularity in many tropical and sub-tropical countries including India (Shukla 1977a and b, Shukla et al. 1981a and b), Indonesia (Kamil 1970, Paribotro and Suwandi-Kliwon 1977), the Philippines (Pablo 1989, Pablo et al. 1996, Soriano et al. 1998, Cabangon et al. 1998, 2002, Eusebio et al. 2002a and b), Venezuela (Anon 1998), Honduras and Costa-Rica (Ramirez-Coretti et al. 1998), all of which face chronic and acute housing shortages. To establish a plant to manufacture structural medium-density WWCBs (1000 kg/m³) requires just 30-40% of the capital necessary to establish a CBP, fibre-cement or OSB plant (Van Elten 2000). The Dutch company Eltomation is establishing new high-capacity (40 000 m³/day), fully automated WWCB plants in Chile, Argentina and Brazil and Mexico for the manufacture of prefabricated housing kits (Anon 1998). The development of small-scale WWCB plants for the manufacture of building panels for low-cost housing is furthest advanced in the Philippines, where the Forest Products Research and Development Institute (FPRDI) has successfully developed simple technologies to manufacture WWCB from indigenous and tropical plantation species (Pablo 1989, Bello et al. 1995, Pablo et al. 1996, Pablo and Cabangon 1997). Fifteen privately funded WWCB manufacturing plants have been established since 1984 (Bello et al. 1995, Pablo et al. 1996). A wealth of experience in manufacturing WWCBs and using the boards in housing construction in the Philippines has been acquired in recent years (Pablo 1995).

Houses constructed from medium-density WWCB in the Philippines use medium- and high-density WWCB in the walls, floors, doors and certain furniture units, and for roof shingles (Pablo et al. 1996). Boards are frequently plastered, tiled or coated after construction to enhance their strength, durability and dimensional stability (Eusebio et al. 1989). Frames often consist of concrete beams in each corner interspersed with wooden battens to which the WWCBs are fastened using nails, as shown in Plates 2.1 (a) and (b). Such houses have been able to withstand wind speeds of 250 km/h during hurricanes (Van Elten 1997). Medium- and high-density WWCB are also used for the manufacture of prefabricated transportable fold-out emergency shelter units in the Philippines (Soriano et al. 2002). Plates 2.2 show new houses in Brazil and the Philippines constructed using wood or concrete framing and WWCB panels for walls.
Plates 2.1 Housing construction using WWCB panels in the Philippines showing (a) house construction and (b) nailing of panels into wooden frame.

Plates 2.2 Rendered houses built from WWCB in (a) Brazil and (b) Philippines.

WWCB is particularly suitable for building construction in developing countries for a variety of reasons. WWCB is manufactured using wood, cement and water; materials that are relatively inexpensive and usually readily available in most tropical and sub-tropical countries. Among the different wood-cement composites, WWCB requires the lowest cement:wood ratio (1-1.5:1 as compared with 2.5 or 3:1 for CBP). This reduces the cost of the boards, since cement is the most expensive major component of wood-cement composites (Moslemi 1989). Although WWCB fabrication can be largely automated in industrialised countries, the process is quite simple and good quality boards can be manufactured using small, local-scale facilities that are labour- rather than capital-intensive (Simatupang et al. 1977, van Elten 1997). The capital cost of establishing a
WWCB plant compares very well with that required to establish most other kinds of wood processing plants such as sawmills, plywood mills and particleboard mills, as shown in Table 2.3.

Table 2.3 Log requirements and capital costs of different types of wood processing plants.

<table>
<thead>
<tr>
<th>Processing plant</th>
<th>Minimum log input (m³/yr)</th>
<th>Capital cost of plant ($US)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WWCB</td>
<td>900</td>
<td>100 000</td>
</tr>
<tr>
<td>Sawmill</td>
<td>20 000</td>
<td>2 000 000</td>
</tr>
<tr>
<td>Plywood</td>
<td>50 000</td>
<td>4 000 000</td>
</tr>
<tr>
<td>Particleboard</td>
<td>100 000</td>
<td>80 000 000</td>
</tr>
<tr>
<td>Medium Density Fibreboard</td>
<td>150 000</td>
<td>100-200 000 000</td>
</tr>
<tr>
<td>Kraft pulp mill</td>
<td>1 000 000</td>
<td>1 000 000 000</td>
</tr>
</tbody>
</table>

(from Anon 1995).

WWCB has generated potential interest in Australia as well. In addition to the factory manufacturing WWCB in Bendigo, Victoria, a Canberra-based engineering firm, Decoin Engineering, is testing a range of wall panel types, including 50-mm WWCB, cement-bonded fibreboard cladding, plywood, weatherboards, log off-cuts and corrugated iron, in a small low-cost prototype dwelling designed for hot, dry Australian conditions. All external panel types consist of three layers with an internal plastic-cell insulating sheet and a gyprock™ interior wall, except for the WWCB which has no insulative backing, and were left either left uncoated, cement-rendered or painted. The WWCBs appear to provide the greatest heat-insulating capacity at minimal cost and assembly time (Stodulka, A. pers. comm. 2000).

2.4.2 Manufacturing WWCBs

WWCB manufacturing around the world ranges from large-scale fully automated production lines such as those installed by Van Elten Engineering and Logistics Ltd to small-scale labour-intensive facilities found in the Philippines. Wood:cement ratios used to manufacture WWCB vary considerably, depending on the target density of the boards and where they are made. The low-density, less compressed insulating boards made in the UK and USA typically use 1 part wood to 2 parts cement (Pinion 1975, Simatupang et al. 1977, Lee 1985, Lee and Hse 1993), whereas in Germany cement content is slightly lower, at 1 part wood to 1.5-1.8 parts cement (Kollman 1963a). A wood:cement ratio of 1:2 is recommended for the manufacture of WWCB from most Indonesian wood species (Kamil and Suwandi-Kliwon 1974, Kamil and Ginoga 1975).

In a typical automated production line the wood wool is produced by a battery of billet-shredding units and fed by a conveyor through a water bath. The wet wood wool is then roller-pressed to remove excess water and deposited into a rotating mixing drum where enough wood wool to form one mat is mixed with dry cement powder and accelerator (if used). The cement-coated wood wool is then metered onto moving trays, cut into individual mats and the trays stacked...
on top of one another. The stack of trays is pressed for 24 hours, the boards de-moulded and stacked indoors to cure for about 20 days prior to shipment. This automated process is illustrated and described in further detail in Chapter 7 in a study of the utilisation of eucalypt wood for low-density WWCB.

In contrast, the more heavily compressed WWCBs manufactured in the Philippines for wall, floor and roof panelling employ a higher wood: cement ratio (Pablo 1989, Soriano et al. 1997). For example, Zamboard Enterprises use a wood: cement ratio of 1:1.5. A ratio of 1:1.2 is recommended by Pablo (1989) for manufacturing boards with a density greater than 400 kg/m$^3$. A wood: cement ratio of 1:1 may be used if the wood wool is pre-soaked prior to manufacture and cement-setting accelerators are used (Soriano et al. 1997). However higher wood: cement ratios lead to increased thickness swelling and water absorption of boards (Pablo and Cabangon 1997).

In contrast to the automated processes used to manufacture lightweight insulation panels in Europe and the USA, most stages of WWCB manufacture in the Philippines, including debarking of logs, mixing of cement and wood, mat forming and stacking, and subsequent board handling, are done by hand (Pablo et al. 1996, Cabangon 1998 pers. comm.). The fast-growing tropical hardwoods Molucca albizia (Paraserianthes falcatoria L. Neilsen), gmelina or white teak (Gmelina arborea Roxb.) and giant ipil-ipil (Leucaena leucocephala (Lam.) de Wit.) are currently used for the manufacture of WWCB in the Philippines (Eusebio et al. 1998b). A schematic diagram showing the steps involved in the manufacture of WWCB in the Philippines is shown in Figure 2.5 and photographs of the process are reproduced in Plates 2.3 (a) to (f). This manual production process can be readily repeated in the laboratory for the purposes of manufacturing and testing WWCBs, as described in Chapter 10.

WWCB is not only economical in terms of cement use, but wood costs can also be minimised by using small-diameter pulp wood. Approximately 1 m$^3$ of wood will produce around 3 m$^3$ of porous WWCB (Heraklith GmbH 1963). Although WWCB can be produced from wood that is unsuitable for sawn timber or plywood, certain log and wood quality requirements are necessary to facilitate the production of good-quality wood wool (Wacker 1960, Chittenden 1972). These include the absence of large knots, reaction wood and decay, which will result in wood wool that is brittle and highly fragmented. Specifications for billets used for WWCB manufacture in the Philippines include a diameter range of 12 to 58 cm, and logs which are bent or contain knots greater than about 5 cm in diameter and/or exposed branches are not acceptable. High levels of silica in certain woods will blunt and damage shredding knives, and wood species of high density require greater energy to shred into wood wool. The ease of shredding of billets into wood wool can also be affected by the presence of interlocking grain which is reported to be a problem in fast-grown plantation species
including *P. falcatoria*, *L. leucocephala* and red mahogany (*Eucalyptus pellita* F. Muell.) (Cabangon, R. 2000 pers. comm.).

Plates 2.3 Partially manual manufacturing of WWCB in the Philippines showing (a) shredding billets and collecting wood wool, (b) pre-soaking wood wool and spreading out to dry, (c) collecting cement-coated wood wool from mixing drum, (d) mat forming by hand using forming boxes, (e) pressing, and (f) outdoor drying and curing for approx. 3 weeks (from FPRDI and Evans, P. 2000 pers. comm.)
Light-coloured woods including spruce, fir and, to a lesser extent, the light hardwoods willow and poplar have traditionally been the species of choice for the manufacture of WWCB in Central Europe. Such species do not greatly inhibit the setting of cement and are easy to shred, producing good quality wood wool (Heraklith GmbH 1963, Kollmann 1963a). *G. arborea* is currently favoured for the manufacture of WWCB in the Philippines because it is readily available in plantations and is easy to convert into wood wool (Eusebio *et al.* 2002a). Its wood wool, however, requires soaking in water at ambient temperature for 24 h to remove sugars and starches from the freshly-prepared wood that inhibit the setting of cement. The use of other readily available Philippines hardwoods for the manufacture of WWCB is under investigation (Pablo 1989, 1996). Fast-growing plantation eucalypt and acacia species in the Philippines may also be suitable (Soriano *et al.* 1997, Cabangon *et al.* 2002, Eusebio *et al.* 2002a and b), and are examined further in this thesis.

### 2.4.4 Properties of WWCBs

As mentioned above, WWCBs make excellent building materials for use in different countries and climates because of their unique features compared with other wood-based composites. An overview of the properties of both structural and non-structural WWCB is given below.

**Density and thickness:** WWCB is lightest of the cement-bonded wood composite family. Panels can be made thick enough to provide the bulk of bricks without the weight and time-consuming
construction (Pinion 1975). Highly porous low-density (375-570 kg/m$^3$) non-structural (non-load-bearing) wood wool boards are traditionally the most common type of WWCB produced in Europe, principally because of their good thermal and sound insulating properties (Heraklith GmbH 1963, Kollmann 1963b). Such WWCBs are manufactured in thicknesses ranging from 15 to 100 mm, with 25 to 50 mm being the most common (Kollmann 1963a). They are commonly used for sound insulation in factories subject to high levels of machine noise (Kuroki et al. 1997). Because these boards are made in moulds with rigid sides, which determine the final thickness, lateral compression during pressing results in denser material at the edges (Pinion 1975). Porous WWCBs are commonly used as insulation for exposed concrete beams, pillars and floors, and as wall fillers (Van Elten 2000).

WWCBs manufactured for structural purposes are more highly compressed, denser (>600 kg/m$^3$) and less porous. For example, products known as ‘medium-density WWCB’ manufactured at Zamboard Enterprises in Zamboanga, Philippines, vary in density from 650 to 750 kg/m$^3$ for boards 0.65 m x 2.5 m in area and 6 mm to 50 mm in thickness. In contrast to low-density WWCB, this type of board is not pressed in moulds but in stacks, with the final products edge-trimmed to size. Low-density, non-structural WWCB is referred to in Britain as Type 'A', whilst the higher density, structural WWCB is known as Type 'B' (Pinion 1975). For comparison, CBPs range in density from about 1000 to 1400 kg/m$^3$.

A third type of WWCB has a density ≥900 kg/m$^3$, which is within the range of CBPs, and is characterised by the smooth surface and high cement content more commonly found in CBP (Simatupang et al. 1977). These boards are heavily compressed with a very dense internal structure, and their applications and properties are similar to those offered by CBP. Hence, this type of WWCB has not assumed an important place in the market for wood-cement composites. This is surprising, since as this Review and following chapters of this thesis show, wood-cement composites containing long strands can have much greater flexural properties and impact strength than composites containing small, discreet particles at a given density and cement content.

**Strength:** Standard specifications for bending strength of WWCB products vary somewhat between countries, as do the testing methods and measurement units. The minimum strength requirement of the low-density, non-structural Type 'A' board according to the British Standard BS 1105 (1981) is to support a static load of 1.0 kN at a span of 450 mm in the air-dry condition. In the case of Type 'B' boards, the minimum requirement is to be able to support a static load of 2.2 kN at a span of 600 mm after soaking in water for 2 hours and draining for 1 hour. The minimum strength properties required by the Philippines National Standard PNS/CTP 07 (1990) for WWCB panels for low-cost housing construction are outlined in Table 2.4 and are based closely on the guidelines set out in Japanese Industrial Standard JIS-A 5404 (1979). As board thickness increases, minimum
load-bearing capacity required by the boards increases greatly. For solid wall and flooring elements 50-mm-thick boards are used while thinner boards are used for non-structural siding and roofing. 8-mm board is used as an internal wall or roof liner. The mechanical properties of WWCB manufactured at the Philippines’ largest manufacturing plant, Zamboard Enterprises in Mindanao, are shown in Table 2.5.

Table 2.4 WWCB minimum mechanical properties PNS/CTP 07 (1990).

<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>Min. Specific Gravity</th>
<th>MOR (N/mm)</th>
<th>Max. Deflection (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.65</td>
<td>150.0</td>
<td>14</td>
</tr>
<tr>
<td>12</td>
<td>0.60</td>
<td>180.0</td>
<td>11</td>
</tr>
<tr>
<td>20</td>
<td>0.55</td>
<td>390.0</td>
<td>9</td>
</tr>
<tr>
<td>30</td>
<td>0.50</td>
<td>635.0</td>
<td>7</td>
</tr>
<tr>
<td>50</td>
<td>0.45</td>
<td>1570.0</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 2.5 Physical and mechanical properties of WWCB manufactured at Zamboard Enterprises, Zamboanga, Philippines.

<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>Density (kg/m³)</th>
<th>MOR (MPa)</th>
<th>24-h thickness swell (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>850</td>
<td>8.3</td>
<td>2.3</td>
</tr>
<tr>
<td>12</td>
<td>800</td>
<td>6.0</td>
<td>2.2</td>
</tr>
<tr>
<td>19</td>
<td>750</td>
<td>5.2</td>
<td>1.9</td>
</tr>
<tr>
<td>20</td>
<td>700</td>
<td>4.8</td>
<td>2</td>
</tr>
</tbody>
</table>

Heat and sound insulation: WWCB has very useful thermal insulation and acoustic absorption and insulating properties, which vary according to the thickness and density of the boards (Kollmann 1963b, Pinion 1975). Thermal conductivity of WWCB is around 0.1 W/m.K (Pinion 1975, Hawkes and Robinson 1978a), which is about a third to a half of the thermal conductivity of materials used specifically for heat insulation purposes, such as roof and wall batts. The thermal conductivity of WWCB can be increased by reducing the pore volume through greater compression of the mat during board manufacture (Lee 1985). The intrinsic thermal and acoustic insulating properties of WWCB boards make them ideal for internal roof lining, with or without supplementary insulating batts (De Wit 1995).

A very important basic property of WWCB is its absorption and dissipation of sound (Kollmann 1963b). Its effectiveness is particularly good for high-frequency noise (Pinion 1975). However, as data from Kollmann (1963b) show, the absorption capacity of low-density WWCB drops markedly in the range 1000 to 2000 Hz. Typical sound absorption coefficients for 50-mm-thick boards range from 0.1 at 125 Hz to 0.75 at 4000 Hz. WWCB is therefore a very useful sound absorption and dissipation panel for use in indoor areas subject to high-frequency noise, especially factories and machine workshops, and halls and restaurants catering for large numbers of people. The acoustics of large rooms with high ceilings, such as gymnasiums, concert halls and churches, are greatly improved by panelling with WWCB to reduce sound reverberation (Kollmann 1963b).
2.5 Cement-bonded particleboard (CBP): applications, manufacture and properties

2.5.1 Applications of CBPs

Despite their high weight:strength ratio, CBPs have become popular, particularly in Europe and Asia, for use in exterior siding, roofing and flooring applications for a variety of reasons. These mainly include increasingly stringent building design regulations for fire, and the need for high resistance to decay and insect attack (Simatupang and Geimer 1991, Kuroki et al. 1995, Wentworth 1997). CBP is particularly well suited to tropical climates where fire, biodeterioration and weathering are more severe (Deppe 1977, Fraser 1977, Kulikov et al. 1983, Schwarz 1989, Wentworth 1997). Non-structural external applications for CBP include agricultural buildings, prefabricated and mobile buildings, flat roofing, industrial and exterior domestic cladding, tunnel linings, highway sound barriers, fire-barriers and paving tiles (Eltomation Engineering and Logistics N.D.).

The manufacture and use of CBPs for domestic dwellings is probably furthest advanced in Russia and Western Europe and Japan. Japanese manufacturers use sophisticated surface embossing and painting techniques to give stone, brick or solid wood-grain finishes to modular exterior CBP cladding (Frick 1989, Kuroki et al. 1995, 1997). An example of surface-embossed and painted CBP external cladding used in a house in Japan is shown in Plate 2.4. In recent years, the manufacture and utilisation of CBP in housing construction has grown in countries such as Mexico where there is a ready market for mass-produced low-cost 'fold-out' kit homes (Solorzano 1989, Buys 1989, 1995). CBP is superior to resin-bonded particleboard in compression, but it must not be used in any structural application which may involve bending, for example book-shelves, where there is the risk of even short-term overload (Kovalchuk et al. 1988).

Plate 2.4 Embossed and painted CBP in domestic housing in Japan (from Kuroki et al. 1995).
2.5.2 Manufacturing CBPs

By the mid-1990s, some 33 CBP plants were in operation worldwide (Pease 1994), with some 20 plants in Russia alone (Van Elten 2000). CBP differs from WWCB in that wood particles are incorporated into a monolithic cement matrix (Wolf and Gjinolli 1997). CBP is generally manufactured in highly automated, process-controlled factories and has a relatively long manufacturing cycle compared to that required to produce resin-bonded particleboards. CBP is usually manufactured using 60% cement, 20% wood and 20% water accompanied by cement-setting accelerators to form a relatively dry furnish which must be pressed, cured and conditioned prior to shipping (Pease 1994). CBP may also be manufactured in smaller scale, labour-intensive plants (Bison-Werke 1976); however unlike WWCB, no current examples of such a process have been found. A schematic diagram of the conventional production process for CBP is shown in Figure 2.6, illustrating the relatively complex plant layout.

The basic process used to manufacture CBP, which has some similarities to conventional particleboard manufacture, particularly in flaking and mat-forming techniques, is summarised from descriptions in Dix (1989), Frick (1989), Anthony and Seymour-Walker (1989) and Solorzano (1989). Pre-seasoned wood (usually softwood) is reduced to particles using flakers and hammer mills, and the particles are then screened into two or more size fractions. The strength properties of CBP are reported to arise from the use of flakes measuring 25 - 35 mm in length and 0.2 - 0.3 mm in thickness (Pease 1994). Metered doses of flakes, cement and chemical additive are mixed using a counter-current mixer and the mat is distributed onto metal caul plates on a continuous conveyor system. Mats are composed of coarse particles in the core and fine particles in the surface layers, and modern mat-forming techniques similar to those used in the manufacture of resin-bonded particleboards ensure the required distribution of particles within the mats. Mats are continuously monitored for thickness, density and moisture content, and below-standard mats are rejected and recycled. Individual caul plates are then stacked in a specially designed cradle and pre-pressed (up to 30 kPa/cm²) for about 5 minutes. The mats are kept under compression in the cradle, which is removed from the press and transferred to a long chamber for heat curing. Cradles containing mats travel at slow speed through the chamber for 5 to 10 h depending on the curing temperature used. In a slightly heated, well insulated chamber, the heat of hydration generated within a large stack of mats keeps the chamber at temperatures of between 80 and 100°C. After curing, the cradle is returned to the press for declamping and removal of boards for curing.

The travel pattern of caul plates, stacks of mats and cradles before and after curing is necessarily complex and requires intelligent plant design to avoid delays in production (Anthony and Seymour-Walker 1989). Boards are then stacked in a warehouse for about 14 days allowing further curing at ambient temperature. After this they are dried and 'equalised' in a warm, humid chamber to between
9 and 12% MC. The process of manufacturing CBP is largely process controlled and is therefore much more difficult to replicate under laboratory conditions than the manufacture of WWCB. The trial manufacture of CBPs from eucalypt and pine species is covered in Chapters 6 and 7 of this thesis.

Figure 2.6 Schematic diagram of plant layout of a CBP plant (from Anthony and Seymour-Walker 1989)

High board density, wood-species specificity and slower setting of cement binder have traditionally favoured the manufacture of CBP on a smaller-scale (<200 m² per day), approximately one fifth the capacity of most resin-bonded particleboard or MDF plants (Pease 1994). This makes CBPs twice to three times as expensive as resin-bonded particleboard in the US (Moslemi 1989, 1993). Hence research in recent years has focussed on reducing the manufacturing cost of CBP by lowering the pressing and curing times while at the same time improving strength properties. Strategies attracting considerable attention include: CO₂-injection pressing (Lahtinen 1991, Simatupang et al. 1991 and 1995, Geimer et al. 1993, Hsu 1993, Simatupang and Habighorst 1993, Yin et al. 1999); supercritical CO₂ pressing (Hermawan et al. 2000, Suh et al. 2000); and the use of
high-temperature pressing and curing (Osinski and Potter 1997, Kats 2001). Additives and cement supplements are also widely used to accelerate pressing and curing times (Schmidt 1988, Aho 1989, Lange et al. 1989, Eusebio et al. 1995, Nagadomi et al. 1996 a-c, Kuroki et al. 1995 and 1997). Some of these techniques are discussed briefly in Section 2.7.

2.5.3 Properties of CBPs

Density and thickness: CBPs are manufactured to a wide range of thicknesses (4 to 40 mm (Eltomation Engineering and Logistics N.D.). Density of standard 12-mm CBP ranges from 1250 to 1450 kg/m$^3$ (Dix 1989, Moslemi 1989, Wolfe and Ginolli 1997). Strength properties (MOR, MOE and IB) of particulate-cement composites are strongly and positively correlated with board density (Sorfa 1984, Badejo 1988, Dinwoodie and Paxton 1989, Fuwape 1995). The high density-to-strength ratio of CBP significantly lowers its attractiveness as a commercial building material, reducing ease of handling, cutting, nailing and transport (Aoki 1991, Zhou and Kamdem 2002), and greatly increasing wear on cutting tools (Darmawan et al. 2001). Also, unlike WWCB, CBP has poor heat-insulating properties, with a heat conduction of 1.3 kcal/m/H$^\circ$C compared to 0.11 kcal/m/H$^\circ$C for WWCB or solid timber (Aoki 1991). Despite this, there are few studies that have attempted to reduce board density while maintaining or improving the elastic and mechanical properties. Strategies that have received some attention include the use of wood and flake types that reduce the overall cement requirement, and the use of foaming agents in the board core (Deppe 1977). A novel system for manufacturing dimensionally stable, light-weight (about 800 kg/m$^3$) CBP made using a combination of coarsely macerated wood fibre, lightweight bulky perlite plus silica has been developed in Japan (Kuroki et al. 1993). Charcoal has also been tested as a lightweight filler in boards (Peng et al. 2000, Bao et al. 2001); however, this appears to result in decreased board flexural properties and resistance to water.

Strength: The bending strength (MOR) of CBPs made to 12 mm thickness is between 9 and 15 MPa (Table 2.2). Despite its high density, the MOR of CBP is generally within the lower range of MOR values exhibited by resin-bonded particleboard; however its stiffness (MOE) is higher (Moslemi 1989). CBP has similar strength properties to medium-density resin-bonded particleboard or medium-density WWCB (~750 kg/m$^3$) of the same thickness, but at the expense of significantly higher board density (almost twice that of conventional particleboard). To compensate, creep deflection in CBPs is significantly lower than that of virtually all other conventional resin-bonded wood panels, including plywood (Dinwoodie and Paxton 1989).

The MOR and MOE of CBPs are significantly affected by flake length and thickness (aspect ratio), and board density, as are resin-bonded particleboards (Iida et al. 1983, Badejo 1988,
Moslemi 1989). Badejo 1988 found that MOR and MOE of CBPs manufactured from pre-treated mixed tropical hardwood flakes showed a significant linear increase with increasing flake length (12.5-37.5 mm) and board density (1050-1200 kg/m³), and significant linear decrease with increasing flake thickness (0.25-0.5 mm). Maximum MOR and MOE of 11.2 MPa and 4800 MPa, respectively, were attained by using 37.5 x 0.25 mm flakes at a board density of 1200 kg/m³. The use of small particles was found to improve the internal bond strength (IB) of cement-bonded composites compared to large elements, but adversely affected flexural properties (Olorunnisola and Adefisan 2002). So contrary to conventional mat structure, the authors suggested that smaller particles should be restricted to the core of panels.

2.6 Challenges associated with the use of wood-cement composites

2.6.1 Creep and deterioration

Portland cement is a good weather-resistant binder for wood-cement composites, including WWCB, giving boards greater resistance to weathering than resin-bonded wood composites (Pinion 1975, Sekino and Suzuki 2002). However, WWCB when used in unsupported ceilings, tends to undergo time-dependent deformation known as 'creep' (Chittenden 1972, Cabangon, R. 2000 pers. comm.). Other cement-bonded composites such as CBP may also creep, especially when subjected to high temperatures and humidities. However, as mentioned above, the high cement content and higher ratio of MOE to MOR make CBP less susceptible to creep than most resin-bonded boards (Kondrup 1990). In the case of WWCB, Chittenden (1972) stressed the importance of overcoming the problem of creep in order to produce WWCBs that are suitable for roofing materials in the tropics and in place of more expensive corrugated iron or fibro-cement (asbestos-cement) sheets.

There were attempts in Europe in the 1930s to improve the rigidity of WWCBs by incorporating a lattice of wooden sticks in the mat (Kollmann 1963b), but this was soon abandoned because of the extra complexity and expense of the manufacturing process as well as the reduced fire resistance of boards containing wooden sticks.

There appear to be no current examples of the use of physical reinforcement mechanisms to improve the load-bearing capacity and creep properties of WWCB, with the exception of the use of steel strips to reinforce wood-cement boards used in roofing applications in China (Xiong 1996). The load-bearing capacity of these thin panels, which were pressed into ribbed structures resembling corrugated iron, was compromised by the low tensile strength of the rib undersurface. Glueing steel strips to the rib undersurfaces greatly improved the flexural properties of the roofing elements (Xiong 1996), enabling them to withstand long-term loading (Xiong 1998). The adhesive for the strips, which consisted of a thick glue made up from unsaturated polyester and silicon powder, provided an adequate physical barrier between the cement and the steel, thereby preventing
corrosion of the strips. The idea of incorporating internal reinforcing lattice made from wood, rattan or bamboo into WWCB to improve its rigidity would be worth examining as a possible solution to the problem of creep of WWCB in the tropics.

Recent research shows that manual orientation of strands during mat formation can significantly improve the flexural and creep properties of WWCBs (Cabangon et al. 2002). The flexural properties (MOR and MOE) of medium density WWCBs made from P. radiata were increased by almost 100% by orienting strands in the surface and core layers of the mats so that they run perpendicular to each other.

Another issue affecting the strength and long-term durability of wood-cement composites is the chemical deterioration of the wood elements over time due to prolonged exposure to the alkaline environment of cement. Damage to wood strands, particles or fibres by alkali is exacerbated by higher temperature and humidity, and can have implications for the use of panels in structural applications (Heraklith GmbH 1963, Pinion 1975, Lempfer and Sattler 1989, Moslemi et al. 1995, Youngquist 1999, Cooke, T. 2001 pers. comm.). A study by Lhoneux et al. (1991) demonstrated that autoclaving wood fibers (both hardwood and softwood) in an alkaline environment results in significant loss of tensile strength (up to 40%) as a result of de-polymerisation of cellulose. Research by Dewitz et al. (1984) found that agents that degrade wood (i.e. alkali and sulphates) can penetrate more than 40 mm longitudinally and 20 mm radially into solid wood blocks from a zone of adjacent cement paste, with greater penetration in drier wood and if a wetter cement mix was used. Cellulose fibres undergo the greatest rate of depolymerisation within the first hour of exposure to alkali and the other constituents of a cement solution (Kühne and Thiele 1986). It has been suggested that the alkalinity of the cement that encrusts the wood elements may also lead to the gradual degradation of lignin and formation of acidic substances, which may reduce the tensile strength of the wood reinforcement causing increased brittleness of WWCBs over time (Heraklith GmbH 1963, Fraser 1977).

Despite these effects, products such as CBP are reputed to have a long service life, retaining and even increasing in strength over time when exposed outside. Boards exposed outdoors to temperatures ranging from -55°C to 55°C in the Moscow region over 12 years retained a high average bending strength of 16 MPa (Sergeev et al. 1995). CBPs coated with a polyurethane-alkyd resin suffered no decrease in mechanical properties after outdoor exposure in Berlin for 12 years, whereas similarly exposed uncoated boards lost about 50% of their initial strength (Deppe and Schmidt 1986). The strength properties of CBPs usually increase with time, depending on storage conditions (Dinwoodie and Paxton 1989). These authors found that the strength of boards stored for 8 years at 20°C and 65% r.h. was 12% greater than their initial strength (4 months after manufacture). A controlled outdoor weathering test of CBPs in Britain over 10 years showed that
their strength properties increased by about 45% over the first 3 to 5 years but then declined by about the same amount over the next 5 to 7 years (Dinwoodie and Paxton 1989). This was thought to be caused by the deterioration and erosion of the wood and portland cement in the surface layers, which was further exacerbated by the growth of lichens on board surfaces.

Enhanced strength of wood-cement composites with ageing has been observed and attributed to the ‘mineralisation’ or ‘petrification’ of the wood elements by cement minerals (Bentur and Ackers 1989). The ‘mineralisation’ of wood elements was studied in the case of aged WWCB using electron microscopy by Parameswaran et al. (1977). However the ageing of wood-cement composites has been most comprehensively studied in relation to wood fibre-cement sheets. Accelerated ageing of such products leads to a significant loss of strength due to rapid fibre damage and de-bonding (Bentur and Ackers 1989), but with long-term natural ageing the deposition of hydration products in the lumens of wood fibres improves stiffness, which more than compensates for the initial strength losses of the fibres. In addition, the densification of the matrix at the wood-cement interface over time enhances the bond strength between the wood and cement.

The presence of organic acids (such as acetic and tannic acids) in woods is believed to be a major cause of deterioration of strength of wood-cement composites over time (Fraser 1977, Blankenhorn et al. 1994). According Heraklith GmbH (1963), this problem does not occur with magnesite binders because of the low alkalinity of the binder. Pinion (1975) noted instances of failure in enclosed roofing elements made of WWCB exposed to high temperatures, due to alkaline degradation of the wood components; however it was suggested that pre-weathering of boards, allowing carbonation of the cement and reduction in alkalinity, would overcome such problems. Other successful strategies for reducing the deterioration of the lignocellulosic component of wood-cement composites include: pre-soaking of wood to remove unstable, acidic constituents; accelerated curing using CO₂ and/or heat; the use of fortifiers such as calcium carbonate and sodium silicate; low alkalinity binders and siliceous natural pozzolanas, such as volcanic ash, fly ash and rice hull ash (Geimer et al. 1993, Moslemi et al. 1995, Youngquist 1999).

The danger of damage caused by elevated temperatures during initial setting and curing of cement is also relevant (Pinion 1975, Simatupang et al. 1977, Flynn and Hawkes 1980). A compounding effect of heat of hydration can occur when freshly pressed WWCB boards are piled in contact with each other in large stacks. To overcome this, stacking of individual boards between stickers is recommended to allow air circulation. However, the curing environment should not dry the boards too quickly as this will reduce the water available for subsequent hydration and strength development during curing (Simatupang et al. 1977).

It can be concluded from the above discussion that there is debate over whether wood-cement composites actually gain or lose strength over time, and there are insufficient long-term studies on
many wood-cement composites, including WWCB, to make conclusive statements about their long-term strength and durability.

2.6.2 Dimensional stability

Wood-cement composites, especially those with higher cement content such as CBP, undergo dimensional change after manufacture, largely as a result of water transfer between the composite and the atmosphere during curing (Fuwape 1992, Mougel et al. 1995, Fan 1997, Fan et al. 1999a and b). Dimensional change or ‘springback’ from the nominal pressed thickness of CBPs can be as high as 25% (Oyagade 1990). This author showed that dimensional change was higher in boards of higher density at any given cement:wood ratio and was further exacerbated by lower cement:wood ratio. Work by Fuwape (1992) showed that moisture-induced dimensional change can be reduced in denser CBPs by increasing the cement content of the composite. It is important to place such findings in perspective with the dimensional changes of other commercial wood composite panels. Samek (1978) exposed a range of commercial resin-bonded particleboards, plywoods, hardboard and CBP to humidity cycling (5 cycles) between 27% and 97% r.h. and measured total and irreversible thickness swelling. CBP showed the lowest dimensional change. Data in Dinwoodie and Paxton (1989) also shows that CBP is more dimensionally stable than resin-bonded particleboard.

The dimensional instability (3-5mm/m) of fibre and particulate wood-cement composites with fluctuating humidity conditions can be effectively reduced by autoclaving, a longer period of stabilisation after manufacture and/or the use of additives (Mougel et al. 1995). The high level of water addition required for wood-cement composites compared to mineral-aggregate concretes results in greater water transfer and evaporation during cement setting and hardening, which leads to a brittle matrix with a propensity to develop surface cracks (Mougel et al. 1995). The problem of cracking of CBP in dry or fluctuating humidity environments has been suggested to be a significant deterrent to their manufacture, and to the use of non-autoclaved wood-cement composites in general in Australia, (Cooke, T. pers. comm. 2001). However, Buys (1995) suggests that in practice the influence of fluctuating humidity and shrinkage of CBP in homes is almost negligible if the design specifications of the dwellings containing CBPs are correct. The effects of high humidity or rainfall on CBP can also be overcome by the application of film-forming surface finishes to exposed panel surfaces (Ahmad-Shakri and Sudin 1989).

Carbonation of the portland cement binder over time is also a contributing factor to the dimensional instability of CBP (Sandermann 1973, Broker and Simatupang 1974a, Fan et al. 1999a and b). Carbonation of portland cement is a slow process involving a complex series of reactions between water, cement hydrates and atmospheric CO₂ that diffuses in through the porous matrix,
resulting in gradual shrinkage and deterioration of the cement matrix (Verbeck 1958, Parrott 1987, Saetta et al. 1993). Work by Fan (1997) and Fan et al. (1999a and b) showed that the inclusion of wood particles facilitated accelerated carbonation and irreversible shrinkage of the wood-cement composite. Carbonation is exacerbated by atmospheric moisture and the contribution of water from wood particles. Periodic wetting of the composite surface, however, significantly reduces the rate of carbonation by reducing the permeability of the cement matrix to CO₂ from the atmosphere.

In contrast, WWCB appears to be less susceptible to the above-mentioned problems. It has been found to possess good dimensional stability compared to solid wood and other kinds of wood-based composites, especially in terms of thickness swelling (Pinion 1975, Lee 1984). Shukla et al. (1981b) undertook a detailed study of the dimensional stability of WWCBs made from species mentioned earlier; west Himalayan fir, Morinda spruce, chir pine and Himalayan white pine (Pinus wallichiana Jackson) manufactured to densities of between 400 and 450 kg/m³. Boards were assessed for shrinkage after the relative humidity (r.h) was reduced from 65% to 40% and subsequent swelling when r.h. was increased from 65% to 90% r.h (all at 27°C). WWCBs were found to be more dimensionally stable in both shrinkage and swelling, regardless of wood species used, than solid wood. Data in Kollmann (1963b) demonstrated that the sorption isotherm for WWCB is quite different to that for solid wood, and that if binders such as magnesite and gypsum are used boards have a much greater sensitivity to moisture than if portland cement is used as the binder.

Opinions differ as to the relative contributions of wood and cement to the dimensional stability of wood-cement composites. Mougel et al. (1995) suggest that the dimensional instability of wood-cement composites is influenced by the wood content, the wood-cement interface and the cement matrix. In contrast, Sandermann (1973) and Broker and Simatupang (1974a) suggest that the dimensional stability of wood-cement composites is largely independent of the wood component but is strongly influenced by the shrinkage and swelling of the porous hydrated portland cement binder. Shrinkage in wood-cement composites can be very effectively reduced by the use of large-sized wood furnish, such as wood wool, and by reducing the cement:wood ratio (Broker 1973, Sandermann 1973, Broker and Simatupang 1974b). These findings may help explain why WWCB has been found to be more stable than small-aggregate, high-cement composites such as CBP in fluctuating moisture conditions.

Pre-treating the wood component with additives has also been found to significantly reduce the dimensional changes in wood-cement composites. Researches by Broker and Simatupang (1974b), Mougel et al. (1995) and Gamage (1997) all found that polyethyleneglycol was particularly effective in reducing humidity and time-induced dimensional change of wood-cement composites. Broker (1973) found that pre-treatment of wood particles with silicone compounds was also
effective. Zoulalian et al. (1995) recommended a two-stage wood pre-treatment process (aqueous pre-washing of particles and impregnation with an organic or mineral compound), in combination with mineral reinforcement of cement and specialised curing, e.g. with CO₂ or humidification, to dimensionally stabilise CBPs. Simpler pre-treatments, including pre-mixing wood particles with waste oil or lime, or simply boiling them in water to remove water-soluble extractives, can also significantly reduce water absorption by wood-cement composites (Ledhem et al. 2000a and b).

Autoclave curing of composites is also very effective (Broker and Simatupang 1974b). Supplementation of portland cement with siliceous pozzolans combined with heat and/or autoclave curing also significantly increases dimensional stability of the binder (Lange et al. 1989, Kawai 1996a and b). Some of these strategies are discussed in more detail in Section 2.7, which examines strategies aimed at enhancing the mechanical properties of cement-bonded wood composites.

2.6.3 Corrosion

Chloride-based cement-setting accelerators are generally the most effective additives for increasing the compatibility of inhibitory woods with cement (Zhengtian and Moslemi 1985, Ma et al. 1997, Wei et al. 2000b, Wei and Tomita 2001). Chloride-based compounds have also been shown to be among the most effective accelerators in improving the strength and water-resistance properties of cement-bonded wood composites, in particular WWCB (Flawes and Chittenden 1967, Kayahara et al. 1979, Moslemi and Pfister 1987, Lee and Short 1989) and CBP (Ma et al. 1997, Zoulalian et al. 1997). Calcium chloride is one of the most efficient and cost-effective accelerators and is therefore widely used in the manufacture of wood-cement composites (Moslemi and Pfister 1987). Because of the wide-spread problem of corrosion of steel reinforcements and other iron-based fastenings in contact with cement there is a high demand for chloride-free accelerators, but it is difficult to find effective, satisfactory relacements for chloride-based salts (Thomas 1987).

While the problem of chloride-induced corrosion of ferrous-based fixings is well known (Thomas 1987, Ramachandran 1994), very few studies on cement-bonded wood composites containing chloride-based additives have addressed the question of corrosion of metal fastenings such as nails and/or framework which may come in contact with the composite. It has been claimed by Ye et al. (2002) that the addition of CaCl₂ during the manufacture of CBPs does not affect the corrosiveness of such boards to nails. However, the corrosiveness of chloride- and nitrate-based cement-setting accelerators to metals places strict limits on the quantities of these types of accelerators that can be used in wood-cement composite panels (Simatupang et al. 1977, Lee and Short 1989, DIN 1101 1989). Because corrosion is potentially important but often neglected in relation to the use of wood-cement composites that contain accelerators it is examined in greater detail in Chapter 10.
2.6.4 Wood-cement interactions and species specificity

Most wood species contain water- and alkali-soluble simple sugars, polysaccharides and polyphenols, all of which have been shown to retard the setting and hardening of portland cement (Sandermann and Brendel 1956, Hachmi and Campbell 1989, Simatupang et al. 1989, Miller and Moslemi 1991a). The type, concentration and pH of wood extractives can play a critical role in determining the compatibility of wood with portland cement (Gnanaharan and Dhamodaran 1985, Hachmi and Moslemi 1990, Miller and Moslemi 1991a). Although several studies have identified which types of wood extractives are responsible for inhibiting cement hydration reactions, the exact mechanisms by which different compounds retard hydration are poorly understood.

The problem of species specificity as it relates to the inhibition of cement hydration reactions by soluble extractives in wood has been one of the most significant barriers to the expansion and adoption of mineral-bonded wood composite technology (Lee 1984, Moslemi and Pfister 1987, Lee and Short 1989, Pazner and Klemarevski 1989). Chittenden (1972) points out that the choice of wood species for use in WWCB is more exacting than for wood aggregate-cement composites because cement is used in much smaller quantities and only coats the wood wool. Any cement-poisoning extractives (compounds which disrupt the normal course of cement hydration) in the wood will therefore have a more deleterious effect on the bonding and final strength of the product.

There is extreme variation in the compatibility of different hardwoods and softwoods with portland cement (Sandermann and Kohler 1964, Hachmi and Campbell 1989); however, hardwoods are generally less compatible with cement than are softwoods (Sandermann 1971, Simatupang et al. 1977, Moslemi 1988). The chemical interactions between wood constituents and cement that lead to the inhibition of cement hydration are complex, and are covered in more detail in Appendix 2.2 (pp. 416-432). Problems posed by acacia heartwood polyphenols, in particular A. mangium, are examined in Chapter 9.

2.6.5 Production and utilisation economics

A variety of other problems have also conspired to prevent wood-cement composites from becoming more widespread (Moslemi 1989). The most significant of these is the long initial and post-press curing time of the portland cement binder, which leads to reduced production capacity and a requirement for a large inventory of boards during curing (Lipinski 1989, Hsu 1992, Mallari et al. 1997). The high weight-to-strength ratio and machine wear of products like CBP (due to their high cement content) compared with resin-bonded particleboards has also reduced their popularity (Lee and Short 1989), despite the greater toughness and durability of the boards. Various methods have been explored in an effort to overcome some of these problems. Since portland cement is the most expensive component of the composite, lower cost substitutes such as pozzolanic and blast
furnace slag cements have also been investigated as a means of reducing the unit cost of boards (Lange et al. 1989). Currently, the cost of manufacturing CBPs is two to three times that of resin-bonded boards. Strategies that can lower the cost of wood-cement composites by increasing the efficiency of production, and that can lead to enhanced properties are discussed next.

2.7 Improving the properties of wood-cement composites

The mechanical properties of composite materials, including wood-cement composites, depend in part on the efficiency of the bonding between the reinforcing elements, but also are greatly affected by the type, content, geometry and arrangement of the reinforcement (Brandt 1995, Razi et al. 1999). Bond strength in wood fibre-reinforced cement composites largely depends on hydrogen bonding between the wood or fibre surface and the cement matrix (Coutts 1983, Coutts and Knightly 1984). Modification of the wood surface as a result of cutting, drying (extractive enrichment, deposition of foreign materials) and reaction with oxygen and light significantly affects its interaction with most binders (Zavarin 1984). Many strategies have been explored with a view to improving the compatibility of wood with cement and other mineral binders and increasing the strength of wood-cement composites, some of which are employed commercially. Strategies include modifying the wood by removing extractives, pre-treatment with chemicals, and modification of wood form and arrangement in the composite. It is also possible to modify the binder and its curing in order to improve the properties of the composite. The amount and composition of cement and its curing conditions (temperature, atmosphere) can be altered, and chemical additives can be used to accelerate hydration and/or fortify the cement matrix. Despite the importance of interfacial bonding in conventional composites, relatively little attention has been paid to the interfacial adhesion of wood and cement in wood-cement composites; however surface roughness of wood elements has been shown to benefit bonding with cement (Kayahara et al. 1979).

Notwithstanding the effect of wood on cement binder strength, the properties of wood-cement composites are also significantly influenced by the content, form, arrangement and other characteristics of the wood reinforcement (Kayahara et al. 1979, Stahl et al. 1997, Bajedo 1988). This effect can be observed by comparing the properties of WWCB with those of CBP. In the former, wood in the form of strands imparts greater flexural properties to boards than do the particles in CBP, which permits a much lower cement content to be used. Perpendicular arrangement of strands or flakes in wood-cement composites has also been found to significantly improve the strength of boards (Elmondorf 1963, 1965, Fuji and Miyatake 1998a, Cabangon et al. 2002a, Kuroki et al. 2002, Ma et al. 2002b). Stahl et al. (1997) and Cabangon et al. (2002a) have used finite element analysis to predict the effects of factors such as strand size, geometry,
orientation and shelling ratio (relative volume and thickness of surface and core layers) on the mechanical properties of WWCB. Other studies have investigated the combining of wood with lightweight inorganic fillers such as vermiculite (Kuroki et al. 1993, 1995, 1997) or foaming agents (Joklik 1983) as a means of improving the weight-to-strength ratio of wood-cement composites. Some studies have tried adding complementary reinforcing materials such as glass and mineral wool (Yue 1999, Wei and Tomita 2001) to improve dimensional stability and strength of the composites. To date, most research attention has been focussed on improving the bonding between wood and cement, and strategies to achieve this are discussed in further detail below.

2.7.1 Wood pre-storage

Although the sapwood of many wood species is recognised as being more compatible with cement than heartwood, the compatibility of sapwood can be greatly affected by the season in which the parent tree is harvested (Weatherwax and Tarkow 1964, Biblis and Lo 1968) and the delay between cutting and use (Shwarz and Simatupang 1984a, Sudin et al. 1989). For example, southern pine sapwood cut and used in spring was found to be less compatible with cement than wood harvested in winter (Weatherwax and Tarkow 1964, Biblis and Lo 1968). This was attributed to the presence of higher levels of carbohydrates in the wood harvested in spring. Sugars and starches present in sapwood, especially in softwoods, have been identified as the main compounds causing incompatibility between wood and cement (Sandermann and Brendel 1956, Sandermann et al. 1960, Bruere 1966, Davis 1966, Biblis and Lo 1968). Accordingly, simple measures like selecting the time of harvesting (i.e. before spring leaf flush) or log pre-storage, which depletes carbohydrates in sapwood, can significantly improve wood-cement board quality (Moslemi and de Almeida 1987, Schubert et al. 1990b). In many cases, the inhibitory effects of sapwood on cement setting can be greatly reduced by allowing the wood to be colonised by blue or brown stain fungi that metabolise carbohydrates in wood (Weatherwax and Tarkow 1964, Davis 1966, Raczkowski et al. 1983, Shwarz and Simatupang 1984a, Moslemi and de Almeida 1987, Kadir and Sudin 1989, Sudin et al. 1989). For example, rubberwood (Hevea brasiliensis Muell.) has high content of inhibitory sugars (1-2.3%) and starches (7.5-10.2%) (Azizol and Rahim 1989), which strongly inhibits the setting of cement in wood-cement composites. Storage of the de-barked billets for 4 weeks reduced sugar and starch contents to 0.5% and 7% respectively (Sudin et al. 1989). Storage of rubberwood billets for 20 weeks reduced sugar and starch levels to 0.2% and 1.1% respectively (Kadir and Sudin 1989), which enabled wood-cement particleboards of acceptable quality to be manufactured from rubberwood. A longer storage time is required to achieve the same effect if billets are stored with their bark intact. Billet or chip pre-storage is commonly used to reduce the carbohydrate content of wood before the manufacture of WWCB and CBP. However, if the wood is
colonised by decay fungi during storage then the wood can become highly incompatible with cement (Davis 1966, Weatherwax and Tarkow 1964, 1967, Biblis and Lo 1968). Accordingly, prolonged storage of wood (more than 1 year) in the tropics, where decay is rapid, greatly reduces the compatibility of wood with cement (Weatherwax and Tarkow 1967, Meier 1990). Work by Simatupang and Handayani (2001) has shown that aerobic fermentation of rubberwood sawdust for seven days can produce a marked reduction in free sugars, from 4.34% to 0.87%, suggesting that pre-storage of wood particles in final form under the right conditions may be a more efficient way of improving the compatibility of wood with cement than log storage.

2.7.2 Adjustment of wood:cement ratio

Although some physical properties of CBP are positively correlated with cement content, studies have shown that there is an optimum cement content that maximises flexural properties of boards. The optimum cement content also needs to be balanced against the high cost of portland cement and its contribution to board weight (Elmondorf 1963, Moslemi and Pfister 1987). The optimum cement content for CBP varies for MOR and MOE (Moslemi and Pfister 1987, Oyagade 1990). The flexural properties of CBPs are also strongly influenced by board density. At any given density, however, MOR is decreased as the cement:wood ratio increases (Oyagade 1990). Moslemi and Pfister (1987) measured MOR, MOE, thickness swelling and water absorption of particleboards containing lodgepole pine (*Pinus contorta* Dougl. ex Loud) particles at cement:wood ratios ranging between 1.5:1 and 3:1. MOR increased significantly as the cement:wood ratio increased from 1.5:1 to 2:1, but decreased as the ratio increased from 2.5:1 to 3:1. In contrast, MOE showed a linear increase as the cement:wood ratio increased from 1.5:1 to 3:1. A similar trend was observed by Simatupang (1979) for CBPs containing spruce (*Picea* spp.) flakes and was attributed to the greater rigidity of cement compared with wood. A linear decrease in water absorption and thickness swelling with increasing cement content was also observed and was thought to be caused by lower board porosity and volume of wood in boards with a higher cement content. Zhou and Kamdem (2002) showed that MOR of CBPs containing CCA-treated red pine (*Pinus resinosa* Ait.) increased as the cement:wood ratio increased from 1:1 (average MOR = 5.1 MPa) to 3:1 (average MOR = 9.5 MPa). MOR decreased again as the cement:wood ratio increased from 3:1 to 4:1 (average MOR = 8.9 MPa). A similar trend was found for MOE, whereas internal bond strength was maximised at 3.5:1 cement:wood ratio.

In the case of WWCB, the relationship between cement:wood ratio and mechanical properties of boards differs from that observed for CBP. Studies on the properties of WWCBs manufactured in the Philippines have shown that board flexural properties can be compromised by using a higher cement:wood ratio, particularly if inhibitory extractives are removed and cement-setting
accelerators are used. WWCBs with cement:wood ratios of 1.4, 1.2 and 1 to 1, and containing accelerators (CaCl₂, Al₂(SO₄)₃ and sodium silicate), were manufactured from A. mangium by Soriano et al. (1997). The MOR increased from 4.5 MPa to 6 MPa as cement:wood ratio decreased from 1.4:1 to 1:1. The high tensile strength of wood probably contributes significantly to its bending properties, particularly MOR. Similar findings were obtained by Moslemi and Pfister (1987) and Eusebio et al. (2002a and b).

The water:cement ratio is also critical to curing and strength development of pure cements and concretes (Lea 1971, Ramachandran 1994, Taylor 1997). The optimum water addition for the hydration of cement in laboratory wood-cement compatibility tests is described in Section 2.9. Simatupang (1979) has given the following formula describing the optimum level of water for the manufacture of CBP:

\[ \text{Water (kg)} = 0.35Wc + (0.3-MCw)Ww \]

where: \( Wc \) = mass of dry cement (kg)  
\( MCw \) = moisture content of wood, expressed as a fraction  
\( Ww \) = oven-dry equivalent mass of wood (kg)

For the manufacture of CBP the MC of the chips can be rapidly determined from their readily measured bulk density (weight/volume) in either a freely poured or compressed, baled state, from which water dosage can be regulated (Akodus et al. 1979). Calibration charts for different species and chip sizes need to be determined first.

It has also been found that wetting and re-drying of certain wood-cement composites such as WWCB after they have been manufactured can result in improved strength (Pinion 1975). This is suggested to arise from renewed hydration of cement that may have dried out during initial curing. Surprisingly, there are very few investigations of this phenomenon in relation to possibly further improving the strength properties of WWCB.

2.7.3 Adjustment of curing time and temperature

For pure cement, the optimum curing time is normally 28 days (Taylor 1997). Accordingly, some studies on mechanical properties of wood-cement composites have also measured board properties after 28 days (e.g. Soriano et al. 1997). Other studies (Lee 1984) have used variable curing times of 2-3 weeks prior to testing. All lignocellulosic materials act as cement-setting retarders, and it follows that the time required to obtain maximum strength properties in a wood-cement composite is likely to be much greater than the 28 days specified for neat cement. This is supported by the suggestion that the adoption of existing cement and concrete strength-time
prediction models is likely to be confounded by the uncontrolled effects of wood-cement interactions (Osinski and Potter 1997). Despite this, relatively few studies have examined the effect of curing time on the strength of wood-cement composites. Moslemi and Pfister (1987) found that increasing the curing time from 14 to 28 days only marginally improved the MOR of CBPs, regardless of wood:cement ratio. The MOE of the CBPs was significantly improved, however, by increasing the curing period from 14 to 28 days. Namioka et al. (1976) tested the mechanical properties of wood-cement composites following curing for up to 12 weeks. Optimum curing time was between 8 and 12 weeks, two to four times the optimum curing time for neat cement. Similarly, Roffael and Dix (1992) and Chen and Hwang (1998) have shown that differences in wood-cement compatibility between species and/or heartwood and sapwood that affect composite strength decrease with increased duration of curing. For example, despite the lower initial compatibility of poplar sapwood with cement, compressive strength of composites containing sapwood was higher after 4 and 8 weeks of curing (Roffael and Dix 1992). Chen and Hwang (1998) tested the compressive strengths of wood flour-cement blocks made from hardwoods of varying compatibility and found that the inhibitory effects of wood on cement hydration decrease over time.

To try to reduce the costs of manufacturing cement-bonded composite materials, considerable research has been done on reducing pressing and curing times of CBP and WWCB. Heat curing by hot pressing (Schwarz and Simatupang 1984b, Lus 2001, Lu et al. 1991), often in tandem with CO₂ generation or injection pressing (Schmidt 1988, Eusebio et al. 1995, Simatupang et al. 1995, Nagadomi et al. 1996c, Kuroki et al. 1995 and 1997), has been extensively investigated to hasten the manufacture of CBP. These techniques enable mat pressing times to be shortened to 10 minutes or less. The combination of hot pressing and CO₂-enhanced curing involves steam-injection pressing and adding a combination of NaHCO₃, which generates CO₂ during pressing, MgCl₂ as a setting accelerator, and sodium silicate and silica fume as fortifying agents. Rapid curing using CO₂ also enables a much wider range of wood species to be used (Simatupang et al. 1995, Mallari et al. 1997). CO₂ gas can also be directly injected into the mats during pressing CBP (Schmidt 1988, Simatupang et al. 1995) or WWCB (Pablo et al. 1995, Mallari et al. 1997). The main technical problem associated with CO₂-injection pressing is the difficulty of obtaining even dispersal of the gas through the CBP mats during pressing and curing (Simatupang et al. 1995); however this problem does not appear to affect CO₂-injection pressing of the more open, springy WWCB mats (Pablo et al. 1995, Mallari et al. 1997).

2.7.4 Chemical additives

There are numerous studies of the effect of cement-hardening accelerators on the hydration of wood-cement mixtures and on the properties of cement-bonded composites. Only those studies that
have utilised accelerators to improve the properties of cement-bonded composites containing inhibitory wood species are discussed here. Additives have been examined as a means of facilitating the use of inhibitory wood species in wood-cement composites and, more recently, to shorten the pressing times for CBP. Accelerators substantially improve the properties of low-density (low-cement-content) composites; however the need for them decreases as the cement content of the composite increases (Sorfa 1984). Accelerators also improve the moisture resistance of cement-bonded composites (Kayahara et al. 1979, Badejo 1989, Wei and Tomita 2001). The most effective accelerator for any particular wood-cement composite depends considerably on wood species, cement type, composite type and processing conditions.

Chloride additives: Chlorides such as CaCl₂ and FeCl₃ are among the most effective additives for overcoming the inhibitory effects of many woods on the hydration of cement (Zoulalian et al. 1997, Wei et al. 2000b, 2001). 3% CaCl₂ has been found to be very effective in improving the strength of CBPs made from inhibitory teak (Tectona grandis L.) and P. falcatoria, both of which inhibit the hydration of cement (Chen and Hwang 1998). The amount of accelerator added improves board properties up to a certain optimum (between 3 and 6%), but with the addition of greater amounts of certain accelerators the properties are adversely affected (Kayahara et al. 1979). These authors added various quantities of AlCl₃ (up to 15% w/w cement) to both WWCB and CBP. MOR reached a maximum (~10 and ~7 MPa from 7 and 5.5 MPa for WWCB and CBP respectively) as the quantity of accelerator used increased to 3%, but decreased thereafter with additions up to 15%. CaCl₂ has long been used as a cement-setting accelerator in concreting applications (Lea 1971, Ramachandran 1994, Taylor 1997) and in wood-cement composites. The MOR of CBP containing grand fir (Abies grandis (Doug. ex D. Don) Lindl.) was increased almost 400% by the addition of 3% CaCl₂ (Ahn and Mosleimi 1980). Lee and Short (1989) tested the addition of 3% CaCl₂ to WWCB manufactured from a range of wood species: compatible eastern cottonwood (Populus deltoides Bartr. ex Marsh) and yellow poplar (Liriodendron tulipifera L.), and incompatible sweetgum (Liquidambar styraciflua L.), southern red oak (Quercus falcata Michx.) and white oak (Q. alba L.). The effect of adding CaCl₂ on the mechanical properties of boards varied significantly among species. The effect was low in the cases of cottonwood and red oak (increases in MOR of 6.3 and 8.6%, respectively), moderate for yellow poplar and white oak (24 and 25%, respectively), and highest for boards containing sweetgum (157% increase in MOR). Sweetgum also had the lowest compatibility with cement. The use of accelerators, including CaCl₂, during the manufacture of wood-cement composites from Australian wood species is examined later in Section 2.9.

Non-chloride additives: Perhaps the most common non-chloride additive used in the manufacture of wood-cement composites is sodium silicate or waterglass (Na₂SiO₃), which has been found to be very effective in improving the properties of CBPs made using the steam-injection pressing
technique discussed earlier. For example, Nagadomi et al. (1996c) found that the properties of CBP made from pre-soaked wood flakes of incompatible Japanese wood species hinoki (*Chamaecyparis obtusa* (Seib. & Zucc.) Endl.) and Japanese cedar (*Cryptomeria japonica* (Thunb. ex L.f.) D. Don.) were optimised by adding 5% Na$_2$SiO$_3$. Al$_2$(SO$_4$)$_3$ is the other main non-chloride additive that has been successfully employed during the manufacture of wood-cement composites. It has proved effective in improving the properties of WWCB made from pre-soaked wood of *A. mangium* (Soriano et al. 1997) and a range of native Philippine hardwoods (Pablo and Cabangon 1997). Al$_2$(SO$_4$)$_3$ has also been shown to be effective in combination with other non-chloride additives (Simatupang et al. 1977, Kühne and Meier 1990) as discussed below.

Additive combinations: There are several published examples of the use of mixtures of chemical additives to improve the properties of wood-cement composites. For example, Na$_2$SiO$_3$ has been used in combination with cement-setting accelerators in several studies. Simatupang et al. (1989) used a mixture of 13% K$_2$CO$_3$ and 5% Na$_2$SiO$_3$ (w/w cement) to reduce mat pressing time of CBP. They found that a mixture of Al$_2$(SO$_4$)$_3$ and lime water (Ca(OH)$_2$) greatly improved the properties of CBP using spruce, but was ineffective with boards made from poplar. Ca(OH)$_2$ and Al$_2$(SO$_4$)$_3$ have also been successfully used in commercial manufacture of CBP (Simatupang et al. 1977). Lee (1985) successfully used a combination of Na$_2$SiO$_3$ and CaCl$_2$ to manufacture WWCB boards from bald cypress (*Taxodium distichum* (L.) L.C. Rich.), a species which is only moderately compatible with portland cement. Kühne and Meier (1990) used solutions of 2% Al$_2$(SO$_4$)$_3$ or MgCl$_2$ with 2-3% sodium silicate to significantly improve the strength properties of cement-bonded fibre boards from an unidentified blend of hardwood fibres. The combination of 2% Al$_2$(SO$_4$)$_3$ with 2% Na$_2$SiO$_3$ was found to be the most effective additive for improving the properties of boards made from unsoaked bamboo culms (which have a high sugar content) (Rahim et al. 1996). 2-3% Al$_2$(SO$_4$)$_3$ in combination with 4-6% CaCl$_2$ has been used in the manufacture of wood-cement aggregate (Arbolit) from larch wood, which on its own strongly retards the setting of cement (Lein and Mokeev 1978). Alternatively, additive mixes, (i) FeSO$_4$, CaCl$_2$ and Ca(OH)$_2$ (ratio 1.5:4:1.5) or (ii) Na$_2$SiO$_3$ and Al$_2$(SO$_4$)$_3$ (ratio 1:1.5) may facilitate the manufacture of moulded wood-cement composites from pre-soaked larch wood (Akodis and Bukharkin 1980).

There are more complex examples of targeted combinations of chemicals that are added to wood-cement composites to counteract the inhibition of cement hydration by wood. A novel method of pre-treating wood flakes was recently patented by Kawai and Nekota (1999), who used a combination of dilute (1-5%) mineral acid (HCl, H$_2$SO$_4$ or H$_2$PO$_4$) and tetrasodium silicate. The initial acid treatment hydrolyses wood sugars, and a subsequent reaction involving Na$_2$O.3SiO$_2$ creates a silicate gel membrane around the wood flakes. This membrane serves two purposes; firstly to reduce any further leaching of sugars into the cement paste, and secondly to react with free Ca$^{2+}$...
ions to form a calcium silicate gel that hardens during curing and acts as a bonding bridge between the wood surface and cement. The pre-treatment is designed specifically for woods that are high in polysaccharides and composites that are cured at high temperatures (60 to 100°C).

The rapid pressing and curing of CBP requires a combination of additives in conjunction with steam-injection pressing. When NaHCO₃ is heated it generates CO₂ which accelerates cement setting and hardening, while MgCl₂ acts as a cement-setting accelerator and sodium silicate as a fortifier of the cement matrix (Eusebio et al. 1995, Nagadomi et al. 1996c). Another example of a mix of additives designed to act in different but complementary ways to overcome low wood-cement compatibility is that tested by Kavouras (1987). A mixture of polar formaldehyde (HCHO) and CaCl₂ was used in the manufacture of cement-bonded flake boards from untreated, inhibitory oak wood (Quercus conferta Kit.). The formaldehyde reacted with and neutralised the alkali-soluble phenolic extractives in oak wood while CaCl₂ accelerated cement setting.

2.7.5 Adjustment of cement type and substitution

Although ordinary portland cement (ASTM Type I) is commonly used in the manufacture of wood-cement composites today, other kinds of portland cement and mineral substitutes have been tested and used to good effect. Since alternative mineral binders to portland cement Type I are not examined in this thesis they are only briefly mentioned here. Quicker setting, high early strength cements (ASTM Type II - high C3S- and C4AF-content-, and ASTM Type III - high C3S-content portland cements) have been shown in numerous studies to result in much improved mechanical properties of cement-bonded wood composites (Kollmann (1963a, Kamil 1970, Schwarz and Simatupang 1983, Lange and Simatupang 1985, Moslemi and Pfister 1987, Schubert et al. 1990, Lee and Hse 1993). Because of this, high C3S-content cements have been widely used for the commercial manufacture of wood-cement composites (Moslemi and Pfister 1987).

The supplementation of portland cement by siliceous reactive pozzolans such as rice-hull ash (RHA), fly ash or blast-furnace slag has also been shown to be capable of reducing the sensitivity of the mineral binder to wood extractives, reduce the setting time and moisture-sensitivity of the binder, and improve the long-term durability of wood-cement composites (Forss 1987, Aho 1989, Lange et al. 1989, Feldman et al. 1991, Hsu 1992 and 1993, Kawai 1996a and b, Sun et al. 1997). Alternative non-portland cement mineral binders such as magnesium oxyphosphate or 'Sorel' cements have also been investigated for use in wood-cement composite manufacture (Paszner 1978, 1987, Paszner and Klemerevski 1989). The problems posed by wood-cement incompatibility and species specificity have been a strong driver for the testing and adoption of supplements and alternative mineral binders to portland cement Type I, and so further information on these can be found in Appendix 2.3 (pp. 432-436).
2.8 Testing for wood-cement compatibility

2.8.1 General studies and testing methods

By far the most appropriate means of assessing wood species for their suitability for use in wood-cement composites is to manufacture and test boards using the species in question. In many instances this is not be possible because of lack of facilities, cost and time constraints (Ma et al. 2002a). Furthermore, the only wood sample material available for testing may be in the form of small blocks or increment cores taken from living trees. The extreme variation among wood species in their compatibility with portland cement and the complexity of the wood-cement-water system necessitate the development of simple methods that can reliably measure and compare the effects of wood on cement hydration. The most common method of assessing wood-cement compatibility is to measure the temperature generated in cement paste containing wood particles and the time taken for the cement to set. It is also desirable to be able to rank different woods in order to compare their potential suitability for the manufacture of wood-cement composites. Over the last 50 years, numerous methods have been developed to assess wood compatibility with cement; however there is still no universal test method. In fact there has been little consistency in the methodology used to determine wood-cement compatibility (Hachmi et al. 1990), making it difficult to compare species rankings produced by different studies. Variation in methodology used to assess wood-cement compatibility has arisen from differences in apparatus used, wood:cement:water ratios, compatibility indices developed and used, as well as wood particle size, shape and composition.

Sandermann and Kohler (1964) were the first to assess the compatibility of different wood species with cement by measuring the hydration temperature generated by mixtures of wood flour, cement and water at fixed ratios. This method has been used in the majority of subsequent studies that have sought to predict the suitability of wood species for the manufacture of wood-cement composites. It has been generally assumed that results obtained from cement hydration tests using wood flour can be used to reliably predict the suitability of wood for cement-bonded composites such as WWCB. For example Yashiro et al. (1968b), Dass and George (1969), Shukla et al. (1984), Jain et al. (1989) and Sutigno and Sulastiningsih (1986) have all used the Sandermann and Kohler (1964) method of measuring hydration temperature in wood flour-cement mixes to predict the potential suitability of wood species for the manufacture of WWCB. Sutigno and Sulastiningsih (1986) grouped 73 woods into suitable (T_{max} >41^\circ C), moderately suitable (36^\circ C to 41^\circ C) and unsuitable (<36^\circ C), and made WWCB boards from all species tested. In contrast to the results from the hydration tests, only 49 of the 61 species classified as suitable met the German Standard for WWCB properties (DIN 1101: 1989). Of the six species classified as moderately suitable, four met the DIN Standard, and of the six species classified as unsuitable, three met the Standard. Not
surprisingly, the relationship between hydration temperature and wood-cement board properties was not significant at the 5% level. The results from Sutigno and Sulastiningsih (1986) strongly suggest that hydration tests using wood flour may overestimate the suitability of some species for WWCB and underestimate the suitability of many others. Possible factors that could cause such discrepancies are examined further in Chapters 3 and 4 of this thesis.

2.8.2 Apparatus used to measure cement hydration temperature

When measuring the hydration temperature of wood-cement mixes the hydration test sample must be placed inside a thermally insulated container from the time of mixing in order to retain all the heat generated by the exothermic hydration reaction (Sandermann and Kohler 1964, Hachmi et al. 1990). Typically, glass vacuum flasks or 'dewars' have been employed for this purpose, with provisions for sealing, extra insulation, and thermometer/thermocouple attachment reaching various degrees of complexity and practicality among different studies. Four schematic examples of hydration test devices are illustrated in Figures 2.7. Although the majority of wood-cement compatibility studies have directly measured temperature increases in wood-cement mixtures using thermometers or thermocouples, a few studies have used isothermal or conduction calorimetry (Bensted 1992, Sauvat et al. 1999, Alberto et al. 2000).

Unlike the standard method, such systems measure the different heat fluxes generated by the hydration of different phases in cement as they occur during the course of cement setting. Total enthalpy is also determined, whereby a wood-cement compatibility index can be calculated using the ratio of enthalpy of the wood-cement mix to that of pure cement. Different woods alter the onset and intensity of hydration of the calcium silicate and calcium aluminate phases or suppress them altogether. However, unlike standard cement hydration tests, measurement of heat fluxes requires specialised and expensive equipment, and hence has rarely been used by researchers in the field of wood-cement composites.

2.8.3 Wood:cement:water ratios for hydration samples

Variation also exists in the amounts of wood, cement and water in hydration samples used in different studies. As can be seen in Table 2.6, the majority of tests used 200 g of cement, which was the amount suggested by early researchers, including Sandermann and Kohler (1964) and Weatherwax and Tarkow (1964); however the amounts of wood and water used vary somewhat. Wood content varies from 4.7% (10 g) to 9.1% (20 g) for 200 g of cement, while the addition of water ranges from 80 g to 100 g per 200 g of cement. The optimum water:cement ratio for wood-cement hydration tests was investigated by Hachmi and Moslemi (1990), who recommended a
water:cement ratio of 0.4:1 for cement, plus an extra amount of water to be added according to how much wood is used. This was set at a water:wood ratio of 0.7:1.

Figures 2.7 Four different kinds of apparatus for monitoring cement hydration temperature in situ; (a) Sandermann and Kohler (1964), (b) Moslemi et al. (1983), (c) Moslemi and Lim (1984), and (d) Tachi et al. (1989).
Table 2.6 Amounts of wood, cement and water used in hydration samples by various authors.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Cement (g)</th>
<th>Wood (g)</th>
<th>Water (g)</th>
<th>Mesh size*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandermann and Kohler (1964)</td>
<td>200</td>
<td>20</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>Weatherwax and Tarkow (1964)</td>
<td>200</td>
<td>15</td>
<td>90</td>
<td>60</td>
</tr>
<tr>
<td>Hofstrand et al. 1984</td>
<td>200</td>
<td>15</td>
<td>variable</td>
<td>20-40</td>
</tr>
<tr>
<td>Moslemi and Lim (1984)</td>
<td>200</td>
<td>15</td>
<td>90.5</td>
<td>20-40</td>
</tr>
<tr>
<td>Zhengtian and Moslemi (1985)</td>
<td>200</td>
<td>15</td>
<td>variable</td>
<td>20-40</td>
</tr>
<tr>
<td>Tachi et al. (1987)</td>
<td>200</td>
<td>15</td>
<td>100</td>
<td>not spec.</td>
</tr>
<tr>
<td>Jain et al. (1989)</td>
<td>200</td>
<td>15</td>
<td>90</td>
<td>60-150</td>
</tr>
<tr>
<td>Sudin and Ibrahim (1989)</td>
<td>200</td>
<td>10</td>
<td>80</td>
<td>35</td>
</tr>
<tr>
<td>Hachmi and Moslemi (1990)</td>
<td>200</td>
<td>15</td>
<td>90.5</td>
<td>20-40</td>
</tr>
<tr>
<td>Hachmi et al. 1990</td>
<td>200</td>
<td>15</td>
<td>90.5</td>
<td>20-40</td>
</tr>
<tr>
<td>Miller and Moslemi (1991b)</td>
<td>400</td>
<td>40</td>
<td>268</td>
<td>40</td>
</tr>
<tr>
<td>Oyagade (1994)</td>
<td>200</td>
<td>15</td>
<td>variable</td>
<td>20</td>
</tr>
<tr>
<td>Blankenhorn et al. (1994)</td>
<td>600</td>
<td>45</td>
<td>272</td>
<td>20</td>
</tr>
<tr>
<td>Fuwape (1994)</td>
<td>200</td>
<td>15</td>
<td>90</td>
<td>'pulverised'</td>
</tr>
<tr>
<td>Alberto et al. (2000)</td>
<td>200</td>
<td>15</td>
<td>90.5</td>
<td>20</td>
</tr>
</tbody>
</table>

*Mesh size 20 = 1-2 mm, 40 = 0.42 mm, 60 = 0.25 mm, 150 < 0.1 mm.

The question of whether the high cement:cement ratio developed for use in hydration tests by Sandermann and Kohler (1964), and used by most subsequent researchers, is relevant to commercial wood-cement composites was examined by Lee et al. (1987). These authors tested the effect of varying the cement:wood ratio from 13:1 (used by Sandermann and Kohler 1964) to 4:1 on maximum cement hydration temperature ($T_{\text{max}}$) and time taken for cement to set. Species used included loblolly pine (Pinus taeda L.), white oak (Quercus alba L.), red oak (Quercus falcata Michx.), yellow poplar (Liriodendron tulipifera L.), sweetgum (Liquidambar styraciflua L.), and mokernut hickory (Carya tomentosa (Poir.) Nutt.), all prepared as 20 to 40 mesh particles. As the cement:wood ratio decreased, $T_{\text{max}}$ decreased markedly, and setting time greatly increased, a trend that was especially pronounced among the less compatible hardwoods (red oak, yellow poplar, sweetgum and hickory). The time required for the wood-cement mix to set was inversely proportional to the maximum hydration temperature reached, as shown in Figure 2.8 from Lee et al. (1987). All sample points with a setting time of less than 5 h and $T_{\text{max}}$ greater than 60°C were those of all species with a cement:wood ratio of 13:1. The results indicate that the high cement:wood ratios used in cement hydration tests can mask essential differences between wood species that would greatly affect their performance in wood-cement composites such as WWCB, which employ a much lower cement:wood ratio.

Another source of variation among wood-cement hydration tests arises from differences in the chemical composition of the portland cement used. Portland cement varies considerably according to country and place of origin, and even among batches produced by the same cement manufacturer. For example, Hachmi et al. (1990) measured average hydration rates of 2.6 and 3.1°C/h, respectively, for two batches of portland cement purchased from the same company, mixed at exactly the same cement:water ratio and measured under exactly the same experimental conditions.
Figure 2.8 Relationships between maximum hydration temperature and time required to reach maximum temperature of wood-cement mixtures (from Lee et al. 1987).

2.8.3 Development of wood-cement compatibility indices

Early attempts to quantify the compatibility of wood with portland cement simply recorded the maximum temperature attained by the exothermic reaction of cement-water-wood samples and the time taken for the maximum temperature to be reached. Sandermann and Kohler's (1964) comprehensive study tested a large number of wood species and recorded their maximum hydration temperature ($T_{\text{max}}$) and the time taken to reach $T_{\text{max}}$.

Weatherwax and Tarkow (1964) developed an inhibitory index ($I$) based solely on the time taken for cement and wood-cement samples to reach $T_{\text{max}}$, i.e.

$$I = \left(\frac{t - t'}{t'}\right) \times 100$$

where $I =$ inhibitory index (%), $t =$ time taken for pure cement to set, $t' =$ time taken for wood-cement mix to set.

This approach appears to make the assumption that $T_{\text{max}}$ is directly correlated with the time taken to set without demonstrating this to be the case for a wide range of hydration samples. The inhibitory index of Weatherwax and Tarkow (1964) was also used in some subsequent studies, including those of Biblis and Lo (1968) and Jain et al. (1989). Hydration time was found to be inversely proportional to hydration temperature for the wood species tested by Hofstrand et al.
(1984) and Lee et al. (1987), whereas this was not the case for the wood-cement samples containing
the chemical additives that were tested by Zhengtian and Moslemi (1985). In a study by Lee and
Hong (1986) there was no correlation between the compressive strength of wood-cement composites and the time taken for them to set, whereas $T_{\text{max}}$ was found to be linearly correlated with compressive strength of samples after 3, 7 or 14 days. Miller and Moslemi (1991b) also found a
good correlation between $T_{\text{max}}$ and the bond strength in wood-cement composites ($r^2 = 0.73$); however, they warned that the correlation was not strong enough for estimating wood-cement compatibility for all wood species and sample types.

In more recent studies, various different formulae have been derived to more 'accurately' quantify wood-cement compatibility. The problem of ignoring $T_{\text{max}}$ in the early compatibility index
developed by Weatherwax and Tarkow (1964) was later rectified by the incorporation of $T_{\text{max}}^\bullet$, time
taken to reach $T_{\text{max}}$, and the maximum slope of the hydration curve (maximum hydration rate) into
an inhibitory index developed by Moslemi and Lim (1984) and Hofstrand et al. (1984);

$$I = \left[ \frac{(t - t')}{t'} \right] x \left[ \frac{(T - T')}{T'} \right] x \left[ \frac{(S - S')}{S'} \right] \times 100$$

where $t$ and $t'$ = time taken to reach maximum temperature for wood-cement mix and pure cement respectively, $T$ and $T'$ = maximum hydration temperature for wood-cement mix and pure cement respectively, and $S$ and $S'$ = maximum rate of increase in temperature during hydration for wood-cement mix and pure cement respectively.

Hachmi et al. (1990) devised and reviewed various different methods of quantifying wood-cement compatibility, which are summarised as follows:

1. Weighted maximum temperature rate ratio ($C_T$)

   This is simply a ratio of the hydration rate of the wood-cement mix to that of pure cement which has been weighted according to the masses of cement, water and wood used in the hydration sample. The weighted maximum hydration rate is calculated first:

   Weighted maximum hydration rate ($R_T$) = $\left( \frac{T_{\text{max}}}{\text{Time}} \right) \times \left[ \frac{(m_w + m_{wd})/m_c} \right]

   where: $m_w$ = mass of water, $m_{wd}$ = mass of wood and $m_c$ = mass of cement used in hydration sample. In calculating the weighted maximum hydration rate for pure cement ($R'_T$), $m_{wd}$ is 0.

   The ratio of weighted maximum hydration rate for a wood-cement mix to that of pure cement is then determined:

   $$\text{Ratio (C}_T\text{)} = \left( \frac{R_T}{R'_T} \right) \times 100$$

   where $R_T$ and $R'_T$ = weighted hydration rates for wood-cement mix and neat cement respectively.
This expression is useful for removing variation arising from differences in composition of wood-cement hydration samples, for example, if differing amounts of wood are used.

2. Maximum heat rate ratio (CH)

This is essentially another ratio of hydration rates of wood-cement mix and neat cement which incorporates a sample mass weighting as well as constants for the specific heats of wood, cement, water and the dewar flask.

\[
RH = \frac{(T_{\text{max}} - T_{\text{room}}) \times [(mc)_w + (mc)_{wd} + (mc)_c + (mc)_d]}{\text{Time}}
\]

where \( T_{\text{max}} \) = maximum hydration temperature, \( T_{\text{room}} \) = room temperature, \( m \) = mass and \( c \) = specific heat of denoted ingredient water (w), wood (wd), cement (c) and dewar flask (d).

Hence, \( CH = (RH/R'\text{H}) \times 100 \)

where \( RH \) and \( R'\text{H} \) = maximum heat rates for wood-cement mix and neat cement respectively.

If the hydration samples being compared are consistent in composition, the 'me' terms become constants.

3. Area ratio method (CA-factor)

The third method of describing wood-cement compatibility devised by Hachmi et al. (1990) was the area ratio or CA-factor. This is the ratio of areas beneath the hydration curves for a wood-cement mix and neat cement, expressed as a percentage.

\[
CA \text{ } (\%) \text{ } = \frac{(A_{\text{wc}}/A_c)}{\times 100}
\]

Where \( A_{\text{wc}} \) = area under the hydration curve of wood-cement mix, \( A_c \) = area under the hydration curve of neat cement.

The derivation of the CA-factor is demonstrated graphically in Figure 2.9 from Hachmi et al. (1990). Of their three methods for calculating wood-cement compatibility, only the area ratio method was found by Hachmi et al. (1990) to produce meaningful values for species of very low compatibility with cement. Hence it was the only method that enabled wood species across a spectrum of compatibility values from 0 to 100% to be effectively ranked. The first two methods could not be applied where no exothermic reaction took place, i.e. the wood severely inhibited cement hydration. They were also unsuitable for hydration tests containing higher wood/cement ratios (Karade et al. 2003 in press).
Hachmi et al. (1990) therefore recommended that the area ratio method (CA-factor) be adopted as a 'standard method' of expressing wood-cement compatibility based on the following stated advantages:

1. The area under the hydration curve takes into account the hydration behaviour of the mix at all stages throughout the duration of the experiment (usually 24 hours);

2. Unlike expressions using only maximum hydration temperature and/or time, the area ratio method enables values to be derived for compatibility of wood species which inhibit the hydration of cement, thus enabling ranking and comparison across a wide range of wood species. Such rankings can then be correlated with other findings such as the mechanical properties of wood:cement composites made from the same wood species; and

3. Unlike simple expressions of maximum hydration temperature or time, CA-factors are comparable across different studies even if the experimental conditions such as wood-cement ratio are different.

This last statement, however, has not been proved. A recent study by Karade et al. (2003 in press) has suggested that the existing methods of assessing wood-cement compatibility which generate compatibility indices based on maximum hydration temperature (T_{max}) and/or time taken to reach this temperature are inaccurate, since T_{max} is influenced by factors such as the type of cement used, the wood:cement:water ratio, wood particle size and water absorption by the wood. The authors also suggested that conventional wood-cement hydration tests are unsuitable for determining appropriate process variables for wood-cement composites, including particle size, wood:cement ratios, mix of wood species and amount of additives.
Karade et al. (2003) correctly point out the problems in comparing results from different wood-cement compatibility tests and relating wood-cement compatibility test results to the properties of wood-cement composites. Their study instead suggested a compatibility index be calculated from wood-cement hydration tests by the use of a maturity function (similar to those used to assess the strength and ‘equivalent age’ of concrete subjected to different curing temperatures and conditions) which is based on maximum heat rate and time taken to reach it. Some sample results were generated for cement mixes containing cork-dust or sand, but their method appeared to unnecessarily complicate the process of making simple and rapid estimates of the compatibility of wood samples with portland cement under fixed conditions. It also made the assumption (without providing any empirical evidence) that the compatibility indices generated would correlate better with the properties of wood-cement composites than other kinds of indices developed for cement hydration tests.

The authors did not present any empirical evidence to demonstrate that variation in this alternative compatibility index would be completely unaffected by the factors expected to influence cement hydration, i.e. cement type and composition, wood:cement:water ratios and amounts and wood particle size. This is why it is important to keep these factors constant in wood-cement compatibility tests. They also did not explain why $T_{\text{max}}$ and time would not be suitable for comparing wood-cement compatibility across samples measured in the same study under identical known and controlled experimental conditions.

For the purpose of experimentation in subsequent Chapters simple compatibility indices such as $T_{\text{max}}$, time, hydration rate and $C_A$-factor have been adopted in keeping with the majority of previous studies that have assessed wood-cement compatibility, and since the wood-cement hydration tests are conducted under uniform conditions throughout the experimental work reported in this thesis. However, the suitability and reliability of the $C_A$-factor for assessing wood-cement compatibility is re-examined in Chapter 4.

In addition few studies have investigated the connection between wood-cement compatibility indices and the mechanical properties of wood-cement composites and none have determined the correlation between results from wood-cement hydration tests and the properties of WWCB. To address this question wood-cement compatibility, as influenced by chemical additives, is correlated with the strength of WWCBs made using the same species and additives and reported on in Chapter 10.

2.8.5 Wood particle size and shape

It has been established that wood extractive content and composition strongly influences its compatibility with portland cement (Sandermann and Brendel 1956, Hachmi and Campbell 1989,
Miller and Moslemi 1991a). The particle size and shape of wood used in hydration tests also strongly influences its 'perceived' compatibility with portland cement. Weatherwax and Tarkow (1964) first studied the effect of wood particle size on the hydration of portland cement using screened particles of southern pine species. Their results (see Figure 2.10) show a steady linear decline in compatibility with decreasing particle size, which changes to an exponential decrease for particles below about 0.1 mm in diameter. The corresponding mesh (sieve size) of particles is shown on the top axis.

![Figure 2.10](image)

Figure 2.10 The effect on wood-cement compatibility (I) of decreasing wood particle size used in wood-cement hydration samples at the same mix ratio (from Weatherwax and Tarkow 1964).

Nevertheless, the numerous laboratory studies that have tested the effect of wood on cement hydration have almost universally used ground wood particles or flour in very low wood:cement ratios. The low ratios are used because wood flour if used in larger quantities severely inhibits cement hydration.

The particle sizes of wood used in hydration tests in different studies are listed in Table 2.6 (p. 52). The sizes used range from 40- to 60-mesh with 20- to 40-mesh wood flour the most commonly used particle size. The effect particles larger than 40-mesh (≈0.4 mm particle diameter) on cement hydration is not shown in the chart from Weatherwax and Tarkow (1964). Some studies have not specified the particle size of the wood used in hydration tests, rather merely stating that 'powder', 'pulverised' or 'hammermilled' wood was used. The variation in wood particle size between the different studies makes meaningful comparisons of wood-cement compatibility data from different studies difficult. It is worth pointing out that wood particle sizes larger than 20- to 40-mesh wood flour have not been used in previous hydration studies, despite of the fact that wood used in wood-cement composites is in a much larger form and quite different geometry, e.g. small flakes in particleboards and strands in WWCB.
No previous studies have tested the compatibility of flakes or strands with cement as being more representative form of wood for predicting the suitability of wood for cement-bonded composites. Instead the use of wood flour appears to have become the generally accepted method of predicting the suitability of wood for all types of wood-cement composites. Chapters 3 and 4 of this thesis examine the effects of wood particle size and form on its behaviour with portland cement and how this can influence the results and inferences made from wood-cement compatibility tests.

2.8.6 Other methods for assessing wood-cement compatibility

Chittenden (1972) has argued that the wood flour-cement hydration test developed by Sandermann and Kohler (1964) and used in most subsequent studies is limited in its ability to predict the suitability of different wood species for use in wood-cement composites and may be reliable only for woods which strongly inhibit the setting of cement or those with very weak effects on cement hydration.

Instead, the use of an even simpler method developed by Sandermann (1966) involving test sticks set in cement was advocated. In this test, no sophisticated hydration temperature-monitoring apparatus is required; rather small uniform sticks are set in cement for 2 days, and if they can be pulled free cleanly from the cement by hand or using pliers then the wood is deemed unsuitable for use in wood-cement composites.

Although not widely used, this method was adopted by Wong and Ong (1982), Rahim and Ong (1983) and Jirayut (1985) to test Malaysian and Thai hardwoods for their compatibility with portland cement and their potential suitability for use in WWCB. Species were ranked according to the pulling force (N) required to remove test sticks set in cement for 24 h. The stick-pull testing method was also used by Schmidt et al. 1994 to test the compatibility of CCA-treated pine with portland cement. Rahim and Ong (1982) state that they adopted this method following the recommendations of Chittenden (1972). Results from stick-pull tests suggest that cement hydration tests may underestimate the compatibility of certain wood species with cement. For example, Sandermann and Kohler (1964) rated Shorea spp. as incompatible with cement on the basis of results from hydration tests (using wood flour), whereas results from Wong and Ong (1982) using the stick-pull tests showed Shorea spp. as being compatible with cement.

Another method that has sometimes been used for assessing the effects of wood on the setting of portland cement is compression testing of cylindrical samples of cement containing small quantities of wood flour (10 parts cement to 1 part wood). Some stated reasons for using this test in preference to other methods include: if the equipment for measuring hydration temperature is not available (Iddi et al. 1992); where an idea of bond strength between wood and cement is desired without having to make test boards (Blankenhorn et al. 1994); and where it is uncertain whether an accurate
assessment of wood-cement compatibility can be given by conventional cement hydration tests (Lee and Hong 1986).

Chittenden (1972) has further suggested that simple wood-cement compatibility tests (including stick-pull tests) are of no great value in determining the overall suitability of timber for the manufacture of wood-cement composites. This is because they give no indication of the important physical characteristics of wood that can affect the properties of composites; including density, grain and knot characteristics and ease of machining, that determine the quality of wood wool or flakes. They also give no indication of strength development in the composite during the curing phase after setting.

2.9 The testing and use of acacias and eucalypts in wood-cement composites

2.9.1 Acacias

Members of the genus *Acacia*, which comprises over 950 species, are poorly represented in wood-cement compatibility studies. Despite the importance of certain species of *Acacia* for wood and non-wood products in numerous countries, very few wood-cement compatibility studies have tested any acacias. The aforementioned stick-pull compatibility study of Rahim and Ong (1983) rated *A. mangium* as unsuitable for use in wood-cement composites. Species that were rated as suitable had pulling forces of not less than 1152 N, whereas the pulling force for sticks of *A. mangium* wood was only 359 N. The bonding strength of *A. mangium* test sticks was improved by pre-soaking them in \( \text{Al}_2(\text{SO}_4)_3 \) solution (resulting in the required pulling force increasing to 1274 N) or \( \text{CaCl}_2 \) solution (888 N). *A. mangium* and other tropical hardwoods (*P. falcatoria* and damar putih (Agathis alba Foxw.)) were used by Firmanti and Subiyanto (1998) to test the effects of different wood pre-treatments on the bond strength of wood-cement composite samples. *A. mangium* was rated as the least compatible with cement, but its compatibility improved after 2 h pre-soaking in 1% NaOH.

Only one species of *Acacia* was represented in the 99 different woods tested for their compatibility with portland cement by Sandermann and Kohler (1964). The sapwood and heartwood flour of a temperate species, green wattle (*Acacia decurrens* Benth.), were found to be highly incompatible with cement and were therefore deemed as being unsuitable for the manufacture of wood-cement composites. The wood of black wattle (*A. mearnsii* de Wild.) has also been shown to be highly incompatible with cement in studies by Hachmi and Moslemi (1989), Hachmi *et al.* (1990) and Hachmi and Sesbou (1991).

The low compatibility of potentially useful tropical acacias such as *A. mangium* with portland cement can be attributed primarily to heartwood extractives (Tachi *et al.* 1988, 1989), which are discussed in greater detail in Chapter 9. The sapwood of *A. mangium* is quite compatible with
Portland cement since it has a much lower soluble sugar content (<0.3%) than the heartwood (>0.5%) (Sudin and Ibrahim 1990). It has been suggested by Solorzano (1989) that if the soluble sugar content of the source wood used in the commercial manufacture of wood-cement composites is above 0.5% it should not be used.

The results of other studies that have tested acacia wood, including the commercially important *A. mangium*, in the manufacture of wood-cement composites appear to be strongly influenced by type of composite made, processing technique and wood pre-treatment, and whether cement-setting accelerators were used. All studies that have examined the manufacture of wood-cement composites from *A. mangium* wood indicate that pre-soaking the wood wool or flakes in cold water for at least 6 to 12 h is necessary to obtain composites of acceptable strength (Jegatheswaran 1989, Tachi *et al.* 1988, Sulastiningsih *et al.* 1990, Soriano *et al.* 1997, Cabangon *et al.* 1998, Eusebio *et al.* 2002b).

Jegatheswaran (1989) found that untreated *A. mangium* wood flakes were highly unsuitable for the manufacture of CBPs, but pre-treatment of the flakes in a 1% NaOH solution greatly improved the strength properties (MOR, MOE, and IB) and dimensional stability (24-h water soak) of boards. In a study Sudin and Ibrahim (1990) CBPs were made from 4-year-old *A. mangium* which met the Malaysian standard for CBP (MS 934, 1986) without the need for chemical additives, provided a high cement:wood ratio (3:1) was used and boards were cured at 65°C for 24 h. Average board MOR in this case was 10.7 MPa. Board properties were further improved by adding 2% Al$_2$(SO$_4$)$_3$. Tachi *et al.* (1988) found that the addition of an accelerator at 2% (either MgCl$_2$, FeCl$_3$ or AlCl$_3$) was necessary to produce CBPs with adequate properties from *A. mangium* flakes. MOR was 11-12 MPa; however the use of CaCl$_2$ did not improve board properties. Subiyanto and Firmanti (1998) pre-treated *A. mangium* wood flakes by boiling them in water for 3 h followed by the addition of CaCl$_2$ at 2.5% w/w cement, which was sufficient to produce boards conforming to Japanese Industrial Standard JIS A-5908. Board MOR was about 8 MPa, and thickness swelling was between 1 and 2% if a wood:cement ratio of 1:2.75 was used.

*A. mangium* has also been investigated in several studies for its suitability for the manufacture of WWCBs. In all cases some form of wood pre-treatment and/or the use of cement-setting accelerators was necessary to produce boards with adequate properties. For example, Sulastiningsih *et al.* (1990) found that *A. mangium* wood wool needed to be soaked in water at ambient temperature for 24 h before making WWCB. The addition of CaCl$_2$ and Ca(OH)$_2$ further improved board properties.

Pre-soaking of *A. mangium* wood wool in water at ambient temperature for 24 h significantly improved the average bending strength of WWCBs made from this species and allowed the substitution by up to 10% (w/w cement) with rice hull ash without significantly compromising board strength properties (Lynch 1997). It was concluded from Lynch's study that *A. mangium* may
be suitable for the commercial manufacture of WWCB provided the wood-cement bonding strength and board density can be increased and thickness swelling reduced to within acceptable limits. Further research into optimising processing conditions such as wood soaking time, post-harvest storage time, pressing time and platen pressure, and water requirement when rice hull ash was used, were strongly recommended to help improve product quality.

Soriano et al. (1997) tested the effects of three wood:cement ratios (0.6:1, 0.8:1 and 1:1) and three accelerators (CaCl₂, Na₂SiO₃ and Al₂(SO₄)₃) added at 3% w/w cement on the properties of WWCBs made from pre-soaked *A. mangium* wood wool. In accordance with the findings of Rahim and Ong (1983), Al₂(SO₄)₃ was found to be the most effective accelerator in improving wood-cement bond strength, particularly if a lower wood:cement ratio (0.6:1) was used. 3% Na₂SiO₃ was relatively ineffective at improving board properties. Boards made using a high wood:cement ratio (1:1) had the highest thickness swelling; however they also had greater bending strength (60 kgf/cm²) than boards made with a wood:cement ratio of 0.6:1. This was thought to be due to the greater reinforcing effect of wood wool on the tensile properties of the former. The study also examined nail-head pull-through strength (NPTS) of boards, which is important for nailed ceiling boards and cladding, especially in wind-prone areas. NPTS values were highest in boards made with a high wood:cement ratio, and were further increased if Al₂(SO₄)₃ and CaCl₂ were added to boards.

Further work on assessing the suitability of *A. mangium* for WWCB in the Philippines includes studies by Cabangon et al. (1998 and 2002b) and Eusebio et al. (2002b). Cabangon et al. 1998 tested the effect of selected cement-setting accelerators (CaCl₂, Al₂(SO₄)₃ and FeCl₃) on the properties of WWCBs made from pre-soaked *A. mangium, E. pellita* and poplar wood. Boards made from *A. mangium* wood wool were consistently stronger than those made from *E. pellita* and responded well to all accelerator types. The addition of accelerators increased the strength properties of boards made from the tropical hardwoods but they had little effect on boards made from poplar wood wool. The superior performance of *A. mangium* in WWCBs compared with *E. pellita* was thought to be primarily due to the lower density of *A. mangium*, which made it easier to shred into good quality wood wool and resulted in a higher mat compression ratio (the pressure exerted to reach desired board thickness) during the pressing of boards.

Cabangon et al. (2002b) investigated whether medium- to long-term outdoor storage of *A. mangium* billets prior to shredding could improve the suitability of this species for use in WWCBs. Debarking and storage of billets for between 12 and 36 weeks improved board properties. Board properties were further improved by prolonged storage of wood (over 9 months) outdoors, and the authors suggested that this might help eliminate the need to use an accelerator during the manufacture of boards.
In a study by Eusebio (2002b), two tropical acacias; *A. mangium* and earleaf acacia (*Acacia auriculiformis* Cunn. ex Benth.), and *G. arborea* were tested for their suitability for the manufacture of WWCBs. All species required pre-soaking of the wood wool and the use of cement-setting accelerators to manufacture boards of acceptable quality. The addition of 3% CaCl₂ did not improve board strength when unsoaked wood wool was used, but it did improve the properties of boards made from wood wool that was pre-soaked for 6 h (or 12 h in the case of *A. auriculiformis*). 3% Al₂(SO₄)₃ was effective with unsoaked wood wool of *G. arborea*, facilitating the production of boards with MOR of about 6 MPa. The highest board quality for the tropical acacia wood was achieved at a wood:cement ratio of 1:1 after wood wool had been pre-soaked for 24 h and an accelerator added. CaCl₂ worked best in boards containing pre-soaked wood wool from *A. auriculiformis* (MOR = 7.6 MPa) whereas Al₂(SO₄)₃ was most effective in boards containing pre-soaked wood wool from *A. mangium* (MOR = 8.2 MPa).

*A. mangium* was found to be more suitable than *E. pellita* for the manufacture of fibre-cement composite panels by Eusebio et al. (1998a). Air-cured panels containing *A. mangium* fibre at 8-10% w/w had a density of 1.44 g/cm³, flexural strength of 20 MPa, fracture toughness of 0.6 kJ/m² and <24% water absorption. At the same fibre loading, panels containing *E. pellita* fibre had MOR of 15 MPa and fracture toughness of 0.3 kJ/m² in. The good potential of *A. mangium* fibre for this kind of composite was considered noteworthy and warranting further investigation.

The only species of temperate acacia that has been tested in wood-cement composites is *A. mearnsii*. Cement-bonded particleboards with satisfactory mechanical properties were reportedly made using *A. mearnsii* flakes of various sizes with portland cement by Teixeira and Pereira (1987). This species was also used to manufacture commercial quality WWCBs by Flawes and Chittenden (1967). It was necessary to pre-soak the wood wool in a 1% solution of CaCl₂ before mixing it with cement, and a 3% solution was recommended to obtain boards with reduced surface friability.

These studies indicate that the timber of *A. mangium* and possibly other fast-grown tropical and temperate acacias is suited to the manufacture of wood-cement composites, provided wood-cement bonding can be improved. Results suggest that pre-soaking wood wool and adding cement-setting accelerators can improve wood-cement bonding. The manufacture of WWCBs from *A. mangium* wood is examined in more detail in Chapter 10 of this thesis.

### 2.9.2 Eucalypts

Wood from fast-grown eucalypts is becoming more popular for use in the commercial manufacture of cement-bonded composite panels around the world (Van Elten 2000). Accordingly, a somewhat wider range of eucalypt species than acacias is represented in laboratory tests of wood-cement compatibility and pilot studies of the manufacture of wood-cement composites. Like the
acacias, however, only a few species have ever been assessed in any one study, and differences in methodology used make it difficult to directly compare results from the different studies. Eucalypt wood has performed well in several wood-cement hydration studies, suggesting that eucalypts may be somewhat better suited to the manufacture of wood-cement composites than many other hardwoods, including acacias. In contrast, results from studies that have attempted to manufacture wood-cement composite boards from various eucalypt species have been mixed.

The compatibility of wood flour from jarrah (Eucalyptus diversicolor F. muell.) and karri (Eucalyptus marginata Donn ex Smith) with cement was measured by Sandermann and Kohler (1964). E. diversicolor was rated as 'unsuitable' for use in wood-cement composites; cement containing its wood flour reached a maximum hydration temperature of only 44°C after 49 h compared with samples containing E. marginata, which reached a maximum hydration temperature of 56°C after 21 h. E. marginata was rated as 'moderately suitable'. By comparison, the least compatible wood species was walnut (Juglans nigra L.) with an initial temperature rise to just 24°C and no subsequent cement hydration and setting.

Samples from 3- and 4-year-old Sydney blue gum (Eucalyptus saligna Smith) trees, an endemic Cuban pine (Pinus tropicalis Morelet), and Caribbean pine (Pinus caribaea Morelet) were tested for their suitability for the manufacture of wood-cement particleboard by Manzanares et al. (1991). These authors prepared hammer-milled wood particles and used maximum hydration temperature to assess the compatibility of the wood with cement. The pines were reported to be suitable, but E. saligna less so. Wood samples from 4-year-old E. saligna trees were more compatible with cement than those from 3-year-old trees.

In contrast, a study by Latorraca et al. (1999) found wood flour samples from lemon-scented gum (Eucalyptus citriodora Hook) to be highly compatible with portland cement (inhibitory index of 4%). This had the highest compatibility of five plantation tree species tested, including Pinus taeda. Fresh wood from G. arborea was the most inhibitory (inhibitory index of 140%), and therefore the least suitable for the manufacture of wood-cement composites. Likewise, wood flour samples from three eucalypts, candlebark (Eucalyptus rubida Dean & Maiden), E. saligna and an unspecified species, were reported to be among the most compatible of a wide range of local and exotic wood species grown for wood production in China (Wei et al. 2000a). Waste sawdust from forest red gum (Eucalyptus tereticornis Smith) was reported to be highly compatible with cement in a wood-cement hydration study by Dutt et al. (1997), whereas milled fresh wood was of only moderate compatibility.

Other eucalypts that have featured in wood-cement compatibility tests include river red gum (Eucalyptus camaldulensis Denh.) and tuart (Eucalyptus gomphocephala D.C.) (Hachmi and Moslemi 1989, 1990). These two species had $C_\lambda$-factors of 69% and 54% and were classed as
'compatible' \((C_A > 68\%)\) and 'moderately compatible' \((C_A\) between 28 and 68\%), respectively. Comparable values for argan \((Argania\ spinosa\ (L.)\ Skeels)\) and lodgepole pine \((Pinus\ contorta\ Dougl.\ ex\ Loud.)\) were 9\% and 85\%, respectively. The two eucalypt species also had intermediate levels of hot-water-soluble extractives, 6.8\% and 8.9\% for \(E.\ camaldulensis\) and \(E.\ gomphocephala\), respectively, compared with 3.1\% and 13.8\% for \(P.\ contorta\) and \(A.\ spinosa\) respectively.

\(E.\ camaldulensis\) was rated among the most suitable of 36 different hardwood species for wood-cement composites that were tested for their compatibility with cement by Shukla et al. (1984) and Jain et al. (1989). Shukla et al. (1984) made cylindrical casts of wood flour-cement mixtures and tested them for compressive strength to assess the compatibility of wood with cement whereas Jain et al. (1989) used Sandermann and Kohler's (1964) method of measuring the heat of hydration of wood flour-cement mixtures.

Wood from flooded gum \((Eucalyptus\ grandis\ Hill\ ex\ Maiden)\) was rated as 'unsuitable' for use in wood-cement composites on the basis of the pulling force required to remove test sticks set in cement (Rahim and Ong 1983). \(E.\ grandis\) required the lowest pulling force \((101\) N\) of all 16 species that were tested and rated as 'unsuitable' for wood-cement composites. The addition of the cement-setting accelerators \(\text{CaCl}_2\) and \(\text{Na}_2\text{SiO}_3\) did not greatly increase the pulling force required to remove the \(E.\ grandis\) test sticks from cement. The most effective accelerator was \(\text{Al}_2(\text{SO}_4)_3\), but this increased the pulling force to only 828 N, below the minimum of 1152 N required to classify a species as 'suitable' for wood-cement composites.

As the above discussion shows, selected eucalypts (especially sub-tropical and tropical species) have been tested for compatibility with portland cement with varied but generally positive results. However, attempts to use eucalypts for the manufacture of cement-bonded composites without some form of pre-treatment have been less successful. The majority of studies that have tested tropical eucalypt species for their suitability for the manufacture of cement-bonded composites have involved the manufacture of WWCBs.

Kamil and Ginoga (1975) found that WWCBs of acceptable quality could not be made from untreated \(E.\ deglupta\) wood. Pariboto and Suwandi-Klivon (1977) showed that the properties of WWCBs made from \(E.\ deglupta\) grown in Indonesia were strongly influenced by the location in which the trees were grown, suggesting strong geographic and/or genetic influences on the chemical constituents in the wood that affect cement setting. In a study by Lynch (1997) \(E.\ pellita\) was used to manufacture WWCBs. Boards of moderate quality could be made without using any pre-treatment or additives \((\text{average board MOR} = 5.5\) MPa\). Pre-soaking the wood in water for 24 h increased the MOR to 9 MPa.

Despite previous findings suggesting that \(E.\ grandis\) wood is unsuitable for use in wood-cement composites (Hawkes and Robinson 1978b, Rahim and Ong 1883), WWCBs of acceptable quality
were reportedly produced from *E. grandis* and *E. tereticornis* providing either a water extraction pre-treatment or a cement-setting accelerator (CaCl₂) was used during the manufacture of the boards (Evans *et al.* 2000). The combination of pre-soaking wood wool and the addition of CaCl₂ resulted in boards with an average MOR of 7.7 MPa.

Wood-cement compatibility tests have all indicated that *E. camaldulensis* should be suitable for the manufacture of wood-cement composites. These findings are, however, contradicted by studies that have manufactured boards from *E. camaldulensis* wood. Yasin and Qureshi (1990) manufactured CBPs from 5-year-old *E. camaldulensis* trees. Wood and bark was converted into small flakes, pre-washed with 3% CaCl₂ followed by the manufacture of CBPs in the laboratory. The resulting boards were of very poor quality. Pre-soaking flakes in cold water for 48 h, followed by pre-washing with 3% CaCl₂ improved the bending strength and water-resistance of boards; however boards with acceptable mechanical properties could only be produced after pre-treating the flakes in boiling water for 1 h. It is not known whether the inclusion of bark in the flakes significantly affected the performance of the wood of *E. camaldulensis* in CBPs.

Latorraca (2000) tested the suitability of eucalypts grown commercially in Brazil for the manufacture of CBP. Species tested included *E. pellita*, swamp mahogany (*Eucalyptus robusta* Smith), Timor mountain gum (*Eucalyptus urophylla* S.T. Blake) and *E. citriodora*. Boards made from *E. urophylla* were the strongest (average MOR = 6.8 MPa provided CaCl₂ was added at 4% w/w cement). The MOR values for boards made from the other species were considerably lower (5.0 MPa for *E. pellita*, 4.6 MPa for *E. robusta* and 3.5 MPa for *E. citriodora*). Steam curing of boards at 60°C for 7 days only slightly enhanced their strength properties. The result for *E. citriodora* contradicts the previous finding from wood-flour cement hydration tests made by Latorraca *et al.* (1999) which indicated that this species was highly compatible with cement. The studies by Latorraca *et al.* (1999) and Latorraca (2000) highlight the large discrepancies that can arise when ranking species for their suitability for the manufacture of wood-cement composites on the basis of results from wood flour-cement hydration tests and pilot-scale studies of the manufacture of test boards.

*E. deglupta* has been tested in the manufacture of CBP by Tachi *et al.* (1988) along with *P. falcataria, A. mangium* and *G. arborea*. The strength properties of CBPs made from *E. deglupta* were poor compared to boards made from the other species. This was attributed largely to unfavourable particle geometry resulting from flaking of the eucalypt wood (using a Pallman Ring Flaker type PZ8). *E. deglupta* wood tended to break up into needle-like particles, which had an adverse effect on board strength properties.

A small number of studies have investigated the suitability of eucalypt wood fibre for the manufacture of cement-bonded fibreboards. Eusebio *et al.* (1998a) found that *E. pellita* had little
potential for such products. The pulping characteristics of *E. pellita* contributed significantly to the poor performance of the composite. *E. pellita* chemi-thermo mechanical pulp (CTMP) had a low fibre yield and shorter, coarser fibres as well as greater retention of inhibitory extractives, all of which adversely affected composite strength.

2.10 Important conclusions

The review of the literature has focussed on two important classes of cement-bonded wood composite materials, cement-bonded particleboard (CBP) and wood wool-cement board (WWCB), and their suitability for use in developing countries. WWCB uses less cement and more wood and, unlike CBP, can be readily manufactured using relatively simple technology. For example, in the Philippines small-scale WWCB manufacturing industries have evolved to help meet the pressing need for low-cost housing materials. The low cement content of WWCB makes the choice of wood species more exacting because of the adverse effect of many woods on the hydration of cement. A wide range of methods for ameliorating low wood-cement compatibility and improving the mechanical and water resistance properties of wood-cement composites were reviewed. These vary greatly in their ease of use. Some of the simplest and most practical methods found in the literature included: prolonged seasoning and storage of wood, extractive removal by soaking wood in water, adjustments to wood:cement ratio and mat compression, and the addition of various cement-setting accelerators, most of which are simple inorganic salts such as $\text{CaCl}_2$ or $\text{Al}_2(\text{SO}_4)_3$.

Laboratory-scale methods for testing the compatibility of wood samples with portland cement (used extensively throughout this thesis) were discussed. It is clear that no universal standard test method has emerged and been used consistently by researchers testing wood-cement compatibility. The most common compatibility testing method, the wood-cement hydration test of Sandermann and Kohler (1964), has been adopted by most studies, however critical factors such as ratios of wood, cement and water, and the particle size of wood is quite variable across studies. Very few hydration tests used wood in any form other than the finely ground wood flour in various mesh sizes. A few studies have questioned the validity of wood flour-cement hydration tests and opted for alternative methods of testing wood-cement compatibility, for example stick-pull tests or compression tests, which provide more direct measures of wood-cement bond strength. Nevertheless, cement hydration tests have been almost universally adopted because of their ease of use, controlled conditions, uniformity and ability to efficiently screen large numbers of samples for their compatibility with cement.

The review reinforces the need to question whether results generated from wood-cement compatibility tests using finely ground wood flour are relevant to the potential performance of wood species in wood-cement composites such as WWCB. In several instances the results from wood
flour-cement hydration or compressive tests of eucalypt and acacia species did not accord with those produced from other compatibility tests such as stick-pull tests, or from studies that manufactured wood-cement composite boards from the same species. A clear example of the discrepancy that can arise was found in the case of *E. camaldulensis*. This illustrated the importance of using wood in hydration tests that is similar in form, age and seasoning history, and condition to that which is likely to be used to manufacture the wood-cement composite material of interest. The review indicated that the size, geometry, age and seasoning history of wood could significantly affect its perceived compatibility with portland cement and its performance in wood-cement composites. These issues are examined in more detail in Chapters 3, 4 and 5 of this thesis.

The review found that, despite their importance in plantation wood production, the representation of species of *Acacia* and *Eucalyptus* in wood-cement compatibility tests was very limited. The performance of selected acacia and eucalypt species in wood-cement composites was highly variable. Attempts to manufacture wood-cement composites (either CBPs or WWCBs) from most acacia and eucalypt woods have been largely unsuccessful unless extractives are removed from the wood (by soaking) and/or cement-setting accelerators are added to the composite during manufacture. Chapters 6 and 7 of this thesis focus on improving the utilisation of selected eucalypts, namely wood waste from short-rotation mallee plantations, and Tasmanian bluegum (*Eucalyptus bicostata* Labill.) in wood-cement composites. Following on from the problems encountered in previous studies with using fresh *A. mangium* wood for wood-cement composites, Chapters 8 to 10 investigate pre-treatments and accelerators aimed at improving the suitability of *A. mangium* for wood wool-cement board.
Chapter 3 Developing appropriate methodology for testing the potential suitability of species of *Acacia* and *Eucalyptus* for cement-bonded wood composites.

3.1 Introduction

The review of literature indicated that only a narrow range of species of acacias and eucalypts have ever been tested for their compatibility with portland cement. Some are represented in wood-cement compatibility tests of various kinds and others have been tested for performance in wood-cement composites. The wide variation in test conditions makes it impossible to directly compare results between studies or make accurate judgements about species suitability for composites of interest, i.e. wood wool cement board (WWCB), cement bonded particleboard (CBP), and cement-bonded flakeboards. The potential suitability of most tropical and temperate acacias and eucalypts for the manufacture of these wood-cement composites is otherwise unknown. The logical first step in determining their suitability is to screen them for their compatibility with cement using the relatively simple laboratory test developed by Sandermann and Kohler (1964), which monitors the effect of the wood on the heat of hydration of cement when wood flour is mixed with portland cement and water.

It has been generally assumed in the literature, however, that results obtained from cement hydration tests using wood flour are relevant to the compatibility of strands or flakes of wood (as used in WWCB and CBP) with cement. Little consideration has been given to whether screening tests that use wood flour actually correlate with the compatibility of wood wool, chips or flakes with cement. This is despite the finding that coarseness of wood flour significantly influences its perceived compatibility with cement (Weatherwax and Tarkow 1964) and that the results of hydration tests using wood flour have been suggested by Chittenden (1972) to be of little practical use, except in extreme cases of low or high compatibility with cement. The stick-pull method (Sandermann 1960) provides information on the bond strength between the wood and cement, but the results from these tests have not been related to the performance of tested species when used in the manufacture of wood-cement composites. Moreover, unlike a cement hydration test, it provides no information about how the wood sample affects hydration as it proceeds. The cement hydration test based on the 'standard' method of Sandermann and Kohler (1964) has therefore been adopted by most workers investigating wood-cement compatibility.

The most obvious factor which might confound the relationship between the results of wood-cement compatibility tests undertaken using wood flour and the suitability of wood for WWCBs or flakeboards in practice is that wood flour is processed into very small particles, resulting in a much larger surface-to-volume ratio than wood wool or flakes. This could affect the ease with which extractives are leached from wood, which is in turn likely to influence its compatibility with...
cement. This could then lead to an underestimation of the compatibility of woods expected to be used as wood wool or large flakes in wood-cement composites. Wood flour is also prepared from dry wood whereas in practice wood wool and flakes are produced from green logs. This difference could influence the effect of the wood on cement hydration and may be overlooked by tests that use wood flour. This Chapter examines these questions and is divided into two parts with two distinct broad objectives:

1. Determine whether wood flour is a reliable predictor of the compatibility of the same wood in the form of wood wool for a small selection of wood species of differing compatibility.
2. Test alternative wood sample preparation techniques for wood-cement hydration tests and select the most appropriate for preparing hydration test samples from limited source material such radial tree cores.

3.2 The suitability of wood flour for assessing suitability of acacias and eucalypts for wood wool or flake based cement composites.

3.2.1 Aims and objectives

The aim of the first section of this Chapter was to determine whether the ‘conventional’ cement hydration test that uses wood flour prepared from dry wood is a reliable method for predicting and comparing potential species (acacias and eucalypts in particular) suitability for WWCB. It is hypothesised that wood flour and wood wool differ significantly in their effects on the hydration of portland cement and that the results generated by the use of wood flour in compatibility tests can produce a misleading assessment of the potential suitability of acacia and eucalypt wood species for the manufacture of WWCB or flake board. Specific objectives were to:

1. Determine whether cement hydration tests using wood flour or wood wool could produce the same ranking of species in their measured compatibility with portland cement. To achieve this, compatibility indices were derived for heartwood, sapwood and a 50% heartwood/sapwood mix prepared in the forms of wood flour and commercially produced wood wool for a tropical acacia (Acacia mangium), a tropical eucalypt (Eucalyptus pellita) and an available species of high compatibility (Populus euramericana) for used as a control.

2. Assess the effects on wood-cement compatibility data and inferences of adding the prepared wood sample (wood flour and wood wool) to cement in different quantities.

3. Assess the possible confounding effects of wood extractive content on wood-cement compatibility results.

4. Consider other factors that could potentially confound the results and interpretation of wood-
cement compatibility tests, including heartwood/sapwood content and their chemical constituents.

### 3.2.2 Materials and methods

#### 3.2.2.1 Source of samples

The tree species used in the experiment were: brown salwood (*Acacia mangium* Willd.) from PNG-West Papua provenance, red mahogany (*Eucalyptus pellita* F. Muell.) from PNG-SW provenance, and plantation black poplar (*Populus euramericana* L.) of unknown geographic origin. *A. mangium* and *E. pellita* were chosen because of their importance as plantation species in Southeast Asia. *P. euramericana* is used to make WWCBs in Australia and was selected as a control. The poplar wood came from 30-year-old trees grown in plantations in central Victoria, Australia. The *A. mangium* and *E. pellita* trees were grown in a seed orchard planted in 1991 at Atherton, Queensland.

#### 3.2.2.2 Preparation of wood wool

Two trees each of *E. pellita* and *A. mangium* were felled and cross-cut into billets measuring 460 mm in length which were then debarked using an axe. The 460-mm billets were shredded in a green condition (MC = 60-100%) into wood wool strands measuring 0.3 x 3 x 460 mm at Woodtex Pty Ltd, Bendigo, Victoria, using a van Elten shredder (Plate 3.1). The wood wool was spread out under cover to air-dry for 7 days at approx. 23°C.

The *P. euramericana* wood was supplied by Woodtex Pty Ltd, Bendigo as two bales of shredded wood wool, cut from an unknown number of trees. Wood wool from *A. mangium* and *E. pellita* was separated into sapwood and heartwood strands on the basis of the distinct colour difference between sapwood and heartwood in both species. As *P. euramericana* does not form visually distinct heartwood (Hillis 1987), separation of sapwood and heartwood in this species was not possible. Wood wool was then cut into pieces measuring approximately 3 cm in length using scissors and placed in open bags in a conditioning room at 20 ± 1°C and 65 ± 5% r.h. for 2 weeks.

#### 3.2.2.3 Preparation of wood flour

Wood flour was prepared from blocks of air-dried heartwood and sapwood sourced from the ends of the billets that had been shredded into wood wool. Small blocks of solid wood measuring approximately 10 x 10 x 5 mm were pre-cut using a small bandsaw. Coarse wood particles were produced by passing the small blocks of wood through a rotary mill grinder (Junior brand) as shown in Plate 3.2(a). The coarse particles were collected in a plastic bag and a portion was further ground in a small Wiley mill (Arthur H. Thomas Co., Plate 3.2(b) to 20-40 mesh size, producing
approximately 50 g of flour from the heartwood and sapwood of each tree. Wood of *P. euramerica*na was unavailable in solid form and test samples were therefore obtained by grinding chopped wood wool through the Wiley mill. All wood flour samples were stored in a conditioning room at $20 \pm 1^\circ C$ and $65 \pm 5\%$ r.h. for two weeks.

Plate 3.1 Van Elten wood wool shredding machine at WoodTex, Pty Ltd, Bendigo.

(a)          (b)

Plates 3.2 Wood sample grinding equipment; (a) rotary mill and (b) Wiley mill.
3.2.2.4 Hydration sample preparation and testing

For each of following amounts of sapwood and heartwood flour and wool from each species, two samples were weighed out (on an oven-dry weight basis) and placed in separate containers: 5 g (low level, 2.4% wood), 10 g (medium level 1, 4.8% wood), 15 g (medium level 2, 7% wood) and 20 g (high level, 9% wood). Within each wood level, three categories of heartwood content were used: 0%, 50% and 100%, resulting in 48 different samples for each species. Once weighed, the wood samples were kept in a conditioning room at 20 ± 1°C and 65 ± 5% r.h.

To prepare each cement hydration sample 100 g of fresh, dry portland cement (Blue Circle Southern Cement Batch No. 99/97) was thoroughly mixed with 43.5 mL of distilled water in a sealable 'Dal grip' polythene bag for 2 minutes. The wood wool or flour sample was then added and massaged through the cement slurry until evenly mixed. The tip of a temperature thermocouple (Type J) was then taped to the outside of the sample bag and enclosed within the body of the cement or wood–cement mix by folding the bag and contents around it. The folded bag was then secured with adhesive tape, placed in a 4-mm-thick polystyrene cup and sealed inside a 1-L capacity Thermos flask. This process was carried out for six samples in turn. A cement hydration temperature logging apparatus (illustrated in Plate 3.3), similar to that used by Irle and Simpson (1993), was used to measure the heat of hydration of six wood–cement samples over 23 hours. The temperature in each sample was recorded at 15-minute intervals. A cement hydration temperature curve for each sample was plotted using the progressive average of each three successive readings. All experiments were done in a controlled temperature room maintained at 20 ± 1°C, because ambient temperature at the time of mixing and setting affects cement hydration and strength (Lea 1971, Dodson and Rajagopalan 1979, Taylor 1997), and day-to-day temperature variation has been shown to significantly affect the results of wood-cement compatibility tests (Miller and Moslemi 1991a).

From each plot of hydration temperature v time, two wood-cement compatibility indices were derived. These were:

1. Maximum heat of hydration temperature ($T_{\text{max}}$); and
2. The $C_A$-factor of Hachmi et al. (1990). As described in Chapter 2 the $C_A$-factor is the area beneath the hydration curve for a wood-cement sample divided by that of pure cement, expressed as a percentage.
Plate 3.3 Cement hydration temperature logging apparatus inside controlled temperature room with schematic diagram of the apparatus below.
3.2.2.5 Experimental design and statistical analysis

The experimental design used factorial principles, investigating the effects of four fixed factors on wood-cement compatibility, i.e. wood form (flour or wool), species, heartwood content and wood level, and also various random effects, including those associated with replicates obtained from different trees. A total of 28 days was required to test all of the samples. Since the factors of greatest interest were the effects of wood form and species on wood-cement compatibility, these factors were randomised within each daily 6-sample run. The next level of randomisation was for wood level and % heartwood with one combination of these two factors tested each day. Wood from the first tree (or bale in the case of P. euramericana) of each species was tested over the first 14 days, followed by the second tree/bale over the next 14 days. Every 7th day four cement control samples were measured, giving a total of 12 control runs over the entire experiment.

The main effects of, and interactions between, each of the four factors on wood-cement compatibility indices were tested for significance by an appropriate multi-factorial ANOVA model at the 5% significance level using Genstat 5 (Lawes Agricultural Trust 1989). Before the final analysis, diagnostic checks on the normality and variance of the data were undertaken. The factorial design of the experiment allowed data to be averaged across non-significant (p > 0.05) effects, thereby giving the experiment greater precision. Significant results are plotted graphically and bars representing the least significant difference (p ≤ 0.05) are included on graphs to facilitate comparison of means.

3.2.2.6 Cold-water-soluble extractive content and determination of sugar content of leachate from sapwood

The method used to determine the cold-water-soluble extractive content of heartwood and sapwood from A. mangium and E. pellita wood wool followed that of Browning (1967). 2 g of conditioned wood flour (20 mesh) of known moisture content and produced by grinding wood wool pieces, was placed in a tall-form beaker to which 300 mL of distilled water was added. The beaker was placed in a water bath maintained at 23 ± 2°C and stirred frequently for 48 h. The contents of the beaker were filtered under suction through a sintered glass crucible of known oven-dry weight and the residual wood was washed with 100 mL of distilled water. The crucible containing the extracted wood was oven-dried at 105°C for 24 h and re-weighed. Extractive content was expressed as a percentage of the calculated oven-dry weight of the unextracted wood. Five samples each of heartwood and sapwood were assayed and averaged. The leachates from the sapwood samples were retained for sugar content analysis.
The sugar content in the leachates from the sapwood samples was determined using a colorimetric method (Dubois et al. 1956). 2 mL of leachate was pipetted into a test tube to which 1 mL of 5% phenol solution was added and then 5 mL of sulphuric acid (Reagent Grade 95.5%) were added quickly using a fast delivery dispenser. Five replicates were taken from each 300 mL leachate. The test tubes were allowed to stand for 10 min and then shaken and placed in a water bath at 27 ± 2°C for another 20 min. 2 mL of the contents of each test tube was placed into a 10 x 10 x 45 mm clear cuvette and its absorbance of UV light at a wavelength of 490 µm was measured using a Unicam SP 1800 Ultraviolet Spectrophotometer. The five absorbance readings were averaged and translated into sugar content (µg/g) using a calibrated regression line constructed for α-D+ glucose (Dubois et al. 1956). Total soluble sugar content was expressed as mg/g of oven-dry unextracted wood.

Plate 3.4 Ultraviolet light spectrophotometer used to determine sugar content of leachates.

3.2.3 Results and discussion

3.2.3.1 Main effects and interactions between factors

The significance of the effects of the different factors (wood form, wood level, % heartwood and species) on T_{max} and C_{A}-factor are shown in Table 3.1. As expected, wood form (flour or wool) and wood level used in cement hydration tests had highly significant (p < 0.005) effects on maximum T_{max} and C_{A}-factor. More importantly, wood form interacted strongly with heartwood content,
species and wood level (Table 3.1), producing different results and interpretations of wood-cement compatibility from tests using wood flour compared with those using wood wool.

Table 3.1 F-probabilities (p-values) for significance of main effects and interactions between factors on the compatibility indices $T_{\text{max}}$ and $C_A$-factor.

<table>
<thead>
<tr>
<th>Effects and interactions</th>
<th>$T_{\text{max}}$</th>
<th>$C_A$-factor.</th>
</tr>
</thead>
<tbody>
<tr>
<td>wood form</td>
<td>&lt;0.001 (s)</td>
<td>&lt;0.001 (s)</td>
</tr>
<tr>
<td>wood level</td>
<td>0.005 (s)</td>
<td>&lt;0.001 (s)</td>
</tr>
<tr>
<td>%heart*wood form</td>
<td>0.002 (s)</td>
<td>0.005 (s)</td>
</tr>
<tr>
<td>species*wood form</td>
<td>0.011 (s)</td>
<td>0.055 (ns)</td>
</tr>
<tr>
<td>wood level*wood form</td>
<td>&lt;0.001 (s)</td>
<td>&lt;0.001 (s)</td>
</tr>
<tr>
<td>%heart*species</td>
<td>0.017 (s)</td>
<td>0.007 (s)</td>
</tr>
</tbody>
</table>

The effect of wood form on wood-cement compatibility can be seen clearly in Figure 3.1, which shows the interaction between wood form and heartwood content, averaged across species, on $T_{\text{max}}$ and $C_A$-factor.

![Figures 3.1 Interaction between heartwood content and wood form for (a) $T_{\text{max}}$ and (b) $C_A$-factor: data averaged across species and wood level.](image)

As the heartwood content of wood wool in cement hydration test samples increased, $T_{\text{max}}$ and $C_A$-factor increased, whereas the opposite occurred in those containing wood flour (Figure 3.1). Heartwood extractives that inhibit cement hydration may be readily leached from wood flour, and this could explain why decreases in wood-cement compatibility were observed to occur as the heartwood content of the wood flour increased. In contrast, wood wool has a much lower surface-to-volume ratio than wood flour, and so the ease with which extractives are removed from wood wool may be lower than for wood flour. Furthermore, the extractives in heartwood may be less susceptible to leaching in the aqueous environment of cement because heartwood is less permeable than sapwood. In contrast, sapwood extractives such as starches and sugars are very soluble and
therefore likely to be easily leached from wood regardless of form. These factors may in part explain the observations shown in Figures 3.1(a) and (b) that as the % heartwood in wood wool increased, wood-cement compatibility increased.

The form of the wood used in the cement hydration tests also influenced the 'perceived' compatibility of the different wood species with cement. Tests using wood flour ranked *E. pellita* as being more compatible with cement than *A. mangium* whereas the ranking was reversed when wood wool was used (Figures 3.2). For example, average $C_A$-factors for *E. pellita* and *A. mangium* flour were 64.5 and 56.5% respectively whereas for wood wool they were 72.4 and 77.5% (Figure 3.2(b)). These compared with *P. eurameriana* wood at 65.4 and 79.8% for flour and wool respectively.

![Graphs](https://via.placeholder.com/150)

**Figures 3.2** Interaction between species and wood form for (a) $T_{\text{max}}$ and (b) $C_A$-factor; data averaged across heartwood content and wood level.

The leachability of extractives from wood flour and wood wool may help explain the observed switch in species compatibility ranking between the two wood forms. The heartwood of *A. mangium* is known to contain distinctive polyphenolic extractives which strongly inhibit cement hydration (Tachi et al. 1989). Such extractives may be easily leached from wood flour with its fine particulate form and very high exposed surface area but less readily from wood wool, and hence it is not surprising that tests using wood flour ranked *A. mangium* as the least compatible of the wood species tested.

The relatively low compatibility of wood wool produced from *E. pellita* sapwood (which can be seen in Tables 3.2 and 3.3) reduced the overall compatibility of *E. pellita* wood in wool form to below that of *A. mangium*. The reduced compatibility of *E. pellita* sapwood compared to its heartwood may have been caused by the presence of inhibitory sugars in and on the surface of the
wood. The age and condition of the wood at the time of preparation for cement hydration samples may therefore influence its perceived compatibility with cement and is discussed further in this Chapter.

As expected, wood form interacted significantly \((p < 0.001)\) with wood level (Table 3.1 and Figures 3.3), whereby compatibility with cement decreased markedly with increasing level of wood flour but less so for wood wool. Wood flour and wood wool were of similar compatibility when added at low or low-medium level; however the two wood types differed significantly \((p < 0.001)\) when added at the medium-high or high level of addition specified in the standard cement hydration test of Sandermann and Kohler (1964). The smaller particle size of wood flour would result in a much greater increase in the ratio of surface area to weight with increasing wood level compared with wood wool, thus affecting wood-cement compatibility to a greater extent.

Finally, Figures 3.4 (a) and (b) show the significant interaction between species and heartwood content whereby wood-cement compatibility increased in \(E. \text{pellita}\) and decreased in \(A. \text{mangium}\) with increasing heartwood content. The trend in \(A. \text{mangium}\) was due to the high average compatibility of its sapwood regardless of form, which can be seen in Tables 3.2 and 3.3, in contrast to the low compatibility of the heartwood in flour form, for reasons already discussed. These results show the potential for inferences about species compatibility with cement from wood cement-compatibility tests to be further confounded by varying proportions of heartwood and sapwood in the cement hydration test samples used.
Figures 3.4 Interaction between heartwood content and species for (a) $T_{\text{max}}$ and (b) $C_{\text{A}}$-factor; data averaged across wood form and wood level.

Statistically significant ($p \leq 0.05$) effects of, and interactions between, wood form, wood level, species and heartwood content on $T_{\text{max}}$ and $C_{\text{A}}$-factor were summarised in Figures 3.1 to 3.4. The same effects can be observed in the ‘raw data’ if $T_{\text{max}}$ (Table 3.3) and $C_{\text{A}}$-factor (Table 3.4) values are averaged across statistically insignificant ($p > 0.05$) results in accordance with the factorial design of the experiment.

Table 3.2 Average $T_{\text{max}}$ for wood flour and wood wool of *E. pellita*, *A. mangium* and *P. euramerican* by % heartwood content and wood level.

<table>
<thead>
<tr>
<th></th>
<th>0% heartwood*</th>
<th>50% heartwood*</th>
<th>100% heartwood*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flour</td>
<td>Wool</td>
<td>Flour</td>
</tr>
<tr>
<td><em>E. pellita</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>66.3</td>
<td>55.4</td>
<td>66.6</td>
</tr>
<tr>
<td>M1</td>
<td>60.8</td>
<td>45.1</td>
<td>62.3</td>
</tr>
<tr>
<td>M2</td>
<td>56.9</td>
<td>40.9</td>
<td>55.3</td>
</tr>
<tr>
<td>High</td>
<td>37.5</td>
<td>40.2</td>
<td>33.5</td>
</tr>
<tr>
<td>Average</td>
<td>55.4</td>
<td>45.4</td>
<td>54.5</td>
</tr>
<tr>
<td><em>A. mangium</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>63.8</td>
<td>64.9</td>
<td>63.1</td>
</tr>
<tr>
<td>M1</td>
<td>57.8</td>
<td>57.6</td>
<td>56.8</td>
</tr>
<tr>
<td>M2</td>
<td>53.8</td>
<td>54.3</td>
<td>48.2</td>
</tr>
<tr>
<td>High</td>
<td>42.9</td>
<td>46.2</td>
<td>33.2</td>
</tr>
<tr>
<td>Average</td>
<td>54.6</td>
<td>55.8</td>
<td>48.9</td>
</tr>
<tr>
<td><em>P. euramerican</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>61.3</td>
<td>60.3</td>
<td>61.7</td>
</tr>
<tr>
<td>M1</td>
<td>52.8</td>
<td>53.5</td>
<td>52.0</td>
</tr>
<tr>
<td>M2</td>
<td>45.3</td>
<td>46.5</td>
<td>48.7</td>
</tr>
<tr>
<td>High</td>
<td>37.8</td>
<td>43.4</td>
<td>33.6</td>
</tr>
<tr>
<td>Average</td>
<td>49.3</td>
<td>54.6</td>
<td>52.8</td>
</tr>
</tbody>
</table>

* 0% heartwood = sapwood; 50% heartwood = 50% heartwood/50% sapwood.
Table 3.3 Average C1-factor for wood flour and wood wool of E. pellita, A. mangium and P. euramericana by % heartwood content and wood level.

<table>
<thead>
<tr>
<th></th>
<th>0% heartwood*</th>
<th>50% heartwood*</th>
<th>100% heartwood</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flour</td>
<td>Wool</td>
<td>Flour</td>
</tr>
<tr>
<td>A. mangium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>91.8</td>
<td>97.7</td>
<td>93.7</td>
</tr>
<tr>
<td>M1</td>
<td>79.6</td>
<td>84.4</td>
<td>70.5</td>
</tr>
<tr>
<td>M2</td>
<td>62.3</td>
<td>78.3</td>
<td>33.3</td>
</tr>
<tr>
<td>High</td>
<td>37.5</td>
<td>61.7</td>
<td>26.7</td>
</tr>
<tr>
<td>Average</td>
<td>67.8</td>
<td>80.5</td>
<td>56.1</td>
</tr>
<tr>
<td>E. pellita</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>93.1</td>
<td>82.5</td>
<td>96.7</td>
</tr>
<tr>
<td>M1</td>
<td>74.6</td>
<td>57.1</td>
<td>82.7</td>
</tr>
<tr>
<td>M2</td>
<td>57.0</td>
<td>47.1</td>
<td>50.2</td>
</tr>
<tr>
<td>High</td>
<td>43.3</td>
<td>42.5</td>
<td>28.3</td>
</tr>
<tr>
<td>Average</td>
<td>67.0</td>
<td>57.3</td>
<td>64.5</td>
</tr>
<tr>
<td>P. euramericana</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>91.8</td>
<td>90.7</td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>74.2</td>
<td>85.0</td>
<td></td>
</tr>
<tr>
<td>M2</td>
<td>53.6</td>
<td>76.0</td>
<td></td>
</tr>
<tr>
<td>High</td>
<td>42.0</td>
<td>67.4</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>65.4</td>
<td>79.8</td>
<td></td>
</tr>
</tbody>
</table>

* 0% heartwood = sapwood; 50% heartwood = 50% heartwood/50% sapwood.

3.2.3.2 Confounding effects of wood extractive content

Explanations for the results observed for E. pellita (above) are less straightforward than those for A. mangium or P. euramericiana. This observation could be due to reduced quantity, reduced leachability or lower 'toxicity' of extractives in the heartwood and/or reduced sapwood compatibility due to the presence and leachability of inhibitory substances such as sugars in the sapwood. To investigate this question further, the average quantities of water-soluble extractives present in the heartwood and sapwood of E. pellita and A. mangium and the quantity of sugars contained in the sapwood leachate were determined and are shown in Table 3.4 below.

Table 3.4 Heartwood and sapwood wood wool extractive contents and sapwood sugar content for A. mangium, E. pellita and P. euramericana.

<table>
<thead>
<tr>
<th>Species</th>
<th>Heartwood Extractive Content (%)</th>
<th>Sapwood Extractive Content (%)</th>
<th>Sapwood Sugar Content (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. mangium</td>
<td>5.8</td>
<td>1.4</td>
<td>5.2</td>
</tr>
<tr>
<td>E. pellita</td>
<td>10.5</td>
<td>4.1</td>
<td>17.3</td>
</tr>
<tr>
<td>P. euramericana</td>
<td>0.9</td>
<td>0.9</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Overall, the heartwood of E. pellita and A. mangium contained greater quantities of extractives than the sapwood. Contrary to expectations, the heartwood of E. pellita contained a greater quantity of extractives (10.5%) than the heartwood of A. mangium (5.8%). This suggests that the extractives present in the heartwood of E. pellita are of a chemical composition that is much less inhibitory of cement hydration than those present in A. mangium. Work by Tachi et al. (1988, 1989) and Hachmi
and Moslemi (1989) has also shown that the chemical composition of heartwood extractives from different wood species has a stronger influence on wood-cement compatibility than the amount present.

The sapwood of *E. pellita* contained a higher quantity of water-soluble extractives than that of *A. mangium*. The sapwood extract from *E. pellita* also contained a very high sugar content (17.3 mg/g of wood) compared to the extract from *A. mangium* sapwood (5.2 mg/g). As can be seen in Table 3.3 the maximum hydration temperature reached for samples containing medium-high level addition of wood wool of *E. pellita* sapwood was 40.9°C ($C_A = 47.1\%$) compared with 54.3°C ($C_A = 78.3\%$) for the same addition of *A. mangium* sapwood wood wool. The wood wool of *E. pellita* may have been made even more incompatible with cement by surface enrichment of inhibitory water-soluble extractives such as sugars. Water-soluble wood sugars can migrate to and deposit on the surface during drying of wood, affecting bonding in a range of wood composites (Long 1978, Zavarin 1984, Miller and Moslemi 1991a). High levels of sugars in and on the surface of sapwood have been shown to reduce its compatibility with cement (Biblis and Lo 1968, Fischer *et al.* 1974).

The results demonstrate that although species, wood form and wood level added are obvious determinants of wood-cement compatibility indices, differences in the quantity and/or chemical composition of extractives in the heartwoods and sapwoods of different wood species, and possibly the condition of the wood when it is prepared, can produce an overlaying and strongly confounding effect on wood-cement compatibility data. Heartwood:sapwood proportion in wood used in hydration samples is a potentially significant determinant of its perceived compatibility with cement and differences could affect species ranking and interpretation of results from wood-cement hydration tests. These considerations are investigated further in later chapters.

### 3.2.4 Conclusions

The findings from this study indicate that for the selected species *A. mangium* and *E. pellita* to be investigated in Chapter 4, conventional cement hydration tests that use wood flour would be unsuitable for measuring and ranking the potential suitability of such species for WWCB or cement-bonded flakeboards. The results confirmed the hypothesis that wood flour and wood wool behave quite differently with cement and generate varying perceptions of wood species compatibility with cement.

The results from the two different kinds of wood-cement compatibility tests were confounded also by the quantity of wood material added and the heartwood/sapwood content of the samples. At low-level addition, the compatibility readings generated from using wood flour or wood wool were similar, whereas at high-level addition the use of wood flour resulted in a much lower ‘perceived’ compatibility of the wood compared to if wood wool was used. Heartwood/sapwood content of
samples also influenced the ‘perceived’ compatibility of a wood species with cement depending on whether wood flour or wood wool was used. Similar compatibility readings arose from the use of wood flour or wood wool if the samples consisted largely of sapwood, whereas the results were very different for the two wood forms if the samples consisted largely of heartwood. This is because the heartwood of A. mangium was significantly less compatible with portland cement when added in the form of wood flour compared to wood wool. In contrast, the compatibility of sapwood from E. pellita was lower in the form of wood wool prepared from fresh green wood compared to the wood flour that had been prepared from dried wood.

Cement hydration tests that use wood flour may underestimate the suitability of a species such as A. mangium for WWCB, as the inhibitory heartwood extractives may not be as easily leached from wood wool compared to wood flour. The results generated from the use of old, dry wood samples may also mask potential problems caused by subsequent drying of wood wool or flakes if they are produced from fresh sapwood, as evidenced in E. pellita. The greatly altered geometry of wood flour also overlooks differences between wood species in structure, permeability and extractive leachability of the wood if prepared as wood wool, larger particles or flakes. Accordingly, cement hydration tests designed to screen wood species for their compatibility with cement should use coarse wood samples with a lower surface-to-volume ratio than wood flour. Hydration samples should also be prepared, if possible, from parent material that reflects the likely condition of wood when prepared and used for the manufacture of wood-cement composites. Such considerations might include when the tree was cut, time elapsed between tree cutting and wood sample preparation for hydration tests, and method of drying.

The results of the wood-cement compatibility tests based on different wood forms were further complicated by differing extractive contents in the heartwood and sapwood of A. mangium and E. pellita. The relatively high extractive content of E. pellita heartwood (10.5%) appears to have had less of a deleterious effect on cement hydration than the lower quantity of water-soluble extractives in A. mangium heartwood (4.3%). However the sapwood of E. pellita contained a high level of water-soluble extractives and high sugar content relative to that of A. mangium, helping to explain its lower compatibility with portland cement.

The extent to which the findings here are relevant to other wood species is not known; however they suggest that compatibility estimates of wood species for WWCBs and possibly other wood-cement composites based on screening tests which use wood flour should be viewed with caution. For this reason, an alternative to hydration tests based on wood flour is to be adopted for subsequent experiments, and alternative methods of preparing wood samples for cement hydration tests are assessed in the second part of this Chapter below.
3.3 Testing and selection of an appropriate wood form for assessing potential suitability of acacia and eucalypt wood for wood wool or flake based cement composites.

The findings from Section 3.2 of this Chapter indicated that results derived from the conventional method of using wood flour in wood-cement hydration tests to assess and rank wood species for compatibility with portland cement could be inaccurate and potentially misleading. The results from such tests could therefore not be extrapolated to the performance of the wood in wood wool or flake-based cement composites. This necessitated closer examination of the effects of wood form on its 'perceived' compatibility with cement, and the development of an alternative method of preparing hydration samples that more accurately predicts the effects of wood wool or flakes on cement hydration. Small, fresh radial tree cores are used for wood-cement compatibility tests in Chapter 4, so it is essential that the preparation technique minimises changes in sample condition and waste of material.

3.3.1 Aims and objectives

The aim of the second section of this Chapter was to develop a suitable alternative to wood flour prepared from dried wood for use in wood-cement hydration tests that can better estimate the effects of wood wool or flakes on cement hydration. It is hypothesised that wood thinly sliced through the tangential longitudinal plane would most closely approximate wood wool or flakes in its hydration behaviour across different wood species, and result in minimal loss of material during preparation. Specific objectives were:

1. To derive compatibility indices for samples prepared in different forms from low to moderately compatible tropical acacia and eucalypt species and compare these with commercially produced wood wool from the same species.

2. To assess the effects of the removal of cold-water-soluble extractives on the compatibility of the different wood forms for each species.

3.3.2 Materials and methods

3.3.2.1 Species and sample collection

Two trees of each of the following species were felled and two adjacent logs each 1.15 m in length were cut from each trunk:

• brown salwoods (*Acacia mangium* Willd. and *Acacia aulacocarpa* Cunn. ex Benth), from PNG-N provenance and PNG-SE provenance, respectively, both planted in 1991 at Damper in North Queensland;
red mahogany (*Eucalyptus pellita* F. Muell.) from PNG-W Papua, planted in 1991 at Ellerbeck in North Queensland; and
cottonwood (*Populus deltoides* Marsh.) clones 'A' and 'B', planted *circa* 1958 at The Australian National University in Canberra.

Each log was further cut to produce two billets measuring 460 mm in length and two discs measuring 40 mm in thickness. One disc was immediately cut into strips 10 mm in width, which were stored in a freezer until further processing. The other was air-dried for 2 weeks and then cut into strips in the same manner as the first disc. The billets were destined for shredding into wood wool.

### 3.3.2.2 Preparation of wood in different forms

Heartwood and sapwood were converted separately into six different forms;

- wood wool: produced at the commercial Woodtex factory in Bendigo as described in Section 3.2. Wood wool could not be prepared from dry wood.
- wood flakes: sliced through the tangential plane to dimensions 10 x 10 x 0.3 mm. Flakes were prepared by hand, using a pedal-operated framers guillotine with extremely sharp cutting blades (*Jyden*, Plate 3.5). These were prepared from both green and air-dry wood samples that had been pre-cut into 10 mm strips.
- coarse-ground particles 1: produced from green wood samples only using a laboratory rotor mill as described in Section 3.2.
- coarse-ground particles 2: produced using a Wiley toothed crushing mill Model No. 54 (Plate 3.6) from samples of green and dry wood. Blocks of both green and dry sapwood and heartwood from all species were first reduced to small blocks measuring approximately 10 x 10 x 5 mm. To prevent the wood being too finely ground the mill was run for a restricted time. Batches of ten blocks each were fed into the top of the mill, the rotor switched on for 10 seconds and then stopped. The particles were collected from the bottom and from within the mill before feeding the next batch of wood into the mill.
- wood flour: produced as described in Section 3.2.2.3 from dry wood samples only.
- wood powder: produced from dry wood flour using a ball mill. Here 40-mesh wood flour produced using a small Wiley mill was ground to a fine powder using a Uni Ball II Micro ball mill (shown in Plate 3.7) with two milling drums each containing seven 2.5 cm diameter steel balls. The wood flour was ground for 6 h at 110 rpm to produce fine particles measuring between 1 and 30 µm in diameter.

The two different types of mills used to produce the coarse wood particles both produced a wide range of particle sizes, necessitating the sieving and isolation of each size fraction. Sieve meshes
used were 7 (3.7 mm aperture), 10 (2.5 mm) and 22 (1.1 mm) according to British Standard (BS 412: 1962).

Plate 3.5 Guillotine used to prepare wood flakes.

Plate 3.6 Wiley toothed crushing mill Model No. 54 used to produce coarse wood particles.
Each sieve fraction was weighed to determine the proportion of each size fraction in the green and dry heartwood and sapwood of each species. The coarse-ground particle samples were compiled from a representative combination of size fractions resulting from sieving, which was kept constant regardless of species, heartwood or sapwood or whether the wood was ground in the green or dry condition. Particles ground using the Wiley Model No. 54 mill contained 7-mesh particles at 70% w/w and 10-mesh particles at 30% w/w. Those prepared using the rotary mill contained 10-mesh and 22-mesh particles at 50% w/w each.

Plate 3.7 Ball mill used to produce fine wood powder.

Plate 3.8 Different forms of wood produced from *A. mangium* heartwood.
The 'Junior'-brand laboratory rotary mill produced much dust and few particles larger than the 20 to 40-mesh wood flour from dry wood, and therefore only green wood samples were used to prepare samples using this technique. The amounts of each mesh size required for heartwood and sapwood for each species and heartwood content to compile unextracted and extracted samples were pre-calculated and all samples were compiled from these figures. All wood samples were stored at 20 ± 1°C and 65 ± 5% r.h. to condition them to a moisture content of 12% prior to testing. The different forms of wood produced are illustrated in Plate 3.8.

3.3.2.3 Aqueous extraction of samples

From each prepared and conditioned wood sample, 7 g of material was removed and soaked in water for 24 h to remove inhibitory extractives. Each sample was placed in a 600-mL plastic container into which 500 mL of distilled water at 23°C was added and stirred to submerge the wood. The water was decanted and replaced with fresh 500-mL aliquots after 6 and 12 h. After 24 h the samples were removed. Wood wool and flake samples were strained through 0.5-mm mesh whereas the wood particles, flour and powder were strained through a sintered glass crucible (Frit 4) under a water tap aspirator, as shown in Plate 3.9. Strained samples were air-dried for 7 days and reconditioned at 20 ± 1°C and 65 ± 5% r.h. to 12% for approx. 3 weeks.

![Plate 3.9 Tap aspirator used to wash and filter fine wood particles.](image)

3.3.2.4 Hydration sample preparation and testing

Three levels of % heartwood were used in the experiment: 0% (100% sapwood), 50% heartwood/sapwood and 100% heartwood. The weights of samples for cement compatibility testing
were first determined for each species using a correction for their basic density so that samples each contained the same volume of wood. \(E.\ pellita\), which had the highest basic density, was set at 5 g of wood per sample. The weights of \(A.\ mangium\), \(A.\ aulacocarpa\) and \(P.\ deltoides\) were then calculated on the basis of their wood density relative to that of \(E.\ pellita\). Hence, the weights used for \(A.\ aulacocarpa\), \(A.\ mangium\) and \(P.\ deltoides\) were 4.6 g, 3.7 g and 3.3 g respectively. This ensured a much greater similarity among species in the surface area of wood used. The mixing of hydration samples and measurement of hydration temperature for each sample over 23 h was undertaken as described in Section 3.2.2.4. Portland cement ASTM Type 1 (Blue Circle Southern Cement Batch No. 053MA99) was used and the 336 wood-cement hydration samples plus 20 cement control samples were tested over a period of approx. 70 days.

3.3.2.5 Experimental design and statistical analysis

In accordance with Section 3.2 of this Chapter, the experimental design for this experiment used factorial principles, investigating the effects of four fixed factors on wood-cement compatibility, i.e. wood form, species, heartwood content and soaking, and also various random effects, including those associated with replicates obtained from different trees. The effects of wood form, heartwood content and soaking on cement compatibility were of primary interest, and these three factors were randomised within each daily 6-sample run. Over each 7-consecutive-day block of 6-sample hydration runs, all 42 combinations of wood form, heartwood content and soaking were run for a randomly selected species and tree. The 20 cement control runs were randomly interspersed throughout the entire experiment.

For this experiment, a wider range of wood-cement compatibility indices were determined, since it was felt that the effects of the wood on the time \(t\) taken to reach \(T_{\text{max}}\) and on the hydration rate (rate of temperature increase, \(R\)) should also be assessed. \(R = (T_{\text{max}} - T_{\text{min}})/t\). The \(T_{\text{min}}\) component of hydration rate is the minimum temperature attained during the first 5 h of the hydration test.

The main effects of, and interactions between, each of the factors, \(T_{\text{max}}\), \(t\), \(R\) and \(C_A\)-factor, were tested for significance using an appropriate multi-factorial ANOVA model at the 5% significance level, using Genstat 5 as in Section 3.2.2.5. Due to non-orthogonality in the combined data set for unsoaked and soaked samples, separate analyses of variance were undertaken for the data sets of the unsoaked and soaked samples. In the analysis, the Wiley-mill and sliced samples from green and dry wood were treated as four different wood forms, allowing a comparison of the effect of form as well as that of wood moisture content during preparation. Before the final analyses, diagnostic checks on the normality and variance of the data were undertaken. The factorial design of the experiment allowed data to be averaged across non-significant \((p > 0.05)\) effects. Significant results are plotted graphically and bars representing the least significant difference \((p \leq 0.05)\) are included.
on graphs to facilitate comparison of means. The four compatibility indices showed similar trends, so hydration rate (a simple composite index that combines $T_{\text{max}}$ and time) has been illustrated.

3.3.3 Results and Discussion

3.3.3.1 Unextracted samples

Of the main effects of wood form, species and heartwood content, only wood form had a highly significant effect ($p < 0.001$) on $T_{\text{max}}$, hydration rate and $C_A$-factor (Table 3.5). Hydration time was significantly influenced by not only wood form ($p < 0.001$), but to a lesser extent, species and heartwood content ($p < 0.05$). Wood form interacted significantly with the factors species ($p < 0.001$) and heartwood content ($p < 0.001$) to influence wood-cement compatibility; however the interaction between wood form and heartwood content was not significant for $T_{\text{max}}$. The interactive effect of wood form and species on wood-cement compatibility is illustrated in Figure 3.5.

Table 3.5 F-probability ($p$-values) for effects of and interactions between species, heartwood content and wood form for unsoaked samples.

<table>
<thead>
<tr>
<th></th>
<th>$T_{\text{max}}$</th>
<th>Time to $T_{\text{max}}$ (t)</th>
<th>Hydration Rate (R)</th>
<th>$C_A$-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>species (Sp)</td>
<td>0.092</td>
<td>0.039</td>
<td>0.047</td>
<td>0.097</td>
</tr>
<tr>
<td>heartwood (H)</td>
<td>0.445</td>
<td>0.009</td>
<td>0.657</td>
<td>0.792</td>
</tr>
<tr>
<td>wood form (F)</td>
<td>$&lt;0.001$</td>
<td>$&lt;0.001$</td>
<td>$&lt;0.001$</td>
<td>0.001</td>
</tr>
<tr>
<td>Sp x H</td>
<td>0.021</td>
<td>$&lt;0.001$</td>
<td>0.022</td>
<td>0.036</td>
</tr>
<tr>
<td>Sp x F</td>
<td>$&lt;0.001$</td>
<td>$&lt;0.001$</td>
<td>$&lt;0.001$</td>
<td>0.001</td>
</tr>
<tr>
<td>H x F</td>
<td>0.120</td>
<td>$&lt;0.001$</td>
<td>$&lt;0.001$</td>
<td>0.013</td>
</tr>
<tr>
<td>Sp x H x F</td>
<td>0.039</td>
<td>0.013</td>
<td>0.018</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Despite the significant compatibility differences among the species, the effects on cement hydration of sliced flakes (Sliced D (dry) and Sliced G (green)) or coarsely ground (Wiley D (dry) and Wiley G (green)) wood for a particular species were not significantly different from those of wood wool (Figure 3.5). Actual compatibility and the relationship between species compatibility in wood wool form were most accurately predicted by the use of dry flakes (Sliced D), whereas the flakes from green wood samples (Sliced G) slightly underestimated wood wool compatibility in the cases of $A. \ aulacocarpa$ and $A. \ mangium$. However this difference was not significant. As with the findings presented in the first part of this Chapter, Figure 3.5 also indicates that a different relationship and compatibility ranking between species could arise if wood flour was used instead of a form more closely resembling wood wool.
The addition of ball-milled (BMill) wood completely retarded cement setting over a period of 24 h, regardless of species, heartwood content or extractive removal. The reason for this is not known, but the finding suggests that there may be a threshold surface area-to-volume ratio above which even the most compatible, extractive-free wood becomes incompatible. Ball milling may also have resulted in chemical and/or physical changes to the wood surface or constituents that could inhibit cement hydration. This finding accords with those of Weatherwax and Tarkow (1964), discussed in Chapter 2, whereby there was a negative linear relationship between hydration inhibition and particle size within the range 0.1 to 0.4 mm, which changed to an exponential increase in inhibitory power with decreasing particle size below 0.1 mm. This characteristic of finely ground wood-based meal is utilised in cement-setting retardants. Finely milled lignosulphonates (a lignin-rich by-product of wood pulping) are well-known cement-setting retardants used in commercial cementing applications (Collepardi 1994).

![Figure 3.5](image)

**Figure 3.5** Effects of species and wood form on the hydration rate of portland cement containing unsoaked wood, averaged across heartwood content (0%, 50% and 100%).

Among the other wood forms, the high variation among species was evident regardless of wood form, with *P. deltoides* having the highest average compatibility and *A. aulacocarpa* the lowest. For species with high average compatibility, the effect of wood form (with the exception of ball-milled wood) from wood flour to wood wool on cement hydration was insignificant, as exemplified by *P. deltoides*. In contrast, for species of low average compatibility (*A. aulacocarpa*), differences in wood form significantly affected wood-cement compatibility (Figure 3.5).
The significant and complex interactive effects between wood form and heartwood content for different species are illustrated in Figures 3.6(a) to (d). In all species except *P. deltoides*, heartwood and sapwood differed significantly in compatibility across one or more wood forms, especially with the finer forms of flour and rotary milled particles. In the case of *A. aulacocarpa*, hydration was inhibited (R = 0) by the presence of inhibitory heartwood in both these forms (Figure 3.6(a)). The heartwood of *A. aulacocarpa* has been shown to contain the leucoanthocyanidin flavonol known as 'teracacidin' (Tindale and Roux 1969). Teracacidin was later found and isolated from the heartwood of *A. mangium* by Tachi *et al.* (1989) and proven by these workers to be the primary agent responsible for inhibiting cement hydration. The results from this study suggest that the effects of this inhibitory compound on cement hydration are greatly exacerbated by the increased wood surface area exposed to the surrounding cement, reasonably explaining the decreased compatibility of the heartwood of these species in finer ground forms.

In contrast to the two acacias, heartwood content in *E. pellita* was of little consequence for compatibility of the fine, dry forms of wood flour and rotary milled wood (Figure 3.6(c)). Section 3.2.3.2 of this Chapter showed that despite its relatively high compatibility with cement, *E. pellita* heartwood also had a high water-soluble extractive content relative to *A. mangium*, suggesting that its extractive chemical composition is not particularly deleterious to cement hydration. In contrast, the sapwood of *E. pellita* was significantly less (p < 0.001) compatible with cement than its heartwood in the cases of Sliced G (green) and Wiley G (green) that had been prepared using fresh, wet sapwood. This same problem was identified in *E. pellita* and discussed in Section 3.2.3. This provides further evidence that wood condition at the time of preparation can also significantly affect its compatibility with portland cement, a phenomenon that is completely overlooked when samples are prepared from dry wood. In another study, Lee and Hong (1986) found that air-dried woods of sweetgum (*Liquidambar styraciflua* L.) and Hickory (*Carya tomentose* (Poir.) Nutt.) were significantly lower in compatibility with cement than if fresh, green wood added to hydration samples. This may also have been caused by surface-enrichment of sugars during drying.

Wood from *P. deltoides* remained consistently high in compatibility (R between 2 and 3°C/h, C_A > 80%) regardless of wood form, except for ball-milled wood (Figure 3.6(d)). This suggests that in the absence of inhibitory extractives wood may be mixed with cement in a finer form with less inhibitory effect on hydration. The less marked reduction in compatibility of the poplar wood in the finer forms F and L can be seen in Figure 3.6(d). *P. deltoides* wood had a low level of water-soluble extractives, and these are likely to have had little effect on cement hydration. Using wood structural and extractive components in isolation as model compound additives, Miller and Moslemi (1991a) showed that powdered lignin and cellulose when added on their own caused only a slight reduction in strength of the exothermic hydration reaction of portland cement. This was in contrast to the
effects of the addition of the same quantities of model wood sugars xylan and glucose and oak tannin (dihydroquercetin), all of which completely inhibited cement hydration.

Figures 3.6 Interactive effect between wood form and % heartwood on compatibility (hydration rate) for (a) *Acacia aulacocarpa*, (b) *A. mangium*, (c) *E. pellita* and (d) *P. deltoides*. 0% = sapwood, 50% = 50% sapwood/50% heartwood, 100% = heartwood.
3.3.3.2 The effect of pre-soaking

The combined analysis of variance for unextracted and extracted samples revealed that, as expected, soaking had a highly significant effect on wood-cement compatibility, as shown in Table 3.6. The interactions between species and soaking and wood form and soaking were highly significant (p < 0.001) and there were also significant complex lower order interactive effects between species, heartwood content and soaking as well as wood form, heartwood content and soaking.

Table 3.6 F-probability (p values) for effects of soaking and interactions between soaking and other factors.

<table>
<thead>
<tr>
<th></th>
<th>$T_{max}$</th>
<th>Time to $T_{max}$ (t)</th>
<th>Hydration Rate (R)</th>
<th>$C_A$-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>soaking (S)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>species x S</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>heartwood x S</td>
<td>0.919</td>
<td>&lt;0.001</td>
<td>0.985</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>form x S</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.119</td>
<td>0.014</td>
</tr>
<tr>
<td>Sp x H x S</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Sp x F x S</td>
<td>0.003</td>
<td>0.003</td>
<td>0.010</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>H x F x S</td>
<td>0.798</td>
<td>0.002</td>
<td>0.323</td>
<td>0.064</td>
</tr>
<tr>
<td>Sp x H x F x S</td>
<td>0.417</td>
<td>0.082</td>
<td>0.198</td>
<td>0.098</td>
</tr>
</tbody>
</table>

Figures 3.7 (a) to (d) illustrate the beneficial effects of soaking on the average compatibility of all wood forms (except ball-milled) for *A. aulacocarpa*, *A. mangium*, *E. pellita* and *P. deltoides*. The most marked effect of extractive removal by soaking was observed for the least compatible wood, *A. aulacocarpa* (Figure 3.7(a)), where the low compatibility of most wood forms was significantly increased ($R \approx 1.7$ to $2.2^\circ C/h$, $C_A \approx 80\%$). The effects of pre-soaking the wood samples were less marked in *A. mangium* and *E. pellita* (Figures 3.7(b) and (c)), in which cases the average compatibility of wood wool was not significantly increased by soaking. In the case of *P. deltoides*, soaking had no significant effect on the already high compatibility of the wood in all forms from wood flour to wood wool. In all species, soaking resulted in consistently high compatibility across all wood forms, except for ball-milled wood. Similarly, water extraction has been found to be effective at improving the compatibility of a highly inhibitory wood such as western larch (*Larix occidentalis* Nutt.) heartwood, with its unusually high levels of water-soluble cement-inhibiting arabinogalactan (Zhengtian and Moslemi 1986, Miller and Moslemi 1991b). Note, however, that hydration rates for soaked wood from the two acacias, *A. aulacocarpa* and *A. mangium*, were around $2^\circ C/h$ or less whereas for *E. pellita* and *P. deltoides* they were between 2.5 and $3^\circ C/h$. This suggests that although pre-soaking was effective, a quantity of inhibitory extractives remained in the acacia wood even after pre-soaking for 24 h. This topic is examined further in Chapter 7, which examines different extraction methods for *A. mangium*. The results from water-soluble extractive removal further demonstrate that small particle sizes greatly reduce the
compatibility of woods containing soluble inhibitory substances because of increased cement exposure to leached inhibitory compounds from the greater surface area of wood.

Figures 3.7 Effect of soaking on compatibility of wood in different forms for (a) A. aulacocarpa, (b) A. mangium, (c) E. pellita and (d) P. deltoides. *green and dry combined.
3.3.4 Conclusions

The forms into which wood samples were converted for wood-cement compatibility testing strongly affected their ‘perceived’ compatibility with cement. Species, heartwood:sapwood proportion and whether the wood was pre-soaked also influenced its effect on cement. It was clear from the findings that the use of samples prepared by slicing the wood through the tangential plane into thin slivers would most closely approximate the behaviour of wood wool with cement across a range of wood species. In most cases wood flakes that had been sliced from green samples were slightly less compatible with cement than those that had been sliced from dried samples.

Preparation of hydration samples by slicing through the tangential plane was also the most controllable in terms of obtaining material of a uniform desired size from a strictly limited sample source such as radial cores. Grinding resulted in considerable loss of sample material both during processing and during sieving to obtain a uniform desired particle-size fraction. The particle-size distribution resulting from grinding was also strongly influenced by the moisture content of the solid wood at the time of preparation.

Wood from less compatible wood species (A. mangium and A. aulacocarpa), as expected, had a more deleterious effect on the hydration of cement when converted into smaller particles than did wood from P. deltoides. The presence of hydration-inhibiting soluble compounds (sapwood sugars and/or heartwood polyphenols) is thought to be primarily responsible for the steep decline in compatibility of the wood when prepared in smaller particle sizes. Once the water-soluble inhibitory compounds were removed, wood form and particle size had little effect on compatibility with cement except ball-milled wood, which was strongly inhibitory regardless of wood species tested or extractive removal. Wood from the two tropical acacias remained slightly less compatible after soaking than that from E. pellita or P. deltoides, suggesting the presence of residual extractives that were not removed during the course of cold-water extraction.

3.4 General discussion

A reliable method of assessing the potential suitability of species for the manufacture of WWCBs was identified as necessary before further experimental work could be undertaken for this thesis. The results from the investigations presented in this Chapter indicated that the effects of wood on cement hydration, and hence its ‘perceived’ compatibility with cement is significantly affected not only by species, but also by wood geometry and particle size. This has strong implications for the preparation of wood samples for wood-cement compatibility testing and inferences made from the data. Results from the first part of this Chapter indicated that the conventional method for testing wood-cement compatibility, i.e. by preparing and adding finely ground wood flour, would be an inaccurate basis for assessing the potential suitability of acacia and
eucalypt species for the manufacture of wood-cement composites such as WWCB. Wood flour and wood wool from selected tropical species (*A. mangium* and *E. pellita*) behaved very differently with cement and resulted in conflicting species rankings between the two wood forms. Findings from the second part of the Chapter indicated that the wood should instead be prepared in a form that closely resembles wood wool. The condition of the wood at the time of preparation (fresh and green or dried) can also significantly influence its behaviour and perceived compatibility with cement. Discussion suggested the phenomenon of redistribution of inhibitory sugars on wood surfaces during drying as a possible reason for the observed reduction in compatibility of freshly prepared flakes from *E. pellita* sapwood.

Therefore, when assessing the suitability of species for wood-cement composites, it is important to specify which type of composite is of interest and to prepare the wood in a size and form most closely resembling that used in composites, rather than using a 'standard' hydration test format based on wood flour from which quite different results and conclusions may be reached. This study confirmed previous doubts about the ability of hydration tests that use wood flour to reliably predict species suitability for the manufacture of wood-cement composites, particularly WWCBs. For predicting the suitability of wood species for WWCBs, it can be clearly seen from Figures 3.6 and 3.7 that thin tangential slivers most accurately represented the effect of wood wool on the hydration of portland cement hydration across a range of wood species of varying compatibility with cement. This was especially so for samples with a fairly even mix of heartwood and sapwood, such as would be present when whole-stem cross sections from trees are sampled for wood-cement compatibility tests. The method of wood conversion to fine tangential slivers was consequently adopted for the wood-cement compatibility testing of acacias and eucalypts described in Chapters 4 and 5.
Chapter 4 Species and intra-species variation in wood-cement compatibility among commercially important tropical species of *Acacia* and *Eucalyptus*.

4.1 Introduction

Reports on the suitability of tropical species of *Acacia* and *Eucalyptus* for wood-cement composites appear to vary considerably depending on the source of the wood, and the type of compatibility test used or test composites made. Although the work of Paribotro and Suwandikliwon (1977) indicated that significant tree and site variation could affect the suitability of *E. deglypta* for wood wool cement board (WWCB), no further studies have considered possible variation stemming from wood source/genotype when testing for wood-cement compatibility. According to Hillis (1987), trees of a particular species can vary significantly in properties such as density, heartwood and extractive content, even within the same plantation. For example, trees within a single plantation of *A. mearnsii* in South Africa showed significant variation in heartwood tannin content among trees. This provides evidence to suggest that among trees of other important acacia species, such as *A. mangium*, there could be considerable variation in the wood properties which affect wood-cement compatibility at the provenance and/or family level. In particular, because *A. mangium* heartwood is naturally incompatible with cement, variation in the proportion of heartwood and/or its extractive content is likely to strongly influence the compatibility of the wood with cement.

In this Chapter information on variation in wood-cement compatibility among and within important tropical species of *Acacia* and *Eucalyptus* is presented. In Chapter 3 it was shown that the 'conventional' methodology for testing wood-cement compatibility would be unsuitable for assessing the potential suitability of wood species (at least selected tropical acacias and eucalypts) for use in wood wool- or flake-based cement composites. Finely ground wood flour was a poor predictor of the effects of larger wood particles or strands on the hydration of portland cement, potentially producing misleading inferences about wood suitability for wood-cement composites. This methodology was therefore abandoned in favour of sliced wood flakes with a geometry and surface area more consistent with that of wood wool or flakes for the purposes of measuring wood-cement compatibility in this study.

Trees representing a range of families and provenances of *A. mangium* were sampled using non-destructive extraction of radial wood cores. The possible effects of wood density, heartwood content and heartwood extractive content on wood-cement compatibility were determined. Other tropical species of *Acacia* (*A. aulacocarpa* and *A. crassicarpa*) and *Eucalyptus* (*E. pellita* and *E. urophylla*) were also sampled, but not as intensively. Within a particular species, variation in wood-cement compatibility may potentially enable the identification and selection of trees whose wood is
less deleterious to cement hydration and hence better suited to the manufacture of wood-cement composites. Methodology that has been described in Chapter 3, such as the measurement and derivation of wood-cement compatibility indices, is indicated throughout this Chapter.

4.2 Aims and objectives

The aim of the research presented in this Chapter was to determine to what extent selected species of tropical acacias and eucalypts that are of importance to commercial forestry and land rehabilitation in South-east Asia, might be suitable for the manufacture of wood-cement composite panels; in particular WWCBs. This was done by sampling trees of different species, provenances and individual families and measuring the compatibility of the wood flakes with portland cement. Specific objectives of the study were to:

1. Rank and compare average species compatibility with portland cement.
2. Identify significant influences on wood-cement compatibility arising from factors such as plantation site, geographic origin of families (provenance) and wood characteristics such as basic density, heartwood content and heartwood extractive content.
3. Test the hypothesis that heartwood and/or extractive content in trees may significantly affect the compatibility of the wood with cement, particularly in the case of the tropical acacias.
4. Identify individual trees of *A. mangium* whose wood may be of higher natural compatibility with portland cement and possible reasons for this.

4.3 Materials and methods

4.3.1 Collection of wood core samples

A summary of the species, provenances, sites and planting dates of the tropical acacias and eucalypts is presented in Table 4.1. The location of the field trials from which the trees were sampled is shown in Figure 4.1. Ten trees (each representing a different seed source or 'family') from each of the 16 species/provenance/site groups (160 trees in total) were sampled throughout January, February and early March, 1998. Two cores per tree were extracted, 320 cores in total. Two 12-mm-diameter cores were extracted from each tree at right angles to each other using a Tanaka motorised corer fitted with a P+N Trecor™ coring head, illustrated in Plate 4.1. The cores were extracted from trees at a height 1.3 m from ground. Clear areas of the bole were sampled and knots and other defects were avoided. The DBHOB (cm) of each tree was recorded. Following extraction, cores were placed in teflon core-holders labelled with species, provenance, family number, location and date of extraction. These were kept in an ice-box in the field and subsequently kept frozen (-10°C) to prevent mould. Cores were shipped to Canberra and kept frozen until use.
Figure 4.1 Location of tropical and eucalypt field trials in North Queensland with inset showing sampling sites between Townsville and Cooktown.

Plate 4.1 Motorised core extraction drill (from manufacturer P&N Trecor).
Plate 4.2 *A. mangium* trees growing at Damper site in North Queensland.

Plate 4.3 *E. pellita* trees growing at Damper site in North Queensland.
Table 4.1 Summary of species, provenances, sites and planting dates of sampled trees.

<table>
<thead>
<tr>
<th>Species</th>
<th>Provenance</th>
<th>Site</th>
<th>Planting Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acacia mangium</td>
<td>PNG-N</td>
<td>Kuranda</td>
<td>1991</td>
</tr>
<tr>
<td>Acacia mangium</td>
<td>PNG-N</td>
<td>Moreton</td>
<td>1991</td>
</tr>
<tr>
<td>Acacia mangium</td>
<td>FNQ</td>
<td>Kuranda</td>
<td>1991</td>
</tr>
<tr>
<td>Acacia mangium</td>
<td>FNQ</td>
<td>Moreton</td>
<td>1991</td>
</tr>
<tr>
<td>Acacia mangium</td>
<td>PNG-SE</td>
<td>Kuranda</td>
<td>1991</td>
</tr>
<tr>
<td>Acacia mangium</td>
<td>QCR</td>
<td>Moreton</td>
<td>1990</td>
</tr>
<tr>
<td>Acacia mangium</td>
<td>PNG-SW</td>
<td>Damper</td>
<td>1991</td>
</tr>
<tr>
<td>Acacia auracocarpa</td>
<td>PNG-SW</td>
<td>Kuranda</td>
<td>1991</td>
</tr>
<tr>
<td>Acacia auracocarpa</td>
<td>PNG-SW</td>
<td>Moreton</td>
<td>1991</td>
</tr>
<tr>
<td>Acacia crassicarpa</td>
<td>PNG-SW</td>
<td>Moreton</td>
<td>1991</td>
</tr>
<tr>
<td>Eucalyptus pellita</td>
<td>IJ</td>
<td>Kairi</td>
<td>1992</td>
</tr>
<tr>
<td>Eucalyptus pellita</td>
<td>IJ</td>
<td>Ellerbeck</td>
<td>1991</td>
</tr>
<tr>
<td>Eucalyptus pellita</td>
<td>PNG-SW</td>
<td>Damper</td>
<td>1992</td>
</tr>
<tr>
<td>Eucalyptus pellita</td>
<td>FNQ</td>
<td>Ellerbeck</td>
<td>1991</td>
</tr>
<tr>
<td>Eucalyptus pellita</td>
<td>PNG-Kiriwo</td>
<td>Etros</td>
<td>1991</td>
</tr>
<tr>
<td>Eucalyptus urophylla</td>
<td>PNG-Wetar</td>
<td>Etros</td>
<td>1991</td>
</tr>
</tbody>
</table>

Provenance boundaries:
PNG-SE: PNG south of Fly River, east of long. 142°E.
PNG-SW: PNG west of Fly River, west of long. 142°E.
FNQ: Far North Queensland (Cape York north of lat. 13°S).
QCR: Queensland Cairns Region (lat. 15° to 19°S).

(From Harwood et al. 1993)
PNG-Kiriwo: Lat. 8°25'S, Long. 141°30'E, Alt. 45 m. Within bounds of PNG-SW
Indonesia-Wetar: Lat. 7°49'-56'S, Long. 125°53'-126°37', Alt. 180-515 m.
(From Doran et al. 1995 and Harwood 1998)
IJ: Bupus and Muting in Irian Jaya, Indonesia.

4.3.2 Measurement of wood properties and wood-cement compatibility

Although the extraction of radial cores is highly suitable for sampling large numbers of trees in a quick and non-destructive manner, disadvantages of this method of sampling can include poor representation of total stem, as the coring height is close to the base of the tree, which contains a greater proportion of heartwood. A radial core also contains an over-representation of the inner portion of the stem, such as heartwood (Downes et al. 1997). To overcome this second characteristic of radial cores, the heartwood content of each core was determined by measuring the entire core length and the length of the heartwood portion (which in all species was visually distinct) using Mitutoyo-brand 50 cm digital calipers. Heartwood percentage of the stem cross section was calculated by considering the core length and heartwood length as the diameters of two circles and calculating the heartwood and total stem areas, from which heartwood content (as %) was derived. The average % heartwood for each tree was obtained by averaging measurements from the two cores. After thawing, each green core was weighed and basic density determined. The green volume of each core was determined using the water displacement (Archimaedian) method suitable for green wood samples, as shown in Haygreen and Bowyer (1982).
Examples of cores from *A. mangium* showing differences in heartwood proportion and colour.

Since the cores could not be oven dried to determine moisture content, average % moisture content (MC) was derived for each core by removing slivers 1 mm in thickness at intervals of approximately 10 mm along the core. The green weight of the slivers was recorded on a tared watch glass immediately after they were cut from the core. The slivers were then oven dried at 105°C for 24 h and re-weighed. The MC was used to estimate the core’s dry weight for the calculation of basic density. Estimation of core oven-dry weight was necessary because further experimentation required the use of the green wood from the cores. The published results from the wood properties survey (Semple et al. 1999) can be found in Appendix 1, p. 341.

Cores from which green volume and heartwood content had already been determined were removed from the freezer to thaw for 30 min prior to slicing. The green weight of the core was measured immediately prior to slicing. The core was then sliced into flakes using the guillotine as described in Chapter 3, keeping heartwood separate from sapwood in plastic containers. The rest of the flakes were air dried indoors at ≈25°C for around 6 days before being transferred to a conditioning room maintained at 20 ± 1°C and 65 ± 5% r.h. to condition them to a target MC of 12% before compiling samples. Since wood destined for use in wood-cement composites is frequently stored for some months prior to use, the wood samples were retained for approximately 4 months in the conditioning room prior to testing them for compatibility with portland cement.

Each wood-cement compatibility sample was compiled by weighing out heartwood and sapwood flakes separately, their individual weight components of the 5-g sample being derived from the calculated proportions of heartwood and sapwood in each tree. A sample of water-extracted flakes (procedure described in Chapter 3) was also prepared for each core. Space constraints allowed only two randomly selected samples from each of the 16 provenance groups, or 32 in total, to be
extracted in each 24-hour extraction cycle. Flake samples and water extraction are shown in Plates 4.5(a) and (b).

Wood-cement compatibility was measured for each sample, using the methodology described in Chapter 3. Portland cement ASTM Type I (Blue Circle Southern cement batch 131/98) was used. The four wood-cement compatibility indices $T_{\text{max}}$, Time to $T_{\text{max}}$ (t), Hydration Rate (R) and C$_A$-factor were determined for each sample.

4.3.3 Hot-water-extractive content of selected samples

To investigate further possible reasons for variation in wood-cement compatibility within *A. mangium* (the species of main interest), hot-water-soluble heartwood extractive contents of selected samples of high and low compatibility with cement were determined. Of the various methods of extractive removal, hot-water-soluble extractive content has been suggested by workers such as Hachmi and Moslemi (1990) to most closely reflect wood compatibility with cement, notwithstanding other factors such as pH and chemical composition. Conditioned, pre-weighed 3-g samples of known MC from the remaining heartwood of those 10 trees shown to have the highest and lowest compatibility with cement (determined using hydration rate) were placed in separate 500-mL beakers to which 400 mL of distilled boiling water was added. The beakers were placed in a hot-water bath set at 80°C. After 1 and 3 hours the samples were drained and refreshed with 500-mL aliquots of boiled water. The samples were removed after 6 h. They were then drained on filter paper of known weight and MC, oven dried at 105°C for 24 h, and then reweighed to determine the amount of extractives removed, expressed as a percentage of the extractive-free wood. The average extractive contents for heartwood from the 10 most and 10 least compatible *A. mangium* trees are shown in Figure 4.5.

4.3.4 Experimental design and statistical analysis

The experimental design used factorial principles to investigate the effects of four fixed factors on wood-cement compatibility, i.e. species, provenance (in the cases of *A. mangium* and *E. pellita*), site and soaking pre-treatment of samples. A total of 74 days was required to test all of the samples. The factors of greatest interest were the effects of species, provenance and soaking treatment, so these factors were randomised within each daily 6-sample run. Because of the length of the experiment, the species were blocked into two groups, i.e. (i) *A. mangium* (which comprised most of the trees sampled) and (ii) other species (i.e. *A. aulacocarpa*, *A. crassicarpa*, *E. pellita* and *E. urophylla*). These two groups were randomised over each 3-day or 18-sample period. Within the *A. mangium* block, four blank hydration runs (no assigned wood sample) were available during each 3-
day period, and this allowed cement control samples to be run. This ensured randomly distributed control runs throughout the duration of the experiment. Variances within the data sets for each of four distinct groups, i.e. unsoaked acacias, soaked acacias, unsoaked eucalypts and soaked eucalypts were significantly different, requiring statistical analyses to be undertaken as four separate models, as indicated in Tables 4.2 and 4.3. For statistical analyses Genstat 5 was used. F-probabilities for significance of factors from each model are shown in Table 4.2. Where averages are obtained from across separate models, i.e. soaked vs. unsoaked samples such as shown in Figure 4.2, standard deviation can be used to compare means. Otherwise least significant difference (LSD) has been included on graphs for this purpose.

4.3.5 Scanning electron microscopy (SEM) assessment of wood-cement interface

The instrument used in this study to examine the effect of wood on the adjacent hydrating cement was a Cambridge Instruments S360 fitted with a high brightness lanthanum hexaboride (LaB₆) electron source (Plate 4.6a). This proved capable of producing high-resolution images of uneven surfaces of both cement and wood, and of measuring the lengths of certain features. Micrographs of SEM images were recorded on Kodak 220 Plus X Plan film using a Leica camera. SEM has been used extensively by previous researchers to examine wood structure and microstructure. It has also been extensively used to study the evolution of cement hydration products during the hydration of cement and concrete. However the methodology used here follows most closely that of Heady (1997). The aim was to assess the effects of wood of different species on the setting of cement adjacent to the wood surface. It was expected that in the case of compatible woods a solid cast of the wood surface would be produced in the set cement. The interfacial zone between the surface of solid wood and cement has not been studied to any great extent. CBP and WWCB were examined by Parameswaran et al. (1977) and Goodell et al. (1997) using SEM to investigate the effects of decay fungi on wood-cement composites. Ahn and Moslemi (1980) used SEM to investigate whether hydrate products can be found in wood cell lumens, and what form these take in the presence of different cement-setting retarders. There are more studies on the microstructure of wood fibre-cement composites (including Davies et al. 1981, Coutts 1987, Coutts and Ni 1995, Bentur and Ackers 1989, Savastano et al. 1992 and Savastano and Agopyan 1999), which have used SEM to study bonding between fibres and cement, fibre pull-out and fracture surfaces. However, no studies have been found that have used SEM to examine the cement relief pattern left by larger pieces of solid wood which might serve as a guide to possible bond strength in wood-cement composites that contain large wood flakes or wood wool.
Sample preparation was carried out approximately one month after hydration samples had been mixed and tested. Small pieces of cement that had been adjacent to the surface of a wood flake were removed from the hydration samples and mounted on 12-mm diameter aluminium stubs using a Nylon-based adhesive (fingernail varnish). Each sample was then coated with a 10-nm layer of gold using an argon gas sputter coating unit (Polaron E5000, Plate 4.6(b)) operating at 20 mA ion current for approx. 3 min. Samples were also painted around their base, avoiding the observation surface, with silver conducting paint to increase electrical conductivity between the sample and the stub.

Plates 4.5 (a) Conditioning prepared heartwood and sapwood flakes, (b) aqueous extraction of flakes.

Plates 4.6 (a) Gold sputter coater, and (b) Cambridge Scanning Electron Microscope located at The Australian National University, Canberra.
4.4 Results and discussion

4.4.1 Species differences in wood-cement compatibility--unextracted samples

The results from the ANOVA models for acacias (soaked and unsoaked) and eucalypts (soaked and unsoaked) are shown in Table 4.2. This Table indicates whether species had a significant effect at the 5% level on compatibility indices. Averages of the wood-cement compatibility indices for the different acacia and eucalypt species are shown in Table 4.3. Unextracted wood from the two eucalypts was more compatible with cement than that from the acacia species. For example, CA-factors for E. pellita and E. urophylla were very similar (81.38% and 81.42% respectively), whereas for the acacias CA-factors were 27.79% for A. crassicarpa, 33.82% for A. mangium and 48.24% for A. aulacocarpa (Table 4.3). Corresponding hydration rates for unsoaked samples are shown in Figures 4.2(a) and (b).

<table>
<thead>
<tr>
<th>Species</th>
<th>Tmax (°C)</th>
<th>Time to Tmax (h)</th>
<th>Hydration Rate (°C/h)</th>
<th>CA-factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acacias unsoaked</td>
<td>0.0015</td>
<td>0.002</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Acacias soaked</td>
<td>N.S.</td>
<td>0.043</td>
<td>N.S.</td>
<td>0.035</td>
</tr>
<tr>
<td>Eucalypts unsoaked</td>
<td>N.S.</td>
<td>0.001</td>
<td>0.011</td>
<td>N.S.</td>
</tr>
<tr>
<td>Eucalypts soaked</td>
<td>N.S.</td>
<td>N.S.</td>
<td>N.S.</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Significant species effects were evident among unsoaked samples from the three Acacia species for all four hydration indices (Table 4.2), and are illustrated graphically for hydration rate in Figure 4.2(a), whereby A. aulacocarpa was most compatible with cement followed by A. mangium and then A. crassicarpa.

Table 4.3 Average wood-cement compatibility indices for unextracted (us) and extracted (s) samples of A. aulacocarpa, A. crassicarpa, A. mangium, E. pellita and E. urophylla.

<table>
<thead>
<tr>
<th>Species</th>
<th>Tmax (°C)</th>
<th>Time to Tmax (h)</th>
<th>Hydration Rate (°C/h)</th>
<th>CA-factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. aulac. (us)</td>
<td>37.6</td>
<td>14.9</td>
<td>0.81</td>
<td>48.24</td>
</tr>
<tr>
<td>A. aulac. (s)</td>
<td>47.3</td>
<td>10.7</td>
<td>1.89</td>
<td>83.76</td>
</tr>
<tr>
<td>A. crass. (us)</td>
<td>32.7</td>
<td>15.6</td>
<td>0.44</td>
<td>27.79</td>
</tr>
<tr>
<td>A. crass. (s)</td>
<td>46.6</td>
<td>10.3</td>
<td>1.81</td>
<td>80.11</td>
</tr>
<tr>
<td>A. mang. (us)</td>
<td>34.6</td>
<td>16.8</td>
<td>0.50</td>
<td>33.82</td>
</tr>
<tr>
<td>A. mang. (s)</td>
<td>46.6</td>
<td>10.2</td>
<td>1.89</td>
<td>78.64</td>
</tr>
<tr>
<td>E. pell. (us)</td>
<td>47.4</td>
<td>11.3</td>
<td>1.82</td>
<td>81.38</td>
</tr>
<tr>
<td>E. pell. (s)</td>
<td>49.1</td>
<td>9.7</td>
<td>2.17</td>
<td>87.57</td>
</tr>
<tr>
<td>E. uro. (us)</td>
<td>46.8</td>
<td>12.3</td>
<td>1.62</td>
<td>81.42</td>
</tr>
<tr>
<td>E. uro (s)</td>
<td>49.2</td>
<td>9.5</td>
<td>2.12</td>
<td>79.25</td>
</tr>
<tr>
<td>Control*</td>
<td>54.1</td>
<td>9.2</td>
<td>2.95</td>
<td>100</td>
</tr>
</tbody>
</table>

*Cement only.
A. aulacocarpa was significantly ($p < 0.001$) more compatible with cement than A. crassicarpa. For A. aulacocarpa $R = 0.81\degree C/h$ and $C_A$-factor = 48.24 %, whereas in the case of A. crassicarpa the average compatibility indices were $R = 0.44\degree C/h$ and $C_A$-factor = 27.79 %, respectively (Table 4.2). The average $C_A$-factor for A. mangium was also significantly lower ($p < 0.001$) than that of A. aulacocarpa. Note also that A. mangium produced the longest delay in cement setting ($t = 16.8$ h).

In the case of the eucalypts, E. pellita was slightly more compatible than E. urophylla ($R = 1.82$ and $1.62\degree C/h$, respectively) as shown in Figure 4.2(b). Time taken to reach $T_{max}$ was also significantly longer ($p = 0.01$) for E. urophylla than E. pellita ($t = 12.3$ and $11.3$ h respectively). The compatibility of E. urophylla with cement was only slightly lower despite the significantly higher proportion of heartwood in the E. urophylla trees (average 52.8%) compared with E. pellita (average % heartwood = 36%) (Semple et al. 1999). A possible reason for this discrepancy may be that sapwood constituents such as sugars affected wood-cement compatibility to a greater extent than the heartwood constituents of these eucalypts, as discussed in Chapter 3. This point is examined further regarding temperate eucalypts in the next chapter.

Unlike the eucalypts, there were no significant species differences in average % heartwood in the trees of the three Acacia species from which the cores were taken for this study (Semple et al. 1999). This suggests that the significant compatibility differences between these three species may be more closely related to differing quantities of heartwood extractives and/or their chemical composition between the species.
Work by Tachi et al. (1988) found that *A. mangium* had similar hot-water-soluble extractive contents to three other species; *Paraserianthes falcataria*, *Eucalyptus deglupta* and *Gmelina arborea*, but its inhibitory index for cement hydration was significantly higher. They subsequently isolated the leucoanthocyanidin known as teracacidin (Clark-Lewis et al. 1961), which had highly inhibitory effects on cement hydration. Despite the fact that the three *Acacia* species in this study, as well as *Acacia auriculiformis* Cunn. ex Benth., are related taxonomically (classified within subsection Falcatae within section Julflorae (Benth.) Maiden and Betch), work by Drewes and Roux (1966) and Tindale and Roux (1969) showed that *A. aulacocarpa* and *A. auriculiformis* heartwood contained different types of flavandiol leucoanthocyanidins. *A. aulacocarpa* heartwood contains the melacacidin-type (3',4',7,8-tetrahydroxy pattern) while *A. auriculiformis* contains the teracacidin-type (4',7,8-trihydroxy pattern) – the same type shown by Tachi et al. (1988) to be highly inhibitory of cement hydration when extracted from *A. mangium*. This provides evidence to suggest that differences in chemical composition of heartwood polyphenols, even among closely related *Acacia* species, could underlie the observed differences in cement compatibility between *A. mangium*, *A. aulacocarpa* and *A. crassicarpa*. The effects of acacia heartwood polyphenols on cement hydration are discussed further in Chapter 9.

It should also be noted that the number of wood samples taken from trees to assess wood characteristics is a compromise between the desired level of accuracy and interpretation and the cost of collecting and processing samples (Downes et al. 1997). The restricted size and nature of the sampling exercise here did not permit the heritability or degree of genetic control of traits affecting cement compatibility to be assessed. The costs of the sampling did not permit individual siblings within each family to be measured and therefore no estimates of within-family variation upon which to base any premises about heritability of specific wood characteristics were generated.

4.4.2 Effects of cold-water-extractive removal by soaking

The removal of extractives by cold water had, as expected, a highly beneficial effect on wood-cement compatibility, especially in the case of the acacias, as shown in Table 4.3 and illustrated for hydration rate in Figure 4.3. Although species means could not be compared statistically because of differing variances between data sets, extracted wood of the two eucalypt species remained higher in compatibility with cement than extracted wood of the acacias (Table 4.3). This difference is particularly evident from hydration rates, which averaged 1.86°C/h for extracted acacias and 2.15°C/h for extracted eucalypts.
Among the acacias, hydration rates increased more than three-fold in most cases after samples were soaked in water. After soaking, however, significant species effects were still evident between the acacias for hydration time and $C_A$-factor (Table 4.3) although the levels of significance ($p$-values) were greatly reduced. In terms of hydration time and $C_A$-factor, extracted $A. mangium$ samples were still slightly but significantly less compatible than $A. aulacocarpa$. The unchanged ranking of the acacias in their compatibility with cement after extractive removal suggests the influence of residual heartwood extractives. It is not clear whether such differences were due to the chemical composition or the amount of extractives left in the wood after soaking.

The overall increase in compatibility with cement after extractive removal was not so marked in the case of the eucalypts, which had high initial compatibility relative to the acacias. Mean $T_{max}$ for $E. pellita$ and $E. urophylla$ increased from 47.4 and 46.8°C, respectively, for unsoaked samples to 49.1 and 49.2°C, respectively, for the extracted samples (Table 4.3). Average hydration rates for $E. pellita$ and $E. urophylla$ after soaking were 2.17 and 2.12°C/h, respectively. Note that $C_A$-factor decreased slightly after soaking in the case of $E. urophylla$, whereas other compatibility indices increased, as shown in Table 4.3. The reliability of the $CA$-factor as a compatibility index for assessing samples of high compatibility with cement is investigated later in Section 4.4.6. For reasons that will be discussed, $C_A$-factor was found to be unsuitable for characterising and comparing samples with relatively high compatibility with cement.

Figure 4.3 Average hydration rate for acacia and eucalypt species before and after soaking; means are from different ANOVA models so standard deviations are used for comparison.
4.4.3 Provenance variation in wood-cement compatibility

In the growth trials from which the A. mangium trees were sampled, the PNG provenances have performed better in terms of growth rate than their North Queensland counterparts (Semple et al. 1999). However, this did not translate into any significant effect of provenance on wood-cement compatibility for either unextracted or extracted samples of A. mangium, irrespective of hydration indices used. This result accords with the previous finding of Semple et al. (1999) that % heartwood in the trees (from which core samples were taken for this study) also did not differ significantly between provenances. The lack of significant provenance differences in wood compatibility with cement could also be due to the very high within-provenance variability in cement compatibility, which is examined and discussed in this Chapter.

In the case of E. pellita, there were also no significant effects of provenance on the compatibility of its wood with cement, either unextracted or extracted. Semple et al. (1999) found that trees from PNG-Kiriwo provenance grown at Etros contained a significantly greater percentage of heartwood than trees from the other provenances. However, this difference was not reflected in the compatibility of the wood core samples with cement, possibly because heartwood in both these species, especially in wood wool or flake form, has only a limited effect on cement hydration.

4.4.4 Relationship between % heartwood and wood-cement compatibility

Hydration rates for unsoaked and soaked A mangium samples are plotted against % heartwood in Figure 4.4(a) and for E. pellita in Figure 4.4(b). No significant relationships were evident between % heartwood in the hydration samples and their compatibility with cement measured by hydration rate in either of the species.

This finding contrasted with the trend for sharply decreasing compatibility with cement with increasing proportion of heartwood in A. mangium if wood flour was used, as was discussed in Chapter 3. In Chapter 3 it was shown that heartwood flour from selected trees of A. mangium, A aulacocarpa and A. crassicarpa was highly incompatible with portland cement, while the sapwood of these tropical species was found to be much higher in compatibility. This finding led to the hypothesis that increasing % heartwood in A. mangium wood samples might have a strong negative effect on their overall compatibility with cement. However, results presented in Chapter 3 also showed that when A. mangium wood was tested in the form of wood wool there were no significant differences in compatibility with cement between samples containing 100% sapwood, 50% sapwood/50% heartwood and 100% heartwood. The wood flakes used in this study were prepared so as to simulate as closely as possible pieces of wood wool.
The absence of any relationship between % heartwood and compatibility with cement across *A. mangium* trees (which contained between 20 and 70% heartwood) accords with the findings for wood wool presented in Chapter 3. In light of this finding, it can be hypothesised that differences in the amount of heartwood extractives and/or their chemical composition among different trees of *A. mangium* are most likely to be primarily responsible for differences in wood-cement compatibility.

The soluble phenolic extractive content of heartwood among the *A. mangium* trees varied significantly, and this appears to have strongly affected wood sample compatibility with portland cement as shown in Figure 4.5. The average hot-water-soluble extractive content of the ten least compatible samples tested was 7.2% compared with an average of 2.45% for the ten most compatible samples. Variability in extractive content and/or composition may be an important governing factor in suitability of acacias for wood-cement composites. Extractive content within *A. mangium* is known to vary with factors such as sample position in the tree (Sudin and Ibrahim 1990), heart rot (Lee et al. 1998, Sudin et al. 1993, Lee 1993), and length of time elapsed since trees were cut (Cabangon et al. 2002b). Heart rot significantly (which was not found in any of the trees sampled in this study) increases the content of water-soluble polar extractives caused by the enzymatic hydrolysis of water-insoluble lignocellulosic and phenolic constituents (Lange and Hashim 2001), resulting in extreme incompatibility with cement (Cabangon and Evans 2002).
A survey of black wattle (A. mearnsii De Wild.) also found very high variation in heartwood extractives yield and composition among trees grown in a single plantation in South Africa (Stephen 1952). A far more comprehensive further assay of heartwood extractive contents within A. mangium would be required to confirm the extent of intra-provenance variability in this important heartwood characteristic and its relationship to cement compatibility.

![Figure 4.5](image)

Figure 4.5 Average hot-water-soluble extractive content of heartwood from the ten most compatible and ten least compatible samples (families) of Acacia mangium.

The results from this study and discussion of previous research suggest that inter- and intra-species variability in heartwood extractive content and composition of wood from tropical acacias in particular could have a strong influence on the suitability of different species for wood-cement composites. Information from a range of other tree species (Hillis 1987) indicates that site as well as genetic factors may play an important role in influencing extractive content and composition in heartwoods of indigenous and exotic plantation trees. The amounts of certain extractives, for example, pinosylvin and tannins, have been found to vary strongly with site in the cases of Scots pine (Pinus sylvestris L.) in Sweden and chestnut (Castanea sativa Mill.) in northern and southern Europe (Erdtmann et al. 1951). Extractive-related heartwood colours in yellow poplar (Liriodendron tulipifera L.) and wild cherry (Prunus serotina Ehrh.) were related to geographic area (Sullivan 1967) and of black walnut (Juglans nigra L.) to soil properties (Nelson et al. 1969), whereas the heritability of another extractive component, oleoresin yield, was found to be very high for slash pine (Pinus elliottii Engelm.) (Franklin et al. 1970, Franklin and Squillace 1973, Squillace and Gansel 1974). The monoterpane composition of oleoresin from P. elliottii varies considerably between trees (Mergen et al. 1955), and the monoterpane composition and constituent ratios in the
wood of this species is under strong genetic control (Squillace 1971, Franklin 1976). Although the amounts and composition of polyphenols present in heartwood is probably largely under genetic control (Hillis 1962), possible confounding effects of growth rate, site and environmental conditions (such as rainfall) on underlying genetic variation cannot be easily separated (Hillis 1987).

Significant inter-provenance variation has also been found in hot-water-soluble wood extractive content of Tasmanian blue gum (Eucalyptus globulus Labill), and provenance was found to strongly affect pulp yield and alkali requirement (Turner et al. 1983). Extractive contents were extremely variable across provenances, ranging from 2.8 to 18.9%. This trait, along with its effect on pulping, could also be closely related to rainfall; however the authors were unable to apportion its variability between genetic and environmental factors. Provenance also significantly influenced % heartwood in the sampled stems of E. pellita used in this study (Semple et al. 1999); however this did not translate into any significant effect on wood-cement compatibility, possibly because of the high overall compatibility of the wood of this species with cement. In contrast, the sampling location of E. deglupta trees within Indonesia strongly influenced the compatibility of the wood with portland cement (Paribotro and Suwandi Kliwon 1977), with extractive content and/or composition the likely factor underpinning the observed variation within this species.

4.4.5 Ranking and identification of 'compatible' families of A. mangium

Table 4.4 lists the ten most compatible families of A. mangium in terms of hydration rate, and their provenance of origin. The distribution of these samples is shown graphically in Figure 4.6. The ten most compatible families were fairly evenly distributed among provenance groups and sites (Table 4.4 and Figure 4.6); however group 2 (PNG-SE at Kuranda) comprised 40% of the top ten samples. Groups 3 (FNQ at Kuranda), 6 (QCR at Moreton) and 7 (PNG-SW at Damper) comprised 20% each. Three of the four trees from PNG-SE at Kuranda came from the same seedlot (15642).

Members from all provenance groups were represented in the ten least compatible samples (Table 4.4), with groups 2 (PNG-SE at Kuranda), 5 (FNQ at Moreton) and 7 (PNG-SW at Damper) comprising 20% each. If C_A-factor (not shown) were used to rank provenances, FNQ at Moreton would comprise 50% of the ten least compatible samples. This result may not be significant in itself, since there are reservations about the validity of the C_A-factor as an accurate wood-cement compatibility index, as will be discussed later. Note that no trees from FNQ at Moreton were represented in the ten most compatible samples (Figure 4.6). This might suggest that more families from this provenance and site may possess heartwood which is ill-suited to wood-cement composites, and that this group should receive lower priority when selecting and growing A. mangium for wood-cement composites. The results suggest that the objective of identifying certain
trees or provenances of *A. mangium* that have a high inherent compatibility with portland cement, and are therefore well suited for selective cultivation for this purpose, may not be met.

Table 4.4 Ranking of the ten most compatible and ten least compatible families of *A. mangium* (unsoaked samples) by hydration rate.

<table>
<thead>
<tr>
<th>10 most compatible</th>
<th>10 least compatible</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Group/Tree</strong></td>
<td><strong>Hydration rate (°C/h)</strong></td>
</tr>
<tr>
<td>2/10</td>
<td>1.49</td>
</tr>
<tr>
<td>3/1</td>
<td>1.36</td>
</tr>
<tr>
<td>7/5</td>
<td>1.02</td>
</tr>
<tr>
<td>7/3</td>
<td>0.98</td>
</tr>
<tr>
<td>6/5</td>
<td>0.93</td>
</tr>
<tr>
<td>2/3</td>
<td>0.91</td>
</tr>
<tr>
<td>3/2</td>
<td>0.89</td>
</tr>
<tr>
<td>2/2</td>
<td>0.84</td>
</tr>
<tr>
<td>6/3</td>
<td>0.83</td>
</tr>
<tr>
<td>2/4</td>
<td>0.82</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>1.01</strong></td>
</tr>
</tbody>
</table>

Key to family identification by Provenance, site and ATSC seedlot No.

Ten most compatible

- 2/2: PNG-SE at Kuranda, 15642-IND5
- 2/3: PNG-SE at Kuranda, 15644-TREE 14
- 2/4: PNG-SE at Kuranda, 15642-TREE 9
- 2/10: PNG-SE at Kuranda, 15642-TREE 8
- 3/1: FNQ at Kuranda, 17701-JM2345
- 3/2: FNQ at Kuranda, 16677-JM1934
- 6/3: QCR at Moreton, 15678-BVG665
- 6/5: QCR at Moreton, 17703-GJM934
- 7/3: PNG-SW at Damper, 17750-KN53
- 7/5: PNG-SW at Damper, 17750-KN107

Ten least compatible

- 1/10: PNG-N at Kuranda, 16938 K2
- 2/8: PNG-SE at Kuranda, 16992 MM995
- 2/9: PNG-SE at Kuranda, 16992 MM981
- 3/9: FNQ at Kuranda, 15677 BH3217
- 4/8: PNG-N at Moreton, 16938 NO. 27
- 5/6: FNQ at Moreton, 15677 BVG650
- 5/8: FNQ at Moreton, 17701 JM2346
- 6/2: QCR at Moreton, 17703 GJM922
- 7/6: PNG-SW at Damper, 16997 BVG1561
- 7/8: PNG-SW at Damper, 16990 BVG1532

Figure 4.6 Distribution of hydration rates for *A. mangium* families (unsoaked samples) by provenance and site group. (11 most compatible families above 0.8°C/h shown by line).
The representation of most provenance groups in both the ten most and the ten least compatible families suggests considerable variability in the wood characteristics governing cement compatibility among the families within each provenance/site group. These characteristics may, as suggested earlier, be more closely tied to heartwood extractive content and/or composition than the overall quantity of heartwood in the stem. This is further supported by the fact that the ten most compatible and ten least compatible families were very similar in average % heartwood, at 51.0 and 49.6% for the ten most and ten least compatible families, respectively. The heartwood traits that affect wood-cement compatibility may also be more consistent across members of closely related families, such as within a seedlot, but this would need to be verified by more intensive sampling.

Figure 4.7 shows the average compatibility (hydration rate) of the ten most compatible and ten least compatible families of *A. mangium* before and after soaking to help illustrate the effects of residual extractives that are not removed in cold water. The unsoaked samples from the ten most and ten least compatible families had average hydration rates of 1.01 and 0.23°C/h, respectively, which increased to 2.25 and 1.65°C/h, respectively, after soaking. The ten least compatible samples remained significantly (p < 0.005) lower in average compatibility even after soaking, suggesting the presence of residual extractives which are insoluble in cold water but may be released when the wood is exposed to the alkaline cement paste.

![Figure 4.7 Average hydration rate for the ten most and ten least compatible *A. mangium* families before and after soaking. (LSD unsoaked = 0.17, LSD soaked = 0.18; Standard deviation indicated by bars).](image-url)
These findings accord with those of Chapter 3, where it was shown that less compatible wood types (such as A. mangium and A. autococarpa) regardless of form, remained less compatible with cement after aqueous extractive removal than more compatible wood types including poplar and E. pellita.

The results could also suggest that the residual extractives left in the wood of less compatible species or trees are of a chemical composition that is more inhibitory of cement hydration than those remaining in the more inherently compatible woods. The questions of how much inhibitory extractive material is removed in cold water from A. mangium wood, and whether this sufficiently improves its compatibility with cement to enable the production of good quality wood-cement composite panels, are investigated further in Chapter 8.

4.4.6 Practical limitations to the use of C_A-factor

The availability of data from a large number of wood samples of differing compatibility with cement has provided an opportunity to identify practical limitations to the use of different wood-cement compatibility indices. The C_A-factor was developed by Hachmi et al. (1990) with the stated objective of developing an accurate and repeatable classification method that could be used as a standard method in all laboratories to measure the compatibility of cement with various wood species. Of a range of different types of compatibility indices compared by Hachmi and co-workers, the C_A-factor facilitated the most effective ranking of different wood species across the complete scale from 0 to 100 (%). C_A-factor was therefore suggested to 'provide the best assessment of the hydration behaviour of any lignocellulosic material mixed with cement'. They did not identify the possibility of inaccuracy resulting from its application to ranking wood samples of relatively high (or low) compatibility with portland cement.

Figures 4.8 show the correlation between C_A-factor and hydration rate for soaked and unsoaked samples of A. mangium (a) and E. pellita (b). Across a wide spectrum of wood-cement compatibility C_A-factor is closely correlated with hydration rate, an inhibitory index that is a direct function of both the maximum hydration temperature and the time taken to reach T_max, as shown for unsoaked A. mangium samples in Figure 4.8(a). In contrast, if all the wood samples being compared were of relatively high compatibility with cement, such as for soaked A. mangium samples or the eucalypt samples (Figure 4.8(b)), then there was no correlation between C_A-factor and the rate of hydration.

This is because hydration curves with a higher hydration rate tail off more sharply after reaching maximum temperature, reducing the area under the curve and hence the C_A-factor. This makes sample ranking and inferences based solely on the C_A-factor unreliable. The C_A-factor was therefore not used to rank individual samples (families) within a species such as A. mangium. The
discrepancy between the hydration rate and the area ratio index meant that among soaked *A. mangium* the samples with highest $C_A$-factors were often not the same samples that would be selected based on highest hydration rate, and vice versa. For this reason, hydration rate was adopted in subsequent Chapters in preference to $C_A$-factor as a more reliable hydration index for ranking and comparing the compatibility of wood samples with portland cement.

Figures 4.8 Correlations between $C_A$-factor and hydration rate for (a) *A. mangium* unsoaked samples, (b) *A. mangium* soaked samples, (c) *E. pellita* unsoaked samples and (d) *E. pellita* soaked samples.
4.4.7 SEM analysis of wood-cement samples

The wide range of wood compatibility among species and the use of flakes in the hydration samples provided a good opportunity to examine closely the interface between the wood surface and cement. Improvements to wood-cement composites have been hampered by a lack of basic understanding of the mechanisms involved in bonding between the portland cement binder and the wood surface (Sandermann and Kohler 1964, Ahn and Moslemi 1980). The early study by Ahn and Moslemi (1980) suggested that the growth of crystals into crevices in the wood contribute significantly to the bonding between the wood surface and the surrounding cement. The interfacial or transition zone between hydrated portland cement and the surface of permeable and semi-permeable vegetable fibres has been subsequently studied far more extensively for cement-bonded fibreboard, by Davies et al. (1981), Coutts and Knightly (1984), Coutts (1987), Coutts and Ni (1995), Bentur and Ackers (1989), Savastano et al. (1992) and Savastano and Agopyan (1999). The hydrated cement at the interfacial zone is characterised by a porous layer of portlandite crystals (calcium hydroxide) and ettringite (hydrated calcium trisulphoaluminate) filaments which, in the case of impermeable filler aggregates or fibres, is believed to be caused by the formation of a water film between the surface of the filler fibre and the cement paste (Wei et al. 1986, Zhang and Gjørv 1999). Research on wood fibre-cement composites indicates that in the case of dry, permeable lignocellulosic fibre (such as wood), there is a net transfer of water from the surrounding cement paste to the fibre surface which results in a greater localised concentration of water at the interface as the cement hydrates, which leads to an even greater porosity and concentration of portlandite growth afforded by greater mobility of Ca\(^{2+}\) ions. The porosity and morphology of this zone is therefore greatly affected by the water:cement ratio used. This porous transition zone can be up to 200 µm in width (in sisal fibre-cement composites) and is believed to be the principal cause of reduced bonding between reinforcing fibres (which in themselves are not inhibitory) and cement since it is in this zone that micro-cracks and fibre de-bonding first occur when the composite is loaded or stressed in any way (Savastano and Agopyan 1999). Coutts (1987), Coutts and Ni (1995) and Zhu (1994) have investigated techniques to temporarily reduce the water:cement ratio at the transition zone during the manufacture of fibre-cement composites, including pressure-moulding, de-watering and autoclaving. However, the wood-cement interface and the control of its water:cement ratio during initial hydration have rarely been investigated in studies dealing with other types of cement-bonded composite materials such as WWCB, CBP or flakeboard.

The relief pattern on the cement left after the wood surface was removed differed markedly among species, heartwood and sapwood within a species, and whether or not the wood sample had been pre-soaked prior to mixing with cement. A. mangium is examined in Plates 4.7(a) to (e), A. crassicarpa in Plates 4.8(a) to (d), and E. pellita and E. urophylla in Plates 4.9(a) to (d)).
In accordance with its low compatibility with cement, the unextracted heartwood of *A. mangium* left a relief of very poorly consolidated cement with no solid cast of the wood flake surface (Plates 4.7(a) and (b)). The morphology of the adjacent cement was similar to that observed by Ahn and Moslemi (1980) in cement affected by the addition of inhibitory sucrose. As suggested by these authors, this would produce poor or non-existent binding between wood and cement in a composite board. The large voids disturbing the pattern (Plates 4.7(a) and (b)) were possibly created by entrained air bubbles produced during initial mixing. However, the bulk of set cement not in contact with the wood surface was not porous, as might be suggested by the frequency of ‘bubbles’ at the wood-cement interface. The voids may also have been formed by the expulsion of air from the wood structure into the surrounding cement; however similar voids were not observed in samples containing wood of higher compatibility with cement. A more plausible theory is that mentioned earlier, i.e. that the accumulation of water adjacent to the wood surface may have dissolved inhibitory extractives from the wood surface, thereby effectively preventing the formation of normal hydration products that characterise the interfacial zone. Once the water was eventually re-absorbed by the hydrating matrix, interfacial air gaps were left unfilled by the usual portlandite and etteringite crystals. However, the exact mechanism for the formation of the large numbers of voids at the interface between cement and unsoaked *A. mangium* heartwood is not known for certain, although observations here suggest a strong influence of inhibitory extractives leached from the wood surface on the morphology of the interfacial zone.

In contrast, the sapwood of *A. mangium* (which was shown to be more compatible with cement in Chapter 3) produced a good relief pattern (Plate 4.7(c)). Once inhibitory extractives were removed, a strong cast of the wood surface was produced (Plate 4.7(d)), suggesting the potential for improved bonding in a cement-bonded composite. Note that the area contacting the wood surface was also greater. Upon closer inspection, the characteristic portlandite and etteringite crystalline hydration products of the transition zone were observed (Plate 4.7(e)).

The unextracted heartwood of *A. crassicarpa* (Plate 4.8(a)) was also deleterious to the setting of cement. The sapwood, on the other hand was of moderate compatibility with cement, producing a rather broken and less defined cast of the wood surface (Plate 4.8(b)). Of particular interest in this case was the presence of hexagonal plate-like hydrates (Plate 4.8(c)). In the presence of retarding sugars a complex interlayered structure of insoluble products often forms around retarded tricalcium aluminate nuclei (Milestone 1977). These take the form of hexagonal hydrates that crystallise as thin, irregularly shaped plates in the presence of retarders (Young 1968, Gupta *et al.* 1973), a similar description to the structures seen here. This suggests the presence of a quantity of inhibitory polysaccharides in the sapwood of *A. crassicarpa*, which is likely to have contributed to the overall low compatibility of this species.
Plates 4.7 Cement reliefs of (a) and (b) unsoaked *A. mangium* heartwood; (c) unsoaked *A. mangium* sapwood; (d) and (e) soaked *A. mangium*. 
Unlike other species, the cold-water-extracted wood from *A. crassicarpa* did not allow good hydration next to the wood surface, as evidenced by the grainy relief shown in Plate 4.8(d). *A. crassicarpa* remained among the least compatible of all species after soaking, and its heartwood is likely to have retained a quantity of inhibitory extractives that were not removed by cold water. It is likely therefore that this species would be less well suited for wood-cement composites even if pre-soaking is applied.

Plates 4.8 Cement reliefs of (a) *A. crassicarpa* heartwood, (b) *A. crassicarpa* sapwood, (c) close-up of plate hydrates (possibly C3A) formed in contact with the sapwood, and (d) soaked wood sample.

Unlike the acacias, the heartwood of *E. pellita*, which has been shown in Chapter 3 to have good compatibility with portland cement, left a clear imprint of the wood surface on the adjacent cement (Plates 4.9(a) and (b)). In this case, features of the tangential surface of the wood flake, including rays, can be clearly seen. Note that the cement paste partially penetrated the rough surface (such as the voids of the ray cells) and set, possibly providing some mechanical interlocking with the
substrate. However, in contrast to the suggestion of Ahn and Moslemi (1980), there was no evidence that individual cement crystals grew into and anchored with the wood surface. The micrographs shown in their paper also did not provide any visual evidence of this phenomenon. The sapwood of both *E. pellita* and *E. urophylla* was less compatible with cement than the corresponding heartwood, leaving only a partial imprint interspersed with areas of poorly hydrated cement, as shown for *E. pellita* in Plate 4.9(c) and *E. urophylla* in Plate 4.9(d). The apparent reduced compatibility of the sapwood with cement may have been caused by preparing and drying fresh sapwood flakes, as discussed in Chapter 3.

Plates 4.9 Cement reliefs of (a) and (b) *E. pellita* heartwood, (c) *E. pellita* sapwood, and (d) *E. urophylla* sapwood.
4.4 Conclusions

Following extensive testing of both unsoaked and pre-soaked samples of tropical acacia and eucalypt wood samples using a selection of wood-cement compatibility indices, it can be concluded that unsoaked tropical eucalypt wood is much more compatible with cement than the unsoaked wood from tropical acacia species. For example, *E. pellita* and *E. urophylla* had R and $C_A$-factor of greater than 1.7°C/h and 80%, respectively, compared with *A. mangium*, *A. aulacocarpa* and *A. crassicarpa* (whose average compatibility indices were $R < 1$ °C/h and $C_A$-factor < 50%). There was also significant variation within the eucalypt and acacia genera in their compatibility with cement. *A. aulacocarpa* had the highest average compatibility ($R = 0.81$ °C/h) of the acacia species tested, followed by *A. mangium* (0.5°C/h) and *A. crassicarpa* (0.44°C/h). *E. pellita* was slightly, but significantly, more compatible than *E. urophylla* in terms of hydration rate ($R = 1.82$ and 1.62°C/h respectively). Within-species provenance or site effects on cement compatibility of unsoaked wood samples were not significant for either *A. mangium* or *E. pellita*. Soaking resulted in a marked increase in average compatibility of acacia samples, along with a reduction in variability. The high initial compatibility of eucalypt samples with cement was not greatly increased by soaking, which suggests that *E. pellita* and *E. urophylla* may be suitable for use in wood-cement composites without the need to pre-soak the wood.

Contrary to initial expectations, % heartwood in the samples was not correlated with wood-cement compatibility in any of the species tested. In the case of *A. mangium*, wood-cement compatibility was, however, strongly linked to the amount of inhibitory water-soluble polyphenolic material present in the heartwood of the samples. The heartwood of the least compatible samples of *A. mangium* contained on average almost three times the quantity of hot-water-soluble material than the most compatible samples.

Among unsoaked wood samples from *A. mangium*, the most compatible samples were dominated by families from PNG-SE at Kuranda, which made up 40% of the ten most compatible families. The ten least compatible samples were predominantly from the FNQ at Morton group. High within-provenance variation in compatibility meant that provenances represented in the ten most compatible samples were also represented in the ten least compatible, highlighting significant intra-provenance variability in wood-cement compatibility.

The large quantity of data obtained from this study allowed the $C_A$-factor of Hachmi et al. (1990) to be tested for its accuracy as a wood-cement compatibility index. $C_A$-factor proved to be an unreliable compatibility index if used to compare samples of relatively high compatibility. Plotting $C_A$-factor against the rate of hydration of cement containing samples spanning a wide range of compatibility resulted in a good correlation between the two indices; however this was not evident among samples of higher compatibility (e.g. soaked acacia samples or among the eucalypt samples).
This resulted in different ranking of samples between $C_A$-factor and hydration rate. Therefore hydration rate rather than $C_A$-factor has been used to rank and make inferences about wood-cement compatibility in subsequent Chapters. $C_A$-factor is used only in certain instances such as when a small number of samples spanning a wide range of wood-cement compatibility are compared.

The use of SEM micrographs taken from wood-cement interfaces of hydration samples approximately 1 month after they were mixed provided information about the nature of the bonding in the wood-cement composites. Samples of high natural compatibility, such as *E. pellita* heartwood, enabled good cement hydration and setting adjacent to the wood surface, leaving a detailed cast of the wood surface imprinted onto the adjacent cement. Higher magnifications showed the presence of a network of portlandite and ettringite crystals that characterised the transition zone between the porous wood surface and hydrating portland cement. In contrast, samples of lower compatibility (such as the heartwoods of the tropical acacias and the sapwood of *E. pellita* and *E. urophylla*) impeded hydration of cement at the wood-cement interface, producing a grainy, pitted zone of unhydrated and poorly hydrated cement. SEM showed that the wood of *A. crassicarpa* did not enable adequate cement hydration adjacent to the wood surface, even after pre-soaking in water, indicating that this species is much less suited to wood-cement composites than *A. mangium* and *A. aulacocarpa*. Based on previous studies of the wood-cement interface, it was hypothesised that voids produced by inhibitory wood types at the interfacial region may have been caused by a layer of inhibitory, extractive-laden water that impeded the normal growth of portlandite and ettringite, leaving empty spaces once the water was re-absorbed by the cement matrix further back from the flake surface. This phenomenon appeared to greatly reduce the contact between the wood surface and the cement, with likely adverse implications for bond strength in wood-cement composite materials containing large wood elements such as wood wool or flakes.

In Chapters 8, 9 and 10, the problem of low compatibility of heartwood from *A. mangium* is investigated further, with a view to overcoming this impediment to the production of wood-cement composites from this readily available wood species. The effects of a variety of physical and chemical pre-treatments on the compatibility of the heartwood are assessed, with the aim of successfully adapting *A. mangium* for the manufacture of wood-cement composites, in particular WWCB.

In Chapter 5 the compatibility of a wider range of temperate acacia and eucalypt species with portland cement is assessed, and possible reasons underlying any observed differences in compatibility among species and genera and between tropical and temperate species of these two genera are discussed.
Chapter 5 The compatibility of temperate species of *Acacia* and *Eucalyptus* with portland cement.

5.1 Introduction

Adaptable, multipurpose temperate acacias such as black wattle (*Acacia mearnsii*), have had a successful history of planting for commercial use overseas, particularly in countries such as China and South Africa where tannin production has been emphasised (Sherry 1971, Hillis 1987). Temperate acacias, *A. mearnsii* in particular, have also attracted considerable attention in countries such as China for their capacity to grow on poor, degraded sites and improve soil fertility (Gao 1989), and where its wood is currently used to produce a wide range of end products including paper, rayon, fuelwood and charcoal, marine posts and mushroom media (Searle 1996). There is also interest in field testing and planting of acacias in agricultural areas of Australia to control salinity and to provide additional farm income through products such as solid timber and firewood (Ryan and Bell 1989, Searle 2000, Clarke et al. 1997).

Experience in growing eucalypts, both in Australia and overseas, has a longer history and is far more comprehensive than other Australian genera (Brown 1993, Eldridge et al. 1993). Selected species such as *E. camaldulensis* and *E. obliqua* have been the most widely domesticated and introduced species overseas because of their extensive geographic distributions and very high intra-specific variation (Eldridge 1975, Brown 1993).

It is not surprising then that both *A. mearnsii* and *E. camaldulensis* are represented in wood-cement compatibility tests and in previous trials of the manufacture of cement-bonded wood composite boards in developing countries. Although previous studies have found the wood from selected temperate acacias (*A. decurrens* and *A. mearnsii*) to be incompatible with cement, utilisation studies indicate that *A. mearnsii* may be well suited to the manufacture of both WWCB (Flawes and Chittenden 1967) and CBP (Teixeira and Pereira 1987). In contrast, wood flour-cement compatibility tests undertaken by Hachmi and Moslemi (1989, 1990), Shukla *et al.* (1984) and Jain *et al.* (1989) have indicated that the wood of *E. camaldulensis* is compatible with portland cement. However an attempt by Yasin and Qureshi (1990) to use *E. camaldulensis* wood particles to make CBP was unsuccessful due to the low compatibility of the untreated wood used in their study. While tropical eucalypts have been better represented in cement-composite research, a small selection of other temperate species such as *E. saligna* (Manzanares *et al.* 1991), *E. citriodora* (Yang and Fan 1992, Latoracca 1999) and *E. globulus* (Valenzuela and Cruz 1982) have also been tested in manufacturing trials of wood-cement composites. Due to the small number of studies and conflicting findings, it is difficult to draw any firm conclusions as to the suitability of most temperate acacias and eucalypts for wood-cement composites.
Furthermore the range of temperate species of *Acacia* and *Eucalyptus* represented in wood-cement compatibility tests is very limited. This study was designed to screen and compare as wide a variety of temperate species as possible. To remove likely confounding effects on wood-cement compatibility arising from variation of tree age, site and environmental conditions, trees of the same age and growing conditions were sampled where possible. Comprehensive field trials of temperate acacias and eucalypts exist in the Australian Capital Territory, with 25 temperate acacia species established in 1994, and 115 species and provenances of eucalypts established in 1984 at two sites (Searle *et al.* 1998, Clarke *et al.* 1997).

5.2 Aims and objectives

The aim of this study was to test for the first time the compatibility with cement of a range of temperate species of acacias and eucalypts grown in controlled field trials in the temperate region of South-Eastern Australia. Specific objectives were to:

1. Identify species of relatively high compatibility that might be suitable for the manufacture of wood-cement composites.
2. Examine possible underlying causes of variation in wood-cement compatibility between acacias and eucalypts and among species, including heartwood/sapwood proportion and extractive content.
3. Consider similarities or differences in compatibility between the tropical acacias and eucalypts investigated in Chapter 4 and the temperate species investigated in this chapter.

For reasons discussed in Chapter 4, hydration rate (which is a direct function of both maximum hydration temperature ($T_{\text{max}}$) and time taken to reach $T_{\text{max}}$), rather than the $C_A$-factor, has been used to rank species for their compatibility with cement.

5.3 Materials and methods

5.3.1 Wood sample collection

Wood samples from a range of temperate eucalypt and acacia species were obtained from controlled species elimination and growth performance trials established by CSIRO Division of Forest Research at two locations within the Australian Capital Territory. The locations of the field trials from which the wood samples were collected are shown in Figure 5.1. Details about the two sites are contained in Table 5.1, since site factors can impact significantly on wood-cement compatibility of a particular species.

Wood samples were collected from the eucalypt trials between 22 Oct. and 1 Nov. 1999 (Uriarra) and 5 to 11 Nov. 1999 (Kowen), and from the acacia trials on 14 Feb. (Kowen) and 6 Mar.
2000 (Uriarra). In both trials, all surviving species were sampled, with one tree per species/provenance seedlot (treatment) cut from each of two replicate blocks at each site. This provided 4 trees per ‘treatment’. A total of 33 species of Acacia plus 4 seedlots of A. mearnsii were sampled, and a total of 41 species of Eucalyptus were sampled. Trees were cut at ground level using a chainsaw and two adjoining discs approximately 25 mm in thickness were cut at breast (1.3 m) height, avoiding branches and knots where possible.

Figure 5.1. Locations of the Uriarra and Kowen field trials of temperate acacias and eucalypts in the ACT, with inset showing the location of the ACT.
Plate 5.1 View of the drier Kowen sampling site.

Table 5.1 Location, climate and soil types for field trial sites at Kowen and Uriarra, ACT.

<table>
<thead>
<tr>
<th></th>
<th>Kowen</th>
<th>Uriarra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latitude</td>
<td>35° 19'S</td>
<td>35° 17'S</td>
</tr>
<tr>
<td>Longitude</td>
<td>149° 19'E</td>
<td>148° 53'E</td>
</tr>
<tr>
<td>Altitude ASL</td>
<td>700 m</td>
<td>680 m</td>
</tr>
<tr>
<td>Mean ann. rainfall</td>
<td>450 - 500 mm</td>
<td>&gt;700 mm</td>
</tr>
<tr>
<td>Mean min. temp.*</td>
<td>-0.2°C</td>
<td>0.12°C</td>
</tr>
<tr>
<td>Mean max. temp.*</td>
<td>26.5°C</td>
<td>27.2°C</td>
</tr>
<tr>
<td>Soil type</td>
<td>Sedimentary shale</td>
<td>Red podzolic merging to silty clay</td>
</tr>
</tbody>
</table>

*mean minimum and maximum temperatures during the coldest (July) and hottest (January) months respectively.

5.3.2 Measurement of % heartwood, basic density and wood-cement compatibility

The discs had their under-bark diameter and heartwood diameter recorded across two axes. These were converted to circular areas and the % heartwood content in the stem calculated. From the first disc the bark was removed and its volume determined using an Archimedian method as used for the core samples in the previous chapter. The disc was then oven dried at 105°C for 24 h, removed and cooled for 5 min in a desiccator and the dry weight used to determine its basic density. The second disc had its bark removed and was cut into wedges using a bandsaw, so that the same proportion of heartwood and sapwood that was present in the tree stem was retained in the cement hydration test sample. The wedges were then sliced using the framers guillotine (shown in Chapter 3) into tangential flakes approx. 0.3-0.5 mm in thickness. In the case of many of the small diameter (<10 cm) discs sampled from the acacia trees, all the wedges from the discs were sliced up. The
flakes were stored at 20°C and 65 ± 5% r.h. to condition them to a moisture content of 12% prior to testing. A 7 g sample of flakes from each tree was pre-soaked in water at 23°C for 24 h, with the water being changed after 6 h and 12 h. Extracted flakes were air dried for approx. 7 days, re-conditioned back to 12% MC and reduced to a 5 g hydration test sample. The measurement of cement hydration temperature vs time reactions and calculation of wood-cement compatibility indices was undertaken as described in Chapter 3 using Blue Circle Southern Cement Batch No. 181MA00. A total of 77 days was required to test all of the samples. A total of 250 unsoaked and soaked eucalypt samples and 210 unsoaked and soaked acacia samples were tested for their compatibility with cement. Every 5 days a cement control sample was randomly interspersed among the 6 hydration samples, resulting in a total of 16 control runs.

5.3.3 Experimental design and statistical analyses

A factorial design was used for this experiment to investigate the effects of four fixed factors on wood-cement compatibility, i.e. genus grouping (eucalypt or acacia), species, site and extraction pre-treatment. Since the factor of greatest interest was the effect of individual species within each genus, species were randomised within each daily six-sample wood-cement hydration test run. The species/provenance treatment groups (i.e. seedlots) were blocked into four genus/site groups which were randomised within two extraction blocks i.e. unsoaked and soaked for trees (Replicates) 1 and 2. All samples from tree 1 were tested, followed by all those of tree 2. The experimental block structure is shown in Table 5.2.

**Table 5.2** Experimental block structure for compatibility testing of temperate acacia and eucalypt species.

<table>
<thead>
<tr>
<th>Tree</th>
<th>Extraction block</th>
<th>Genus/site block</th>
<th>Species/prov. groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>un-extracted</td>
<td>Euc. Uriarra</td>
<td>42</td>
</tr>
<tr>
<td>1</td>
<td>un-extracted</td>
<td>Aca. Kowen</td>
<td>24</td>
</tr>
<tr>
<td>1</td>
<td>un-extracted</td>
<td>Euc. Uriarra</td>
<td>23</td>
</tr>
<tr>
<td>1</td>
<td>un-extracted</td>
<td>Aca Uriarra</td>
<td>44</td>
</tr>
<tr>
<td>1</td>
<td>extracted</td>
<td>Euc. Uriarra</td>
<td>42</td>
</tr>
<tr>
<td>1</td>
<td>extracted</td>
<td>Aca. Kowen</td>
<td>24</td>
</tr>
<tr>
<td>1</td>
<td>extracted</td>
<td>Euc. Kowen</td>
<td>23</td>
</tr>
<tr>
<td>1</td>
<td>extracted</td>
<td>Aca Uriarra</td>
<td>44</td>
</tr>
<tr>
<td>2</td>
<td>un-extracted</td>
<td>Euc. Uriarra</td>
<td>42</td>
</tr>
<tr>
<td>2</td>
<td>un-extracted</td>
<td>Aca. Kowen</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>un-extracted</td>
<td>Euc. Kowen</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>un-extracted</td>
<td>Aca Uriarra</td>
<td>44</td>
</tr>
<tr>
<td>2</td>
<td>extracted</td>
<td>Euc. Uriarra</td>
<td>42</td>
</tr>
<tr>
<td>2</td>
<td>extracted</td>
<td>Aca. Kowen</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>extracted</td>
<td>Euc. Kowen</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>extracted</td>
<td>Aca Uriarra</td>
<td>44</td>
</tr>
</tbody>
</table>
To examine species effects, separate ANOVA models were generated for unsoaked samples and for soaked samples to reduce the complexity inherent in the composite model. Two separate ANOVA models were also adopted because of the very different variances between the data sets for the unsoaked and soaked samples, as was the case with the data sets analysed in Chapter 4.

Relationships between wood-cement compatibility (expressed as hydration rate (R) for the reasons explained in Chapter 4) and possible influencing factors including % heartwood in the trees and extractive content of the wood, were analysed for significance using regression analyses.

5.3.4 Determination of hot-water-soluble extractive content

For samples with sufficient material left over after conducting the hydration tests, hot water soluble extractive content was determined. The samples were pre-conditioned for several months in a climate controlled room maintained at 20 ± 1°C and 65 ± 5% r.h. to condition them to a consistent MC of 12%. A 3 g sample (where possible) of conditioned flakes was weighed, then placed in a 500 mL beaker and 500 mL of boiled water was added and stirred. The water was decanted after 1 h, 2 h and 3 h, replacing it with another 500 mL of fresh boiling water. After the third water change the samples were left covered for another 20 h until cool. The samples were then filtered using a 10 mm diameter funnel and a piece of filter paper (Whatman No. 1, 15 mm diameter) of known weight and moisture content and then oven dried at 105°C overnight. The sample was cooled in a desiccator and reweighed. The extractive content was expressed as a percentage of the oven-dry weight of the extracted wood sample.

5.4 Results and discussion

5.4.1 Wood-cement compatibility: main effects

The levels of significance for main factors (site, genus and soaking) and interactions between factors are shown for a preliminary accumulated ANOVA (all samples) in Table 5.3.

Table 5.3 Levels of significance from the accumulated ANOVA for main factors (site, genus, soaking) and interactions between factors.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Temperature</th>
<th>Time to $T_{\text{max}}$</th>
<th>Hydr. Rate</th>
<th>$C_A$-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>site</td>
<td>&lt;0.001</td>
<td>0.035</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>genus</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>soaking</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>site x genus</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>genus x ssp</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>site x soak</td>
<td>&lt;0.001</td>
<td>0.03</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>genus x soak</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>site x genus x ssp.</td>
<td>N.S.</td>
<td>N.S.</td>
<td>N.S.</td>
<td>N.S.</td>
</tr>
<tr>
<td>site x genus x soak</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>genus x ssp. x soak</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>
All main factors significantly affected compatibility of wood samples with portland cement ($p < 0.001$), as did interactions between factors. The site x genus x species interaction was not significant, indicating that, overall, average compatibility of species across the two genera were not significantly affected by the site at which they were grown.

Table 5.4 shows the main effects and interactions between factors for hydration rate only from the ANOVA models for unsoaked and soaked samples as separate data sets.

Table 5.4 F-probabilities (p-values) for main effects and interactions between factors on hydration rate for unsoaked and soaked wood samples.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Unsoaked samples</th>
<th>Soaked samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>site</td>
<td>&lt;0.001</td>
<td>0.767</td>
</tr>
<tr>
<td>genus</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>site.genus</td>
<td>&lt;0.001</td>
<td>0.095</td>
</tr>
<tr>
<td>genus.species</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>site.genus.species</td>
<td>0.447</td>
<td>0.734</td>
</tr>
<tr>
<td>genus.Acacia spp</td>
<td>&lt;0.001</td>
<td>0.239</td>
</tr>
<tr>
<td>genus.Eucalyptus spp</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

For the unsoaked samples of temperate acacias and eucalypts all factors and interactions had highly significant effects on wood-cement compatibility except for the site x genus x species interaction, indicating that among unsoaked samples site did not affect overall compatibility of species across both genera. However, a significant site effect on wood-cement compatibility was apparent in the case of the eucalypts, which is discussed in more detail in Section 5.4.4.

The average compatibilities (expressed as hydration rate) of wood samples from the two genera *Acacia* and *Eucalyptus* before and after soaking are plotted in Figure 5.2. As a group, the unsoaked samples from the acacias were significantly ($p < 0.001$) less compatible with cement than those from the eucalypts. The average hydration rate for samples containing acacia wood was 0.57°C/h compared with those containing eucalypt wood, which averaged 1.57°C/h. In a similar trend to that found among the tropical species investigated in Chapter 4, the eucalypts retained a significantly higher average compatibility than the acacias after soaking, which can also be seen in Figure 5.2. Hydration rates were in the range of 1.9 to 3.3°C/h for soaked eucalypt samples compared with 1.7 to 2.5°C/h for soaked acacia samples. The acacia samples may have retained greater quantities of residual cold-water-insoluble extractives than did the eucalypt samples. Alternatively, the extractives retained in acacia wood after soaking may have been more inhibitory of cement hydration than those retained in the eucalypt wood, as suggested by the initial low compatibility of the acacia wood with cement.

In addition significant species differences were still evident among the eucalypts after extractive removal, as indicated by the significant ($p < 0.001$) genus x species interaction among soaked
samples of eucalypt species shown in Table 5.4. Differences between acacia and eucalypt species in wood-cement compatibility and possible reasons for these differences are discussed further in Section 5.4.4.

Figure 5.2 Average compatibility (Hydration rate) for samples from the genera Acacia and Eucalyptus before and after soaking. (Means are from different ANOVA models, so standard deviation is used for comparison; means from the same models (i.e. ‘soaked’ and ‘unsoaked’) are significantly different at the 0.1% level).

5.4.2 Wood-cement compatibility of temperate acacias

The average compatibility of each sampled acacia species is shown in Table 5.5 for both unsoaked and soaked wood samples. Species have been placed into three broad compatibility classes: ‘compatible’ $R > 2°C/h$, ‘moderately compatible’ $1.5 < R < 2°C/h$, and ‘incompatible’ $R < 1.5°C/h$. The unsoaked samples from all species could be classed as ‘incompatible’ with cement except for *A. elata*, which was of ‘moderate’ compatibility (average $R = 1.72°C/h$).

Another compatibility study (Sandermann and Kohler (1964)) found both the sapwood and heartwood flour of *A. decurrens* to be highly incompatible with cement and unsuitable for wood-cement composites. In their study, cement setting was delayed for 46 and 38 hours for the sapwood and heartwood respectively, with equivalent hydration rates of 0.71 and 1.0°C/h, respectively. *A. mearnsii*, which performed well in the growth trials, exhibited high variation in wood-cement compatibility among trees from the relatively small number of different seedlots (representing
different provenances) sampled. Seedlot 18979 achieved the second highest hydration rate (1.4°C/h) whereas seedlot 16621 was among the lowest (0.22°C/h) (Table 5.5).

Table 5.5 Ranking of *Acacia* species by hydration rate for unsoaked and soaked samples across both sites.

<table>
<thead>
<tr>
<th>Species</th>
<th>Average Rate (unsoaked)*</th>
<th>Species</th>
<th>Average Rate (pre-soaked)#</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>A. elata</em></td>
<td>1.733</td>
<td><em>A. elata</em></td>
<td>2.509</td>
</tr>
<tr>
<td><em>A. mearnsii</em></td>
<td>1.396</td>
<td><em>A. binervia</em></td>
<td>2.389</td>
</tr>
<tr>
<td><em>A. macrodealbata</em></td>
<td>1.336</td>
<td><em>A. impexa</em></td>
<td>2.338</td>
</tr>
<tr>
<td><em>A. blayana</em></td>
<td>1.135</td>
<td><em>A. mearnsii</em></td>
<td>2.239</td>
</tr>
<tr>
<td><em>A. melanoxylon</em></td>
<td>1.04</td>
<td><em>A. parvippinula</em></td>
<td>2.206</td>
</tr>
<tr>
<td><em>A. melanoxylon</em></td>
<td>0.926</td>
<td><em>A. melanoxylon</em></td>
<td>2.204</td>
</tr>
<tr>
<td><em>A. chrysostricha</em></td>
<td>0.88</td>
<td><em>A. sysestris</em></td>
<td>2.187</td>
</tr>
<tr>
<td><em>A. fulva</em></td>
<td>0.846</td>
<td><em>A. mearnsii</em></td>
<td>2.184</td>
</tr>
<tr>
<td><em>A. parvippinula</em></td>
<td>0.807</td>
<td><em>A. melanoxylon</em></td>
<td>2.178</td>
</tr>
<tr>
<td><em>A. dealbata</em></td>
<td>0.794</td>
<td><em>A. dealbata</em></td>
<td>2.167</td>
</tr>
<tr>
<td><em>A. mearnsii</em></td>
<td>0.781</td>
<td><em>A. blayana</em></td>
<td>2.162</td>
</tr>
<tr>
<td><em>A. irrorata</em></td>
<td>0.748</td>
<td><em>A. chrysostricha</em></td>
<td>2.162</td>
</tr>
<tr>
<td><em>A. obliquina</em></td>
<td>0.739</td>
<td><em>A. irrorata</em></td>
<td>2.159</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>A. velutinella</em></td>
<td></td>
</tr>
<tr>
<td><em>A. decurrens</em></td>
<td>0.659</td>
<td><em>A. dealbata</em></td>
<td>2.114</td>
</tr>
<tr>
<td><em>A. glauccarpa</em></td>
<td>0.601</td>
<td><em>A. cangalensis</em></td>
<td>2.108</td>
</tr>
<tr>
<td><em>A. dealbata</em></td>
<td>0.598</td>
<td><em>A. melanoxylon</em></td>
<td>2.101</td>
</tr>
<tr>
<td><em>A. trachyphloia</em></td>
<td>0.593</td>
<td><em>A. parramatensis</em></td>
<td>2.095</td>
</tr>
<tr>
<td><em>A. binervia</em></td>
<td>0.589</td>
<td><em>A. binervia</em></td>
<td>2.075</td>
</tr>
<tr>
<td><em>A. filicifolia</em></td>
<td>0.585</td>
<td><em>A. dealbata</em></td>
<td>2.072</td>
</tr>
<tr>
<td><em>A. dealbata</em></td>
<td>0.488</td>
<td><em>A. leucocleda</em></td>
<td>2.071</td>
</tr>
<tr>
<td><em>A. melanoxylon</em></td>
<td>0.487</td>
<td><em>A. decurrens</em></td>
<td>2.059</td>
</tr>
<tr>
<td><em>A. binervia</em></td>
<td>0.461</td>
<td><em>A. irrorata</em></td>
<td>2.039</td>
</tr>
<tr>
<td><em>A. irrorata</em></td>
<td>0.444</td>
<td><em>A. nano-dealbata</em></td>
<td>2.028</td>
</tr>
<tr>
<td><em>A. implexa</em></td>
<td>0.421</td>
<td><em>A. leucocleda</em></td>
<td>2.024</td>
</tr>
<tr>
<td><em>A. falciformis</em></td>
<td>0.418</td>
<td><em>A. dealbata</em></td>
<td>2.018</td>
</tr>
<tr>
<td><em>A. sysestris</em></td>
<td>0.415</td>
<td><em>A. trachyphloia</em></td>
<td>2.018</td>
</tr>
<tr>
<td><em>A. dealbata</em></td>
<td>0.391</td>
<td><em>A. fulva</em></td>
<td>2.003</td>
</tr>
<tr>
<td><em>A. parramatensis</em></td>
<td>0.366</td>
<td><em>A. mearnsii</em></td>
<td>1.988</td>
</tr>
<tr>
<td><em>A. mearnsii</em></td>
<td>0.266</td>
<td><em>A. glaucocarpa</em></td>
<td>1.98</td>
</tr>
<tr>
<td><em>A. parramatensis</em></td>
<td>0.251</td>
<td><em>A. filicifolia</em></td>
<td>1.972</td>
</tr>
<tr>
<td><em>A. mearnsii</em></td>
<td>0.221</td>
<td><em>A. mearnsii</em></td>
<td>1.956</td>
</tr>
<tr>
<td><em>A. leucocleda</em></td>
<td>0.191</td>
<td><em>A. parramatensis</em></td>
<td>1.944</td>
</tr>
<tr>
<td><em>A. cangalensis</em></td>
<td>0.088</td>
<td><em>A. obliquina</em></td>
<td>1.92</td>
</tr>
<tr>
<td><em>A. leucocleda</em></td>
<td>0.081</td>
<td><em>A. irrorata</em></td>
<td>1.882</td>
</tr>
<tr>
<td><em>A. irrorata</em></td>
<td>0.057</td>
<td><em>A. dangarensis</em></td>
<td>1.839</td>
</tr>
<tr>
<td><em>A. velutinella</em></td>
<td>0.055</td>
<td><em>A. falciformis</em></td>
<td>1.835</td>
</tr>
</tbody>
</table>

LSD = 0.326, *LSD* = 0.189.

Other compatibility studies by Hachmi and Moslemi (1989), Hachmi *et al.* (1990) and Hachmi and Sesbou (1991) have tested *A. mearnsii* and have found this species to be highly incompatible
with cement. In the study by Hachmi and Moslemi (1989) wood flour from *A. mearnsii* was given a \(C_A\)-factor of 14 compared with 85 for lodgepole pine (*Pinus contorta* var. *latifolia* (Engelm.) Critchfield). Despite its low compatibility, Hachmi and Moslemi (1989) found the wood of *A. mearnsii* to be relatively low in hot water soluble extractives (7.7%) compared with other species of higher compatibility, including Holm oak (*Quercus ilex* L.) with an extractive content of 14.2% and a \(C_A\)-factor of 37%. Arabinogalactan (known to be responsible for the low compatibility of larch heartwood with cement) have also been isolated from the wood of *A. mearnsii* by Aspinall *et al.* (1968), however this has not been mentioned in any compatibility studies of this species.

*A. mearnsii* is the only one of the sampled temperate acacia species reported to have been tested in the manufacture of cement-bonded composite panels. Wood-wool from this species was reported to be suitable for the manufacture of commercial quality wood wool-cement boards providing the wood wool was soaked in a 1% calcium chloride solution before mixing with cement (Flawes and Chittenden 1967). However a 3% solution was recommended as being necessary to obtain boards with reduced surface friability. According to Teixeira and Pereira (1987) CBP has also been made successfully from wood flakes of *A. mearnsii*. It was not specified whether they used fresh or old wood or added an accelerator; however, it appears that the use of a simple compound such as calcium chloride may be sufficient to manufacture quality cement-bonded composites from this species.

Pre-soaking of wood-wool in water at ambient temperature for 24 h had a significant beneficial effect on compatibility of wood from the acacias, as shown in Table 5.3 and Figure 5.2). After soaking, most of the acacias became 'compatible' (\(R > 2^\circ\mathrm{C}/\mathrm{h}\)) with cement (Table 5.5). Apart from *A. elata*, certain seedlots from *A. mearnsii* (15329 and 18789) and *A. melanoxylon* (15863 and 18980) were also ranked as highly compatible after soaking. By contrast, *A. mearnsii* seedlots 17928 and 16621 achieved only 'moderate' compatibility after soaking. *A. dangarensis* retained its relatively low compatibility even after soaking, suggesting that this species may contain higher levels of inhibitory extractives which are not readily soluble in cold water. Like *A. crassicarpa*, this species retained a hydration rate of under 2\(^\circ\mathrm{C}/\mathrm{h}\) after pre-soaking three times in fresh water and is therefore unlikely to be suited to the manufacture of wood-cement composites without more comprehensive pre-treatment.

### 5.4.3 Wood-cement compatibility of temperate eucalypts

The average compatibility of each species of eucalypt sampled is shown in Table 5.6. Only unsoaked samples are shown since the compatibility of pre-soaked samples was high. As a group, the average compatibility of unsoaked wood of the eucalypts was significantly (\(p < 0.001\)) higher than that of the acacias, as shown in Figure 5.2.
In comparison to the acacias, the unsoaked eucalypt wood samples were also highly variable in their compatibility with cement, with 14 out of the 39 species being classed as 'compatible' with cement (Table 5.6). Species such as *E. piperita*, *E. oreades* and *E. regnans* were highly compatible with cement (hydration rate > 2.3°C/h) with little improvement in compatibility resulting from pre-soaking the wood. 13 eucalypt species were 'moderately compatible' and 12 were classed as 'incompatible'. The better known commercial species *E. regnans*, *E. obliqua*, *E. sieberti* and *E. grandis* all attained a high compatibility ranking, whereas others such as *E. bicostata*, *E. saligna* and *E. viminalis* were of 'moderate' compatibility. The species better known for their success in planting overseas, *E. tereticornis* and *E. camaldulensis* (section Exertae) were both ranked as 'incompatible' with cement. *E. camaldulensis* is known to contain polymerised leucoanthocyanids (which inhibit cement hydration) and its extractive composition is subject to significant site-related variability (Hillis 1972).

Table 5.6 Ranking of *Eucalyptus* species by hydration rate (°C/h) for unsoaked samples averaged across sites.

<table>
<thead>
<tr>
<th>Compatible</th>
<th>Moderately Compatible</th>
<th>Incompatible</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species</td>
<td>H Rate</td>
<td>Species</td>
</tr>
<tr>
<td><em>E. piperita</em></td>
<td>2.57</td>
<td><em>E. bicostata</em></td>
</tr>
<tr>
<td><em>E. oreades</em></td>
<td>2.38</td>
<td><em>E. saligna</em></td>
</tr>
<tr>
<td><em>E. regnans</em></td>
<td>2.36</td>
<td><em>E. polyanthemos</em></td>
</tr>
<tr>
<td><em>E. dendromorpha</em></td>
<td>2.35</td>
<td><em>E. sideroxylon</em></td>
</tr>
<tr>
<td><em>E. laevojinea</em></td>
<td>2.30</td>
<td><em>E. glaucescens</em></td>
</tr>
<tr>
<td><em>E. fastigata</em></td>
<td>2.27</td>
<td><em>E. mannifera</em></td>
</tr>
<tr>
<td><em>E. obliqua</em></td>
<td>2.27</td>
<td><em>E. viminalis</em></td>
</tr>
<tr>
<td><em>E. sieberti</em></td>
<td>2.25</td>
<td><em>E. brookeriana</em></td>
</tr>
<tr>
<td><em>E. decim</em></td>
<td>2.15</td>
<td><em>E. nortonii</em></td>
</tr>
<tr>
<td><em>E. grandis</em></td>
<td>2.10</td>
<td><em>E. muelleriana</em></td>
</tr>
<tr>
<td><em>E. quadrangulata</em></td>
<td>2.10</td>
<td><em>E. resinifera</em></td>
</tr>
<tr>
<td><em>E. elata</em></td>
<td>2.09</td>
<td><em>E. cinerea</em></td>
</tr>
<tr>
<td><em>E. botryoides</em></td>
<td>2.01</td>
<td><em>E. nova-anglica</em></td>
</tr>
<tr>
<td><em>E. cypellocarpa</em></td>
<td>2.01</td>
<td><em>E. malaccocylon</em></td>
</tr>
</tbody>
</table>

Standard Error Difference = 0.442

In keeping with the trend for unsoaked wood samples, the average compatibility of soaked samples of eucalypts was also higher than that of soaked samples of acacias (Figure 5.2). In contrast to the results here, previous compatibility studies have found wood flour of *E. camaldulensis* to be 'compatible' with portland cement, with a $C_A$-factor of 69% (Hachmi and Moslemi (1989, 1990). Its equivalent $C_A$-factor here was 33%. Wood flour from *E. camaldulensis* was also rated among the most suitable of 36 different hardwoods tested for their compatibility with cement (Shukla *et al.* 1984, Jain *et al.* 1989). The age and history of the wood samples used by these workers is unknown but may have influenced their findings if only heartwood or very old samples were used.

Despite the encouraging results from laboratory wood-cement compatibility tests, attempts to use wood from *E. camaldulensis* in cement-bonded panels have not been successful. Cement-
bonded particleboards were made from 5-year-old plantation-grown *E. camaldulensis* wood by Yasin and Qureshi (1990). In their study, both cold-water-extracted (48-hour soak) and hot-water-extracted (1-hour soak) wood flakes were tested in boards with a wood:cement ratio of 1:2. All wood flakes were pre-treated with a 3% calcium chloride solution for 5 minutes, and then dried to between 10 and 15% MC before mixing with cement. Unsoaked wood produced poorly bonded boards of low strength and dimensional stability, despite the pre-treatment with calcium chloride. The cold-water-extracted (CWE) wood flakes produced boards of somewhat better quality than the unextracted flakes, whilst the hot-water-extracted (HWE) flakes produced the best boards. The swelling (% linear expansion) of boards containing the CWE flakes was 45% higher than that of boards containing the HWE flakes, and their mean MOR was 90 kg/cm² compared to 111 kg/cm² for HWE boards. The boards containing CWE flakes did not adhere to standard requirements for dimensional stability and bending strength. The results of Yasin and Qureshi (1990) accord better with the findings of the present study and suggest that fresh wood of *E. camaldulensis* (or at least certain provenances or families of this species) may be unsuitable on its own for wood-cement composites. In addition, information in the literature suggests that simple accelerators such as calcium chloride may be relatively ineffective in wood-composites containing woods such as *E. camaldulensis*. The efficacy of calcium chloride as a conventional, low cost cement set accelerator with woods that contain high quantities of polyphenols is examined in Chapters 8 to 10.

The compatibility results for *E. grandis* sampled in this study from the ACT trials indicated relatively high natural compatibility with portland cement. In previous compatibility studies *E. grandis* has been found to be relatively incompatible with cement. It was rated as 'unsuitable' for wood-cement composites on the basis of the pulling force required to remove test sticks set in cement (Rahim and Ong 1983). *E. grandis* required the lowest pulling force (101 N) of all of the 16 species also rated as unsuitable. *E. grandis* was also found to be unsuitable for the commercial manufacture of wood wool-cement panels in a study by Hawkes and Robinson (1978b). However, WWCBs of acceptable quality have been manufactured from *E. grandis* and also *E. tereticornis* grown in the Philippines, but only if cold water extraction or calcium chloride were used to pre-treat the wood wool (Eusebio et al. 2002a).

The above discussion indicates that results from laboratory wood-cement compatibility tests provide only a very general guide to potential species suitability for wood-cement composites, and most judgements are usually only based on one or two samples from wood of a species that may exhibit wide variation in compatibility depending on its geographic origin and growing conditions, season and tree age at cutting, storage condition and time elapsed between cutting and testing, preparation technique, and even the hydration testing procedure used, as evidenced in Chapter 3.
5.4.4 Effects of wood properties including heartwood content and hot water extractive content

There was a slight but non-significant relationship between % heartwood and hydration rate among the temperate acacias, as shown in Figure 5.3(a). In contrast, for the temperate eucalypts there was a significant ($p < 0.001$) positive relationship between the amount of heartwood in the tree stem and the compatibility of the wood with portland cement, as shown in Figure 5.3b. Heartwood content in the samples of eucalypt species ranged from 0% (in *E. polyanthemos*) to almost 80% (in *E. sieberi*) of the stem. Note that many of the samples represented in the lower range of % heartwood and compatibility with cement were from smaller diameter trees grown at Kowen.

Figures 5.3 Correlation between hydration rates and % heartwood content for individual unsoaked and soaked samples of (a) acacias and (b) eucalypts.

As can be seen in Table 5.7, the average % heartwood among trees of a particular species grown at Kowen was in most cases lower than that for the same species grown at Uriarra. This observed effect was tested for statistical significance only among those species that were sampled from both sites. The site effect was found to be highly significant ($p < 0.001$) for both % heartwood in the trees and for hydration rate. This indicates that trees of a particular species sampled at Kowen were significantly less compatible with portland cement than those of the same species sampled at Uriarra, which appears to have been caused by their significantly higher proportion of sapwood in the stem.

A similar result was found in a published pilot study (Semple et al. 2000, Appendix 1, p 362) of wood-cement compatibility among a smaller selection of 8 temperate eucalypt species grown at the same two sites. In that study, trees from the same seed stock growing at Kowen were smaller in
size, contained significantly less heartwood, and were significantly less compatible with cement than those grown at Uriarra. The results suggest that the heartwoods of many eucalypt species may contain more benign extractives and/or lower quantities of extractives than the sapwood.

Table 5.7 Average % heartwood content in *Eucalyptus* species grown at Kowen and Uriarra.

<table>
<thead>
<tr>
<th>Species</th>
<th>% HW Uriarra</th>
<th>% HW Kowen</th>
<th>Species</th>
<th>% HW Uriarra</th>
<th>% HW Kowen</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>E. agglomerata</em></td>
<td>68.3</td>
<td>--</td>
<td><em>E. robusta</em></td>
<td>42.4</td>
<td>--</td>
</tr>
<tr>
<td><em>E. siebert</em></td>
<td>62.5</td>
<td>--</td>
<td><em>E. aggregata</em></td>
<td>41.9</td>
<td>44.3</td>
</tr>
<tr>
<td><em>E. oreades</em></td>
<td>59.3</td>
<td>--</td>
<td><em>E. chapmanii</em></td>
<td>39.9</td>
<td>19.0</td>
</tr>
<tr>
<td><em>E. globulus</em></td>
<td>58.2</td>
<td>33.4</td>
<td><em>E. brookerana</em></td>
<td>39.9</td>
<td>24.2</td>
</tr>
<tr>
<td><em>E. nitens</em></td>
<td>57.1</td>
<td>32.9</td>
<td><em>E. dalyrmpleana</em></td>
<td>38.7</td>
<td>35.0</td>
</tr>
<tr>
<td><em>E. laevopinea</em></td>
<td>56.6</td>
<td>44.2</td>
<td><em>E. deansii</em></td>
<td>38.0</td>
<td>--</td>
</tr>
<tr>
<td><em>E. acaciformis</em></td>
<td>54.9</td>
<td>26.4</td>
<td><em>E. piperita</em></td>
<td>36.0</td>
<td>--</td>
</tr>
<tr>
<td><em>E. fastigata</em></td>
<td>52.7</td>
<td>--</td>
<td><em>E. dendromorpha</em></td>
<td>35.5</td>
<td>--</td>
</tr>
<tr>
<td><em>E. delegatensis</em></td>
<td>51.3</td>
<td>46.7</td>
<td><em>E. cinerea</em></td>
<td>35.4</td>
<td>24.0</td>
</tr>
<tr>
<td><em>E. cupella</em></td>
<td>50.9</td>
<td>--</td>
<td><em>E. quadrangulata</em></td>
<td>33.5</td>
<td>--</td>
</tr>
<tr>
<td><em>E. saligna</em></td>
<td>49.3</td>
<td>--</td>
<td><em>E. nortonii</em></td>
<td>30.4</td>
<td>21.4</td>
</tr>
<tr>
<td><em>E. regnans</em></td>
<td>48.6</td>
<td>--</td>
<td><em>E. angophoroides</em></td>
<td>28.2</td>
<td>8.9</td>
</tr>
<tr>
<td><em>E. nova-anglica</em></td>
<td>48.4</td>
<td>32.8</td>
<td><em>E. stenostoma</em></td>
<td>28.0</td>
<td>--</td>
</tr>
<tr>
<td><em>E. botryoides</em></td>
<td>48.3</td>
<td>--</td>
<td><em>E. melliodora</em></td>
<td>23.6</td>
<td>--</td>
</tr>
<tr>
<td><em>E. elata</em></td>
<td>48.1</td>
<td>35.2</td>
<td><em>E. tereticornis</em></td>
<td>15.8</td>
<td>27.7</td>
</tr>
<tr>
<td><em>E. mannifera</em></td>
<td>47.9</td>
<td>44.9</td>
<td><em>E. polyanthemos</em></td>
<td>14.5</td>
<td>21.6</td>
</tr>
<tr>
<td><em>E. nicholii</em></td>
<td>47.4</td>
<td>32.8</td>
<td><em>E. resinifera</em></td>
<td>13.6</td>
<td>--</td>
</tr>
<tr>
<td><em>E. viminalis</em></td>
<td>45.8</td>
<td>22.9</td>
<td><em>E. sideroxylon</em></td>
<td>11.3</td>
<td>--</td>
</tr>
<tr>
<td><em>E. glaucescens</em></td>
<td>45.6</td>
<td>--</td>
<td><em>E. camaldulensis</em></td>
<td>7.4</td>
<td>23.6</td>
</tr>
<tr>
<td><em>E. obliqua</em></td>
<td>44.0</td>
<td>--</td>
<td><em>E. longiflora</em></td>
<td>6.1</td>
<td>--</td>
</tr>
<tr>
<td><em>E. grandis</em></td>
<td>43.8</td>
<td>--</td>
<td><em>E. gunnii</em></td>
<td>31.8</td>
<td>--</td>
</tr>
<tr>
<td><em>E. dunnii</em></td>
<td>42.6</td>
<td>33.1</td>
<td><em>E. malacoxylon</em></td>
<td>25.0</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 5.8 ranks most of the eucalypt and acacia species by their hot-water-soluble extractive content. The correlation between hot-water-soluble extractive content of the wood and its effect on hydration rate of portland cement is shown for acacias in Figure 5.4(a) and for eucalypts in Figure 5.4(b).

The acacias generally contained higher quantities of hot-water-soluble extractives, which is believed to have contributed to their lower compatibility with portland cement (not withstanding the likely effects of extractive chemical composition). The amount of extractives is likely to be a significant determining factor in compatibility in the case of the acacias, since there was a significant ($p < 0.001$) negative correlation between extractive content and hydration rate, as shown in Figure 5.4(a) among the temperate acacias. Some species (e.g. *A. leucoclad*, *A. parramatensis* and *A. dangarensis*) had a hot-water-soluble extractive content of up to 10%. From Table 5.5 it can be seen that these species were also among the 10 least compatible species of temperate acacias.
tested (R < 0.3°C/h). Many of these contained distinctive yellow-coloured sapwood which is shown for *A. dangarensis* and *A. leuclada* in Plate 5.2.

### Table 5.8 Average content of hot-water-soluble extractives in species of *Acacia* and *Eucalyptus.*

<table>
<thead>
<tr>
<th></th>
<th>Acacias</th>
<th>Extr. cont. (%)</th>
<th>Eucalypts</th>
<th>Extr. cont. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>A. leuclada</em></td>
<td>11.0</td>
<td><em>E. cinerea</em></td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td><em>A. parramatensis</em></td>
<td>10.5</td>
<td><em>E. obliqua</em></td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td><em>A. dangarensis</em></td>
<td>9.9</td>
<td><em>E. muelleriana</em></td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td><em>A. mearnsii</em></td>
<td>8.3</td>
<td><em>E. fastigata</em></td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td><em>A. parvipinmula</em></td>
<td>8.0</td>
<td><em>E. camalderensis</em></td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td><em>A. melanoxyylon</em></td>
<td>7.6</td>
<td><em>E. botryoides</em></td>
<td>4.8</td>
<td></td>
</tr>
<tr>
<td><em>A. irrorata ssp. velutinella</em></td>
<td>7.3</td>
<td><em>E. nortoni</em></td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td><em>A. dealbata</em></td>
<td>5.9</td>
<td><em>E. acaciiformis</em></td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td><em>A. trachyploia</em></td>
<td>5.8</td>
<td><em>E. polyanthemos</em></td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td><em>A. falciformis</em></td>
<td>5.7</td>
<td><em>E. laeopinea</em></td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td><em>A. fulva</em></td>
<td>5.6</td>
<td><em>E. angophoroides</em></td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td><em>A. cangaiensis</em></td>
<td>5.4</td>
<td><em>E. malacoxyylon</em></td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td><em>A. deccurens</em></td>
<td>5.1</td>
<td><em>E. piperita</em></td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td><em>A. dealbata</em></td>
<td>4.8</td>
<td><em>E. quadangulata</em></td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td><em>A. mearnsii</em></td>
<td>4.5</td>
<td><em>E. dalrympleana</em></td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td><em>A. parramatensis</em></td>
<td>4.5</td>
<td><em>E. tereticornis</em></td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td><em>A. deccani</em></td>
<td>4.4</td>
<td><em>E. elata</em></td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td><em>A. binervata</em></td>
<td>4.2</td>
<td><em>E. melliodora</em></td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td><em>A. irrorata</em></td>
<td>3.9</td>
<td><em>E. resinifera</em></td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td><em>A. dealbata</em></td>
<td>3.8</td>
<td><em>E. cyphlocarpa</em></td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td><em>A. syvvestris</em></td>
<td>3.7</td>
<td><em>E. mappifera</em></td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td><em>A. glaucocarpa</em></td>
<td>3.6</td>
<td><em>E. dunnii</em></td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td><em>A. elata</em></td>
<td>3.6</td>
<td><em>E. nova-anglica</em></td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td><em>A. melanoxyylon</em></td>
<td>3.5</td>
<td><em>E. longifolia</em></td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td><em>A. mearnsii</em></td>
<td>3.2</td>
<td><em>E. saligna</em></td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td><em>A. filicifolia</em></td>
<td>3.2</td>
<td><em>E. viminalis</em></td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td><em>A. melanoxyylon</em></td>
<td>3.0</td>
<td><em>E. chapmaniana</em></td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td><em>A. chrysotricha</em></td>
<td>2.6</td>
<td><em>E. deccani</em></td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td><em>A. binervia</em></td>
<td>2.6</td>
<td><em>E. aggregata</em></td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td><em>A. mearnsii</em></td>
<td>2.2</td>
<td><em>E. biconostata</em></td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td><em>A. irrorata</em></td>
<td>2.0</td>
<td><em>E. delegatensis</em></td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td><em>A. obliquinervia</em></td>
<td>1.8</td>
<td><em>E. grandis</em></td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td><em>A. nano-dealbata</em></td>
<td>1.3</td>
<td><em>E. glaucescens</em></td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>E. sieberi</em></td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>E. regrans</em></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>E. oreades</em></td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>E. nitens</em></td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>E. Gunnii</em></td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>E. brookeriana</em></td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>E. dendromorpha</em></td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>
Figures 5.4 Correlation between hydration rate and wood extractive content for (a) acacias and (b) eucalypts.

Plate 5.2 Distinctive yellow colouring of sapwood in *A. dangarensis* (top) and *A. leucoclada* (bottom). Yellow colouring disappeared after soaking (samples on right).

Acacia species containing a lower quantity of extractives were mostly higher in compatibility with cement. The average hydration rate for acacias containing less than 2.5% extractives was 1.05°C/h, while that of acacias containing over 5% extractives was 0.35°C/h. The extractives in the
wood of acacias are likely to be more potent inhibitors of cement hydration than those present in eucalypt wood. This is evidenced by the fact that the average hydration rate in cement produced by wood samples from acacia species containing a moderate level of hot-water-soluble extractives (between 3 and 4%) was 0.65°C compared with 1.57°C for eucalypt wood species within the same range of extractive contents.

Work by Hachmi and Moslemi (1989), Hachmi et al. (1990) and Hachmi and Seshou (1991) found that among equally incompatible wood species A. mearnsii, Quercus suber and Stipa tenacessima, the acacia had the lowest hot-water-soluble extractive content (7.7%) compared with over 12% in the other two species. The results here and the above-mentioned studies suggest that although some acacias may contain relatively low levels of extractives, their chemical composition can make them potent inhibitors of cement hydration. Hemicelluloses such as arabinogalactan in A mearnsii (and possibly other temperate species) were mentioned earlier as a possible cause of low compatibility.

In contrast to the temperate acacias, there was no significant relationship between the hot-water-soluble extractive content of eucalypt wood samples and their compatibility with cement (Figure 5.4). This is because some of the most compatible species (e.g. E. fastigata and E. botryoides) had relatively high quantities of hot-water-soluble extractives (5.4% and 4.8% respectively) while others (e.g. E. gunnii and E. nitens) had very low levels of hot-water-soluble extractives (0.5% and 0.7%, respectively) but were still of very low compatibility with cement as shown in Table 5.5. These were in contrast to other species which had very low levels of extractives (e.g. E. regnans (1%) and E. oreades (0.78%)) but were highly compatible with cement. Some eucalypts have been shown to contain very high levels of hot-water-soluble heartwood extractives; for example E. obliqua can contain up to 26.6% of its dry weight as hot-water-soluble extractives (Hillis 1987). This species was of high compatibility with cement (R = 2.26°C/h) in this study, despite its relatively high extractive content. It would be worthwhile testing for the sugar and polyphenolic contents of the extracts from the eucalypts, since this could be more closely related to the compatibility of eucalypt wood rather than the overall quantity of extractives present in the wood.

As discussed earlier, eucalypts with a higher proportion of sapwood were mostly less compatible with cement than those containing less sapwood, despite the fact that the overall quantity of extractives did not significantly affect wood-cement compatibility. Hachmi and Moslemi (1989), when testing a range of different wood species, also found that extractive content alone could not account for all of the variation observed in wood-cement compatibility. They did however forward a theory that there is a threshold level of extractives (7%) above and below which woods could be classified as ‘incompatible’ or ‘compatible’, respectively, with cement. The results from eucalypts here did not neatly fit this theory and suggest the presence of distinctly different kinds of
compounds in the woods of different eucalypt species that may strongly influence the effect of the wood on cement hydration. The extractives of eucalypts largely consist of polymerised polyphenols (tannins) and carbohydrates that vary according to taxonomic grouping (Hillis 1966, 1972). Some eucalypt woods (e.g. E. camaldulensis) are rich in tannins and ellagitannins which vary greatly in composition and quantity according to species and the geographic origin of the samples (Yazaki and Hillis 1976, Conde et al. 1995, Cadahia et al. 1997) and even within a species, which has been demonstrated in E. globulus (Pereira 1988). This variation in chemical composition and content may have contributed significantly to the observed variation in wood-cement compatibility among the species tested in this study.

5.4.5 Comparison with tropical acacias and eucalypts

As reported in Chapter 4, the tropical acacias A. mangium, A. crassicarpa and A. aulacocarpa and tropical eucalypts E. pellita and E. urophylla were tested for compatibility with portland cement. Hydration rates for A. mangium and A. crassicarpa were less than 0.5°C/h, whereas for A. aulacocarpa it was 0.81°C/h. Almost 50% of the temperate species also had average hydration rates less than 0.5°C/h. After soaking, the tropical species attained moderate compatibility (1.8 to 1.9°C/h) under the classification system used here. An important difference to note between the tropical and temperate acacias is that the tropical species were sampled as much larger and older trees with a higher content of heartwood (up to 70%) than the temperate species. This may have accounted for their relatively low compatibility even after soaking.

In Chapter 3 it was shown that the sapwood of A. mangium was more compatible than the heartwood, and a supplementary study by Semple and Evans (1998), which can be found in Appendix 1, p. 340, showed that the sapwood flour of three tropical acacias, A. mangium, A. auriculiformis and A. crassicarpa was significantly higher in compatibility with cement than heartwood (C_A-factors of between 73 and 82%). The same study showed that the sapwood flour of two important temperate acacia species, A. mearnsii and A. melanoxylon was as compatible or less compatible with cement than the heartwood, which is similar to the trend found by Sandermann and Kohler (1964) for A. decurrens. All sapwood samples were given a C_A-factor of less than 25%. The sapwoods of A. mearnsii and A. melanoxylon were found to have high quantities of soluble sugars (8.5 and 16.6 mg/g dry wood, respectively) compared with A. mangium (5.2 mg/g). The very low compatibility of many of the temperate acacias and the lack of any correlation between compatibility and heartwood/sapwood proportions in the trees suggest that, in contrast to tropical species like A. mangium, both the sapwood and heartwood of many temperate species is incompatible with cement. The inhibitory sugars and heartwood polyphenols in the temperate species were mostly soluble in water and most of the temperate species were reclassified as
compatible (R > 2°C/h) after soaking. However, the finding that almost one third of the temperate species attained only moderate compatibility after soaking suggests the retention of some inhibitory extractive material and that cold-water soaking may not sufficiently ameliorate the low compatibility of these woods for the manufacture of wood-cement composites. The removal of heartwood extractives by cold and hot water is examined further for *A. mangium*, in Chapter 8.

The fresh wood of the two tropical eucalypts described in Chapter 4 could be classed as being of 'moderate' compatibility with cement (R between 1.5 and 2°C/h) under the classification system used here and similar to *E. saligna* and *E. viminalis*. In accord with the trend in *E. pellita* for compatibility to increase as sapwood content decreased, the results from this study showed that among a much wider range of eucalypts compatibility with cement also increased with decreasing sapwood content. The results from Chapter 3 and the SEM micrographs shown in Chapter 4 demonstrate that the heartwood of *E. pellita* is of high natural compatibility with cement, resulting in a hydration rate of 2.4°C/h, despite its high quantity of extractives. In contrast, the sapwood was only of low to moderate compatibility, averaging 1.4°C/h. The heartwoods of many other eucalypt species may also be of similar high natural compatibility with portland cement compared with the sapwood. Although fresh sapwood may be often of low compatibility with cement, the wood of several tropical and temperate eucalypt species may be well suited for the manufacture of wood-cement composite materials, particularly if the levels of inhibitory polysaccharides in the sapwood can be reduced either by extraction or pre-storage. As discussed in Chapter 2, the normally high content of inhibitory sugars and starches in rubberwood (*Hevea brasiliensis* Muell.), which is currently used in Malaysia to manufacture cement-bonded composite panels, can be reduced to within acceptable limits by simply pre-storing de-barked billets for between 4 and 20 weeks. This is taken into consideration in Chapter 7, which examines the manufacture of WWCB and cement-bonded flakeboards from the important temperate eucalypt species, *E. bicostata*.

5.5 Conclusions

In this study a wide range of tropical and temperate species of *Acacia* and *Eucalyptus* were screened for compatibility with portland cement, most of which have never been tested previously. Overall, wood samples from all species of acacia were rated as 'incompatible' with cement, except for *A. elata*, which was of 'moderate' compatibility. In contrast, the eucalypts as a group were of significantly higher natural compatibility, with one third of the species tested being classed as 'compatible' with cement (R>2°C/h). The research has also indicated that different wood properties such as heartwood content, extractive content and composition can significantly influence wood-cement compatibility among trees and species of these two genera. In the case of the temperate acacias, % heartwood in the samples did not significantly affect wood-cement compatibility,
suggesting that both heartwood and sapwood were of very low compatibility. The quantity of hot-water-soluble extractives in the wood did, however, significantly influence sample compatibility, with a higher content of hot-water-soluble extractives leading to decreased compatibility. In the case of the eucalypts, the findings were quite different, i.e. wood-cement compatibility was positively correlated with increasing % heartwood, indicating that higher sapwood content is primarily responsible for reduced overall wood-cement compatibility. Differences in extractive chemical composition between eucalypt species may play a more important role since, unlike the acacias, there was no correlation between wood extractive content and its compatibility with cement.

Where a range of different trees from different provenances of a species were available for testing, as in the case of *A. mearnsii*, the results indicated significant variation in wood compatibility with cement among different provenances and individuals of a species sampled from the same plantation. These findings accord with examples discussed in the literature showing that intra-specific variation in wood chemical constituents that influence wood-cement compatibility can be very high for acacia and eucalypt species. This suggests that it is difficult to make definite statements about the exact suitability of a species for wood-cement composites where a wide range of individuals from different seed-stocks have not been tested to establish possible intra-specific variation in wood-cement compatibility.

It can be concluded from this study that selected temperate acacia species (for example *A. elata* and certain provenances of *A. mearnsii*) and several temperate eucalypt species may be quite well suited to cement-bonded wood composites with minimal need for wood pre-treatment. However, many of the acacias and eucalypts commonly planted in developing countries, such as *A. mangium*, *A. aulacocarpa*, *A. crassicarpa*, certain provenances of *A. mearnsii*, *E. camaldulensis* and *E. tereticornis* appear to be of very low natural compatibility with portland cement. Past experience has shown that wood-wool, particles or flakes from many of these species require pre-treatments such as soaking and/or the addition of chemical cement set accelerators before the wood can be used to manufacture wood-cement composites.

Chapter 6 completes the section on wood-cement compatibility testing of acacias and eucalypts, and examines the compatibility of mallee eucalypt species with cement and their potential suitability for the manufacture of wood-cement boards. The wood was in the form of small-diameter stem residues of short-rotation mallee eucalypt trees left over from the harvesting of leaves for extraction of leaf oils.
Chapter 6 Compatibility of Western Australian species of mallee eucalypt and melaleuca with portland cement.

6.1 Introduction

Rising water tables in the wheat belt of Western Australia (WA) due to extensive clearing of native soil vegetation over the last 100 years are transferring salts from ancient marine sediments to the upper soil horizons, with devastating effects on agricultural productivity. Almost 10% or 1.8 million ha of wheat-belt soils are now affected to some extent by salinity (Government of Western Australia 1996). This is forecast to increase to 50% over the next 50 years unless large-scale revegetation of affected areas is undertaken (Ferdowsian et al. 1996). To help rectify this problem an ambitious to large-scale tree plantations has put in place, and it is hoped that such plantations will have the dual effects of ameliorating rising water tables and accompanying soil salinity and providing income for farmers through the sale of eucalypt leaf oils and wood (Berry 1997, Shea 1998). Some 45 species of eucalypts and acacias are currently being tested for their ability to grow on salt-affected land throughout the wheatbelt of WA (Shea 1998). Preliminary results suggest that mallee eucalypts, which are hardy, lignotuberous, multi-stemmed eucalypts adapted to the semi-arid zones of eastern and western Australia are well suited for planting on salt-affected sites and have the potential to generate significant volumes of wood and essential leaf oils (Markham and Noble 1989, Wildy et al. 2000).

Five species in particular; Eucalyptus polybractea R.T. Baker, E. angustissima F. Muell ssp. angustissima, E. kochii Maiden and Blakely ssp. plenissima (Gardner) Brooker, E. horistes Johnson & Hill and E. loxophleba ssp. lissophloia (Benth.) show great promise. E. polybractea is the premier source of high grade cineole oils (1,8-cineole is the principal active constituent of medicinal oils) in Australia (Boland et al. 1991). Leaf oil is the main commercial product derived from mallee plantations in Australia, but at present it is only sold in niche markets for high quality pharmaceutical oils, the much larger market for general purpose eucalyptus oil being mainly supplied at lower cost by China (McKelvie et al. 1994). In future Australia could potentially supply large markets for 'new generation' industrial solvents based on eucalyptus oil (Wildy et al. 2000).

There are currently around 10 000 ha of mallee eucalypt plantations in WA, with projections for sharp increases in planting rates (Bartle, J. pers. comm. 1999). The trees coppice readily and subsequent harvesting could take place as frequently as every 1 to 2 years (Shea 1998). However, cineole yields from mallee leaves are highest in older leaves around 5 years of age (Eastham et al. 1993). Later harvest of trees is therefore the preferred option, resulting in the generation of larger
quantities of woody biomass left over after stripping the leaves for distillation. Economic analysis indicates that the financial viability of oil production from mallee plantations depends on farmers finding a commercial outlet for the woody residues (Bartle et al. 1996). Around 3 t/ha/year of clean dry woodchips can be produced at most sites under a 3-5 year rotation (Bartle 2001), and in addition plantations of oil-mallee eucalypts have the potential to generate around 13 million m$^3$ of woody biomass annually in WA (Shea 1998). A preferred option for disposing of the woody residue is by chipping, which provides a ready source of fuel for distillation, electricity generation, carbonisation into activated charcoal products (Evans 1997, Fung 1999), and possibly raw material for the manufacture of wood-based composites (Bartle 2001).

The genus *Melaleuca* (fam. Myrtaceae) comprises an estimated 200 species endemic to Australia, mainly WA, and about another eight from islands to Australia's north (Holliday 1989). Species and provenances span a very wide range of sites from the arid interior to swampy, saline estuarine and coastal sites (Holliday 1989, Doran and Turnbull 1997). Certain species of melaleuca are of considerable economic importance in several developing countries, particularly in S.E. Asia, as sources of essential oils (Brophy and Doran 1996), flowers and pollen for honeybees and also, in Australia, as ornamental plants. The wood is also an important source of fuel in some countries (Wang et al. 1981, Gardner 1989). Importantly, many melaleuca species are adapted to salty, low-lying water-logged soils and are among the only large plants which will tolerate such conditions (Holliday 1989). The introduction of melaleucas into the agricultural landscape in WA for 'farm-forestry' is still in the species and provenance testing stage, and there is considerable potential for melaleucas to effectively combat waterlogging and salinity on farmland and to be cultivated by farmers for the commercial production of leaf oils.

There is almost no information about the suitability of mallee or melaleuca residues for the manufacture of wood-based composites. This Chapter deals specifically with the compatibility of chipped mallee and melaleuca residues with portland cement and their potential utilisation for the manufacture of cement-bonded composite panels. In this study the chipped wood and bark residues of mallee eucalypt and melaleuca species were first tested to determine their effect on the hydration of portland cement. As shown in Chapters 3 to 5, cement hydration tests provide a useful guide to the potential capacity of woods to inhibit setting of portland cement, but on their own are insufficient to fully assess whether wood is suitable for the manufacture of cement-bonded composites. Unlike the sampling of tropical and temperate acacia and eucalypt species in Chapters 4 and 5, the sampling of mallee eucalypts provided an opportunity to manufacture cement-bonded particleboards (CBPs) in the laboratory from chipped residues and determine their strength and physical properties. However insufficient source material meant that the same could not be done for the melaleucas. Results were compared with those obtained from testing CBPs manufactured from
radiata pine (*Pinus radiata* D. Don) particleboard flakes, a species that is used commercially for the manufacture of wood-cement composites (Semple and Evans 2000).

### 6.2 Aims and objectives

The overall aim of this study was to test the potential suitability of selected Western Australian mallee eucalypt and melaleuca species for the manufacture of wood-cement composite panels. Specific objectives of the research presented in this Chapter were to:

1. Measure and calculate wood-cement compatibility indices for chipped wood and bark residues from five potentially important oil mallee species, determining the effects of species, tree age, growing site and the presence/absence of bark in the chipped residues.

2. Measure and calculate wood-cement compatibility indices for chipped wood and bark residues from three potentially important melaleuca species, determining the effects of species, presence/absence of bark, and aqueous extractive removal from the residues.

3. Manufacture and assess the mechanical and water resistance properties of wood-cement composites made from chipped mallee wood and bark residues.

### 6.3 Materials and methods

#### 6.3.1 Wood sample collection and preparation

The mallee trees available for sampling were multi-stemmed, shrub-like, and less than 3 m in height. Stem diameters were about 10 to 40 mm; and all of the stems present were removed at 0.3 m from ground level. The bottom 1 m portions of all stems were removed for chipping. Species sampled were *E. polybractea*, *E. angustissima* ssp. *angustissima*, *E. kochii* ssp. *plenissima*, *E. horistes* and *E. loxophleba* ssp. *lissophloia*. Wood was obtained from the mallee field trials in April/May 1999 from two of the blocks present at each of five sites, one block containing the 2.5-year-old coppice and the other containing 6-year-old seedling trees. Two trees were cut at random from each block. The five sampling sites were Kalannie, Trayning, Beverley, Newdegate and Esperance (shown in Figure 6.1). Insufficient material was available for sampling from a sixth site, Canna, due to cyclone damage in 1998, and only 2.5-year-old trees were available from Newdegate.

The melaleucas were available only from native populations growing along riparian strips that are subject to periodic waterlogging. Wood samples were collected from native populations of three species of potential commercial interest; *Melaleuca lateriflora* Benth, *Melaleuca acuminata* F. Muell. and *Melaleuca uncinata* R. Br. Three small-diameter (<10 cm) trees from each species were destructively sampled. For comparison, wood residues from a ubiquitous crop fodder tree, tagasaste or tree lucern (*Chamaecytisus proliferus* var. *palmensis* (Christ) Hansen & Sunding), were also
sampled. The melaleuca and tagasaste trees were multi-stemmed, reaching around 2 m in height. Stems from three trees of each species were sampled using a chainsaw in a similar manner to that described above for the mallees. Mallee eucalypt trees on farmland and typical sampled trees are shown in Plates 6.1 (a) to (c).

![Map of Western Australia showing sampling locations for mallee and melaleuca trees](image)

Figure 6.1 Sampling locations for mallee and melaleuca trees in Western Australia. Rainfall: Kalannie, Trayning 300 mm; Canna, Newdegate 350 mm; Beverley 500 mm; and Esperance 600 mm per annum.

Due to the youth and small diameter of the sampled mallee and melaleuca trees, the wood represented was all sapwood and could not be converted to flakes by hand slicing as was done in Chapters 4 and 5. The residues were instead converted into large particles using a chipper-shredder. Once the stems were cut, the leaves were removed and the stems separated into two portions, one of which was stripped of bark by hand. The wood was then air dried for 2 weeks, and the barked and de-barked portions of each tree were chipped separately in a MTD Chipper-Shredder. The residues were bagged and sent to Canberra where they were separated by sieving (Plate 6.2(a)) into four size classes (>3.86 mm, 2.4 to 3.86 mm, 1.68 to 2.4 mm and <1.68 mm). The 1.68 to 2.4 mm fraction from each tree (with and without bark) was retrieved and kept in a conditioning room maintained at 20 ± 1°C and 65 ± 5% r.h. for 3 weeks. This size class was used to examine the effects of mallee eucalypt and melaleuca wood on the hydration of cement. Two 5 g samples from each tree (one with bark and one without) were placed in open-topped plastic tubes. Samples were again kept in the conditioning room until used. Two samples of commercial radiata pine sapwood particleboard flakes were also prepared and tested in the same manner for their compatibility with cement.
Typical small-diameter mallee wood stems that were shredded, the resulting sieved chips, and radiata pine particleboard flakes are shown in Plate 6.2(b).

Plates 6.1 (a) mallee hedgerows, (b) hedgerow ready for harvest, and (c) stems to be utilised for composites after chipping.

6.3.2 Removal of extractives and measurement of wood-cement compatibility

The removal of cold-water-soluble extractives from the screened wood and bark residues from the sampled melaleuca trees was carried out using the same methodology as described in Chapter 3. After this treatment the particles were air-dried for 7 days and re-conditioned at 20 ± 1° C and 65 ± 5% r.h. for 3 weeks prior to weighing out into 5 g (ODW basis) samples in preparation for wood-cement compatibility testing. The mixing of cement hydration samples and measurement of cement hydration temperature profiles and the derivation of compatibility indices were carried out as described in Chapter 3.
Plates 6.2 (a) sieves used to screen chipped mallee particles for desired size, and (b) typical particles produced from mallee residues, with radiata pine core particleboard flake sourced from CSR, Tumut as a comparison.

6.3.3 Manufacture of cement-bonded particleboards from mallee in the laboratory

Cement-bonded particleboards (CBPs) were manufactured from chipped and screened mallee eucalypt residues. There was insufficient material to allow the manufacture of boards from melaleuca residues. Due to restrictions on tree removal from the growth trials, there was also insufficient material to allow the manufacture of boards from separate trees obtained from each site and age class. Therefore, for each species, the 2.4 to 3.8 mm (large) and the 1.7 to 2.4 mm (small) size fractions were combined in the proportions of 65% and 35% across site and age class respectively to produce bulk samples each weighing approximately 700 g, sufficient for the manufacture of two boards (replicates). This was done separately for residues with and without bark. The small size (<10-50 mm diameter) of mallee eucalypt stems may potentially restrict the options for converting the wood into engineered wood particles designed to maximise the strength of particleboards (Maloney 1977). Hence, it was important to compare the mechanical properties of CBPs made from chipped mallee eucalypt residues with those of boards made from commercially produced radiata pine particleboard flakes.

The manufacture of CBPs followed the methodology used by Yasin and Quereshi (1990) and Sudin and Ibrahim (1990). Boards contained 325 g of wood (oven dry basis), 650 g of portland cement ASTM Type 1 (wood:cement ratio of 1:2), 250 g of water and 13 g of CaCl₂ (2% w/w cement). The wood residue for each board was first sprayed evenly with water containing dissolved CaCl₂ and cement was sprinkled through the wet wood particles. The cement and wood were mixed
by hand to evenly coat all particles with cement. The mix was then immediately transferred to a steel mould measuring 240 x 300 mm placed on a rectangular sheet of plywood measuring 340 x 420 x 17 mm. The mat was evenly spread and flattened using a wooden block, the mould removed and another piece of plywood placed on top of the mat. Two wooden spacing rods measuring 12 x 12 x 300 mm were placed at either end of the two plywood sheets to ensure that pressed board thickness was 12 mm. The resulting assemblage was pre-pressed while the mat for the next board was mixed. This process was repeated to produce a sandwich of three mats. This stack of mats was placed between two steel plates measuring 340 x 470 x 15 mm and pressed to approximately 60 kN using a PHI 101.6 mm RAM hydraulic operated press, which is shown in Chapter 7. The pressed mats were kept under constant pressure for 24 h by bolting the two steel plates together using four 8-mm-thick bolts. After 24 h the boards were de-clamped, stacked vertically and conditioned for approx. 8 weeks at 20 ± 1 °C and 65 ± 5% r.h. to allow the cement to cure and gain strength.

In addition to the 20 boards made from mallee residue, two boards were manufactured in exactly the same manner from commercial radiata pine particleboard flakes obtained from Carter-Holt Harvey in Tumut, NSW. During the manufacture of mallee eucalypt boards, replicate 1 of all species and bark content combinations were manufactured in random order over the first 5 days, followed by replicate 2 over the next 5 days.

6.3.4 Determination of mechanical properties of CBPs

Each conditioned board measuring 240 x 300 x 12 mm was sawn into four test samples measuring 230 x 50 mm. Samples 1 and 3 were tested for bending strength (modulus of rupture, MOR) and stiffness (modulus of elasticity, MOE) in the dry condition. Samples 2 and 4 were tested for MOR and MOE after they had been soaked in water at ambient temperature (20°C) for 24 h. Before soaking, the samples were weighed and their thickness measured at three points along their length using a Mitutoyo digital calliper. After soaking, the samples were drained for 15 min to remove excess water. The sample weights and thickness were re-measured and the absorption of water (WA %) and thickness swelling (TS %) of samples were calculated (expressed as percent of original weight and thickness, respectively). Three-point flexural testing was carried out using an Instron 4505 Universal Testing Machine (shown in Chapter 7) with a span of 180 mm, cross-head and bearer diameter of 25 mm and loading speed of 5 mm/min.

6.3.5 Experimental design and statistical analysis

Wood samples from the mallee eucalypts and melaleucas were collected, prepared and tested for compatibility with cement in two different experiments. Therefore results, which were analysed
separately, are presented separately here. However, a general comparison between the results can be made since the tests were undertaken using the same experimental conditions. The experimental designs employed factorial principles. The effects of four fixed factors (species, site, age and the presence/absence of bark) on wood-cement compatibility of mallee wood was analysed, taking into account various random effects, including those associated with replicates obtained from different trees. The design of the experiment reflected the nesting of species/age class plots within sites (locations) and the availability of wood from two trees (replicates) per species and plots. At each location there were three plots each containing trees of a different age class. Therefore it was not possible to replicate each age class at the site level, as the two trees from each species/age class plot were taken from within the same plot. During assessment of the effect of wood and bark residues on cement hydration, each daily run of six cement hydration samples contained three species/age class combinations and samples 'with' and 'without' bark. Every 16 successive hydration samples contained all species/age class combinations randomised for one tree and site. All site, species, age class and bark combinations were assayed for the first tree followed by all of those for the second. A total of 180 mallee samples were tested over a period of about 45 days.

The smaller experiment to test the compatibility of the three melaleuca species with cement examined the effects of three fixed factors; species, presence/absence of bark, and extractive removal. The design contained 12 species/bark/soaking combinations, each of which contained two hydration samples from each of three trees per species. A total of 72 melaleuca and 4 tagasaste samples were tested over a period of 15 days. Species/bark/soak combinations were fully randomised for each tree over the duration of the experiment. Within each daily 6-sample run, three tree/bark content combinations were tested, incorporating the unextracted and extracted sample for each. Four cement control runs were randomly interspersed throughout the experiment.

The main effects of, and interactions between, each of the three factors on $T_{\text{max}}$, Time taken to reach $T_{\text{max}}$ (t), Hydration Rate (R), and $C_A$-factor were tested for significance using an appropriate multi-factorial ANOVA model at the 5% significance level. Before the final analysis, diagnostic checks on the normality and variance of the data were undertaken. The factorial design of the experiments allowed data to be averaged across non-significant ($p > 0.05$) effects. Significant results are plotted graphically, and bars representing the least significant difference or LSD ($p \leq 0.05$) are included on graphs to facilitate comparison of means.

The experimental design for the manufacture of cement-bonded particleboards from mallee wood and bark residues was constructed to examine the effects of three factors on board properties i.e. species, the presence of bark, and the effect of exposure of board samples to water. 'Species' was represented by chipped material pooled across all trees, sites and age class for each species. Two boards (replicates) for each treatment combination were manufactured, resulting in a total of 20
boards. All species/bark combinations were manufactured in randomised order for board 1 followed by board 2. The analysis of variance models for MOR and MOE used transformed data (log_e) to make statistical inferences; however the actual values are also presented and discussed.

Again, significant results are plotted graphically and bars representing LSD are included on graphs to facilitate comparison of means.

6.4 Results and discussion

6.4.1 Effect of mallee wood and bark residues on cement hydration

The hydration of portland cement was significantly affected (p < 0.001) by species of mallee eucalypt and whether bark was present in the wood residue (Table 6.1). Compatibility indices for the mallee wood and bark residues and radiata pine (RP) are shown in Table 6.2. The effects of selected mallee eucalypt wood and bark residue samples on the hydration of portland cement are also illustrated in Figure 6.2. The maximum rate of increase in temperature during the heat evolution stage for neat cement and water was 3.4°C/h (C_A = 100%). Note that a sample of higher compatibility (illustrated by E. polybractea) reduced the maximum temperature attained by about 8°C, resulting in a decreased hydration rate (from 3.4°C/h to 1.6°C/h), but did not greatly increase the time taken for the cement to set. In the scheme used in Chapters 4 and 5, such samples could be classed as 'moderately compatible' with cement (R between 1.5 and 2°C/h). In the cases of samples of lower compatibility (E. angustissima and E. loxophleba with bark), both T_max and time taken to reach T_max were significantly altered. Note from Table 6.1 that the age of the residues and growing site did not significantly influence compatibility of mallee wood with cement, however there was a detectable effect on hydration (T_max, hydration rate and C_A-factor) arising from an interaction between age and bark content (Table 6.1).

Table 6.1 F-probabilities (p-values) for main effects and interactions between factors on cement hydration reaction indices.

<table>
<thead>
<tr>
<th>Factor</th>
<th>T_max</th>
<th>Time to T_max</th>
<th>Hydr. Rate</th>
<th>C_A-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>Age</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>Species</td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
</tr>
<tr>
<td>Age x Species</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>Bark</td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
</tr>
<tr>
<td>Age x Bark</td>
<td>p = 0.041</td>
<td>n.s.</td>
<td>p = 0.017</td>
<td>p = 0.041</td>
</tr>
<tr>
<td>Species x Bark</td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
<td>p &lt; 0.001</td>
</tr>
<tr>
<td>Age x Species</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>Bark</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 6.2. Typical hydration temperature vs time curves for pure cement and cement containing mallee eucalypt wood residue of selected species (all examples shown are for 2.5 y.o. residues from Beverley site).

6.4.1.1 Species differences and the effect of bark

Table 6.2 and Figure 6.3 illustrate the effects of different mallee eucalypt species (with and without bark) on the hydration rate of portland cement. In the absence of bark, all species inhibited cement hydration to a similar extent and could be ranked as 'moderate' in compatibility with cement. *E. horistes* had the highest average compatibility (*R* = 1.78°C/h, *C_A* = 70.8%), while *E. angustissima* had the lowest (*R* = 1.52°C/h, *C_A* = 59.9%). The hydration rate for radiata pine was 1.88°C/h (*C_A* = 78%); not significantly higher than that of mallee residue without bark.

Table 6.2 Cement compatibility indices of mallee eucalypt wood species (with and without bark) and radiata pine (RP).

<table>
<thead>
<tr>
<th>E. angustissima</th>
<th>E. horistes</th>
<th>E. lox. ssp. liss.</th>
<th>E. plenissima</th>
<th>E. polybractea</th>
<th>RP</th>
</tr>
</thead>
<tbody>
<tr>
<td>n.bark</td>
<td>bark</td>
<td>n.bark</td>
<td>bark</td>
<td>n.bark</td>
<td>bark</td>
</tr>
<tr>
<td>T_max</td>
<td>42.6</td>
<td>45.5</td>
<td>44.0</td>
<td>44.7</td>
<td>43.5</td>
</tr>
<tr>
<td>Time</td>
<td>14.3</td>
<td>13.2</td>
<td>12.3</td>
<td>13.7</td>
<td>12.7</td>
</tr>
<tr>
<td>Rate</td>
<td>1.5</td>
<td>1.8</td>
<td>1.7</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td>C_A</td>
<td>59.9</td>
<td>70.8</td>
<td>64.8</td>
<td>68.5</td>
<td>62.5</td>
</tr>
</tbody>
</table>

N.B. Indices for cement control were 55.7°C, 9.6 h, 3.4°C/h and 100%.
As can be seen in Figure 6.3, the presence of bark in most mallee eucalypt residue samples had no significant effect on their compatibility with cement, except for the case of *E. loxophleba* ssp. *lissophloia*, whereby the presence of bark strongly inhibited cement hydration. Bark in the wood samples of *E. angustissima* also inhibited cement hydration, but not to the same extent as for *E. loxophleba* ssp *lissophloia*. Wood samples of *E. horistes*, *E. kochii* ssp. *plenissima* and *E. polybractea* all retained their moderate compatibility (*R* = 1.5, 1.7 and 1.6°C/h respectively) with cement even when bark was present, suggesting that the complete removal of bark from these species may not be necessary in order to manufacture well-consolidated cement-bonded composites. The chemical composition of bark varies greatly among wood species (Jensen et al. 1963), and the results here for *E. loxophleba* ssp. *lissophloia* compared to the other mallee species suggests that this may be the case even among relatively closely related eucalypt species such as mallies.

Note from Table 6.2 that the compatibility indices for many of the mallee species, particularly *E. horistes*, *E. plenissima* and *E. polybractea* were similar (not statistically different) to those of radiata pine. Radiata pine is considered suitable for wood-cement composites and is used in Australia for the commercial manufacture of wood-wool cement boards (Woolley, J. pers. comm. 1998). This suggests that from the point of view of wood-cement compatibility, these mallee species (with or without bark) may also be potentially suitable for wood-cement composites, not...
withstanding possible confounding effects of bark, and wood flake or particle size and geometry on board mechanical properties, which will be examined later in this Chapter and again in Chapter 7.

6.4.1.2 Site and age effects

Despite the variation in average annual rainfall among the five different trial sites throughout the wheat belt zone from which material was sampled, the location at which the mallee trees were grown exerted no significant influence on wood-cement compatibility (Table 6.1). This finding is in accordance with that found for other eucalypts investigated in this thesis, for example *E. pellita* and *E. urophylla* in Chapter 4, whereby site also did not the influence the compatibility of wood with cement. However, it contrasts with findings for selected eucalypts grown at different temperate sites in South-Eastern Australia in Chapter 5, where trees of the same species and seed stock from a wetter, more productive site were significantly higher in compatibility than those grown on a drier site. Similarly, variation among trees of *E. deglupta* grown on different sites in Indonesia (at different altitudes) was found to have a highly significant effect on the compatibility of the wood with cement (Paribotro and Suwandi-Kliwon 1977).

However, there was a small influence (p = 0.04) on cement hydration (T\text{max}, hydration rate and C\text{A}-factor) due to an interaction between age and bark (Table 6.1). This may have occurred because there was a greater proportion of bark present in the younger coppice trees, which led to samples from young trees in which bark was present having a more inhibitory effect on cement hydration than wood obtained from older trees.

6.4.2 Effect of melaleuca and tagasaste wood and bark residues on cement hydration

Unadulterated wood samples from the melaleuca species and the tagasaste were very low in compatibility with cement compared with the mallee species. These were classed as 'incompatible' with portland cement according to the ranking system used for acacias and eucalypts in Chapters 4 and 5. The results of the ANOVA for the effects of species, bark content, extractive removal and interactions between factors are shown in Table 6.3. Melaleuca species did not significantly affect T\text{max} or hydration rate but they did significantly influence setting time and, by extension, the C\text{A}-factor (Table 6.3). Water-soluble carbohydrates in sapwood can greatly delay the setting time of portland cement. The chipped residues from melaleuca were less compatible with cement than the majority of the mallee residues, reducing the hydration rate of cement from 3.4°C/h (without wood) to an average of 1.15°C/h (C\text{A} = 61%). This compares with the 'moderate' compatibility of mallee wood from *E. polybractea* and *E. horistes* (R = 1.75°C/h). The addition of unextracted residues from tagasaste resulted in the complete inhibition of cement hydration, i.e. the mixes did not set
within 24 h. In the absence of compatibility indices for this species, it was omitted from the ANOVA model.

Table 6.3 F-probabilities (p-values) for effects of main factors, species, extraction and bark content, and interactions between factors on compatibility indices of melaleuca species.

<table>
<thead>
<tr>
<th></th>
<th>Temperature</th>
<th>Hydration Rate</th>
<th>Time to $T_{max}$</th>
<th>$C_A$-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species (s)</td>
<td>N.S.</td>
<td>N.S.</td>
<td>&lt;0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>Extraction (e)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Bark (b)</td>
<td>N.S.</td>
<td>N.S.</td>
<td>0.028</td>
<td>N.S.</td>
</tr>
<tr>
<td>s X b</td>
<td>N.S.</td>
<td>N.S.</td>
<td>&lt;0.001</td>
<td>0.019</td>
</tr>
<tr>
<td>s X e</td>
<td>N.S.</td>
<td>N.S.</td>
<td>&lt;0.001</td>
<td>0.028</td>
</tr>
<tr>
<td>b X s</td>
<td>0.012</td>
<td>N.S.</td>
<td>0.002</td>
<td>0.017</td>
</tr>
<tr>
<td>s X b X e</td>
<td>0.008</td>
<td>N.S.</td>
<td>&lt;0.001</td>
<td>0.007</td>
</tr>
</tbody>
</table>

*Level of significance p ≤ 0.05.

The presence of bark and the interactions between species and bark also influenced setting time and $C_A$-factor (Table 6.3). These effects are illustrated graphically in Figures 6.4 for (a) time to $T_{max}$ and (b) $C_A$-factor.

Figures 6.4 The effects of melaleuca species, bark content and extractive removal on (a) time taken to set cement and (b) $C_A$-factor ('s' denotes pre-soaked samples).

There was a significant interaction between species and bark content on time to $T_{max}$ (p < 0.001), as illustrated in Figure 6.1 (a). Wood (without bark) from *M. uncinata* was significantly (p < 0.001) less compatible than the other species, with a delayed setting time of 22 h ($C_A = 32\%$); however when bark was present its compatibility was greatly increased, reducing setting time to 17 h ($C_A = 66\%$). Bark also increased the compatibility of *M. lateriflora*, but to a lesser extent, significantly reducing setting time from 17 h to 14.5 h. In this case there was a small but not significant increase
in $C_A$-factor from 63% to 75%. In contrast, the presence of bark made M. alternifolia slightly less compatible (denoted by increased setting time from 15 to 17 h). $C_A$-factor was also reduced but this was not significant at the 5% level. For comparison, setting time for portland cement on its own was about 9 h, and setting times ranged from 12.7 to 14.3 h for mallee samples without bark.

The most significant effect on wood-cement compatibility was that of extractive removal ($p < 0.001$), which can be clearly seen in Figures 6.4(a) and (b). As a result of aqueous extractive removal, average hydration rate for cement containing residues was increased to 2.5 °C/h (i.e. 'compatible') and setting time was reduced from an average of 16.7 h to 9.9 h. It should be noted that despite the very low compatibility of the melaleuca species before soaking, their average compatibility with cement after cold water soaking was considerably higher than that of tropical and temperate acacias examined in Chapters 4 and 5, many of which were still below 2°C/h in hydration rate even after pre-soaking. This indicates that most of the inhibitory constituents of the melaleuca wood are readily soluble in water and effectively removed by cold water soaking. With appropriate tree size and availability, correct wood conversion and pre-soaking, melaleuca wood is likely to be well suited to wood-cement composites. Other methods of reducing the effects of soluble inhibitory constituents in sapwood, including pre-storage of wood and the addition of simple salts such as CaCl$_2$, would be worth further investigation in the case of melaleucas.

An interesting aspect of the results was that the bark of two of the three tested melaleuca species appeared to be as or more compatible with cement than the wood itself. In these cases partial supplementation of wood by bark may improve the compatibility of residues with cement. Melaleuca has a thick, spongy, multi-layered bark that comprises 15 to 20% of total stem volume (Chiang and Wang 1984). Because the bark is of much lower density than the wood, the samples containing bark had up to 50% less wood (w/w) than samples that contained no bark. This made a significant difference to the hydration of cement containing M. uncinata, whose wood was less compatible than its bark or of the wood of other species. The suitability of melaleuca species for the manufacture of cement-bonded composites may be considerably improved if it is not necessary to remove all the bark from the wood; however, the effects of bark on board mechanical and moisture sorption properties would need to be determined.

The finding that the presence of bark improved wood-cement compatibility of melaleucas runs counter to the general trend that bark of many tree species is incompatible with cement as it contains much higher levels of water-soluble, and, particularly, alkali-soluble constituents than the wood. Extractives in bark often constitute between 40 and 60% w/w of material and include polysaccharides and pectins, phenolic compounds such as tannins and resin acids, and suberins (Wenzl 1970, Sjostrom 1981). Bark structure and chemical composition also vary greatly among species (Jensen et al. 1963), and the high tannin-containing bark of woods such as pine has been
shown to have highly inhibitory effects on the setting of portland cement (Yoshimoto and Minami 1976a). The solubility of reactive bark polyphenols is highest in alkaline solutions (Yazaki 1985, Yazaki and Collins 1994), such as that found in hydrating cement paste. Melaleuca bark from the species *M. quinquenervia* (Cav.) Blake has also been shown to contain very high levels of phenolic extractives, as suggested by its high methanol-soluble fraction (22.5%) compared to that of sapwood (2.7%) (Wang and Huffman 1982). Melaleuca bark also contains many layers of suberised cells (Chiang and Wang 1984). Suberin in bark cells is a natural water-repellent barrier to pathogens (Laks 1991). Another interesting characteristic of melaleuca bark is its high content (~16%) of fatty substances (lipids), giving it the highest known calorific content of any tree material (Wang and Huffman 1982, Wang et al. 1982). Non-polar fats and terpenes have been shown by Miller and Moslemi (1991a) to have little adverse effect on cement setting. These peculiar characteristics of melaleuca bark may have influenced its compatibility with cement; for example high levels of fats and suberin may have reduced the solubility and mobility of the phenolic extractives in the bark that inhibit cement-setting reactions.

Attempts have been made to utilise stem wastes from other kinds of oil-producing tree species in wood-cement composites with little success. The wood from the Moroccan culinary oil crop tree, argan (*Argania spinosa* (L.) Skeels), was found to be highly incompatible with cement by Hachmi and Moslemi (1989, 1990). $C_A$-factor for the wood was 9%, and its high hot-water-soluble extractive content (13.8%) was suggested to be responsible for the reduced compatibility with cement.

6.4.3 Mechanical properties of CBPs made from mallee residues

CBPs manufactured from mallee residues using an accelerator (CaCl$_2$) were generally well consolidated; however their mechanical properties (MOR and MOE) were significantly ($p = 0.005$) affected by species and whether board samples were tested in the dry or wet condition (Table 6.4). These effects are illustrated for transformed (log$_e$) MOR and MOE in Figures 6.5 (a) and (b), respectively. The average strength properties of boards made from mallee and pine particles are given in Table 6.5. Although the presence of bark in boards slightly reduced their mechanical properties, its effect was not significant ($p > 0.05$). *E. horistes*, *E. kochii* ssp. *plenissima* and *E. polybractea* produced the strongest boards (average dry MOR = 1.29, 1.44, and 1.48 MPa, respectively), in accordance with the higher compatibility of these species with cement. In comparison, boards containing radiata pine flakes had an average MOR of 5.72 MPa, even though they were of similar compatibility with cement to the mallee particles. The strength properties, particularly MOR, of boards made from radiata pine were also not significantly affected by soaking of samples in water for 24 hours prior to testing (Figure 6.5a).
Table 6.4 F-probabilities (p-values) for main effects and interactions between factors influencing mechanical properties of CBPs made from mallee and radiata pine wood species.

<table>
<thead>
<tr>
<th>Species (Sp.)</th>
<th>Bark (Ba.)</th>
<th>Sp. x Ba.</th>
<th>Test Condition</th>
<th>Test x Sp.</th>
<th>Test x Ba.</th>
<th>Test x Sp. x Ba.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In MOR</td>
<td>In MOE</td>
<td>Thickness</td>
<td>Water Abs.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>0.006</td>
<td>0.075</td>
<td>0.199</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.080</td>
<td>0.111</td>
<td>0.050</td>
<td>0.013</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.660</td>
<td>0.674</td>
<td>0.504</td>
<td>0.974</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>N.A</td>
<td>N.A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.087</td>
<td>0.01</td>
<td>N.A</td>
<td>N.A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.173</td>
<td>0.286</td>
<td>N.A</td>
<td>N.A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.112</td>
<td>0.07</td>
<td>N.A</td>
<td>N.A</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figures 6.5 Flexural properties (a) In MOR and (b) In MOE of CBPs manufactured from mallee eucalypt residues as affected by testing condition (wet or dry); results averaged across site, age class and bark content.

Table 6.5 Average strength and mechanical properties for CBPs made from mallee with and without bark and radiata pine particles without bark.

<table>
<thead>
<tr>
<th>Species</th>
<th>Bark</th>
<th>MOR (MPa)</th>
<th>MOE (MPa)</th>
<th>TS (%)</th>
<th>WA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E. angus.</td>
<td>N</td>
<td>1.08</td>
<td>455.3</td>
<td>5.2</td>
<td>29.6</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>0.83</td>
<td>302.1</td>
<td>10.0</td>
<td>35.3</td>
</tr>
<tr>
<td>E. horistes</td>
<td>N</td>
<td>1.66</td>
<td>825.6</td>
<td>4.5</td>
<td>23.7</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>0.92</td>
<td>446.5</td>
<td>6.7</td>
<td>29.2</td>
</tr>
<tr>
<td>E. lox. ssp. liss.</td>
<td>N</td>
<td>0.93</td>
<td>525.4</td>
<td>6.2</td>
<td>26.8</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>0.46</td>
<td>250.9</td>
<td>6.4</td>
<td>32.9</td>
</tr>
<tr>
<td>E. kochii ssp. plen.</td>
<td>N</td>
<td>1.57</td>
<td>675.1</td>
<td>4.3</td>
<td>26.1</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>1.30</td>
<td>644.2</td>
<td>5.4</td>
<td>29.4</td>
</tr>
<tr>
<td>E. polybractea</td>
<td>N</td>
<td>1.53</td>
<td>870.6</td>
<td>4.5</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>1.42</td>
<td>720.1</td>
<td>5.5</td>
<td>28.0</td>
</tr>
<tr>
<td>P. radiata</td>
<td>N</td>
<td>5.72</td>
<td>2848.2</td>
<td>1.8</td>
<td>22.2</td>
</tr>
</tbody>
</table>

In contrast, boards made from E. loxopleba and E. angustissima had the lowest strength (average dry MOR = 0.69 and 0.96 MPa, respectively) and were most affected by exposure to water. These
species were clearly less suitable for the manufacture of wood-cement composites than the other mallee eucalypts.

As Figures 6.6 (a) and (b) show, the thickness swelling (TS) and water absorption (WA) of boards were not significantly affected by species; however when bark was present in the residue, average WA of boards increased from 26.1% to 31.0% and TS from 4.7% to 6.5%. Note in Table 6.5 that boards containing *E. angustissima* with bark had the highest TS (10%) and WA (35%). The bark from this species constituted up to 40% of the total volume of residue used to manufacture boards and was much more fibrous than the bark of the other mallee species. Note also that CBPs made using residues from species of relatively low compatibility (i.e. *E. loxopleba* and *E. angustissima*) were also more susceptible to deterioration of flexural properties after exposure to water, as can be clearly seen in Figures 6.5 (a) and (b). This was probably because the cement binder was poorly consolidated, more easily penetrated by water and weakened by the swelling of wood particles.

![Graph](image)

**Figures 6.6** Effect of bark in residue on average (a) water absorption and (b) thickness swelling of CBPs manufactured from mallee eucalypt residues; results averaged across species, site and age class.

The international standard for cement-bonded particulate composite panels (ISO 8335) specifies a maximum TS for boards of 2%. The CBPs manufactured in this study failed to meet this standard despite the addition of CaCl₂. This may have been due to a combination of factors, including their relatively low cement content for particulate-cement composites, the use of wood of only 'moderate' compatibility with cement, and the exacerbating effects of bark in the residue. Although the
presence of bark did not significantly affect the wood-cement compatibility of three of the five mallee eucalypt species, nor significantly reduce the flexural properties of CPBs, its adverse effect on the water resistance of boards detracts significantly from the potential utility of residues that contain bark. This effect is likely to have arisen from the fibrous, spongy nature of the bark leading to greatly increased water absorption compared with the wood on its own. Aggregates (such as bark) that contain high levels of water-soluble constituents significantly reduce the dimensional stability of cement-bonded composites (Ledhem 2000a, b). As a result, these types of aggregates either require pre-treatment to remove water-soluble constituents or the addition of stabilising agents such as silicone compounds or polyethylene glycol to improve the dimensional stability and water resistance of cement-bonded composites (Broker 1973, Broker and Simatupang 1974b, Mougel et al. 1995, Gamage 1996, Ledhem 2000a, b).

It is clear that the flexural properties of CBPs made from the chipped mallee eucalypt residues were very low (1 to 1.5 MPa in MOR and 250 to 900 MPa in MOE) compared with those of boards made from commercially produced radiata pine wood flakes (MOR = 5.72 MPa, MOE = 2850 MPa) and of commercially produced CBPs, whose flexural properties range from 8 to 15 MPa in bending and 4000 to 6000 MPa in elastic modulus (Dinwoodie 1978, Moslemi 1989, Wolfe and Gjinolli 1997). This is despite the fact that the woods of radiata pine and mallee eucalypts were similar in their compatibility with cement. Furthermore, the CBPs manufactured in this study did not conform to the minimum strength properties set out in ISO 8335, which covers particulate cement-bonded boards of this type, despite the addition of CaCl₂ during board manufacture. Minimum MOR and MOE required by this standard are 9 and 3000 MPa, respectively, and minimum MOR after 24 hours exposure to water is 5.5 MPa.

The observation that mallee eucalypt wood residues (particularly those of E. polybractea and E. kochii ssp. plenissima) were of the same compatibility with cement as radiata pine but produced boards of significantly lower strength suggests a strong confounding effect of particle geometry. The chipped mallee residues consisted of small but bulky particles, with a much lower slenderness or aspect ratio than the radiata pine particleboard flakes. This can be clearly seen by viewing a typical cross-section of CBP manufactured from chipped mallee residue (in this case E. polybractea without bark) compared with that of a board made from radiata pine flakes (Plates 6.3 (a) and (b)). From Plate 6.3 (b) it appears as though the geometry of the mallee eucalypt particles did not permit adequate horizontal alignment throughout the board cross-section nor adequate compression to eliminate voids. The size, geometry and arrangement of wood elements in particleboards strongly influences their packing behaviour during pressing, contact and bonding between particles and the horizontal density distribution in the composites (Kelly 1977, Wang and Lam 1998).
Because of their irregular shape the poor packing and contact between the mallee eucalypt particles is likely to have contributed to the lower strength properties of the mallee eucalypt boards since there is a strong correlation between the slenderness ratio (the length of a particle divided by its thickness) of wood flakes used in particleboards and the mechanical properties of the boards (Fisher 1972, Maloney 1977). Some previous attempts to utilise eucalypt wood in cement-bonded composites have also been hampered by difficulties in converting the wood to particles with the correct geometry. For example, Tachi et al. (1988) found that poor strength properties of CBP made from *Eucalyptus deglupta* compared with other hardwood species (*Paraserianthes falcataria*, *Acacia mangium* and *Gmelina arborea*) was caused by unfavourable particle geometry rather than lower wood-cement compatibility.

Plates 6.3 Sanded cross-sections of cement bonded boards made from (a) radiata pine particleboard flake, and (b) chipped residues from *E. polybractea*.

The radiata pine particleboard flakes were of similar thickness to the mallee particles; however they were generally longer and wider or more plate-like (as can be seen in Plate 6.2(a) which shows
particles from radiata pine and mallee), enabling greater capacity to stack and compact in a horizontal arrangement throughout the mat.

The conversion of small-diameter mallee residue into particles or flakes with a greater slenderness ratio would be desirable, although smaller particles from mallee residue may, however, be suitable as a surface material for particleboards whose central layer contains larger sized material from different wood species. Alternatively, small mallee eucalypt stems may be better suited to conversion into composites composed of longitudinally split strands such as those used in 'Scrimber' (Hutchings and Leicester 1988), produced by crushing and splitting stems through a series of rollers. Composites based on strands such as 'sliced strand timber' or SST (Miyatake and Fujii 1997), which are made using sharp roller shredders to convert small diameter stems into strands measuring 2-4 mm in thickness, may also be suitable. In the absence of such purpose-designed equipment, alternative methods of converting mallee stems using conventional equipment are explored in Chapter 7, where cement boards are made from mallee wood that has been converted to flakes and particles using a knife flaker. Optimum size and distribution of particles and flakes in wood-cement composites is also discussed in greater detail in Chapter 7, which aims to improve the properties of cement-bonded boards made from mallee and other plantation eucalypt wood.

6.5 Conclusions

The wood from five leaf-oil producing species of mallee eucalypt had moderate to good compatibility with portland cement (hydration rate almost 2°C/h for wood of most species). The wood from mallee eucalypt species was similar in compatibility to that of radiata pine, a wood that is commonly used in the manufacture of wood-cement composites such as WWCB in Australia. The presence of bark made residues from *E. loxophleba* ssp. *lissophloia* and to a lesser extent *E. angustissima* less compatible with cement, reducing their potential suitability for use in wood-cement composites. The bark of *E. loxophleba* ssp. *lissophloia* may have contained higher quantities of inhibitory polyphenols (such as tannin), which were responsible for its highly inhibitory effect on cement hydration. Unlike other eucalypts in this study, the geographic location and age of mallee trees exerted little influence on the compatibility of the wood with cement, although the higher proportion of bark in the younger (2.5-year-old) material resulted in a slight reduction in its compatibility with cement.

Average compatibility of the melaleuca and tagasaste residues was lower than that of the mallee eucalypts; the average compatibility indices for debarked wood from melaleuca species were 1.5°C/h and 65% for hydration rate and CA-factor, respectively. Woods from melaleuca and tagasaste that had not been pre-soaked in water prior to testing was highly incompatible with cement, making the fresh wood from these species unsuitable for wood-cement composites. The
wood of *M. uncinata* was significantly lower in compatibility than that of the other melaleuca species; however the compatibility of the residue was significantly increased by the partial substitution of the wood by its bark. Substitution of wood for bark had little effect, however, on the compatibility of *M. acuminata* or *M. lateriflora* wood with cement. The most critical factor affecting compatibility of melaleuca wood and bark with cement was the removal of extractives by soaking in water. Pre-soaking of melaleuca wood in water at ambient temperature greatly improved its compatibility with cement, making it more compatible than pre-soaked wood of other hardwoods (such as the acacia species examined in Chapters 4 and 5). Such a simple pre-treatment is likely to make melaleuca wood well suited for use in cement-bonded composites provided is sufficient source material available. The effects of any wood conversion and of included bark on board mechanical properties (particularly water resistance) would need to be investigated as part of any feasibility study on the performance of melaleuca wood in wood-cement composites.

The flexural properties of CBPs made from chipped mallee eucalypt residues were significantly influenced by species but, surprisingly, not by the presence of bark. Water absorption and swelling of boards, on the other hand, were not significantly influenced by species but were significantly increased by the presence of bark in the boards. Being spongy and fibrous, the bark from the mallee eucalypt stems is likely to have absorbed water easily, resulting in increased water absorption and thickness swelling of boards containing bark. Although well-consolidated CBPs could be manufactured from the residue of most of the mallee eucalypt species tested, the boards had very low flexural properties compared to commercially produced CBPs or those made from radiata pine particles. The small particle size and slenderness ratio of chipped mallee eucalypt residues is believed to have been the primary cause of the low strength of the boards. From the results of this study, two challenges were identified in order to improve board quality. These were firstly to find alternative methods of preparing small-diameter wood such as mallee eucalypt residues for the manufacture of cement-bonded composite panels, and secondly to reduce the content and effects of incorporated bark on board properties. These questions are investigated in Chapter 7, which reports on the manufacture of cement-bonded flakeboards and CBPs, not only from mallee waste wood and bark residues, but also from commercial species of eucalypt and pine grown in Western Australia, which are normally used for solid timber and pulp.
Chapter 7 The manufacture of cement-bonded flake, particle and wood wool boards from Western Australian mallee eucalypt, blue gum and commercial pine species.

7.1 Introduction

The research presented in Chapter 6 showed that the wood and bark residues of selected mallee eucalypt species were of 'moderate' compatibility with portland cement; not significantly less so than wood of radiata pine, a species that is currently used for the manufacture of wood-cement composites in Australia. The outstanding exception to this was *E. loxophleba* ssp. *lissophloia*, which was incompatible when the wood residues contained its bark. In contrast to the mallee eucalypts, the compatibility of untreated wood and bark residues from three melaleuca species was low unless it was first soaked in water. The very high bark content and limited availability of melaleucas currently limits their suitability as a raw material for the manufacture of wood-cement composites. Wood-cement composites were therefore not manufactured from melaleuca residues and the work reported in this Chapter focuses instead on mallee eucalypts and commercially important plantation species grown in Western Australia (WA).

In Chapter 6 the manufacture of cement-bonded boards from chipped wood and bark residues of mallee eucalypts demonstrated that in-field chipping of the residues using a chipper-shredder could not produce particles with the size and geometry necessary to optimise the strength properties of wood-cement composite boards. However, the presence of bark (with the exception of *E. loxophleba*) did not significantly affect the strength properties of boards but resulted in unacceptably high water absorption and swelling of boards when they were exposed to water. Mallee eucalypt stems are very small in diameter (<10 cm), often crooked and with a high proportion of bark (up to 50%) that is difficult to remove using conventional log debarking machinery. The use of this type of 'whole stem' residue is often problematic in conventional panel manufacturing due to the problem of fines and its high bark content (Hakkila 1989).

To try to overcome some of these problems and manufacture better quality cement-bonded composites, the mallee eucalypt stems were partially dried and then converted with the bark still on into screened flakes of different sizes, using a knife-flaker that is used to prepare wood for particleboard manufacture. In this Chapter, the properties of wood-cement boards manufactured from such flakes produced from mallee eucalypts (*E. polybractea* and *E. horistes*) were examined. The properties of the composites were compared with those of similar boards manufactured from commercial plantation timbers grown in WA, Tasmanian blue gum (*Eucalyptus bicostata*), radiata pine (*Pinus radiata*) and maritime pine (*Pinus pinaster*). While mallee eucalypt residues were not suitable for conversion to wood wool because of their small diameter, crookedness and difficulty in removing bark, blue gum and pine logs were suitable. Therefore a commercial trial was undertaken...
to manufacture non-structural wood wool-cement boards from these species. This was undertaken in a factory located in Victoria, Australia, that produces this product from radiata pine.

This is the first report on the utilisation of the commercially important blue gum timber for wood-cement composite boards such as CBP and WWCB. A feature of blue gum and other fast-grown plantation eucalypts is that after just a few years they generate merchantable volumes of timber which can contain a high proportion of juvenile wood unsuitable for the manufacture of solid wood products because of its poor sawing and drying characteristics (Hillis 1978, Waugh and Rozsa 1991). The suitability of eucalypt wood for conventional resin-bonded composite panels is also adversely affected by high levels of water- and alcohol-soluble phenolic heartwood extractives that affect glueing (Hillis 1978, Yazaki et al. 1993). Young plantation-grown blue gum wood is a light yellow-brown in colour, open textured, commonly with interlocked grain, and is often used for the manufacture of paper and rayon pulps (Hall et al. 1970, Turnbull and Pryor 1978). Unbleached blue gum kraft fibre (grown in Spain) was used as part of a study by Lhoneux et al. (1991) that examined the effects of autoclaving in lime-water on the tensile properties of a range of reinforcing fibres for use in cement-bonded fiberboard. Otherwise, as mentioned above, the suitability of blue gum wood for particulate, flake or wood wool cement composites is unknown.

7.2 Aims and Objectives

To follow on from the findings of Chapter 6, the aim of the research presented in this Chapter was to produce better quality wood-cement composite boards from mallee eucalypt wood wastes and commercially important plantation timber species grown in WA i.e. blue gum, radiata pine and maritime pine. The research included three major experiments with the following specific objectives which were addressed in three separate experiments:

1. To determine which commercially important WA species, including mallee eucalypts, would be best suited to the manufacture of wood-cement flakeboards (Experiment 1). The effects of species and flake pre-treatment (extraction or addition of accelerators) were assessed.

2. To improve the strength properties of flakeboards made from each species by manipulating wood element size, wood pre-treatment and board curing temperature (Experiment 2). The effects of species, the use of flakes or particles, flake and particle pre-treatment (extraction or addition of accelerators), and board curing temperature (20 or 65°C).

3. To determine the suitability of WA-grown blue gum, radiata pine and maritime pine for the commercial-scale manufacture of non-load-bearing WWCB insulating slabs (Experiment 3). Flexural and impact strength tests were undertaken to compare the properties of factory-made boards of these species with those of commercial products manufactured from radiata pine.
7.3 Materials and Methods

7.3.1 Log harvesting

Mallee eucalypt (*E. polybractea* and *E. horistes*), Tasmanian blue gum (*E. bicostata*), radiata pine (*P. radiata*) and maritime pine (*P. pinaster*) logs were obtained from trees growing on different sites in the south-west of WA (described in Figure 7.1 and Table 7.1) in June/July 2001. For all species, wood from ten individual trees was obtained and pooled to ensure a representative mix of parent material. The mallee eucalypt wood was sourced from seedlings grown from seed collected from native stands. Trees were sampled from hedgerows spaced 40 to 50 m apart on pastureland. These trees being multi-stemmed, one large stem (1 to 2 m long and 7 to 10 cm in diameter) was harvested at ground level from each of the ten trees. The stems were cut to a length of 1 m for transporting to Canberra. The Tasmanian blue gum and the two pine species were sampled from plantations during commercial harvesting operations. One log measuring 1.2 m in length was cut from a different height in each tree to ensure a mixed sample of wood representing different trees and positions in trees. Blue gum trees at the Eckersley plantation were of two different DBH as a result of harvesting of dominant (30-45 cm; blue gum 1) and suppressed (7-15 cm; blue gum 2) trees from the stand (Table 7.1). The soil type was fairly consistent across the sites from which the trees were sampled; however tree age among the species varied considerably at the time of harvest.

![Figure 7.1](image_url)  
*Figure 7.1 Sampling locations for eucalypt and pine species in the south-west of Western Australia.*
Table 7.1 Summary of species, planting dates and sites for wood species used to manufacture flakeboards.

<table>
<thead>
<tr>
<th>Species</th>
<th>Site</th>
<th>Soil</th>
<th>Planting date</th>
<th>Tree Height</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>E. polybractea</em></td>
<td>Narrogin</td>
<td>Gravel/loam</td>
<td>1995</td>
<td>5-6 m</td>
</tr>
<tr>
<td><em>E. horistes</em></td>
<td>Narrogin</td>
<td>Gravel/loam</td>
<td>1995</td>
<td>2-5 m</td>
</tr>
<tr>
<td><em>E. bicostata (A)</em></td>
<td>Eckersley</td>
<td>Gravel/loam</td>
<td>1988</td>
<td>≈25 m</td>
</tr>
<tr>
<td><em>E. bicostata (B)</em></td>
<td>Eckersley</td>
<td>Gravel/loam</td>
<td>1988</td>
<td>≈15 m</td>
</tr>
<tr>
<td><em>P. radiata</em></td>
<td>Stirling Dam</td>
<td>Gravel/loam</td>
<td>1988</td>
<td>≈25 m</td>
</tr>
<tr>
<td><em>P. pinaster</em></td>
<td>Harvey Weir</td>
<td>Gravel/loam</td>
<td>1981</td>
<td>30-35 m</td>
</tr>
</tbody>
</table>

7.3.2 Preparation of wood flakes and particles

Log samples were converted into flakes and particles using a pilot-scale disk flaker (Bezner No. 6577, shown in Plate 7.1) located at the Carter-Holt Harvey particleboard factory in Oberon, NSW, Australia. The blue gum and pine logs were first debarked by hand using an axe and then cross-cut using a chainsaw into rounds measuring 200 mm in length. These were then further reduced to pieces measuring about 200 x 50 x 100 mm using a block splitter. As it was difficult to debark the mallee eucalypt stems, they were cut into 200-mm-long rounds which were flaked with the bark on. The disk flaker contained a steel disc that measured 80 cm in diameter and contained eight separate knife blades each set at a 45° angle to cut flakes along the grain to a nominal size of about 60 x 45 x 0.4 mm. The flakes were collected in 1-m³-capacity Nylon wool-bales, dried in a large oven at 50°C for around 48 h to reduce their moisture content to approximately 10%, and then stored undercover in the wool-bales for 4 months. They were then screened, first through a 10-mm-mesh sieve to retain those flakes larger than about 10 x 50 mm, and then through a 7-mm-mesh sieve to retain those smaller than about 7 x 30 mm. The large 10-mm-mesh sieve is shown in Plate 7.2(a) and the 7-mm-mesh round sieve is shown in Plate 7.2(b). Although the larger flakes were cut to a nominal thickness of 0.4 mm, there was noticeable variation between species in the appearance and thickness of the flakes. Close-up photos of flakes from maritime pine, blue gum and mallee are shown in Plates 7.3 (a) to (c). To quantify this variation and how it might impact on the mechanical properties of cement-bonded flakeboards, an assessment of variation in flake thickness within each of the wood species was made as part of this study.

Another potential source of inconsistency in flake quality among the different species was the inability to remove the bark from the mallee stems prior to flaking. After air-drying the stems for about 3 weeks, most of the bark from the mallee eucalypt rounds formed fine flakes and dust during flaking, and these were separated from the large-flake fraction during sieving. However, this meant that the quantity of bark in the small-flake fraction used to make CBPs was around 40-50% by volume. The effects of this higher bark content on the strength and water resistance of CBPs made from mallee eucalypt residues was determined in this study.
Plate 7.1 Disk flaker used to produce flakes and particles from log samples.

Plates 7.2 Sieving flaked mallee eucalypt wood to separate (a) large flakes and (b) small flakes.
7.3.3 Manufacture and testing of cement bonded flakeboards, CBPs and WWCBs

7.3.3.1 Experiment 1: Species and pre-treatment (flakeboards)

Cement-bonded flakeboards were manufactured using the large flakes to test the effects of two factors on the properties of boards, i.e:
• species (mallee (*E. polybractea*/E. horistes mix), blue gum 1 (low-density wood), blue gum 2 (high-density wood), radiata pine and maritime pine); and
• flake pre-treatment (none; cold-water soak for 24 h; hot-water soak for 8 h; addition of CaCl₂ or MgCl₂ at 2% w/w cement).

A total of 55 flakeboards were manufactured as shown in Plates 7.4(a) to (e)) over a period of about 25 days. The boards measured 380 x 300 x 15 mm, using a wood:cement ratio of 1:3, and a water:cement ratio of 1:2. 450 g of air-dry wood flakes were placed in the rotating drum of a cement mixer (Plate 7.4(a)) while water was sprayed onto the flakes. About 500 mL of water was sprayed in at first and the flakes were then mixed for 2-3 min to facilitate even wetting of flakes. Cement powder (1350 g) was then slowly added by hand to the tumbling flakes and the remaining
water (175 mL) was sprayed onto the wood-cement mix to moisten the cement powder and to ensure even coating of flakes with cement. The cement-coated flakes were tumbled for a further 5 min and they were then removed and distributed as evenly as possible by hand into a formply mould measuring 300 x 380 mm (Plate 7.4(b)) which was placed on a rectangular sheet of formply measuring 340 x 420 x 17 mm. Cement-coated flakes were added to the mould to evenly build up the mat. The mat was smoothed and flattened using a small 3-pronged gardening fork. The mould was then removed and another piece of formply was placed on top of the mat. Two wooden spacing rods measuring 15 x 15 x 300 mm were placed at either end between the two formply sheets to allow for a pressed final board thickness of 15 mm. The resulting assemblage was pre-pressed while the mat for the next board was mixed, and the process repeated to produce a sandwich of two mats between three sheets of formply. The stack of mats was placed between two steel plates measuring 340 x 470 x 15 mm and pressed at ambient temperature at approximately 60 kN using a PHI 101.6 mm RAM hydraulic operated press (Plate 7.4(c)). The pressed mats were kept under constant pressure for 24 h by bolting the two steel plates together using four 8-mm-thick bolts. After 24 h the boards were de-clamped, stacked and conditioned for 10 weeks at 20 ± 1 °C and 65 ± 5 % r.h. to allow the composites to cure and increase in strength.

After curing, each flakeboard was cut into five samples each measuring 50 x 230 x 12 mm. Due to the high cement content of the boards they had to be cut using a diamond-edged saw (Plate 7.4(e)). This type of saw is water-lubricated, and to minimise the wetting of boards their surfaces were first sprayed with petroleum ether to disperse the water from the surface. Excess moisture was removed from the samples immediately after cutting, using a sponge, and samples were further dried using compressed air. Any remaining moisture was removed by air-drying samples in the sun for about 2 h. Samples (some of which are shown in Plate 7.4(f)) were kept in a conditioning room at 20 ± 1 °C and 65 ± 5% r.h. for 14 days prior to the testing of board physical and mechanical properties.

Samples 1 and 3 were tested for modulus of rupture (MOR) and modulus of elasticity (Young's modulus or MOE) in the dry condition. Samples 2 and 4 were tested for MOR and MOE in the wet condition after they had been soaked in water at ambient temperature (23°C) for 24 h. Before soaking, the samples were weighed and their thickness measured at three points along their length using a Mitutoyo digital caliper. After soaking, the samples were drained on paper towels for 15 min to remove excess water. The sample weights and thickness were re-measured and the absorption of water (WA %) and thickness swelling (TS %) of samples were calculated (expressed as percentage of original weight and thickness, respectively). Three-point flexural testing was carried out using an Instron 4505 Universal Testing Machine (Plate 7.5) with a span of 180 mm, cross-head and bearer diameter of 25 mm and loading speed of 5 mm/min.
7.3.3.2 Experiment 2: Flake size and curing temperature (flakeboards and CBPs)

In this experiment cement-bonded flake boards and CBPs were manufactured to examine the effects of two further variables, flake size (flakes or particles) and board curing temperature (20°C or 65°C), on the strength and water resistance of cement-bonded boards. The species used were radiata pine, blue gum and mallee eucalypts, except in this experiment only the low-density blue gum 2 wood was used. The flaking equipment available was unable to produce particleboard flakes, and therefore in the case of radiata pine commercial particleboard flakes were obtained from Carter-Holt Harvey, Oberon, and were used in the experiment. In the case of the mallee and blue gum wood, small flakes and splinters that were produced during the flaking were separated from larger residues by sieving as described in Section 7.3.2, and these were used for the manufacture of CBPs from eucalypt wood.

The flakeboards and CBPs were manufactured using the procedures described above for Experiment 1. The CBPs were manufactured using the same proportions of wood:cement and water as for the flakeboards. The equation normally used to determine the quantity of water that is required to hydrate cement during the manufacture of CBPs (Simatupang 1979) would have required the addition of 571 mL of water to the wood-cement mix. This figure is considerably lower than that used to manufacture cement-bonded flakeboards, and in trials it was found to be insufficient for boards made using the commercial radiate pine particleboard flake and the cement mixer. This discrepancy was probably caused by loss of water to the inside surface of the cement mixer and evaporation of the fine spray used to wet the particles. When 571 mL of water was added to the wood particles and fines it was rapidly absorbed by the wood, producing a very dry mix and friable boards. It was therefore decided to increase the water content to a level similar to that used in the manufacture of the flakeboards, i.e. 700 mL. During the manufacture of CBPs, coating of the small wood particles in the cement mixer took longer because they tended to stick to the sides and bottom of the mixer and had to be scraped away periodically during mixing. Particles also tended to clump together the longer the mix was tumbled.

To cure boards at 65°C, the mats were clamped between two bolted steel plates as described above for Experiment 1 and the clamped stack was then placed in a large bread-baking oven for 16 h. After 24 h they were de-clamped, stacked and conditioned for 10 weeks at 20 ± 1°C and 65 ± 5% r.h.

The mechanical properties of all boards made in Experiment 2 were determined as described for Experiment 1. Samples of a typical CBP and flakeboard manufactured in this study are shown in Plate 7.4(d).
Plates 7.4  (a) to (f) Manufacturing and testing process for cement-bonded flakeboards.
Plate 7.5 Three-point testing jig fitted to an Instron 4505 Universal Testing Machine used to determine board flexural properties.

7.3.3.3 Experiment 3: Commercial WWCBs

WWCBs were manufactured only from those species whose trees were of sufficient diameter to convert into wood wool; i.e. radiata pine, maritime pine and low density blue gum. Ten logs each measuring 1.2 m from the same trees that were used in Experiments 1 and 2 were sent to WoodTex Pty Ltd in Bendigo, Victoria, in July 2001. The logs were debarked, cut into 360-mm billets and converted in the green condition to 'coarse' wood wool measuring 3 x 0.5 mm as described in Chapter 3. After shredding, the wood wool was fed through a rotating drum sieve that separated and removed the short wood wool pieces from the long strands that were used to manufacture boards. The wood wool from each species was kept separate, and it was then loosely packed into large (1-m³-capacity) aerated plastic bags and stored under cover for 9 months prior to manufacture of WWCBs.

Low-density WWCBs measuring 270 x 160 x 25 cm were manufactured from the wood wool of each species in the same manner that WoodTex Pty Ltd uses to manufacture commercial insulating WWCBs from radiata pine. The wood:cement:water ratio was 1:2:1 using air-dried (=10% MC) wood wool. The wood wool was first manually fed from the bags in small batches onto a conveyor that passed it under a toothed rotating drum through a bath of cold water. Excess water was removed from each batch of wood wool by passing it through a wringer. As a result of this, each batch of wood wool contained a consistent quantity of water. Batches of wet wood wool were then fed up into a rotating spiked drum that evenly mixed the wood wool and cement. Cement-coated wood wool was then dropped onto a load cell where it was collected into batches of uniform weight (about 2 kg) before being dispensed into moulds measuring 270 x 160 x 25 cm. An end-to-end train
of moulds passed under the wood wool mat dispenser, forming a continuous mat that was then cross cut using an automated chain saw bar to separate the individual mats. Each mat was then passed into a stacker capable of stacking up to 30 mats. As each mat passed on to the stacker, any large clumps in the mat were redistributed by hand and any large solid wood pieces from the shredding process were removed.

Radiata pine was run through the board manufacturing process first, followed by maritime pine and finally blue gum. One stack of mats for each species was produced, with the available wood allowing the production of 26 boards from radiata pine, 19 boards from maritime pine and 11 boards from blue gum. About 50% less wood wool was produced from the blue gum logs for two reasons. Firstly some of the billets could not be shredded due to excessive defects such as large knots, and secondly the wood was denser (≈500-600 kg/m³), resulting in higher losses due to the occurrence of numerous short pieces and chips during shredding.

Each stack of mats was pre-pressed by the stacker for about 5 min before being removed using a forklift to an under-cover curing bay. A concrete block measuring 270 x 170 x 20 cm and weighing 1.1 tonne was placed on top of each of two stacks of mats using a forklift, and the stacks were left to cure for 7 days undercover at ambient temperature. The mats were then de-moulded and stacked vertically outdoors in a steel rack to dry for a further 3 weeks, followed by under-cover storage at ambient temperature for 4 weeks. Each panel was then trimmed to 1200 x 600 mm. The manufacturing process is shown in Plates 7.6 (a) to (g).

Four adjacent samples each measuring 600 x 75 x 25 mm were cross-cut from each trimmed panel, using a circular saw, and conditioned for about 2 weeks at 20 ± 1°C and 65 ± 5% r.h. The dimensions of each piece were accurately determined using Mitutoyo digital calipers, and the conditioned weight of each piece was recorded. The density of each piece was calculated and basic density estimated from pre-determined sample moisture content. Pieces 1 and 4 were then tested for flexural properties (MOR and MOE) using a 3-point static bending test, following ASTM D 1037 (1999), for panels 25 mm in thickness. Samples were mechanically tested using the Instron 4505 Universal Testing Machine operating with a span of 470 mm, nominal depth of 25 mm, nominal breadth of 75 mm, loading speed of 10 mm/min, bearer diameter of 50 mm, and loading nose diameter of 40 mm, as shown in Plate 7.7(a).

The remaining portion of each panel, measuring 600 x 900 mm, was destructively tested for impact strength as specified in British Standard (BS 1105: 1981). This Standard specifies that boards > 50 mm in thickness should be able to withstand the impact of a 45-kg load dropped from a height of 1.2 m, and a static load of 1.32 kN. The impact tests were modified to suit the thinner, weaker panels used here. The panel was fixed to two saw-horses using four G-clamps and two strips of 21-mm-thick medium-density fibreboard as shown in Plate 7.7(b). The span was 750 mm and the loads were Nylon bags containing sand, one weighing 5 kg and the other 8 kg.
Plates 7.6 (a) to (g) Commercial WWCB manufacturing process at WoodTex Pty Ltd, Bendigo.
The ability of the boards to withstand impact caused by dropping a 5-kg load through 50 and 100 mm was recorded. If the board did not break under the 5-kg load, the test was repeated using an 8-kg load, first from 50 mm and then from 1 m. If failure still did not occur then the 8-kg test from 100 mm was repeated until failure. The static bending test is shown in Plate 7.7 (a) and the impact test is shown in Plate 7.7 (b).

Plates 7.7 (a) 470 mm span 3-point bending test jig for WoodTex panel samples and (b) impact test rig for 600 x 900 mm panels showing the 5 kg load.

7.3.4 Experimental designs and statistical analyses

Experiment 1 used a balanced factorial design to examine the effects of species and wood pre-treatment on the properties of flakeboards cured at ambient temperature only. For Experiment 1 two boards (replicates) for each treatment were manufactured in blocks of species in random order, with all permutations for board 1 manufactured followed by all those for board 2. Some treatment combinations involved the manufacture of an extra one or two boards if there was any inconsistency caused during manufacture. Experiment 1 also contained an assessment of the effect of species (maritime pine, radiata pine, blue gum 1 and 2, and mallee eucalypt) on the average thickness of randomly sampled large screened flakes. For the analysis of variance model, flake thickness was transformed (log_e); however the true averages are shown in Table 7.7.

Experiment 2 also used a balanced factorial design to examine the effects of species (pine, blue gum 1 and mallee eucalypt) and pre-treatment (none, hot water or accelerator) on the properties of flake and particle boards cured at either ambient (20°C) or elevated temperature (65°C). For Experiment 2, three boards for each treatment combination were manufactured, blocked into groups of two size (flake or particle)/wood pre-treatment combinations that were randomly assigned within each species/curing temperature combination.
Experiment 3 (Commercial WWCBs) was restricted to an investigation of species (maritime pine, radiata pine and blue gum 1) on the density, thickness and mechanical properties of low density WWCBs, and therefore involved a simple design, i.e. manufacturing runs blocked by species, with a variable number of boards manufactured according to the quantity of wood wool produced from each species.

The statistical analyses of board mechanical properties of all three experiments involved the use of mixed linear models and REML variance components analyses (as described in Chapter 4). This approach is best suited to the analysis of unbalanced data sets from experiments that contain both fixed and random effects, and hence was highly suitable for the analysis of data here. A chi-squared distribution was used to obtain significance levels (shown in Tables 7.2 and 7.4 for Experiment 1 and Table 7.10 for Experiment 2) for fixed effects and interactions between factors determined from Wald tests for variance component estimates. In Experiment 1, the effects of the broader categories, 'wood type' (pine or eucalypt) and 'treatment type' (none, soaking or accelerator), were incorporated into the analysis of variance. A separate analysis of variance was also conducted to assess the effects of board condition (dry or after immersion in water for 24 h) on mechanical properties, and whether there were interactive effects between species and wood pre-treatment. Significant results are plotted graphically and bars representing the least significant difference (p ≤ 0.05) are included on graphs to facilitate comparison of means.

7.4 Results and Discussion

7.4.1 Experiment 1- Species and pre-treatment (flakeboards)

7.4.1.1 Mechanical properties

Species, wood pre-treatment and interaction between these two factors had highly significant (p < 0.001) effects on all physical and mechanical properties of flakeboards, except for thickness swelling, as shown in Tables 7.2 and 7.4. Wood type (pine or eucalypt) did not significantly influence board density or thickness swelling, but it did significantly affect board strength properties and water absorption by boards. In contrast, treatment type (none, soaking or accelerator addition) had highly significant effects on all board properties including strength and water resistance. Since there was no treatment type x individual treatment interaction, the effect of treatment type on the strength properties of flakeboards (MOR) made from the different species has been combined and is illustrated graphically in Figure 7.2. Averages for MOR and other board properties, as influenced by species and wood pre-treatments, are contained in Tables 7.3 and 7.5 to 7.8.
Table 7.2 Chi-squared probabilities for the significance of effects of species, flake pre-treatment and interactions. N.S. = not significant at the 5% probability level (p > 0.05).

<table>
<thead>
<tr>
<th></th>
<th>Density</th>
<th>MOR</th>
<th>MOE</th>
<th>TS</th>
<th>WA</th>
<th>WMOR</th>
<th>WMOE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species (S)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>N.S.</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Treatment(T)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>N.S.</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>S x T</td>
<td>0.009</td>
<td>0.003</td>
<td>&lt;0.001</td>
<td>0.042</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.007</td>
</tr>
<tr>
<td>Wood type (WT)</td>
<td>N.S.</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>N.S.</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Treatm. type (TT)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.015</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>WT x S</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>N.S.</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>WT x TT</td>
<td>0.022</td>
<td>0.053</td>
<td>&lt;0.001</td>
<td>N.S.</td>
<td>0.002</td>
<td>&lt;0.001</td>
<td>0.003</td>
</tr>
<tr>
<td>TT x T</td>
<td>N.S.</td>
<td>N.S.</td>
<td>N.S.</td>
<td>N.S.</td>
<td>N.S.</td>
<td>N.S.</td>
<td>N.S.</td>
</tr>
<tr>
<td>WT x S x TT</td>
<td>N.S.</td>
<td>&lt;0.001</td>
<td>0.003</td>
<td>N.S.</td>
<td>0.005</td>
<td>N.S.</td>
<td>N.S.</td>
</tr>
<tr>
<td>WT x TT x T</td>
<td>N.S.</td>
<td>N.S.</td>
<td>N.S.</td>
<td>N.S.</td>
<td>0.011</td>
<td>N.S.</td>
<td>N.S.</td>
</tr>
<tr>
<td>WT x S x TT x T</td>
<td>0.004</td>
<td>N.S.</td>
<td>N.S.</td>
<td>0.005</td>
<td>&lt;0.001</td>
<td>0.015</td>
<td>0.007</td>
</tr>
</tbody>
</table>

TS = Thickness Swelling, WA = Water Absorption, WMOR = WetMOR, WMOE = WetMOE.

All flakeboards manufactured in Experiment 1 exceeded the minimum density of 1000 kg/m³ stipulated by ISO 8335 for cement-bonded boards, ranging in density between 1080 and 1300 kg/m³. The average basic density of flakeboards as affected by species and wood pre-treatment is shown in Table 7.3. Despite the relatively low range in board density over-all, species, pre-treatment and interaction between these factors significantly influenced board density. For example, addition of accelerator significantly increased the density of boards made from blue gum and mallee eucalypt, but not those made from maritime pine, as shown in Table 7.3.

The average strength properties (MOR and MOE) of boards as affected by species, flake treatment and test condition are shown in Table 7.4. There were no significant first or second order interactive effects between test condition (wet or dry) and the other factors—species and treatment—indicating that species and flake treatment did not influence the strength losses by boards after 24 h immersion to water at ambient temperature.

Table 7.3 Average basic density (kg/m³) of flakeboards as influenced by species and flake treatment.

<table>
<thead>
<tr>
<th></th>
<th>No Treatment</th>
<th>Cold Water</th>
<th>Hot Water</th>
<th>CaCl₂</th>
<th>MgCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>maritime</td>
<td>1137</td>
<td>1142</td>
<td>1126</td>
<td>1143</td>
<td>1164</td>
</tr>
<tr>
<td>radiata</td>
<td>1156</td>
<td>1143</td>
<td>1150</td>
<td>1206</td>
<td>1214</td>
</tr>
<tr>
<td>blue gum 1</td>
<td>1095</td>
<td>1098</td>
<td>1154</td>
<td>1218</td>
<td>1114</td>
</tr>
<tr>
<td>blue gum 2</td>
<td>1154</td>
<td>1205</td>
<td>1187</td>
<td>1220</td>
<td>1270</td>
</tr>
<tr>
<td>mallee eucalypt</td>
<td>1104</td>
<td>1152</td>
<td>1161</td>
<td>1201</td>
<td>1259</td>
</tr>
</tbody>
</table>

Least Significant Difference = 62

Table 7.4 Chi-squared probabilities (p-values) for effects of species, wood pre-treatment and test condition (wet or dry) on strength properties MOR and MOE of flakeboards.

<table>
<thead>
<tr>
<th></th>
<th>MOR</th>
<th>MOE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species (S)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Treatment (T)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Test condition (TC)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>S x T</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>S x TC</td>
<td>0.089</td>
<td>0.095</td>
</tr>
<tr>
<td>T x TC</td>
<td>0.169</td>
<td>0.180</td>
</tr>
<tr>
<td>S x T x TC</td>
<td>0.155</td>
<td>0.070</td>
</tr>
</tbody>
</table>
As can be seen from Table 7.4, the differences between treatment types (soaking or accelerator) were not significant within each species. Therefore the performance of the different species and the average effects of pre-soaking or addition of accelerator on MOR are summarised in Figure 7.2. Pre-treatment did not significantly affect the strength of boards made from pine wood; however the use of accelerator (CaCl₂ and MgCl₂) significantly increased the strength of boards made from blue gum 1 and mallee eucalypt wood. In contrast, boards made from higher density blue gum 2 did not respond to the addition of accelerator. The highest average board strength was achieved using the lower density wood from blue gum 1 and adding accelerator, suggesting that lower density blue gum as well as the pine wood is well suited for the manufacture of cement-bonded flakeboard.

The average dry MOR, dry MOE and wet MOR of boards, as influenced by species and pre-treatment, are shown in Tables 7.5 to 7.7. The shading denotes samples that did not meet the ISO 8335 Standard strength properties of 9 MPa for MOR (dry samples), 5.5 MPa for MOR (after exposure to water for 24 h) and 3000 MPa for MOE for cement-bonded boards.

Boards made from untreated flakes of maritime and radiate pine exceeded the ISO standard, and no marked increase in MOR resulted from pre-soaking the flakes or adding cement-setting accelerators (Table 7.5 and Figure 7.2). In contrast, there was a 20% gain in MOE of maritime pine boards as a result of adding MgCl₂ (Table 7.6). Over-all, the best flake pre-treatment for maritime pine was the addition of CaCl₂ whereas the best pre-treatment for radiata pine was extractive removal by hot water. The latter may result from the deleterious effect of untreated heartwood on
the mechanical properties of cement composites made from radiata pine (Semple and Evans 2000), since the flakes used contained both heartwood and sapwood.

Table 7.5 Average dry MOR (MPa) of flakeboards as influenced by species and flake treatment.

<table>
<thead>
<tr>
<th>Species</th>
<th>No Treatment</th>
<th>Cold Water</th>
<th>Hot Water</th>
<th>CaCl₂</th>
<th>MgCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>maritime pine</td>
<td>10.5</td>
<td>9.9</td>
<td>11.2</td>
<td>13.8</td>
<td>12.1</td>
</tr>
<tr>
<td>radiata pine</td>
<td>11.1</td>
<td>12.9</td>
<td>13.1</td>
<td>11.9</td>
<td>9.6</td>
</tr>
<tr>
<td>blue gum 1</td>
<td>7.2</td>
<td>11.0</td>
<td>13.0</td>
<td>12.2</td>
<td>15.5</td>
</tr>
<tr>
<td>blue gum 2</td>
<td>5.8</td>
<td>8.7</td>
<td>9.0</td>
<td>7.2</td>
<td>7.0</td>
</tr>
<tr>
<td>mallee eucalypt</td>
<td>2.6</td>
<td>4.4</td>
<td>5.3</td>
<td>7.8</td>
<td>8.4</td>
</tr>
</tbody>
</table>

Least Significant Difference = 3.2

Table 7.6 Average dry MOE (MPa) of flakeboards as influenced by species and flake treatment.

<table>
<thead>
<tr>
<th>Species</th>
<th>No Treatment</th>
<th>Cold Water</th>
<th>Hot Water</th>
<th>CaCl₂</th>
<th>MgCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>maritime pine</td>
<td>4112</td>
<td>4175</td>
<td>4307</td>
<td>4870</td>
<td>4902</td>
</tr>
<tr>
<td>radiata pine</td>
<td>4492</td>
<td>4764</td>
<td>4792</td>
<td>4990</td>
<td>3879</td>
</tr>
<tr>
<td>blue gum 1</td>
<td>1887</td>
<td>3487</td>
<td>4310</td>
<td>4595</td>
<td>3809</td>
</tr>
<tr>
<td>blue gum 2</td>
<td>2068</td>
<td>2888</td>
<td>3062</td>
<td>2694</td>
<td>3880</td>
</tr>
<tr>
<td>mallee eucalypt</td>
<td>592</td>
<td>1691</td>
<td>2340</td>
<td>3359</td>
<td>3939</td>
</tr>
</tbody>
</table>

Least Significant Difference = 1038

While boards made from the untreated low-density blue gum 1 flakes did not meet the ISO minimum dry MOR of 9 MPa, pre-soaking and addition of accelerator significantly (p < 0.001) improved the mechanical properties of boards. Average dry MOR increased from 7.2 MPa to between 11 and 15.5 MPa as a result of flake pre-treatment. In the case of the higher density blue gum 2 and the mallee flakes, neither cold-water soaking nor the addition of accelerators was sufficient to produce boards exceeding 9 MPa in bending strength (Table 7.2). However, variation in MOR (shown by standard deviation in Figure 7.2) indicates that some of the mallee eucalypt boards containing CaCl₂ and MgCl₂ met the standard, suggesting that an increase in the quantity of accelerator used might allow boards of acceptable quality to be manufactured from the mallee eucalypt flakes. Other reasons for reduced strength of boards containing mallee eucalypt and blue gum 2 flakes are discussed in Section 7.4.1.3. Note from Table 7.4 that mallee eucalypt boards containing cement-setting accelerators were above the ISO standard of 3000 MPa in dry MOE.

In accordance with the main aim of this study, the strength properties of flakeboards made from mallee eucalypts were markedly higher than those of boards manufactured from chipped mallee eucalypt wood in Chapter 6, particularly after addition of accelerator. This suggests that flakes rather than particles should be used for the manufacture of cement-bonded boards where the aim is to produce boards of high strength. The good performance of blue gum (especially the lower density wood) in cement-bonded flakeboards is also significant since it represents a considerable improvement on previously cited examples of poor performance of eucalypt wood in cement-bonded composites (e.g. Tachi et al. 1988, Yasin and Qureshi 1990). The potential of blue gum is supported by another study on the use of eucalypt wood for the manufacture of cement-bonded
boards (Warden et al. 2002). In their study, eight temperate eucalypt species, including blue gum, were tested in the manufacture of cement-bonded flakeboards and particleboards. The wood:cement ratio used was 1:3 and the water:cement ratio was 0.38:1, considerably lower than that used here (0.5:1), and CaCl₂ was added at 2% w/w cement to some boards. Board densities were between 1200 and 1400 kg/m³ after curing. Only boards made from blue gum had MOR above 8 MPa, averaging 10.8 MPa. The greatly reduced board strength among other species was attributed to poor flake geometry (low aspect ratio) and a high quantity of fines in the boards.

7.4.1.2 Board dimensional stability and resistance to water

The average bending strengths of boards after soaking in water for 24 h are shown in Table 7.7. All boards made from pine or low-density blue gum exceeded the minimum wet MOR of 5.5 MPa specified in ISO 8335; however no boards made from mallee eucalypt met the standard, possibly because of their low initial strength. Pre-soaking of higher density blue gum flakes or the addition of accelerator (CaCl₂) was necessary to prevent a reduction in bending strength to below 5.5 MPa after exposure of boards to water. The wet MOR values of boards made from mallee eucalypt were generally significantly lower than those of other species, except when accelerator was used.

| Table 7.7 Average wet MOR (MPa) of flakeboards as influenced by species and flake treatment. |
|---------------------------------------------|----------------|----------------|----------------|----------------|----------------|
|                                       No Treatment | Cold Water | Hot Water | CaCl₂ | MgCl₂ |
| maritime | 8.4 | 8.8 | 5.9 | 8.7 | 7.7 |
| radiata  | 7.6 | 7.1 | 9.9 | 8.7 | 7.7 |
| blue gum 1 | 6.0 | 7.4 | 7.2 | 8.6 | 7.8 |
| blue gum 2 | 5.8 | 6.0 | 5.9 | 6.3 | 5.3 |
| mallee eucalypt | 1.4 | 2.7 | 2.4 | 4.9 | 5.0 |

Least Significant Difference = 2.3

Thickness swelling of boards was not significantly affected by species or pre-treatment (Table 7.2), but the interaction between species and pre-treatment was significant (p = 0.042). Thickness swelling and associated water absorption by boards made from the different species and subject to the various flake pre-treatments are shown in Table 7.8. ISO 8335 has a requirement for maximum thickness swelling of cement-bonded particleboards boards after soaking in water at ambient temperature for 24 h of 2%. Most boards manufactured here exceeded this value, but usually not by a wide margin (Table 7.8). Hot-water soaking, CaCl₂ and MgCl₂ treatments were effective in many cases in reducing thickness swelling of boards to within standard limits. ISO 8335, however, has no maximum specified water absorption. There were highly significant differences and interactions between species and flake pre-treatment which influenced water absorption (Table 7.2). Water absorption by boards containing pine wood was not significantly affected by flake pre-treatments and ranged from about 10 to 13%. Boards made from eucalypt wood were highly variable in water
absorption; in some cases water absorption exceeded 20% but was generally between 12 and 14% when a cement-setting accelerator was used in boards.

Table 7.8 Average thickness swelling (%) of flakeboards as influenced by species and flake treatment; water absorption, %, in parentheses.

<table>
<thead>
<tr>
<th>Species</th>
<th>No Treatment</th>
<th>Cold Water</th>
<th>Hot Water</th>
<th>CaCl₂</th>
<th>MgCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>maritime</td>
<td>2.2 (11.8)</td>
<td>2.3 (7.9)</td>
<td>2.2 (12.1)</td>
<td>2.2 (7.0)</td>
<td>2.0 (7.0)</td>
</tr>
<tr>
<td>radiata</td>
<td>2.1 (12.3)</td>
<td>2.0 (12.3)</td>
<td>2.0 (12.9)</td>
<td>1.7 (9.4)</td>
<td>1.8 (9.9)</td>
</tr>
<tr>
<td>blue gum 1</td>
<td>2.9 (20.1)</td>
<td>2.7 (26.2)</td>
<td>1.6 (16.3)</td>
<td>1.5 (13.3)</td>
<td>2.6 (13.1)</td>
</tr>
<tr>
<td>blue gum 2</td>
<td>2.9 (16.5)</td>
<td>2.1 (13.0)</td>
<td>2.0 (15.4)</td>
<td>1.6 (12.8)</td>
<td>1.9 (12.1)</td>
</tr>
<tr>
<td>mallee eucalypt</td>
<td>2.9 (23.3)</td>
<td>3.0 (17.2)</td>
<td>3.3 (16.7)</td>
<td>2.2 (13.9)</td>
<td>2.0 (12.7)</td>
</tr>
</tbody>
</table>

Least Significant Difference for TS = 0.98, Least Significant Difference for WA = 3.01.

Warden et al. (2002) found that the size and shape of wood elements strongly influenced thickness swelling of wood-cement flakeboards. Thickness swelling increased significantly with increasing flake thickness (from 0.3 to 0.9 mm), and decreasing flake length. The use of thicker flakes resulted in greater heterogeneity throughout the board cross-section and a more irregular 'open' board surface that was more easily penetrated by water, similar to the features of boards made from the high-density blue gum 2 and mallee eucalypt flakes in this study.

7.4.1.3 The effects of wood density, flake parameters and mat structure

The size and thickness of the flakes, the small size of the mould and the manual mat-forming technique also made it difficult to evenly distribute flakes in the boards manufactured here. Notwithstanding this problem, the mechanical properties of commercially produced flakeboards are mainly determined by flake geometry, quality and alignment together with wood density and resin content (Hakkila 1989). There was noticeable variation in flake quality and thickness produced during conversion of the different woods in this study, and this is believed to have been responsible for further reducing board quality, particularly in the case of the blue gum 2 and mallee wood. Boards produced from mallee eucalypt and blue gum 2 flakes had greater heterogeneity and surface roughness. These boards were weaker and failure tended to occur at less compacted zones. The relationship between MOR and MOE for all flakeboards is shown in Figure 7.3. There was significant variation in MOE among boards exceeding about 7 MPa in MOR. Localised variation in mat distribution and density arising from the hand-forming of mats and the variation in flake thickness may have accounted for this. Some examples of variation in board structure and vertical density profile can be seen in the sanded board cross-sections shown in Plate 7.6.
Figure 7.3 MOR vs MOE for cement-bonded flakeboards manufactured from pine and eucalypt wood.

Better control of flake thickness and automatic mat-forming equipment could overcome this problem, leading to enhanced board flexural properties. Warden et al. (2002) also observed significant variation in the mechanical properties of cement-bonded flakeboards, which they attributed to manual mat formation and to the relatively large wood-element size used to make the boards. Flake length and thickness significantly affect the mechanical properties of resin-bonded oriented strand board or OSB (Youngquist 1999, Barnes 2000, 2001), but according to Warden et al. (2002), these parameters do not appear to greatly influence the same properties of cement-bonded flakeboards. While there is no recommended minimum flake length (particularly in the panel sub-surface) for use in flakeboards, the slenderness ratio (i.e. high length:thickness ratio) is critical to achieving good strength properties (Barnes 2000). The lower strength of boards made from mallee eucalypt and high-density blue gum 2 (even after extractive removal) was likely to have been strongly influenced by their high average and highly variable flake thickness (as shown in Table 7.9), geometry and reduced compressibility. The density of the wood that goes into compressed cement panel products can significantly affect bending strength through its effect on compression ratio, with less dense woods resulting in higher mat compression during pressing and enhanced panel strength (Roffæl and Dix 1994).

The average thickness of flakes for the different species is shown in Figure 7.4 and Table 7.9. Results show that the blue gum 2 and mallee eucalypt flakes were on average significantly thicker than those of blue gum 1, radiata pine or maritime pine. Average flake thickness of blue gum 1 was significantly lower than that of the two pine species.
The size, form and density of the wood used to produce flakes greatly influences their geometry and quality, and hence the bending properties of flakeboards increase proportionally with flake length and decrease proportionally with flake thickness (Hakkila 1989). Flaking of small-diameter mallee eucalypt and high-density blue gum 2 produced flakes of variable thickness, ranging from less than 0.15 mm to over 3 mm, as shown in Table 7.9. The thicker flakes had a tendency to scroll up during drying (as shown in Plate 7.3(c)). This adversely affected flake slenderness ratio, mat homogeneity, compression and evenness of board surfaces. In contrast, pine and low-density blue gum flakes were significantly ($p < 0.001$) thinner, averaging 0.3 to 0.36 mm. They were less variable in thickness and remained flat during drying. The thin flakes from low-density blue gum 1
tended to separate longitudinally into a more fibrous form that did not seem to adversely affect board strength.

Therefore, both pine and blue gum 1 flakes produced a more compact mat structure. Eucalypt wood has been suggested to have good potential for flake-based wood composites provided flaker-knife settings are set to produce flakes that are 10 to 15% thinner than flakes from lower density species (such as pine or aspen that are currently used in the manufacture of flakeboards and waferboards (Klemerewski et al. 2000). This suggestion accords well with our findings and highlights the need for adjustment of flaker-knife parameters to better suit dense woods and produce more even flakes with a higher slenderness ratio as a means of optimising the mechanical properties of flakeboards. The use of thinner flakes also improves flakeboard dimensional stability by reducing thickness swelling, springback and linear expansion. A practical size range from the standpoint of flake production, handling and mat formation is 50 to 75 mm in length, 0.4 to 1.3 mm in thickness, and 12 to 25 mm in width (Geimer and Price 1978).

The effects of high variation in flake thickness on mat consolidation and board microstructure can be seen in images of sanded board cross sections shown in Plates 7.8 (a) to (d). The greater degree of uniformity and consolidation in pine and blue gum 1 boards can be seen in Plates 7.8(a) and (b), compared with the reduced uniformity and greater void space in boards made from the thicker and more variable flakes produced from the higher density wood of blue gum 2 or mallee eucalypt, as shown in Plates 7.8 (c) and (d).

Other research on cement-bonded boards also indicates that flake thickness significantly influences board properties. A study on the mechanics of the wood reinforcing elements in cement-bonded wood composites by Kayahara (1985) indicates that as flake thickness decreases the 'critical flake length' required to optimise composite strength also decreases. Badejo (1988) showed that MOR and MOE of cement-bonded boards manufactured from pre-treated mixed tropical hardwood flakes showed a significant linear decrease with increasing flake thickness, which ranged from 0.25 to 0.5 mm. The longer and thinner the flakes, the stronger, stiffer and more dimensionally stable were the resulting cement-bonded boards, with maximum MOR and MOE of 11.5 MPa and 4820 MPa, respectively, resulting from the use of 37.5 x 0.25 mm flakes. The research by Warden et al. (2002) did not examine the effects of flake thickness on board properties but noted that boards made from flakes with relatively high aspect ratios may enable better stress transfer between wood elements with the board during loading, resulting in improved flexural properties. The effect of flake morphology on the mechanical properties of cement-bonded flakeboards, particularly the distribution of aspect ratios and flake sizes, was suggested by the authors to be worthy of further investigation.
Plates 7.8 Cross sections of flakeboards made from (a) pine, (b) blue gum 1, (c) blue gum 2, and (d) mallee eucalypts.
7.4.2 Experiment 2- Flake size and curing temperature (flakeboards and CBPs)

7.4.2.1 Mechanical properties

The chi-squared probabilities for the effects of the main factors—species, flake size, pre-treatment, curing temperature, and interactions between factors—are shown for each mechanical property in Table 7.10. Results are shown graphically for MOR only and averages for other properties of the flakeboards and CBPs manufactured in this experiment are shown in Tables 7.11 and 7.12.

Table 7.10 Chi-squared probabilities (p-values) for effects of species, flake size, flake pre-treatment, curing temperature and interactions on board properties. N.S. = not significant at the 5% probability level (p > 0.05).

<table>
<thead>
<tr>
<th>Species (S)</th>
<th>Dens</th>
<th>MOR</th>
<th>MOE</th>
<th>WMOR</th>
<th>WMOE</th>
<th>TS</th>
<th>WA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flake Size (F)</td>
<td>N.S.</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>N.S.</td>
<td>&lt; 0.001</td>
<td>0.008</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Pre-treatment (T)</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>Curing Temperature (C)</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>S x F</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>S x T</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>F x T</td>
<td>N.S.</td>
<td>N.S.</td>
<td>&lt; 0.001</td>
<td>0.025</td>
<td>N.S.</td>
<td>0.025</td>
<td>N.S.</td>
</tr>
<tr>
<td>S x C</td>
<td>&lt; 0.001</td>
<td>0.006</td>
<td>0.003</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>0.005</td>
</tr>
<tr>
<td>F x C</td>
<td>N.S.</td>
<td>N.S.</td>
<td>N.S.</td>
<td>N.S.</td>
<td>0.011</td>
<td>N.S.</td>
<td>0.030</td>
</tr>
<tr>
<td>T x C</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>0.025</td>
<td>0.003</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>S x F x T</td>
<td>&lt; 0.001</td>
<td>0.006</td>
<td>&lt; 0.001</td>
<td>0.011</td>
<td>0.004</td>
<td>&lt; 0.001</td>
<td>0.010</td>
</tr>
<tr>
<td>S x F x C</td>
<td>&lt; 0.001</td>
<td>0.037</td>
<td>0.015</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
<td>&lt; 0.001</td>
</tr>
<tr>
<td>S x T x C</td>
<td>N.S.</td>
<td>N.S.</td>
<td>&lt; 0.001</td>
<td>0.006</td>
<td>0.002</td>
<td>0.017</td>
<td>0.001</td>
</tr>
<tr>
<td>F x T x C</td>
<td>N.S.</td>
<td>0.002</td>
<td>0.003</td>
<td>N.S.</td>
<td>N.S.</td>
<td>N.S.</td>
<td>N.S.</td>
</tr>
<tr>
<td>S x F x T x C</td>
<td>0.009</td>
<td>0.043</td>
<td>0.014</td>
<td>N.S.</td>
<td>0.023</td>
<td>0.001</td>
<td>0.008</td>
</tr>
</tbody>
</table>

WMOR = wet MOR, WMOE = wet MOE, TS = Thickness Swelling, WA = Water Absorption

All board properties except MOE were significantly affected by species and flake size (flakes or particles). As might be expected, board density was not influenced by flake size, since the weights of cement, wood and water used to manufacture boards remained the same regardless of flake size used. All board properties were strongly influenced by flake pre-treatment (none, hot water or accelerator) and initial curing temperature (20 or 65°C). The interactions of species x flake size, species x pre-treatment, species x curing temperature, and pre-treatment x curing temperature had highly significant effects on all board properties. The effects of flake pre-treatment and curing temperature on the MOR of flakeboards and CBPs are illustrated in Figure 7.5.

Although both flakeboards and particleboards responded in a similar manner to wood pre-treatments and curing, the CBPs were significantly (p = 0.002) lower in strength. At ambient temperature, flakeboards generally did not require pre-soaking or accelerator to significantly increase board strength, whereas in the case of CBP board strength was significantly increased by hot-water extraction of particles and particularly by the addition of accelerator. Contrary to expectations, the strength of both flakeboards and CBPs was greatly reduced by curing at 65°C, especially when the wood was not pre-treated with hot water or an accelerator added. The curing of
boards that did not contain an accelerator at 65°C resulted in localised zones of powdery, unconsolidated cement. This was particularly apparent in boards made from unextracted wood flakes and particles of either pine or eucalypt. This effect may have arisen from localised de-watering of cement paste caused by over-heating before the cement had a chance to set.

Another study (Manzanares et al. 1989) that compared heat curing (75°C for 8 h) with curing at ambient temperature for wood-cement aggregate blocks found that composite strength was higher for blocks cured at ambient temperature. Research by Oblivin et al. (1992), Schwartz and Simatupang (1984b) and Lange and Simatupang (1985) indicates that accelerated heat curing of CBPs (particularly at temperatures over 50°C) results in a reduction of final composite strength. Therefore heating should only be used to maintain ambient temperature of the hydrating composite at, or just above, the maximum hydration temperature generated by the cement during initial curing (about 40 to 50°C). Also the composites should not be cooled too quickly. It would certainly be worthwhile testing the addition of deliquescent and/or heavily hydrated accelerators such as $\text{Al}_2(\text{SO}_4)\cdot 9\text{H}_2\text{O}$ with accelerated curing using heat, so that extra water can be provided to compensate for the rapid drying that apparently takes place.

![Figure 7.5](image)

**Figures 7.5** The average effects of wood pre-treatment and curing temperature on MOR of (a) flakeboards and (b) CBPs manufactured from eucalypt (blue gum and mallee eucalypt) and pine (radiata) wood.

The interactive effects of wood pre-treatment and flake size on MOR of boards are shown for each of the three species used (pine, mallee eucalypts and blue gum) in Figure 7.6. In contrast to the flakeboards (even without wood pre-treatment), none of the CBPs met the ISO standard of 9 MPa for MOR, except for those made from blue gum 1 containing particles cured at 20°C and an accelerator (MgCl$_2$). In this case, average MOR was 9.8 MPa. Similar boards made from mallee
Eucalypts had the second highest average MOR of 8.4 MPa, suggesting that further addition of accelerator may bring these boards up to standard strength requirements for CBPs.

![Graphs showing interactions between wood pre-treatment and 'treatment type' (size and curing temp.) on MOR for boards made from (a) pine, (b) blue gum, and (c) mallee eucalypt.](image)

Figures 7.6 Interactions between wood pre-treatment and 'treatment type' (size and curing temp.) on MOR for boards made from (a) pine, (b) blue gum, and (c) mallee eucalypt.

These findings suggest that wood in the form of particles (particularly those designed for resin-bonded particleboard) is far less satisfactory than flakes (at least under the experimental conditions used here) for the manufacture of cement-bonded boards. The average strength of the CBPs
produced in this study may also have been reduced by their lower mat compression ratio, since the mats had a lower volume than the flakeboards but were pressed to the same thickness.

Wolfe and Gjinolli (1997) also found that laboratory-made CBPs which used the same wood:cement ratios as commercial products had poor bending properties (MOR between 0 and 3 MPa). Although the effects of particle size and geometry on mechanical properties are claimed to be similar for resin- and cement-bonded particleboards (Pease 1994), the findings here and other work on CBP suggest otherwise, and indicate that cement-bonded boards may require a much larger particle size than resin-bonded panels. As discussed in Chapter 2, research by Badejo (1988) showed that MOR and MOE of CBPs manufactured from pre-treated mixed tropical hardwood flakes showed a significant linear increase with increasing flake length from 12.5 to 37.5 mm, and board density from 1050 to 1200 kg/m$^3$; and a significant linear decrease with increasing flake thickness between 0.25 to 0.5 mm. Maximum MOR and MOE of 11.2 MPa and 4800 MPa, respectively, were attained by using 37.5 x 0.25 mm flakes, with a board density of 1200 kg/m$^3$. These results suggest that particle slenderness ratio greatly impacts on the flexural properties of CBP. An important difference between the ‘fines’ generated from flaking the eucalypt wood and the factory-produced particles of radiata pine was their geometry. The length of the pine particles obtained from the particleboard factory varied from 5 to 15 mm, and ranged in thickness from 0.2 to 1.5 mm. The small ‘flakes’ of eucalypt wood were longer (between 5 and 30 mm), wider (up to 10 mm), and much thinner than the pine particles. The nature of the particle alignment in board cross-sections in the CBPs made from pine and eucalypt are shown in Plates 7.9 (a) to (c). In the case of CBPs made from radiata pine particles, there was minimal interlaying and contact between wood elements; rather the particles appeared to be arranged more like an aggregate filler rather than multi-layered fibrous reinforcement. This may have been why CBPs made from the pine particles did not meet the ISO standard of 9 MPa for MOR even when cement-setting accelerators were used. In the case of resin-bonded particleboard, fines are used in the surface layers to produce a smooth finish that requires minimal sanding and does not adversely affect panel strength. Fines in the surface layers of cement-bonded boards, however, have been shown to significantly detract from their bending strength (Fuwape and Fuwape 1994), and more recent research shows that the placement of longer strands in the surface layers and smaller strands in the core layer enhances the strength properties of wood-cement panels (Kuroki et al. 2002).
Plates 7.9 Cross-sectional profiles of CBPs made from (a) factory-produced particles of radiata pine, and screened small-sized elements of (b) blue gum and (c) mallee eucalypt.

The effects of species, particle pre-treatment and board curing temperature on the corresponding MOE of flake and particleboards are shown in Table 7.11. Despite the propensity of CBPs to break under relatively low loading, their ability to resist deflection under a given load (expressed as MOE) was often higher than that of the flakeboards, especially in the case of boards made from eucalypt wood subjected to pre-treatment, as shown in Table 7.11. This may be why MOE was not significantly affected by flake size, unlike MOR (Table 7.10). In most cases (particularly after hot-water or accelerator treatment), the average MOE for CBPs of a given species and treatment exceeded the 3000 MPa required by ISO 8335.
Table 7.11 Average MOE of flakeboards and CBPs made from radiata pine, blue gum 1 and mallee eucalypt according to wood pre-treatment and board curing temperature. Shading denotes boards that did not meet ISO 8335.

<table>
<thead>
<tr>
<th>Flakeboards</th>
<th>No Treatment</th>
<th>Hot Water</th>
<th>Accelerator</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
<td>65°C</td>
<td>20°C</td>
</tr>
<tr>
<td>radiata pine</td>
<td>4764</td>
<td>4200</td>
<td>4990</td>
</tr>
<tr>
<td>blue gum 1</td>
<td>3630</td>
<td>3330</td>
<td>4595</td>
</tr>
<tr>
<td>mallee</td>
<td>1651</td>
<td>2322</td>
<td>3359</td>
</tr>
<tr>
<td>CBPs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>radiata pine</td>
<td>3878</td>
<td>3880</td>
<td>4298</td>
</tr>
<tr>
<td>blue gum 1</td>
<td>1382</td>
<td>1391</td>
<td>3139</td>
</tr>
<tr>
<td>mallee</td>
<td>2603</td>
<td>883</td>
<td>4713</td>
</tr>
<tr>
<td>LSD = 948</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This trend is also clearly illustrated by comparing the relationship between MOR and MOE among the flakeboards (Figure 7.3) and the particleboards (Figure 7.7), where the slope of the regression line for particleboards was higher than that for flakeboards. The most likely reason for this observation is that the finer wood elements in the particleboards produced a much more compact mat structure upon pressing, which resulted in reduced void space and irregularities. However, this better compaction of mats was offset by the negative effects on cement setting produced by the fineness and much larger surface area-to-volume ratio of the wood in small particle form.

![Figure 7.7 MOR vs MOE for CBPs manufactured from pine and eucalypt wood.](image-url)
7.4.2.2 Board dimensional stability and resistance to water

The average wet MOR values of flakeboards and CBPs after soaking in water for 24 h are given in Table 7.12. Because of their higher initial strength, more of the flakeboards retained MOR above 5.5 MPa after exposure to water than did the CBPs. Flakeboards cured at 65°C, however, were especially susceptible to loss of bending strength after soaking, particularly if they did not contain an accelerator.

Table 7.12 Average wet MOR of flakeboards and CBPs made from radiata pine, blue gum 1 and mallee eucalypt according to wood pre-treatment and board curing temperature. Shading denotes boards that did not meet the ISO 8335 requirement of 5.5 MPa.

<table>
<thead>
<tr>
<th>Flakeboards</th>
<th>No Treatment</th>
<th>Hot Water</th>
<th>Accelerator</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
<td>65°C</td>
<td>20°C</td>
</tr>
<tr>
<td>radiata pine</td>
<td>7.5</td>
<td>2.9</td>
<td>9.5</td>
</tr>
<tr>
<td>blue gum 1</td>
<td>6.1</td>
<td>1.8</td>
<td>7.1</td>
</tr>
<tr>
<td>mallee</td>
<td>1.4</td>
<td>1.5</td>
<td>2.4</td>
</tr>
<tr>
<td>CBPs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>radiata pine</td>
<td>3.7</td>
<td>0.6</td>
<td>5.0</td>
</tr>
<tr>
<td>blue gum 1</td>
<td>4.7</td>
<td>1.9</td>
<td>4.2</td>
</tr>
<tr>
<td>mallee</td>
<td>2.5</td>
<td>0.5</td>
<td>4.0</td>
</tr>
<tr>
<td>LSD = 1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

No CBPs had wet MOR above 5.5 MPa, except for one case. In keeping with the trend for dry samples, only boards made from low-density blue gum particles using MgCl₂ and cured at ambient temperature exceeded 5.5 MPa in wet MOR as required by ISO 8335. Boards cured at 65°C were significantly lower in bending strength after exposure to water, particularly those made from radiata pine and mallee eucalypt particles which were not subject to pre-treatment. ISO 8335 has no specified minimum MOE of boards after 24 h exposure to water. Average wet MOE ranged from 392 MPa for boards made from untreated radiata pine cured at 65°C to 3850 MPa for boards made from mallee eucalypt particles containing accelerator and cured at 20°C.

Table 7.13 shows the average thickness swelling of flake and particleboards made from radiata pine, blue gum 1 and mallee eucalypt. The thickness swelling of CBPs was generally lower than that of the flakeboards, with most CBPs falling within the 2% limit specified in ISO 8335. Exceptions to this were the poorly consolidated boards made from untreated particles from all species cured at 65°C. The lower thickness swelling of particleboards accords well with the findings of Warden et al. (2002) who also found that flakeboards swelled more than CBPs on exposure to water because of the rough surface and greater internal void-space in the flakeboards. Fuwape and Fuwape (1994) attempted to rectify this problem in cement-bonded flakeboards made from sitka spruce (Picea sitchensis (Bongard) Carriere) by using sawdust in the top and bottom layers. Such an approach improved dimensional stability but significantly reduced the bending strength and stiffness of boards. This finding accords with the results of other work on CBP, which support the
notion that increased flake length improves the flexural properties of cement-bonded boards, particularly if they are located in the surface layers.

Table 7.13 Average thickness swelling of flakeboards and CBPs made from radiata pine, blue gum and mallee eucalypt according to wood pre-treatment and board curing temperature. Shading denotes boards that did not meet the ISO 8335 limit of 2%.

<table>
<thead>
<tr>
<th>Flakeboards</th>
<th>No Treatment</th>
<th>Hot Water</th>
<th>Accelerator</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
<td>65°C</td>
<td>20°C</td>
</tr>
<tr>
<td>radiata pine</td>
<td>2.4</td>
<td>4.5</td>
<td>2.0</td>
</tr>
<tr>
<td>blue gum 1</td>
<td>2.9</td>
<td>6.4</td>
<td>1.6</td>
</tr>
<tr>
<td>mallee</td>
<td>2.9</td>
<td>3.0</td>
<td>3.3</td>
</tr>
</tbody>
</table>

CBPs

<table>
<thead>
<tr>
<th>Flakeboards</th>
<th>No Treatment</th>
<th>Hot Water</th>
<th>Accelerator</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
<td>65°C</td>
<td>20°C</td>
</tr>
<tr>
<td>radiata pine</td>
<td>0.5</td>
<td>3.1</td>
<td>0.8</td>
</tr>
<tr>
<td>blue gum 1</td>
<td>1.0</td>
<td>2.3</td>
<td>1.2</td>
</tr>
<tr>
<td>mallee</td>
<td>1.9</td>
<td>3.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>

LSD = 0.66

7.4.3 Experiment 3: Commercial WWCBs

7.4.3.1 Physical properties and static bending tests

Chi-square probabilities were calculated for effects of the factor 'species' on all WWCB properties, i.e. basic density, board thickness, breaking load, deflection, MOR and MOE. Of all board properties, only density was significantly (p = 0.025) affected by species from which the wood wool was produced to make boards.

The average density and strength properties of WWCBs made from Western Australian-grown blue gum, maritime pine and radiata pine are shown in Table 7.14. Results can be compared with those of commercial 'WoodTex' manufactured to the same specification (using locally-grown radiata pine wood). In the absence of an Australian standard for this type of panel product, the board properties are compared with the British and Japanese standards for insulating WWCB.

Table 7.14 Average density, thickness and flexural properties for factory-made WWCBs of blue gum, maritime pine, radiata pine and commercial 'WoodTex' boards (standard deviation in parentheses).

<table>
<thead>
<tr>
<th>species</th>
<th>Basic Density (kg/m³)</th>
<th>Breaking Load (N)</th>
<th>Deflection (mm)</th>
<th>MOR (MPa)</th>
<th>MOE (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>blue gum</td>
<td>366.6 (44.4)</td>
<td>83.0 (27.0)</td>
<td>6.8 (1.4)</td>
<td>1.21 (0.47)</td>
<td>438.0 (246.3)</td>
</tr>
<tr>
<td>maritime pine</td>
<td>351.3 (32.1)</td>
<td>91.6 (49.2)</td>
<td>6.2 (1.6)</td>
<td>1.23 (0.43)</td>
<td>457.7 (219.7)</td>
</tr>
<tr>
<td>radiata Pine</td>
<td>337.4 (33.0)</td>
<td>89.1 (38.1)</td>
<td>6.1 (1.1)</td>
<td>1.29 (0.46)</td>
<td>475.9 (177.9)</td>
</tr>
<tr>
<td>WoodTex</td>
<td>356.5 (31.0)</td>
<td>86.3 (30.4)</td>
<td>5.9 (1.2)</td>
<td>1.23 (0.41)</td>
<td>454.2 (122.7)</td>
</tr>
</tbody>
</table>

Thickness (mm)
18.4 to 29.6
21.6 to 29.1
22.3 to 26.6
23.2 to 26.7

Contrary to expectations, despite the significant variation in board density, the average bending strength and variation among WWCBs made from pine and eucalypt wood were very similar to
each other and to the commercial product; average MOR was between 1.21 and 1.29 MPa (Table 7.14). All except seven of the 160 board samples tested, however, had MOR below the 2 MPa specified in the British Standard (BS 1105: 1980) for low-density insulating WWCB slabs. None of the samples from the commercial batch of 'WoodTex' met this standard. No minimum MOE is specified in BS 1105; however, as Figure 7.8 shows, MOE was very closely correlated with MOR in the lower range of MOR but, like the flakeboards examined earlier, became more variable as bending strength of boards increased. From Figure 7.8 it might be reasonable to expect that a corresponding MOE for boards with MOR ≥ 2 MPa should not be below 800 to 1000 MPa. The Japanese Industrial Standard for insulating wood wool board (JIS-A 5404: 1979) does not specify minimum bending or stiffness values for boards (at various nominal thicknesses) but instead specifies a breaking load of not less than 490 N and deflection of not more than 8 mm for boards 25 mm in thickness. Although the boards here were well below this minimum breaking load (Table 7.14), average deflection prior to breaking was below 8 mm.

Surprisingly, the WWCBs manufactured in this study displayed wide variation in thickness, particularly those made from blue gum and maritime pine. Thickness tolerance specified in JIS-A 5404 is +1 and -2 mm above and below a nominal thickness of 25 mm. Commercial and experimental boards made from radiata pine were within the lower limit but slightly above the upper limit, whereas some of those made from blue gum and maritime pine were outside the upper or lower limits. Variation in board thickness may have arisen from imprecise edge heights of the

Figure 7.8 MOR vs MOE for all WWCBs manufactured at WoodTex Pty Ltd.
moulds and/or from variation in the volume and distribution of wood wool in the mats, possibly influenced by such factors as density and grain of the parent wood.

Average board density did not vary greatly between species, ranging from an average of 351 kg/m$^3$ for maritime pine to 367 kg/m$^3$ for blue gum. The average density of blue gum boards was slightly but significantly ($p = 0.004$) higher than that of maritime pine boards. There was wide variation in sample density, particularly in the cases of blue gum (whose boards ranged in density from 284 to 552 kg/m$^3$) and maritime pine (280 to 501 kg/m$^3$). In contrast, density variation among the commercial 'WoodTex' panels was smaller (302 to 415 kg/m$^3$). This suggests greater heterogeneity in the distribution of cement-coated wood wool from blue gum and maritime pine and highlights a need for 'fine-tuning' of the manufacturing process to better suit these wood species.

BS 1105 specifies a minimum mass/m$^2$ of slabs 25 mm in thickness of 18 kg/m$^2$. The equivalent average mass of boards manufactured in this study ranged from 9.7 kg/m$^2$ for boards made from radiata pine to 7.8 kg/m$^2$ for boards made from blue gum. These values are only 53 to 60% of the minimum mass/m$^2$ of slab required by BS 1105 and may explain why the MOR values of boards were below the minimum of 2 MPa. Increasing the amount of cement-coated wood wool distributed into each mould and increasing the average board density would probably increase average bending strength and stiffness of boards regardless of wood species used. The relationship between board density and bending strength is shown below in Figure 7.9.

![Figure 7.9 MOR vs basic density of WWCBs manufactured at WoodTex Pty Ltd.](image)

Figure 7.9 suggests that, while there is a positive relationship between board strength and density, board density alone does not explain all the variation in MOR. During sample testing, there were noticeable differences in distribution and packing of wood wool along the sample length, i.e.
through the board cross section. Although samples were loaded at mid-point along their length, they tended to fracture at the lower density regions. This suggests that improvements to the mat distribution process designed to prevent the occurrence of such low-density zones would also lead to increased board strength.

A third possible source of variation in strength within and among boards is poor mixing of wood wool of different compatibility with portland cement. This has been shown to reduce the strength of WWCBs made from radiata pine (Semple and Evans 2000) and could have affected the properties of boards here. This paper can be found in Appendix 1 (This Vol., p. 355).

Given that the manufacturing process was kept constant for all wood batches, the main factor that is likely to have influenced mat quality at the time of board manufacture was variation in wood wool bulk density and quality (length and thickness variation and wood wool content) among species. In the case of blue gum, mat height was about 5 cm compared with 10 cm in the case of the two pines, which was due to the smaller volume of blue gum wood wool deposited in each mould. Mats of blue gum wood wool appeared to be somewhat less continuous and less interlocked, probably because of shorter, heavier strands and greater frequency of solid chips produced by the shredding process. There may also have been a smaller volume of cement-coated blue gum wood wool per batch weighed by the load cell (which was a fixed weight designed for pine wood wool). Both of these factors could have influenced mat quality and board structure.

Although these observed differences in mat characteristics at the time of manufacture were expected to translate into reduced board strength in the case of blue gum, this does not appear to have been the case when the properties of blue gum boards are compared with those of the commercial product manufactured from radiata pine. On the contrary, certain strength properties were increased in boards made from blue gum, as shown below.

7.4.3.2 Impact Resistance of WWCBs

The percentages of each type of WWCB that broke under each weight and drop height are shown in Table 7.15. Shaded cells denote the majority response of boards made from each species. The majority of boards (95%) made from blue gum survived the 5-kg-load drops followed by the 8-kg load dropped from a height of 50 cm, and 35% of the boards survived one or more drops of the 8-kg load from a height of 1 m. Impact resistance was lower among boards made from pine wood, especially among the low-density panels. About 50% of all boards made from pine wood survived the 5-kg load dropped from 1 m but broke when the 8-kg load was dropped from 50 cm. Fracture of some boards made from radiata pine was often clean through the middle of the panel and at the clamping points, resulting in the total destruction of the board. Most of the other boards fractured through the middle and at the clamp joints without completely breaking, leaving it still supporting the weight through mechanical interlocking of the wood wool strands, as shown in Plate 7.7(b).
Less than 20% of the boards made from pine wood survived the 8-kg load dropped from 1 m. The strongest boards were the thicker and higher density boards with a more compacted mat structure. The stronger blue gum wood wool strands may also have contributed to the higher impact resistance of boards made from this species.

Table 7.15 Percentage of wood wool boards that failed after dropping different weights from different heights. Shading highlights the limit of the majority of boards of each species.

<table>
<thead>
<tr>
<th></th>
<th>5 kg</th>
<th></th>
<th>8 kg</th>
<th></th>
<th>multiple drops</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50 cm</td>
<td>100 cm</td>
<td>50 cm</td>
<td>100 cm</td>
<td></td>
</tr>
<tr>
<td>blue gum</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>60</td>
<td>35</td>
</tr>
<tr>
<td>maritime pine</td>
<td>6</td>
<td>30</td>
<td>55</td>
<td>15</td>
<td>--</td>
</tr>
<tr>
<td>radiata pine</td>
<td>0</td>
<td>30</td>
<td>50</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>WoodTex</td>
<td>10</td>
<td>40</td>
<td>50</td>
<td>10</td>
<td>--</td>
</tr>
</tbody>
</table>

Possible reasons for the lower impact strength of boards made from pine wood include the above-mentioned problem of low heartwood compatibility with cement. Zones of friable, less well consolidated wood-cement bonding were noticed in many of the weakest boards made from pine wood. In contrast, the heartwood of eucalypts does not appear to have adversely affected its compatibility with portland cement, in accordance with their mostly good compatibility with cement, which was shown in Chapters 3 to 5. Another possible reason for the higher impact strength of boards made from blue gum was the reduced volume of wood wool in the mats, resulting in a higher cement:wood ratio when considered on a volume basis. This may have led to enhanced consolidation of boards and improved bonding between the wood wool and cement, enabling greater load distribution across board surfaces and thus increasing impact resistance.

7.4.4 Current interest in and further potential for, cement-bonded flakeboards

Results from this study show that cement-bonded flakeboards manufactured using relatively simple techniques can surpass those of CBPs produced under the same conditions. Despite their relative ease of manufacture and favourable properties, there are still relatively few studies on the manufacture and utilisation of cement-bonded flakeboards of the type investigated here. Despite the increased thickness swelling of flakeboards compared to CBPs, the use of larger sized flakes has a number of advantages. This study has shown that boards with acceptable mechanical properties can be manufactured using relatively simple processing technology, with minimal need for wood pretreatment or accelerators, especially if the wood is naturally compatible with cement, such as the radiata and maritime pine wood flakes tested here. The use of large flakes is also a very effective way of reducing carbonation-induced shrinkage in wood-cement composites (Sandermann 1973, Broker and Simatupang 1974a, b).
Cement-bonded flakeboards were first developed as a building material by El mondor (1963 and 1966). However, since then relatively little further research and commercialisation of this type of wood-cement composite has taken place until quite recently. There is increasing interest and use of wood-cement flakeboards or ‘waferboards’ in China and Korea due to their combination of favourable properties, including: strength, resistance to moisture, biodeterioration and fire, low manufacturing cost and energy efficiency (Kim and Lee 1987, Zhou 1992, Tu 1995), but there are few published reports in English on this subject. The wood-cement flakeboards referred to by Zhou (1992) and Xiong (1996) are made from either portland cement, blast furnace slag or a mix of both, using a wood:cement ratio of 0.3:1, a high water:cement ratio of 0.6-0.7:1, and cement-setting accelerators (CaCl₂, Na₂SiO₃ or Al₃(SO₄)₃ + Ca(OH)₂) at between 3 and 8% w/w cement. Wood flakes produced from sawmill wastes and branches are reported to be 18 to 25 mm in length, 4 to 6 mm wide and 0.2 to 0.5 mm in thickness. Mats are compressed at between 1 and 3 MPa and cured by autoclaving for 6-8 h followed by curing at ambient temperature for 14 days. Superior board properties were reported to result from the use of higher cement content, higher compression ratio, and the lower water:cement ratio. MOR and MOE for such boards were ≈7 and 5570 MPa, respectively, within the range of strength values of boards manufactured in this study.

Large flakes also provide much greater scope for flake or strand orientation to impart higher flexural properties to boards. The most recent researchers of wood-cement flakeboards has revisited the idea of flake alignment (Kim and Lee 1987, Bach and Kolker 1995, Mat et al. 2002b, Kuroki et al. 2002), with significant beneficial effects on board strength properties. Wood is an anisotropic material with significantly higher mechanical strength and dimensional stability in its longitudinal direction (Panshin and De Zeeuw 1980, Kajita and Mokudai 1993). Modern oriented strand composites attain their high strength properties through a combination of high slenderness ratios and close-to-parallel flake orientation in the surface layers (McNatt et al. 1992, Barnes 2000). The idea of manufacturing oriented and layered wood-cement flakeboards was first developed and patented by Elmondorf (1963 and 1966) to produce a high-strength panel product (termed Embedded Fiber Board) at a fraction of the cost of producing plywood, and before resin-bonded OSB was developed. This is the earliest published example of wood-cement flakeboard being produced as a viable commercial product, so it is discussed in depth here. A pilot plant at Palo Alto, California, produced 12-mm-thick boards containing flakes measuring 2.5 and 5 cm in length, a wood:cement:water ratio of 1:2.5:1 and pressed at up to 200 psi to a target density of between 1000 and 1200 kg/m³. The wood:cement ratio could be varied to between 1:2 and 1:5 to balance durability, weather resistance and strength against cost, ease of machining and ease of handling on building sites. Two board types were manufactured: type A, composed of a single mat containing randomly oriented flakes; and type B, composed of a three-layered mat formed much like oriented strand board or OSB. In the top and bottom layers the flakes were aligned with each other, whereas
in the middle layer the flakes were either randomly orientated or aligned perpendicular to the orientation of flakes in the top and bottom layers. The flexural properties of type A boards were MOR of 14.8 MPa and MOE of 2071 MPa, whereas those for type B boards were 22.7 MPa and 6560 MPa for MOR and MOE respectively. The increase in bending strength after strand orientation was 53%. Flake orientation was also investigated and applied in the USSR to improve the strength properties of their ‘Arbolit’ mineral-bonded boards (Klar and Vankov 1975), with flexural properties reportedly improved by 2 to 3 times compared with those of boards with random flake distribution.

A recent study (Ma et al. 2002b) also used the above-mentioned production technique (i.e. aligned surface flakes and randomly oriented core flakes) to greatly improve the strength properties of cement-bonded flakeboards made from sugi (Cryptomeria japonica (L. f.) D. Don); a species normally considered unsuitable for wood-cement composites. Strength properties were maximised by adding 3.75% CaCl₂ and using a surface to core or ‘shelling’ ratio of 1 to 4. The average MOR of the resulting boards was almost 50 MPa and the average MOE was 8 GPa. The gain in strength from using surface orientation in this instance was 250%. These values are the highest cited in the literature for wood-cement composites, and compare with average strength values of resin-bonded OSB of 47 MPa for MOR and 8300 MPa for MOE (Youngquist 1999). Cement-bonded boards that employ conventional OSB manufacturing technology and combine the high production rate and flexural properties of OSB with high fire resistance are also attracting renewed interest in the North American construction market (Bach and Kolker 1995). Here a combination of rapid setting magnesite cement, a highly reactive MDI (isocyanate) resin and hot pressing is used to achieve the production rate of OSB. Experimental cement-bonded OSB made by Kuroki et al. (2002) contained yeddo spruce (Picea jezoensis Carr) flakes and had a wood:cement ratio of 1:2.5, a water content of 40%, and 10% silica fume (fly ash). Injected CO₂ gas was used to accelerate curing during pressing, and boards were hardened for 24 h at 50°C. Board flexural properties were between 25 and 30 MPa for MOR and between 3500 and 4500 MPa for MOE.

The early work of Elmondorf (1963) demonstrated that mechanical strand orientation can be readily applied during the manufacture of cement-bonded flakeboards; however the moisture present in and on the strands is critical to the success of the process. There must be just enough moisture to bind the cement powder to the strands during mat formation or ‘air-felting’ but not enough to enable the flakes to clump together. Particles or flakes can be oriented either mechanically or electrostatically depending on the size of the wood elements. Mechanical strand orienters are designed for long, thin and slender flakes whereas electrostatic alignment of the furnish in the mat is designed for small particles (Kajita et al. 1982, Kajita and Mokudai 1993). Mechanical orientation involves dropping cement-coated flakes down through a regularly spaced series of parallel reciprocating plates, discs or vanes, usually aligning the flakes parallel to mat
length (Kajita and Mokudai 1993). The degree of strand alignment is controlled by adjusting the free-fall distance from the bottom of the grille to the mat surface as it travels beneath the dispenser (Kajita et al. 1982, Kajita and Mokudai 1993). A simple mat-forming box containing regularly spaced plates was used by Kuroki et al. (2002) to orient the layers of surface and core flakes perpendicular to each other.

The other major simple avenue for improving cement-bonded flakeboard properties, including dimensional stability, without resorting to siliceous cement supplements, autoclaving, CO₂ and/or hot pressing, is flake pre-treatment with inorganic and/or organic additives. The results here showed that the addition of cement-setting accelerators was the only effective method of increasing the strength of cement-bonded flakeboards, particularly in the case of boards made from higher-density eucalypt wood where the flake thickness was sub-optimal. Novel methods exist for preparing wood flakes for use in wood-cement composites by pre-mixing them with relatively inexpensive minerals. A patent by Walter and Walter-Gurzeler (1991) describes a process of pre-mineralising small wood flakes using a 13-15% solution of Al₂(SO₄)₃ followed by a water-based suspension of finely ground kaolin (Al₂O₃·2SiO₂) to significantly improve the performance of wood-cement composites. An Australian patent lodged by Gamage (1997) involving the pre-treatment of sawdust with sodium metasilicate powder, MgCO₃, MgSO₄, polyethylene glycol and lime claims to achieve a similar effect. Relatively simple pre-mineralisation methods such as these deserve to be tested on mallee eucalypt wood and bark residues with the aim of further improving board strength and resistance to water.

7.5 Conclusions

This study investigated the utilisation of eucalypt wood (both small-diameter waste stems from oil mallee eucalypt and commercial plantation blue gum timber) for cement-bonded composite boards, using boards made from pine wood (radiata and maritime pines) as controls. In keeping with the overall objective of the study, the cement-bonded boards made from mallee eucalypt wood flakes were much better than those of the CBPs in Chapter 6. Flakeboards manufactured from pine and low-density blue gum 1 at a wood:cement ratio of 1:3 were of good quality. The addition of accelerators (CaCl₂ or MgCl₂) further improved the properties of boards made from blue gum. Average MOR of boards made from commercial blue gum and containing MgCl₂ was 15 MPa, indicating that this eucalypt species has very good potential for the manufacture of cement-bonded flakeboards. Thickness swelling of boards made from untreated wood flakes of all species was above 2%, the maximum level permitted by ISO 8335; however hot-water extraction of flakes and the addition of accelerators reduced thickness swelling in most cases.

The effects on board properties of using smaller particles and elevated curing temperature (as is employed during the commercial manufacture of CBP) were also examined. The results showed
that the use of large flakes resulted in boards with significantly higher bending strength (MOR) than those composed of small particles. This was probably due to improved strand contact and interlocking, and the higher mat compression ratio of flakeboards compared to particleboards. Board stiffness (MOE) was not significantly affected by small flake size, but the dimensional stability of boards was generally improved by the use of small flakes. The elevated-temperature curing regime recommended for the manufacture of CBP reduced board properties under the manufacturing conditions used here. Similar problems were reported in other studies as well.

The flexural properties of flakeboards were greatly reduced in the cases where boards were made from flakes of higher density wood species (blue gum 2 and mallee eucalypt). Addition of accelerators at 2% w/w cement significantly improved the strength of boards made from mallee eucalypt flakes, but the improvements were not sufficient to ensure that boards met the minimum properties specified for cement-bonded boards in ISO 8335. Adjustment of flake thickness, geometry and alignment, and the use of simple cement-setting accelerators would be sufficient to improve the properties of boards made from mallee flakes so that they meet the standard.

A commercial-scale manufacturing run of low-density WWCBs from pine and blue gum wood was undertaken as part of this study. In contrast to the negative expectations of board quality that arose from observing the conversion of blue gum wood to wood wool, the wood from this species proved to be as well suited to the manufacture of WWCBs as wood from radiata or maritime pine, even without the use of cement-setting accelerators. The mechanical properties of factory-produced WWCBs made from lower density blue gum wood were very similar to those of boards made from the commercially used radiata pine wood and the impact resistance of WWCBs made from blue gum was higher. The factory-made boards did not meet standard requirements for strength; however this was probably due to their below-standard density rather than any inherent unsuitability of species tested for the manufacture of wood-cement composites.

The improved strength properties conferred by the use of larger flakes in cement-bonded composites and the ability to orient flakes to further improve strength properties have not gone unnoticed by other researchers, and there is renewed interest in developing oriented cement-bonded flakeboards. The results from this study help show that small-diameter, fast-grown plantation eucalypt wood may be well suited to the manufacture of wood-cement flakeboards, provided the wood is flaked correctly and other manufacturing variables are optimised.

Chapters 8 to 10 of this thesis deal with improving the suitability of *A. mangium* wood for the manufacture of wood-cement composites and facilitating the manufacture of WWCBs from this species. Chapter 8 begins by investigating a range of different kinds of pre-treatments aimed at improving the low compatibility of *A. mangium* heartwood with cement.
Chapter 8 Pre-treatment of *Acacia mangium* heartwood to improve its compatibility with portland cement.

8.1 Introduction

The problem of inhibition of cement hydration reactions or 'cement poisoning' by extractives in many woods, resulting in poor bonding at the wood-cement interface, has been identified as a major deterrent to the expansion of mineral bonded wood composite technology (Pazner and Klemarevski 1989). This problem has greatly hampered the adoption of otherwise readily available wood resources such as *Acacia mangium* for use as a raw material for the manufacture of cement-bonded composites. The findings from Chapter 4 indicated that the heartwood of *A. mangium*, almost regardless of its proportion in the tree, can significantly reduce the compatibility of the wood with portland cement and is therefore the primary cause of inadequate consolidation and bond strength development in cement-bonded composites manufactured from this species.

The successful establishment and availability of *A. mangium* in South East Asia has provided impetus for research into the use of its wood as a raw material for the manufacture of wood wool-cement board (WWCB) in countries such as the Philippines (Soriano et al. 1997, Eusebio et al. 2002a, b). *A. mangium* has also been tested for its suitability for the manufacture of cement-bonded particleboard (CBP) in Malaysia (Tachi et al. 1988, 1989, Sudin and Ibrahim 1990). The main deterrent to its use in wood-cement composites is the presence of water- and alkali-soluble polyphenols present in the heartwood of *A. mangium* that severely retard the normal course of cement hydration, as investigated by Tachi et al. (1989). As shown in Chapter 4, these strongly impede the development of normal hydration products at the wood-cement interface, leaving little or no contact between the wood surface and the cement. Previous studies have demonstrated that untreated wood of *A. mangium* has a deleterious effect on the strength of WWCB (Soriano et al. 1997, Cabangan et al. 1998, Eusebio et al. 2002b). CBP strength is also adversely affected (Jegatheswaran 1989, Tachi et al. 1988, Sudin and Ibrahim 1989). *A. mangium* wood wool or particles therefore require some form of pre-treatment, usually either by pre-soaking in water and/or the addition of cement-setting accelerators to improve compatibility with cement. However other strategies such as post-harvest storage of logs have also been tested (Cabangan et al. 2002b).

Pre-soaking in large shallow baths of water at ambient temperature is currently used to prepare wood wool for the manufacture of structural WWCB in the Philippines (Pablo 1989, 1996, Pablo et al. 1996). Unlike some tropical hardwoods, some if not most, of the inhibitory polyphenol content in *A. mangium* heartwood is water-soluble (Tachi et al. 1988, 1989), enabling extractives to be removed from wood wool by soaking in water at ambient temperature. However, the question of whether cold water removes enough of the inhibitory extractives from *A. mangium* heartwood to
enable the manufacture of wood-cement composites that meet standard specifications is unclear. WWCBS made in previous experimental studies by Soriano et al. (1997), Cabangon et al. (1998) and Eusebio et al. (2002b) using wood wool pre-soaked in water at ambient temperature without the further addition of a cement-setting accelerator were only between 2 and 6 MPa in MOR. These values are below the minimum of 7 MPa for non-structural WWCBS set out in the Philippine National Standard (PNS/CTP 07: 1990), and therefore suggest that cold water soaking of A. mangium wood wool may not remove sufficient extractives to enable WWCBS with satisfactory properties to be manufactured from this species.

It is well known that hot water and dilute alkali will remove a much greater proportion of extractives from most woods than does cold water (Hillis 1962, 1987, Goldstein 1984, Hillis 1987, Alberto et al. 2000). Hot water or dilute alkali is necessary to manufacture cement boards from inhibitory woods including Eucalyptus camaldulensis (Yasin and Qureshi 1989), Tectona grandis (Sutigno 2000) and a Japanese larch (Larix leptopsis Gordon) (Yashiro et al. 1968a). Pre-soaking wood wool or flakes of these species in cold water was found to be insufficient to remove enough of the inhibitory extractives to facilitate the manufacture of sound cement-bonded boards; instead extraction in either hot water or alkali was necessary. Boiling sawdust from wood in a mineralising solution of Fe(SO₄)₃ has been recommended by Parker (1947) as a simple, practical way of neutralising inhibitory tannins and removing fatty substances prior to manufacturing cement-bonded composites.

An alternative to the lengthy process of pre-soaking wood in water involves dipping the wood in a mineralising fluid that accelerates cement hydration prior to manufacture of wood-cement composites. Pre-dipping wood wool of Acacia mearnsii in 3% CaCl₂ proved to be a simple and effective way of improving the quality of non-structural WWCBS slabs made from Acacia mearnsii (Flawes and Chittenden 1967). Other alternatives include the application of a coating that impedes access to the wood surface by the alkaline solution of cement paste, potentially reducing the leaching of inhibitory polyphenols from heartwood into the surrounding cement. Oils have been tested as water repellents for larch wood flakes with the aim of reducing extractive leaching and water absorption in wood-cement composite materials (Yamagishi et al. 1980, 1983, Ledhem et al. 2000a, b). Wood flakes of inhibitory oak can be pre-treated with high quantities of Al₂(SO₄)₃ to block leaching and act as a cement-setting accelerator (Walter and Walter-Gurzeler 1991). Pre-treating the wood by heating, exposure to sunlight or electrical plasma could be used to induce possible changes in the inhibitory extractives in A. mangium heartwood. Coloured polyphenols in other inhibitory heartwoods such as western red cedar (Thuja plicata Donn ex D. Don) undergo photo-induced colour changes that may alter their effect on cement setting; however there appear to
be no published examples of attempts to use such pre-treatments to improve the compatibility of wood with portland cement.

8.2 Aims and objectives

The aim of this study was to test the effects of simple pre-treatments on the compatibility of *A. mangium* heartwood with portland cement with a view to identifying the most effective and practical treatment that might have potential application in the manufacture of low-cost wood-cement composites, in particular WWCB, from this species. Based on findings from previous studies on the manufacture of WWCB from *A. mangium*, it was hypothesised that certain conventional methods of pre-treating the wood wool (such as cold water soaking) may not remove enough of the inhibitory heartwood extractives to enable good quality WWCBs to be produced. Specific objectives of the study were to:

1. Test the effects on the compatibility of *A. mangium* heartwood of four different classes of wood pre-treatments including (i) Chemical Dip (pre-dipping in cement-setting accelerators), (ii) Extractive Removal (in water at different temperatures, dilute NaOH or alcohol), (iii) Water Repellent (coating strands with water repellents such as oil or wax), and (iv) Radiation treatments (heat, sunlight or electrical plasma).

2. Investigate the question of how much heartwood extractive material is removed by increasing the water temperature or using alternative solvents such as alcohol or alkali. Determine a more appropriate water temperature for the pre-soaking of *A. mangium* wood wool prior to the manufacture of WWCBs.

8.3 Materials and methods

8.3.1 Wood sample collection and preparation

Wood wool was obtained from two 8-year-old trees of brown salwood (*Acacia mangium*) grown in provenance trials at Damper in North Queensland, Australia (location shown in Chapter 4). Tree 1 was from the provenance PNG-North, and contained distinctly lighter-coloured heartwood than tree 2, which was from the provenance PNG-SE and contained darker coloured heartwood. Two end-matched logs each measuring 1.15 m in length were removed from each felled tree for handling and transport. From these, two end-matched billets, 0.46 m in length were cut from the middle. Billets from tree 1 were labelled with pink paint and those from tree 2 were labelled with purple paint, to keep track of the wood identity during transport, debarking and conversion into wood wool strands. The eight billets were shredded in the green condition into wood wool strands, as described in Chapter 3, keeping wood wool from the two trees separate. The wood wool was then air dried
under cover for around 2 weeks and grab-samples were then randomly taken for sorting to isolate and retain strands of pure heartwood. The heartwood strands were cut into pieces approximately 50 mm in length using scissors and kept for a minimum of 3 weeks in a conditioning room maintained at 20 ± 1°C and 65 ± 5% r.h. to condition the wood to a constant moisture content of 12% MC before use.

8.3.2 Pre-treatments for heartwood wood wool samples

The pre-treatments applied to samples of *A. mangium* heartwood strands are outlined in Table 8.1. The methods used to apply them are described below. Two samples of heartwood wood wool from each of the two trees (replicate) were subjected to each pre-treatment.

Table 8.1 Pre-treatments applied to *A. mangium* heartwood strands.

<table>
<thead>
<tr>
<th>Treatment category</th>
<th>Medium</th>
<th>Treatment Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Dip</td>
<td>SnCl(_2) 0.1 M in water</td>
<td>5 seconds</td>
</tr>
<tr>
<td>Chemical Dip</td>
<td>CaCl(_2) 0.1 M in water</td>
<td>5 seconds</td>
</tr>
<tr>
<td>Chemical Dip</td>
<td>FeCl(_3) 0.1 M in water</td>
<td>5 seconds</td>
</tr>
<tr>
<td>Water Repellent</td>
<td>Petroleum jelly 10% or 50% in mineral turpentine</td>
<td>2 min</td>
</tr>
<tr>
<td>Water Repellent</td>
<td>Linseed oil (LO) 20% or 70% in mineral turpentine</td>
<td>2 min</td>
</tr>
<tr>
<td>Water Repellent</td>
<td>Paraffin wax (PW) 10% or 30% in mineral turpentine</td>
<td>2 min</td>
</tr>
<tr>
<td>Water Repellent</td>
<td>LO (50%) + PW (30%) in mineral turpentine</td>
<td>2 min</td>
</tr>
<tr>
<td>Water Repellent</td>
<td>LO (25%) + PW (10%) in mineral turpentine</td>
<td>2 min</td>
</tr>
<tr>
<td>Extractive Removal</td>
<td>Water 23°C</td>
<td>1, 6, 12, 24, 48 h</td>
</tr>
<tr>
<td>Extractive Removal</td>
<td>Water 40°C</td>
<td>1, 6 h</td>
</tr>
<tr>
<td>Extractive Removal</td>
<td>Water 50°C</td>
<td>1, 6, 12, 24, 48 h</td>
</tr>
<tr>
<td>Extractive Removal</td>
<td>Water 60°C</td>
<td>1, 6 h</td>
</tr>
<tr>
<td>Extractive Removal</td>
<td>Water 80°C</td>
<td>1, 6 h</td>
</tr>
<tr>
<td>Extractive Removal</td>
<td>Water 100°C</td>
<td>1, 6 h</td>
</tr>
<tr>
<td>Extractive Removal</td>
<td>NaOH 0.01 M</td>
<td>5, 20 min</td>
</tr>
<tr>
<td>Extractive Removal</td>
<td>NaOH 0.01 M</td>
<td>1, 6, 12, 24, 48 h</td>
</tr>
<tr>
<td>Extractive Removal</td>
<td>acetone:ethanol:toluene mix 4:1:1</td>
<td>1, 6 h</td>
</tr>
<tr>
<td>Exposure to Radiation</td>
<td>Dry heat 105°C</td>
<td>24 h</td>
</tr>
<tr>
<td>Exposure to Radiation</td>
<td>Sunlight</td>
<td>200 h</td>
</tr>
<tr>
<td>Exposure to Radiation</td>
<td>Plasma chamber 10 watts</td>
<td>1 min</td>
</tr>
<tr>
<td>Exposure to Radiation</td>
<td>Plasma chamber 100 watts</td>
<td>1 min</td>
</tr>
</tbody>
</table>

8.3.2.1 Chemical dip

100 mL solutions of each chemical (SnCl\(_4\), CaCl\(_2\) and FeCl\(_3\)) were prepared at 0.1 M concentration using distilled water at room temperature. This ensured that the concentration of active ingredient was not affected by the degree of hydration (water content) of each chemical. A 5-g sample of heartwood strands was then immersed in the solution for 5 seconds and retrieved by
straining through a 2-mm sieve. The strands were separated, drained and dried on absorbent paper for one week.

8.3.2.2 Application of water repellents

The inexpensive and readily available water repellents; petroleum jelly, paraffin wax and linseed oil, were dissolved separately or as mixtures on a percentage volume basis as indicated in Table 8.1 in 15 mL of mineral turpentine. The paraffin wax was melted first before stirring it into the mineral turpentine solvent. The dissolved water repellent was then applied to a 5-g sample of wood wool by combining the solution and wood wool in a 375-mL capacity glass jar with a lid. The mixture was shaken and stirred for a few minutes to evenly coat the wood wool strands, after which the wood wool strands were separated and placed on absorbent paper to dry.

8.3.2.3 Removal of extractives

To heat and maintain water at the different temperatures and times indicated in Table 8.1, a 40-L capacity water-bath was used, shown in Plate 8.1(a). Covered beakers containing 500 mL of distilled water, two for each time period at a particular temperature, were heated to the target temperature in the water bath. Once the beakers of water reached the desired temperature a 7-g sample of heartwood strands was added, stirred, and heated in the covered beaker for the desired period of time. For the pre-treatment in boiling water, a beaker containing 500 mL of distilled water was brought to the boil on a hotplate, to which a 7-g sample was added and boiled for the desired period. Once the pre-treatment was complete, the strands were strained using a 0.5-mm sieve and transferred to absorbent paper to dry.

For alkali removal of extractives 500 mL aliquots of 0.01 M strength solutions of NaOH were prepared at room temperature in 600 mL beakers, two for each soaking period. To each beaker of solution a 10-g sample of wood wool was added, stirred, and soaked for the required period of time, after which the samples were strained, dried, conditioned and re-weighed as described above.

For solvent extraction of heartwood, 7 g of chopped wood wool was eluted for 1 or 6 hours with 500 mL of acetone, ethanol and toluene at the ratio 4:1:1 using a Soxhlet apparatus as shown in Plate 8.1(b). A sample from each tree was extracted separately. Once complete, the wood wool was removed from the Soxhlet apparatus and placed onto absorbent paper to dry.

The amounts of extractives removed by soaking at different temperatures were assessed using separate heartwood wood wool samples. Pre-conditioned (12% MC) samples of wood wool strands weighing 3 g from each tree were subjected separately to the aforementioned extractive removal treatments, drained on absorbent paper and oven dried at 105°C overnight to determine their oven-dry weight. The moisture content of the strands at the time of treatment was verified using the oven-dry method on sub-samples from the source material. This was used to calculate the oven-dry
weight of the un-extracted wood sample to in order to determine amount of extractives removed by each extraction treatment.

8.3.2.4 Exposure to pre-heating, sunlight or plasma

Pre-heating was done by placing 7 g of heartwood strands from each tree on separate Petri-dishes and heating in an oven set at 105°C for 24 hours. Sunlight exposure was carried out during the summer months (January and February) in Canberra, ACT. 7-g samples were exposed to sunlight over a period of around 40 days to accumulate approx. 200 hours of exposure. Plasma treatment involved placing 7 g of wood wool on Petri-dishes and exposing them to electrical plasma under vacuum, either 10 or 100 watts power, for one minute. The apparatus is shown in Plate 8.2.

(a)

(b)

Plates 8.1 (a) Water extraction of A. mangium heartwood strands using a temperature controlled water bath, and (b) Soxhlet apparatus used for solvent extraction of A. mangium heartwood strands.

Plate 8.2 The apparatus used to expose wood strands to plasma.
8.3.3 Preparation of hydration test samples

After exposure to their respective pre-treatments, samples were dried at room temperature for around one week (if the pre-treatment involved dipping or extractive removal) and then re-conditioned back to constant weight (MC = 12%) in the conditioning room at 20 ± 1°C and 65 ± 5% r.h. for approx. 3 weeks. All pre-treated samples of heartwood strands were reduced in weight to 5-g cement hydration test samples. The measurement of cement hydration temperature as influenced by each treated wood sample used the methodology described in Chapter 3. A total of 104 samples were measured.

8.3.4 Experimental design and statistical analysis

The experiment was designed to assess the effects of four different kinds of wood pre-treatment on the compatibility of *A. mangium* heartwood with portland cement. Wood-cement compatibility was expressed in terms of Hydration Rate, (total increase in temperature in the wood-cement mix as a function of time taken, °C/h). The four broad classes of pre-treatment included ‘Chemical Dip’ (3 treatments), ‘Water Repellent’ (4 treatments), ‘Extractive Removal’ (15 treatments), and ‘Exposure to Radiation’ (3 treatments). Each treatment contained four heartwood samples (two from each tree). Four samples containing cement only and 4 containing untreated wood + cement used as controls. The statistical analysis used a nested factorial design to assess the effects of treatment class and the effects of different treatments within each class. The average effects on compatibility of each treatment class are shown in Figure 8.1. Because of the very different numbers of samples represented in each treatment class, means have been compared using 95% confidence interval for each. Non-overlapping means are significantly different at the 1% probability level. The effects of each treatment are graphed separately for ‘Extractive Removal’ and ‘Non-Extractive Removal’ treatment types (incorporating ‘Chemical Dip’, ‘Water Repellent’ and ‘Exposure to Radiation’) in Figures 8.1 and 8.2, respectively, with LSD used to compare means.

8.4 Results and discussion

8.4.1 Treatment class

As expected, pre-treatment type, and the individual pre-treatments had highly significant (p < 0.001) effects on the compatibility of *A. mangium* heartwood with cement. The average effect on compatibility of *A. mangium* heartwood (expressed as Hydration Rate, °C/h) is shown in Figure 8.1. Overall, a pre-treatment that either removed extractives or added a cement-setting accelerator proved to be the most effective of the four different classes of heartwood pre-treatments. For these two treatment types the average increase in compatibility was over 100%, i.e. from 1°C/h to over
2°C/h, and they conferred significantly greater compatibility to *A. mangium* heartwood than did the application of water repellents to the wood wool, or exposure of wood wool to heat, sunlight or plasma.

![Graph showing average effect on compatibility of *A. mangium* heartwood of different types of wood pre-treatment; bars indicate 95% confidence interval.](image)

Figure 8.1 Average effect on compatibility of *A. mangium* heartwood of different types of wood pre-treatment; bars indicate 95% confidence interval.

Water repellents and exposure to radiation resulted in relatively minor increases in wood-cement compatibility, and the means were not significantly different from those of the untreated heartwood samples. Pre-dipping the heartwood strands in a solution of cement-setting accelerator doubled the hydration rate of cement containing the heartwood; however the high variation arose from the poor result achieved from dipping heartwood strands in CaCl₂ solution compared that of dipping in FeCl₃ or SnCl₄.

### 8.4.2 Extractive removal pre-treatments

Of the different types of wood pre-treatments tested, the removal of inhibitory extractives was the most effective means of improving the compatibility of the wood with portland cement. Figure 8.2 shows the average effects on wood-cement compatibility of pre-soaking heartwood strands in water at different temperatures, NaOH and the ethanol/acetone/toluene mix (‘Alcohol’) for 1 and 6 hours. As expected, increasing the water temperature resulted in a steady increase in the compatibility of the heartwood with cement, due possibly to the removal of greater quantities and/or a wider range of inhibitory heartwood extractives.
Pre-soaking the heartwood strands in water at 23°C resulted in approximately 50-60% increase in compatibility with cement, whereas pre-soaking in water at 50°C increased compatibility by over 100%, significantly greater than the compatibility of cold-water-soaked wood wool (Figure 8.2). Boiling the heartwood strands in water or pre-soaking in dilute NaOH at ambient temperature increased the compatibility of the heartwood by 250% (R = 2.5°C/h).

Apart from its immediate effect on initial setting of cement over 24 h, extractive removal is also suggested to be beneficial to the longer term durability of wood-cement composites since it involves the removal of organic acids (which include phenolic constituents such as tannins) that can slowly attack the bonds between wood and cement, causing reduced composite strength over time (Fraser 1977, Moslemi 1989, Blankenhorn et al. 1994).

The organic solvent mix was about as effective as pre-soaking in water at 40-50°C but not as effective as warmer water or dilute alkali. 0.01 M NaOH (pH 11-12) was the most effective medium for removing inhibitory extractives over a period of 1 to 6 h, and significantly better than 'Alcohol' (Figure 8.2). The reason for this is unclear, but according to Hillis (1987), solvent type can interact strongly with wood species and age, influencing its ability to remove all extraneous materials from the wood. For example age-related polymerisation of heartwood polyphenols reduces their solubility in many organic solvents including methanol, as indicated by the increasing proportion of methanol-insoluble extractives towards the inner heartwood of Quercus rubra (Nelson 1975).

![Image](image-url)
Phenolic heartwood extractives occur largely in a less soluble polymerised form, with monomeric polyphenols found in largest quantities at the outer (younger) heartwood boundary of tree stems (Hillis 1987). Large quantities of polymeric, intractable condensed tannins can be found in the heartwoods of acacias, e.g. *A. sparsiflora* (Clarke-Lewis and Dainis 1967). Furthermore, insoluble membranes lining cell walls can impede the removal of much of the alcohol-soluble (in this case ether) extractives from cell lumens, resulting in underestimation of ether-soluble extractive content (Erdtman 1943).

The capacity of alkali to remove greater quantities of inhibitory extractives is supported by the fact that among many woods, especially eucalypts, the dilute-alkali-soluble heartwood extractive content can be up to 15 times higher than ethanol soluble extractive content, particularly for those species with leucoanthocyanidin-containing red heartwoods, which require dilute alkali (0.1M) to remove most of the extractives (Hillis 1987). The polyphenols in *A. mangium* heartwood also belong to the leucoanthocyanidin series (Clarke-Lewis et al. 1961, Tachi et al. 1989), and the same may therefore be true for *A. mangium* heartwood also. *A. mangium* polyphenols are discussed further in Chapter 9. Data from Campbell and Bamford (1939) presented in Thompson (1969) showed that 1% NaOH (0.01M) will remove around 15% of the oven-dry weight of loblolly pine wood (*Pinus taeda* L.), whereas cold water, hot water and alcohol-benzene will remove 2.3, 3.5 and 1.7% w/w of extractives, respectively. Alkali is particularly effective because it partially destabilises lignin, exposing interspersed hemicelluloses and other extractive materials to further leaching (Hoffmann and Parameswaran 1976). Indeed, Jegasethwaran (1989) found pre-treatment of *A. mangium* flakes in 1% NaOH to be the most effective extraction pre-treatment for producing good quality CBPs from this species.

Running counter to its beneficial effect on extractive removal and wood-cement compatibility of *A. mangium* heartwood, exposure to alkali has a significant effect on wood strength that is exacerbated by increasing length of exposure, and is far greater than that of acid at the same concentration (Gobie 1954, Ross 1956, Stamm 1964). Prolonged exposure to strong alkali (2 to 10%) at room temperature will result in the dissolution of part of the hemicellulose fraction, with up to 20% of the lignin being converted to soluble alkali-lignin complexes, resulting in up to 50-60% loss in strength (Wise and Jahn 1952, Wanggaard 1966). For this reason, the concentration of NaOH used to extract *A. mangium* heartwood was kept to the minimum necessary to have a beneficial effect on wood-cement compatibility. According to data presented in Kollmann (1951), the weakening effect on wood caused by exposure to alkali is not significant below pH 10, which is lower that that in the environment of cement paste or 0.01 M NaOH.

Figure 8.3 illustrates the effects of solvent type and temperature as well as duration of extraction on the improvement of the compatibility of *A. mangium* heartwood with portland cement. The effect
of increasing water temperature during soaking on the compatibility of heartwood with cement can be clearly seen, and was discussed earlier. Duration of extraction was also a significant determinant of compatibility, particularly when NaOH or water at lower temperatures was used. If water at 23°C was used, compatibility with cement was generally increased with increasing duration of soaking, with maximum effect occurring after 24 h of soaking. No change in compatibility resulted from soaking the heartwood strands for 5 min in cold water. After 24 h of soaking, hydration rate reached only 1.8°C/h, or 'moderate' compatibility with cement using the ranking system adopted in Chapters 4 and 5. This suggests a limit to the amount and/or type of inhibitory extractives that can be removed by water at 23°C. The optimum duration for pre-soaking in water at 50°C and 100°C was reduced to 6 h, with no further increase in compatibility to be gained by soaking for longer periods of time (at least at 50°C). Similarly, a study by Eusebio et al. (2000b) on strength properties of WWCB made from soaked A. mangium wood wool found no significant increase in MOR of boards if soaking time was extended from 6 h to 12 or 24 h.

The maximum hydration rate was achieved by pre-soaking the wood wool in NaOH for 1 h, after which no further increase was achieved. In fact the compatibility of the wood underwent a steady decline with increasing exposure to mild alkali. A similar trend was observed by Blankenhorn et al. (1994) whereby the compressive strength of red oak (Quercus rubra L.), and sugar maple (Acer saccharum Marsh.) wood flour-cement plugs decreased significantly with increased duration of

![Figure 8.3](image-url)
exposure of the wood flour (and accompanying weight loss) to 0.25% NaOH. These observations were explained by the accumulation of alkali degradation products in and on the wood surface that had adverse effects on its compatibility with cement. This phenomenon, along with the deterioration in wood strength with increasing exposure to alkali, is likely to adversely affect the strength of cement-bonded composites manufactured using alkali-treated wood; however no studies are available to confirm this.

Removal of extractives by hot water has been found in several other studies to result in significant increases in wood-cement compatibility of inhibitory woods and their performance in wood-cement composites (Schwarz and Simatupang 1984a, Zhengtian and Moslemi 1986, Moslemi and Lim 1984, Moslemi et al. 1983, Hachmi and Moslemi 1989). Cold water soaking for 48 h was, however, insufficient to remove enough inhibitory extractives from flakes of *E. camaldulensis* to make cement-bonded particleboards of acceptable quality from this species (Yasin and Qureshi 1990). Their study found that soaking flakes in hot water for 1 h was sufficient to facilitate the production of boards of acceptable strength and dimensional stability. Likewise for inhibitory teak (*Tectona grandis*) wood, Sutigno (2000) found that soaking wood wool in hot water for 1 h removed around 30% more extractives than did soaking in cold water for 24 h, and resulted in significantly stronger WWCBs. Badejo (1989) showed that the higher the water temperature (50 or 75°C), the higher the resulting strength of CBPs made from teak. Some studies indicate that the amount of hot-water-soluble extractives in woods, notwithstanding the confounding effect of extractive chemical composition, is far more closely correlated with their inherent compatibility with portland cement than the quantity of extractives removed in cold water (Yasin and Qureshi 1990, Hachmi and Moslemi 1990).

Figure 8.4 indicates the effect of temperature on the amount of extractives removed from *A. mangium* heartwood by water. Even after only 10 min of treatment with hot water (100°C), more extractives were removed than after 48 h soaking at 23°C or 24 h soaking at 50°C. This explains the high compatibility attained by the heartwood (>2°C/h) after pre-treatment with hot water for just 5 to 10 min. As can be seen from Figures 8.2 and 8.3, the quantity of extractives removed and subsequent compatibility with cement of *A. mangium* heartwood was still lower after 48 h of pre-soaking in water at 23°C than that produced by pre-treating with water at 100°C for a few minutes. This may help explain why sound WWCBs made from *A. mangium* wood wool soaked in cold water could not be produced without the further aid of cement-setting accelerators in previous studies by Soriano et al. (1997), Cabangon et al. (1998) and Eusebio et al. (2002b).

Treatment with very dilute NaOH (0.01M) at ambient temperature had a similar effect as treatment with water at 50°C for the same period of time. Note from Figure 8.4 that hot water removed a greater quantity of extractives from the heartwood than did the alkali, irrespective of
treatment time, whereas dilute alkali resulted in a greater increase in compatibility of the heartwood with cement than did pre-soaking in hot water for 1 h, as shown in Figure 8.3. The reason for this anomaly is unclear since this was the only instance where alkali-treated wood wool was higher in compatibility than the hot-water-treated wood. In all cases, the highest rate of extractive loss occurred within the first 6 hours of treatment. These results suggest that soaking in cold water for between 12 and 24 h would be necessary to remove the extractives that may otherwise be removed in the dilute alkali present in cement paste (pH 11-12 or 0.01 M) and inhibit cement hydration. The same level of extractive removal could be achieved over a much shorter time period by soaking the wood wool in water at 50°C for between 1 and 6 h. If hot water (at or near 100 °C) were available then this could be achieved within a few minutes, possibly by passing the wood through a bath as part of a continuous automated manufacturing process.

Compatibility of *A. mangium* appears to have responded well to warm or hot water extraction. This is in contrast to certain other kinds of inhibitory hardwoods, such as hickory, sweetgum and yellow poplar, which were shown by Moslemi and Lim (1984) to retain only moderate compatibility even after hot-water soaking. There are even more extreme cases where extraction in hot water or alkali makes little difference to the extremely low compatibility of some tropical hardwoods with portland cement. An outstanding example of this is the African hardwood, chanfuta (*Afzelia quarzenzis* Welw.), which remained a strong inhibitor of cement hydration even after extraction in boiling water for 2 h or soaking for 24 h in a strong (10g/L) solution of NaOH. (Alberto et al. 2000),

![Figure 8.4](image)

Figure 8.4 Effect of extraction of *A. mangium* heartwood wood wool in water at different temperatures and in 0.01 M NaOH at ambient temperature (20°C) on the amount of extractives removed from the dry weight of wood.
**8.4.3 Non-extractive removal pre-treatments**

Pre-treatments which did not involve the removal of extractives, (i.e. heating, plasma modification or the addition of water repellents such as waxes and oils) all increased wood-cement compatibility but only to a relatively small and usually insignificant degree, as shown in Figure 8.5. Pre-dipping the wood wool in a solution containing a cement-setting accelerator was a simple approach that had been successfully used to make *Acacia mearnsii* wood wool suitable for WWCB slab production by Flawes and Chittenden (1967). CaCl₂ was used to good effect in this particular species, however pre-dipping in this accelerator here had little effect on the compatibility of *A. mangium* heartwood. Of the chemical dips, SnCl₄ and FeCl₃ significantly (*p < 0.001*) improved the compatibility of the heartwood whereas CaCl₂ had no effect. Average hydration rate achieved by pre-treating heartwood with SnCl₄ was almost 2.5°C/h whereas after pre-treatment with CaCl₂, hydration rate was 1.1°C; not significantly greater than that of untreated wood wool. The amount of CaCl₂ added to the wood wool may have been too small to accelerate cement hydration. In contrast, pre-treatment with solutions of SnCl₄ and FeCl₃ of the same concentration as that of CaCl₂ resulted in an increase in compatibility greater than that produced by pre-soaking the wood wool in water at 23°C for 24 to 48 hours. The increase in compatibility produced by dipping in SnCl₄ or FeCl₃ was similar to that achieved by pre-soaking in hot water (80-100°C) for 1 to 6 hours. This marked increase in the compatibility of the heartwood with cement is likely to have resulted from chemical interaction between the accelerator and inhibitory heartwood polyphenols. This question is examined further in relation to utilising *A. mangium* wood wool for WWCBs in Chapters 9 and 10.

![Figure 8.5](image-url)  
**Figure 8.5** Effect on wood-cement compatibility of different pre-treatments that do not involve the removal of extractives from *A. mangium* heartwood.
Of the water repellents, the addition of petroleum jelly to wood wool resulted in the greatest increase in the compatibility of the heartwood, a slight but significant increase in hydration rate from 1 to 1.43°C/h. This suggests that a fine layer of petroleum jelly may have retarded the leaching of extractives into the cement paste to a certain degree. Pre-treatment of wood wool with water repellents was expected to produce a greater increase in wood-cement compatibility than the results found here. Pre-treatment of highly inhibitory larch (Larix ssp.) wood with hydrophobic substances has been shown to accelerate cement hardening and significantly improve bending strength of cement-bonded boards by ‘sealing in’ the inhibitory extractives (Yamagishi et al. 1980). Contrary to expectations, none of the other water repellents resulted in any significant increase in the compatibility of A. mangium heartwood with cement. It is possible that the quantity of water repellent added to the heartwood strands was insufficient to block the leaching of inhibitory heartwood constituents into the surrounding cement paste. Alternatively, the oils added to the wood wool surface may have been degraded by the alkali in the cement paste. The wax might have given better protection against leaching but it tended to form globules on the surface of the wood wool and hence did not evenly coat the surface.

Heating, sunlight and plasma pre-treatments resulted in no significant increases in compatibility of the heartwood with cement. This is probably because they did not remove, modify or block access by cement paste to inhibitory extractives in the wood. In contrast to our results, exposure to sunlight is known to further reduce wood-cement compatibility, resulting in poor setting of cement adjacent to exposed plywood formwork (Yoshimoto et al. 1966, Yoshimoto and Minami 1975, 1976b). This was suggested by the authors to be caused by photo-induced changes in chemical constituents of wood, resulting in increased quantities of inhibitory low molecular weight sugars (particularly arabinose) in and on the wood surfaces of both sapwood and heartwood. Although the surface of sunlight-exposed A. mangium heartwood strands were slightly weathered and grey in appearance, this suggested phenomenon does not appear to have further reduced the already low compatibility of A. mangium heartwood.

8.5 Conclusions

The investigation of the effect of different kinds of wood pre-treatments on the compatibility of A. mangium heartwood with portland cement revealed that only those that involved the partial or total removal of soluble inhibitory extractives were effective in increasing the compatibility of the heartwood with cement. Based on the poor results of previous studies that have manufactured WWCBs from pre-soaked A. mangium, it was hypothesised that cold-water soaking may not remove sufficient quantities of inhibitory extractives from A. mangium wood wool prior to making boards. In accordance with this hypothesis, pre-soaking A. mangium heartwood in water at 23°C for
48 h removed only half the quantity of extractives that was removed by pre-soaking in mild alkali (NaOH 0.01 M) for 48 h, or soaking in boiling water for 6 h. Post-treatment compatibility of heartwood strands soaked in cold water with cement was therefore one third to one half less than that of strands treated with hot water or dilute alkali. Regardless of extraction duration, the hydration rate of cement containing A. mangium heartwood pre-soaked in water at 23°C never exceeded 2°C/h.

Because pre-soaking of wood wool uses large quantities of fresh water, which requires disposal after use, some alternative pre-treatments that did not involve extractive removal were also investigated. The pre-treatment of wood by direct heating or exposure to sunlight or plasma had little effect on the low compatibility of the heartwood, indicating that these pre-treatments did not remove or chemically interfere with the cement-poisoning action of heartwood polyphenols. The addition of water-repellent substances such as waxes and oils to the wood wool surface was attempted with a view to creating a physical barrier between the wood and cement and thereby restricting the leaching effects of cement paste at the wood surface. This technique was quite complicated, requiring that the water repellent be pre-dissolved in a flammable solvent such as kerosene or mineral turpentine and ensuring that the wood wool strands were evenly coated with the emulsion by using an atomising spray. Contrary to expectations, this approach was only mildly effective and did not greatly improve the compatibility of A. mangium heartwood with cement. Furthermore, it was not possible to evenly coat the wood wool strands with the wax emulsion. Other reasons as to why the water repellents, including oil, were not effective could be insufficient quantity and/or the degradation of the coating by the alkali in the cement paste.

Pre-dipping the wood wool in a mineralising solution of cement-setting accelerator was found to be almost as effective at improving the compatibility of the heartwood as extractive removal; however, this depended very much on which compound was used. Pre-dipping in CaCl₂ produced no change in the inhibitory effect of the heartwood, whereas treatment using acidic solutions containing FeCl₃ and SnCl₄ proved to be far more effective, more so than pre-soaking the wood wool in cold water. Reasons for the differences between CaCl₂ and the other two chlorides, and the possible effects of different kinds of accelerators on heartwood compatibility are investigated further in Chapters 9 and 10. The experiments in Chapter 9 deal specifically with testing the capacity of a wider range of cement-setting accelerators to ameliorate the low compatibility of unsoaked A. mangium heartwood with cement. Chapter 10 reports on the manufacture of good quality WWCBs from this species without the need to pre-soak the wood wool.
Chapter 9 Additives to improve the compatibility of *A. mangium* heartwood with portland cement.

9.1 Introduction

In Chapter 8 it was shown that the only pre-treatments likely to be effective in improving the low compatibility of *A. mangium* heartwood with portland cement were the removal of inhibitory extractives from the wood or the addition of compounds that ameliorate the inhibitory extractives present in the heartwood, allowing accelerated hydration of cement. Pre-soaking the wood wool in hot water or dilute alkali were the most effective pre-treatments, however these are less practical than soaking in cold water. Although cold water soaking of wood wool in large, shallow baths is currently used to prepare wood wool for the manufacture of WWCB in the Philippines (Pablo 1989, 1996, Pablo et al. 1996), results in Chapter 8 suggested that cold water soaking may not remove sufficient extractives to permit the manufacture of good quality WWCBs from *A. mangium*. Pre-soaking of wood also adds an extra step to the manufacturing process, requiring extra time, space, and the need to dispose of tannin-laden water (Youngquist 1999). The availability of large quantities of fresh water required for pre-soaking of wood wool may also be disrupted at certain times of the year, thus causing the suspension of manufacturing operations for WWCB plants that rely on this form of wood pre-treatment. It is necessary therefore to investigate alternative wood pre-treatments that can effectively ameliorate the inhibitory effects of the *A. mangium* heartwood on cement setting.

Results in Chapter 8 also showed that pre-treating *A. mangium* wood wool with a compound that may interact with heartwood polyphenols and accelerate cement hydration could be a simple and effective way of improving its low compatibility with cement. It has long been known that simple compounds such as CaCl₂, AlCl₃, and MgCl₂ judiciously added to portland cement will accelerate the hydration reactions, particularly the tri-calcium silicate (C₃S) phase, reducing setting time and, in some cases, increasing maximum hydration temperature (Lea 1971, Ramachandran 1994). Such compounds, in particular CaCl₂, have been successfully used to improve the strength properties of WWCB (e.g. Kayahara et al. 1979, Lee and Short 1989, Soriano et al. 1997). Pre-dipping wood wool in aqueous solutions of simple compounds such as 2 to 3% Na₂SiO₃ and/or CaCl₂ has been found to significantly improve the quality of commercially produced light-weight wood wool boards made from a range of woods, including acacia (Flawes and Chittenden 1967), southern pine and sweetgum (Lee 1984, Lee and Hse 1993).

However, pre-dipping *A. mangium* heartwood wood wool in CaCl₂ was found to be relatively ineffective in counteracting the inhibition of cement hydration by the extractives found in *A. mangium*. This same problem has also been observed by Tachi et al. (1988), who found that MgCl₂
was far more effective than CaCl₂ at counteracting the inhibitory effects of *A. mangium* heartwood on cement hydration. Pre-treatment with CaCl₂ has also been shown to be ineffective in improving the properties of WWCBs manufactured from pre-soaked *A. mangium* wood wool (Eusebio et al. 2002b). These observations suggest that compounds like CaCl₂, which simply accelerate cement hydration, may not be sufficient to enable adequate consolidation and strength development of wood-cement composites manufactured from wood species with high polyphenol contents, such as *A. mangium*. Compounds with the ability to chemically interact with water- and alkali-soluble inhibitory polyphenolic constituents of the heartwood may be necessary to enable the manufacture of WWCB and other wood-cement composites from untreated *A. mangium* wood. This study was therefore designed to test the effects of such compounds on the hydration of cement and compare them with conventional accelerators such as CaCl₂.

### 9.2 Aims and objectives

The aim of the research presented in this Chapter was to test a wide range of inorganic compounds for their ability to improve the strength of hydration of portland cement containing inhibitory *A. mangium* heartwood strands. It was hypothesised that compounds which only accelerate cement setting but do not chemically interact with *A. mangium* heartwood polyphenols may be less effective in counteracting the inhibitory effect of the heartwood on cement hydration. Specific objectives were to:

1. Identify simple, effective compounds that could be used in low quantities to manufacture quality WWCBs from untreated *A. mangium* wood; which has not previously been possible. The addition of one or more simple water-soluble compounds will hopefully eliminate the need for any billet or wood wool pre-treatments such as soaking, prolonged storage or the addition of a non-water-soluble repellent coating of strands prior to the manufacture of WWCBs.

2. Determine whether the most effective compounds chemically interact (via precipitation) with heartwood polyphenols from *A. mangium* in an alkaline medium.

### 9.3 Materials and methods

The laboratory scale hydration test developed by Sandermann and Kohler (1964) has been successfully adopted by subsequent researchers as a means of testing the effects of different chemicals on cement hydration. In studies by Zhengtian and Moslemi (1985) and Wei et al. (2000b) additives were screened using this method to try to ameliorate the highly inhibitory effects on cement hydration of extractives from other wood species such as western larch (*Larix occidentalis* Nutt.) and Chinese red birch (*Betula albo-sinensis*). Cement hydration tests are used in
this study as well, and wood wool was produced and prepared for testing as described in Chapters 3 and 8 using the same two *A. mangium* trees sourced from North Queensland.

9.3.1 Preparation of compounds

All compounds were prepared for testing at the same concentration, i.e. 0.1 M. Previous studies that have compared the effects of accelerators on cement hydration (e.g. Zhengtian and Moslemi 1986) or on the properties of cement composites (e.g. Wei *et al.* 2000b) have added and compared compounds at a fixed percentage of cement weight regardless of compound molecular weight and its water content. The concentration of active ingredient in a cement admixture affects its efficacy, and therefore compounds should be compared at the same concentration (Thomas 1987). Compounds tested in this study were therefore prepared and added to cement hydration samples at the same molar concentration of 0.1 M. A second deficiency of previous studies is that none of them have tested the effect of each compound on the hydration of pure cement on its own, making it difficult to estimate the degree to which the compounds accelerate cement hydration in the absence of wood.

In total, 137 inorganic compounds were tested and are shown in Tables 9.2 and 9.3. These included selected chlorides, sulphates, nitrates, acetates, oxides, carbonates and/or fluorides of Ag⁺, Al³⁺, Ba²⁺, Ca²⁺, Co²⁺, Cr³⁺, Cu⁺, Cu²⁺, Fe²⁺, Fe³⁺, K⁺, Li⁺, Mg²⁺, Mn²⁺, Na⁺, Ni²⁺, Pb²⁺, Sr²⁺, Zn²⁺ and Zr⁴⁺. Several miscellaneous compounds including citrates, tartrates, bromides and oxalates of Na⁺ and K⁺ were also assayed. The solubility in water (20°C) of each compound was checked against its properties as given in Weast (1970) to determine whether to add it to the cement hydration sample as a solid or liquid. The water-soluble compounds were first dissolved in distilled water at room temperature to 0.1 M strength in a 250-mL capacity volumetric flask. Four 40-mL aliquots of the compound solution were poured into separate 50 mL capacity vials for addition to cement hydration samples: two for addition to wood–cement samples and two for addition to samples containing cement only. The two vials to be added to wood–cement samples were prepared with an extra 0.7 mL of distilled water per gram of wood used, in accordance with the recommendations of Hachmi *et al.* (1990).

Those compounds that were insoluble in cold water were pulverised using a mortar and pestle and four equal amounts were weighed out into four 5-mL capacity vials for addition as a dry powder to cement hydration samples. The amount of each compound used in a hydration test corresponded to the amount that would be present in 40 mL of a 0.1 M solution if the compound were soluble in water. This ensured consistency in concentration of additives across soluble and insoluble compounds.
9.3.2 Addition of compounds to cement hydration samples

Each aliquot of compound solution was first mixed with 100 g of fresh dry portland cement Type I (Blue Circle Southern brand, Batch No. 090MA99) at 20°C in a sealable 'Dalgrid' polyethylene bag by hand kneading for about 2 minutes. Each sample of insoluble compound was added as a dry powder to 100 g of dry cement in a 'Dalgrid' polythene bag and evenly tumbled though the cement, after which distilled water was added to mix the cement and compound slurry as described above. For samples containing only pure cement or cement + compound without wood, 40 mL of distilled water or compound solution was added. For each sample to which wood was to be added, 43.5 mL of distilled water or compound solution was first added to the cement and mixed, then 5 g of chopped A. mangium heartwood wool was added and massaged though the cement slurry until evenly coated. The measurement of cement hydration temperature and the derivation of wood-cement compatibility indices were undertaken as described in Chapter 3.

9.3.3 Experimental design and statistical analysis

In addition to four cement control (cement only) and four wood-cement control samples, the 137 compounds were tested with two replicates for pure cement and two replicates (trees) for wood-cement samples. The experimental design contained a nested structure of cement and cement + wood hydration samples within the 'compound' stratum. In each daily six-sample run of hydration samples, three compounds were tested at random. For each compound, two matched samples were run, one with cement + compound and the other with cement + compound + wood. All compounds were run in random order for replicate 1 (cement) and tree 1 (cement + wood) over the first 46 days followed by replicate 2 and tree 2, again randomised by compound over the next 46 days.

Compounds were ranked in order of their efficacy in improving the strength (expressed as \(T_{\text{max}}\) and hydration rate) of the exothermic reaction of cement containing A. mangium heartwood strands. The ranking for the 20 most effective compounds in improving the compatibility of A. mangium heartwood with cement is shown in Table 9.1, and the rankings of all of the compounds tested in this study according to their effect on the hydration rate of cement containing A. mangium heartwood strands are shown in Tables 9.2 and 9.3. Compounds were also assessed comparing the compatibility indices \(T_{\text{max}}\) and hydration rate of cement + wood + compound with those of cement + compound only. The effects of different compound types (separated by anion and cation content) on hydration rates of pure cement and of wood-cement mixes are shown in Figures 9.1 and 9.2, respectively. LSD is shown for comparison of means. For each compound the \(T_{\text{max}}\) and hydration rate of the wood-cement mix were plotted against those obtained for samples containing cement + compound only and are shown in Figures 9.3 and 9.4.
9.3.4 Determination of polyphenol-metallic complexes

Freshly mixed cement slurry is highly alkaline (pH 11-12) and increases in alkalinity with time as calcium hydroxide is produced (Lea 1971, Taylor 1997). This has a strong leaching effect on wood and will dissolve and remove more than just the water-soluble heartwood extractives (Goldstein 1984). Therefore, dilute NaOH matching the alkalinity of cement paste was used to obtain a leachate containing alkali-soluble inhibitory polyphenols from A. mangium heartwood. A small amount of soluble compound solution was added to diluted heartwood extract to test its ability to form an insoluble precipitate with heartwood polyphenols in alkaline medium. To obtain the heartwood leachate 10 g of chopped A. mangium heartwood wool was placed in a beaker containing 300 mL of alkaline solution at pH 11.5-12 (0.01 M NaOH) and soaked in a waterbath for 6 h at 25°C. After soaking, the wood wool was removed and the leachate was filtered using a water tap aspirator through a 40-mm-diameter sintered glass crucible (frit no. 3) to remove any sludge and solids such as wood fibre, as described in Chapter 3. 100 mL of the dark leachate was then diluted with 150 mL of 0.01 M NaOH to produce a transparent brown liquid in which any insoluble precipitate if formed could be clearly seen. 3-mL aliquots of this solution were placed in small 7-mL capacity glass vials to which 2 drops of compound solution was added. The strength and colour of any precipitate and the time taken to form the precipitate were noted. To illustrate the effect of complexes formed with heartwood polyphenols in the extract, 10 drops of selected compound solutions were added to diluted extract in 25 mL test-tube bottles, as shown in Plate 9.2.

9.4 Results and discussion

9.4.1 Compound ranking

Several of the 137 compounds tested markedly strengthened the hydration of cement containing inhibitory A. mangium heartwood wool. Approximately 50 of the compounds raised the average \( T_{\text{max}} \) and hydration rate of cement containing wood wool from 31°C and 0.5°C/h to over 37°C and doubled the hydration rate to \( \geq 1 \)°C/h. The 20 compounds that resulted in the greatest increase in hydration rate for cement containing inhibitory A. mangium heartwood strands were all water-soluble and are listed in Table 9.1, and all of the compounds tested can be found in Table 9.2 and 9.3, depending on whether they accelerated or retarded the hydration of pure cement. CaCl\(_2\) performed moderately well as an accelerator in the hydration tests; however several compounds were found to be more effective than CaCl\(_2\) at increasing the strength of cement hydration in the presence of A. mangium heartwood (Table 9.1). The top 6 compounds that resulted in R > 3°C/h were SnCl\(_4\), AlCl\(_3\), FeCl\(_3\), Zr(NO\(_3\))\(_4\), Al(NO\(_3\))\(_3\) and MgCl\(_2\). The capacity of each compound to precipitate A. mangium heartwood polyphenols is ranked from 0 (no precipitate) to 5 (very strong
precipitate formed within seconds). In accordance with the suggested hypothesis, all compounds in the top 6 except MgCl$_2$ (ranked 6th) strongly interacted with A. mangium heartwood polyphenols by forming an insoluble precipitate in alkaline medium. CaCl$_2$, which formed a very weak precipitate, was ranked 13th in terms of hydration rate, lower than two other compounds that also formed no precipitate, including MgCl$_2$ and BaCl$_2$.

In a study by Zhengtian and Moslemi (1985), 30 compounds, mainly chlorides and sulphates, were tested for their effects on the hydration of portland cement containing western larch (Larix occidentalis) heartwood flour. The heartwood of western larch is one of the least compatible with cement (Sandermann and Kohler 1964, Hofstrand et al. 1984). The most effective compounds for ameliorating cement inhibition identified by Zhengtian and Moslemi (1985) were the chlorides SnCl$_2$, FeCl$_3$, AlCl$_3$ and CaCl$_2$, in accordance with findings here. A more recent study by Wei et al. (2000b) using birch (Betula sp.) also found FeCl$_3$, SnCl$_2$ and CaCl$_2$ to be the most efficient accelerators of cement hydration in wood-cement mixes. However neither of these studies tested the effects of the additives on pure cement containing no wood sample.

Table 9.1 Top 20 compounds ranked by hydration rate of wood-cement mix, with corresponding maximum hydration temperature and time.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hydration rate ($^\circ$C/h)</th>
<th>Max. Temp. ($^\circ$C)</th>
<th>Time (h)</th>
<th>Precipitate*</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl$_2$</td>
<td>5.3</td>
<td>59.9</td>
<td>6.9</td>
<td>5</td>
</tr>
<tr>
<td>AlCl$_3$</td>
<td>4.5</td>
<td>53.6</td>
<td>6.9</td>
<td>5</td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td>3.6</td>
<td>51.5</td>
<td>8.1</td>
<td>5</td>
</tr>
<tr>
<td>Zr(NO$_3$)$_4$</td>
<td>3.5</td>
<td>54.6</td>
<td>7.2</td>
<td>5</td>
</tr>
<tr>
<td>Al(NO$_3$)$_3$</td>
<td>2.9</td>
<td>48.4</td>
<td>6.4</td>
<td>4</td>
</tr>
<tr>
<td>MgCl$_2$</td>
<td>2.8</td>
<td>48.9</td>
<td>9.5</td>
<td>0</td>
</tr>
<tr>
<td>BaCl$_2$</td>
<td>2.6</td>
<td>47.2</td>
<td>9.4</td>
<td>0</td>
</tr>
<tr>
<td>NiCl$_2$</td>
<td>2.5</td>
<td>46.6</td>
<td>9.2</td>
<td>4</td>
</tr>
<tr>
<td>Al$_2$(SO$_4$)$_3$</td>
<td>2.3</td>
<td>48.5</td>
<td>8.9</td>
<td>4</td>
</tr>
<tr>
<td>Fe(NO$_3$)$_3$</td>
<td>2.3</td>
<td>47.3</td>
<td>8.9</td>
<td>4</td>
</tr>
<tr>
<td>SrCl$_2$</td>
<td>2.1</td>
<td>47.1</td>
<td>10.0</td>
<td>0</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>2.1</td>
<td>45.4</td>
<td>9.9</td>
<td>1</td>
</tr>
<tr>
<td>PbCl$_2$</td>
<td>2.1</td>
<td>46.0</td>
<td>22.9</td>
<td>5</td>
</tr>
<tr>
<td>Na$_2$CrO$_7$</td>
<td>2.0</td>
<td>47.8</td>
<td>11.4</td>
<td>4</td>
</tr>
<tr>
<td>Ni(C$_2$H$_3$O$_2$)$_2$</td>
<td>1.9</td>
<td>46.6</td>
<td>11.0</td>
<td>3</td>
</tr>
<tr>
<td>Co(NO$_3$)$_2$</td>
<td>1.9</td>
<td>44.2</td>
<td>13.9</td>
<td>4</td>
</tr>
<tr>
<td>AgNO$_3$</td>
<td>1.9</td>
<td>47.4</td>
<td>11.6</td>
<td>4</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>1.8</td>
<td>45.7</td>
<td>11.4</td>
<td>4</td>
</tr>
<tr>
<td>Ba(NO$_3$)$_2$</td>
<td>1.8</td>
<td>43.4</td>
<td>10.4</td>
<td>0</td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$</td>
<td>1.7</td>
<td>44.6</td>
<td>10.7</td>
<td>0</td>
</tr>
</tbody>
</table>

*0 none, 1 very slight, 2 weak, 3 moderate, 4 strong, 5 very strong.

CaCl$_2$, a by-product of sodium carbonate manufacture, has long been favoured as a cement setting accelerator because of its low cost, availability and predictability (Lea 1971, Taylor and Fuessele 1994, Taylor 1997). The anion-cation combination in CaCl$_2$ acts as an accelerator mainly on the tri-calcium silicate (C$_3$S) phase in portland cement and is one of the most effective anion-
cation combinations for use in pure cement (Ramachandran 1994). However, the findings from this study and others that have tested the effect of accelerators on the hydration of cement containing woods with high tannin content suggest that there are several inorganic salts that may be more effective than CaCl$_2$. AlCl$_3$ was found to be more effective than MgCl$_2$, FeCl$_3$, and CaCl$_2$ in the manufacture of wood-cement composites from the inhibitory wood of Shorea spp. (Kayahara et al. 1979). Soriano et al. (1997) found that Al$_2$(SO$_4$)$_3$ was a more effective additive for the manufacture of WWCB from pre-soaked _A. mangium_ wood than CaCl$_2$ or waterglass (sodium silicate, Na$_2$O.3SiO$_2$).

A key difference between this study and others that have screened chemical additives for their ability to ameliorate the effects of low-compatibility woods on the cement hydration is that a tannin-containing wood was used rather than one whose principal cement-inhibiting substances are hemicelluloses (such as arabinogalactan in larch and acetylated xylans in birch). The action of CaCl$_2$ may not be adversely affected by non-tannin inhibitory constituents such as wood hemicelluloses evidenced by the findings of Wei et al. (2000b). In their study, birch wood was used and CaCl$_2$ was found to be the most effective additive tested, and more so than AlCl$_3$ and SnCl$_4$. Ma et al. (1997) also found that CaCl$_2$ was among the most effective accelerators in ameliorating the inhibitory effects of bamboo powder on cement hydration.

Tables 9.2 and 9.3 show the hydration rates of all the compounds tested in pure cement and cement containing heartwood. The compounds are listed in order of their effects on the hydration rate of pure cement, with the corresponding hydration rate produced in cement containing heartwood in the adjacent column. All those that accelerated the hydration of pure cement are listed in Table 9.2 and all those that reduced the hydration rate of cement to below that of pure cement are listed in Table 9.3. All compounds that had a marked positive effect on the hydration of cement containing _A. mangium_ heartwood strands (i.e. increased $R$ to $>2^\circ$C/h) are shaded in bright blue, and those that accelerated hydration of cement containing wood to $R > 1^\circ$C/h are shaded pink.

From Table 9.2, of the 69 compounds that accelerated the hydration of pure cement, 14 strongly accelerated the hydration of cement containing inhibitory _A. mangium_ heartwood to $R > 2^\circ$C/h (denoted by bright blue), while another 12 resulted in a moderate increase in the hydration rate of cement containing wood to $R$ between 1 and $2^\circ$C (denoted by pink). Interestingly, of the 68 compounds that retarded the hydration of pure cement, 13 resulted in an increase in hydration rate of cement containing inhibitory heartwood to $R > 1^\circ$C/h (Table 9.3).

This indicates that there was no direct correlation between the accelerating or retarding effect of a compound on the hydration of pure cement and the rate of hydration of cement containing _A. mangium_ heartwood. Many of the compounds that accelerated the hydration of pure cement had little effect on the hydration of cement containing _A. mangium_ heartwood (Table 9.2). In addition,
many of the compounds that retarded the hydration of pure cement (such as those containing Pb\(^{2+}\), Ag\(^+\) and Ni\(^{2+}\)) nevertheless had a positive effect on the hydration rate of cement containing the inhibitory heartwood (Table 9.3). A possible reason for this is that all these compounds formed insoluble precipitates with *A. mangium* heartwood extractives (as shown in Table 9.1 for nickel-containing accelerators). This suggests that the ability of a compound to accelerate the hydration of pure cement does not in itself fully explain the capacity of the compound to ameliorate the inhibitory effect of *A. mangium* heartwood on cement hydration. The effects of compounds on pure cement and wood-cement mixes, and the confounding effects of wood content, are illustrated graphically in Figures 9.1 to 9.4.

Table 9.2 The average hydration rates (for pure cement and cement + wood) for compounds that accelerated the hydration of pure cement, listed in descending order of their effect on the hydration of pure cement.

<table>
<thead>
<tr>
<th>Compound with cement</th>
<th>R (°C/h)</th>
<th>Compound with wood</th>
<th>R (°C/h)</th>
<th>Compound with cement</th>
<th>R (°C/h)</th>
<th>Compound with wood</th>
<th>R (°C/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlCl3</td>
<td>7.87</td>
<td>AlCl3</td>
<td>4.42</td>
<td>Co(NO3)2</td>
<td>4.11</td>
<td>Co(NO3)2</td>
<td>1.87</td>
</tr>
<tr>
<td>SnCl4</td>
<td>6.88</td>
<td>SnCl4</td>
<td>5.29</td>
<td>ZnSO4</td>
<td>4.09</td>
<td>ZnSO4</td>
<td>0.00</td>
</tr>
<tr>
<td>FeCl3</td>
<td>6.57</td>
<td>FeCl3</td>
<td>3.62</td>
<td>Al(NO3)3</td>
<td>4.07</td>
<td>Al(NO3)3</td>
<td>2.90</td>
</tr>
<tr>
<td>BaCl2</td>
<td>6.34</td>
<td>BaCl2</td>
<td>2.57</td>
<td>FeF3</td>
<td>4.04</td>
<td>FeF3</td>
<td>0.28</td>
</tr>
<tr>
<td>K2CrO4</td>
<td>5.67</td>
<td>K2CrO4</td>
<td>1.71</td>
<td>KNO3</td>
<td>4.01</td>
<td>KNO3</td>
<td>0.89</td>
</tr>
<tr>
<td>SrCl2</td>
<td>5.61</td>
<td>SrCl2</td>
<td>2.37</td>
<td>Na2CrO7</td>
<td>3.97</td>
<td>Na2CrO7</td>
<td>1.98</td>
</tr>
<tr>
<td>NiCl2</td>
<td>5.47</td>
<td>NiCl2</td>
<td>2.45</td>
<td>TiO2</td>
<td>3.96</td>
<td>TiO2</td>
<td>0.40</td>
</tr>
<tr>
<td>CaCl2</td>
<td>5.38</td>
<td>CaCl2</td>
<td>2.34</td>
<td>SrO3</td>
<td>3.95</td>
<td>SrO3</td>
<td>0.73</td>
</tr>
<tr>
<td>NACl</td>
<td>5.33</td>
<td>NACl</td>
<td>0.62</td>
<td>LiNO3</td>
<td>3.93</td>
<td>LiNO3</td>
<td>1.05</td>
</tr>
<tr>
<td>KCl</td>
<td>5.30</td>
<td>KCl</td>
<td>0.97</td>
<td>MgO</td>
<td>3.93</td>
<td>MgO</td>
<td>0.70</td>
</tr>
<tr>
<td>AlK(SO4)2</td>
<td>5.26</td>
<td>AlK(SO4)2</td>
<td>0.80</td>
<td>Al2O3</td>
<td>3.89</td>
<td>Al2O3</td>
<td>0.73</td>
</tr>
<tr>
<td>LiCl</td>
<td>5.24</td>
<td>LiCl</td>
<td>0.69</td>
<td>MnO2</td>
<td>3.89</td>
<td>MnO2</td>
<td>0.54</td>
</tr>
<tr>
<td>NaNCO3</td>
<td>5.12</td>
<td>NaNCO3</td>
<td>1.42</td>
<td>Co Acetate</td>
<td>3.88</td>
<td>Co Acetate</td>
<td>1.20</td>
</tr>
<tr>
<td>Zn(NO3)4</td>
<td>5.10</td>
<td>Zn(NO3)4</td>
<td>3.55</td>
<td>CoSO4</td>
<td>3.88</td>
<td>CoSO4</td>
<td>0.77</td>
</tr>
<tr>
<td>NaBr</td>
<td>4.97</td>
<td>NaBr</td>
<td>0.58</td>
<td>Sodalime</td>
<td>3.87</td>
<td>Sodalime</td>
<td>0.54</td>
</tr>
<tr>
<td>Na2SO4</td>
<td>4.97</td>
<td>Na2SO4</td>
<td>0.34</td>
<td>Fe(NO3)3</td>
<td>3.86</td>
<td>Fe(NO3)3</td>
<td>2.16</td>
</tr>
<tr>
<td>K oxalate</td>
<td>4.89</td>
<td>K oxalate</td>
<td>0.65</td>
<td>BaSO4</td>
<td>3.85</td>
<td>BaSO4</td>
<td>0.43</td>
</tr>
<tr>
<td>KBr</td>
<td>4.86</td>
<td>KBr</td>
<td>0.65</td>
<td>NiO</td>
<td>3.85</td>
<td>NiO</td>
<td>0.58</td>
</tr>
<tr>
<td>Al2(SO4)3</td>
<td>4.78</td>
<td>Al2(SO4)3</td>
<td>2.18</td>
<td>CaO</td>
<td>3.84</td>
<td>CaO</td>
<td>0.51</td>
</tr>
<tr>
<td>Na2SO4</td>
<td>4.75</td>
<td>Na2SO4</td>
<td>0.42</td>
<td>CaSO4</td>
<td>3.78</td>
<td>CaSO4</td>
<td>0.94</td>
</tr>
<tr>
<td>K2SO4</td>
<td>4.63</td>
<td>K2SO4</td>
<td>0.27</td>
<td>BaF</td>
<td>3.77</td>
<td>BaF</td>
<td>0.66</td>
</tr>
<tr>
<td>MgCl2</td>
<td>4.57</td>
<td>MgCl2</td>
<td>2.78</td>
<td>NiO3</td>
<td>3.74</td>
<td>NiO3</td>
<td>0.55</td>
</tr>
<tr>
<td>Na Tungstate</td>
<td>4.52</td>
<td>Na Tungstate</td>
<td>0.57</td>
<td>KF</td>
<td>3.71</td>
<td>KF</td>
<td>0.47</td>
</tr>
<tr>
<td>Li2CO3</td>
<td>4.50</td>
<td>Li2CO3</td>
<td>0.47</td>
<td>Sr Acetate</td>
<td>3.69</td>
<td>Sr Acetate</td>
<td>1.68</td>
</tr>
<tr>
<td>Na2SO2O3</td>
<td>4.40</td>
<td>Na2SO2O3</td>
<td>0.47</td>
<td>Ba Acetate</td>
<td>3.69</td>
<td>Ba Acetate</td>
<td>1.61</td>
</tr>
<tr>
<td>KHCO3</td>
<td>4.38</td>
<td>KHCO3</td>
<td>1.18</td>
<td>MgCO3</td>
<td>3.68</td>
<td>MgCO3</td>
<td>0.57</td>
</tr>
<tr>
<td>Zn(NO3)2</td>
<td>4.38</td>
<td>Zn(NO3)2</td>
<td>0.27</td>
<td>SrF2</td>
<td>3.68</td>
<td>SrF2</td>
<td>0.43</td>
</tr>
<tr>
<td>Ba(NO3)2</td>
<td>4.37</td>
<td>Ba(NO3)2</td>
<td>1.77</td>
<td>BaO</td>
<td>3.68</td>
<td>BaO</td>
<td>0.69</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>4.35</td>
<td>Cr2O3</td>
<td>1.78</td>
<td>ZrO</td>
<td>3.66</td>
<td>ZrO</td>
<td>0.59</td>
</tr>
<tr>
<td>Na Acetate</td>
<td>4.27</td>
<td>Na Acetate</td>
<td>1.63</td>
<td>Sr(NO3)2</td>
<td>3.61</td>
<td>Sr(NO3)2</td>
<td>2.80</td>
</tr>
<tr>
<td>Zn Acetate</td>
<td>4.21</td>
<td>Zn Acetate</td>
<td>0.00</td>
<td>NaSO2</td>
<td>3.60</td>
<td>NaSO2</td>
<td>0.80</td>
</tr>
<tr>
<td>CaCl2</td>
<td>4.15</td>
<td>CaCl2</td>
<td>1.26</td>
<td>Mg Silicate</td>
<td>3.59</td>
<td>Mg Silicate</td>
<td>0.44</td>
</tr>
<tr>
<td>NaNO3</td>
<td>4.15</td>
<td>NaNO3</td>
<td>0.82</td>
<td>Li Acetate</td>
<td>3.58</td>
<td>Li Acetate</td>
<td>0.49</td>
</tr>
<tr>
<td>K Acetate</td>
<td>4.14</td>
<td>K Acetate</td>
<td>0.44</td>
<td>KI</td>
<td>3.58</td>
<td>KI</td>
<td>0.51</td>
</tr>
<tr>
<td>KIO2</td>
<td>4.13</td>
<td>KIO2</td>
<td>0.38</td>
<td>Cem. control</td>
<td>3.57</td>
<td>Cem. control</td>
<td>3.57</td>
</tr>
</tbody>
</table>
Table 9.3 The average hydration rates (for pure cement and cement + wood) for compounds that retarded the hydration of pure cement, listed in descending order of their effect on the hydration of pure cement.

<table>
<thead>
<tr>
<th>Compound</th>
<th>R (°C/h)</th>
<th>Compound</th>
<th>R (°C/h)</th>
<th>Compound</th>
<th>R (°C/h)</th>
<th>Compound</th>
<th>R (°C/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>with cement</td>
<td></td>
<td>with wood</td>
<td></td>
<td>with cement</td>
<td></td>
<td>with wood</td>
<td></td>
</tr>
<tr>
<td>Ca(NO₃)₂</td>
<td>3.55</td>
<td>Ca(NO₃)₂</td>
<td>1.67</td>
<td>Mn Acetate</td>
<td>2.61</td>
<td>Mn Acetate</td>
<td>0.56</td>
</tr>
<tr>
<td>CaS</td>
<td>3.54</td>
<td>CaS</td>
<td>0.47</td>
<td>KH₂PO₄</td>
<td>2.55</td>
<td>KH₂PO₄</td>
<td>0.24</td>
</tr>
<tr>
<td>Ca₃(PO₄)₂</td>
<td>3.54</td>
<td>Ca₃(PO₄)₂</td>
<td>0.70</td>
<td>Fe₂O₄</td>
<td>2.38</td>
<td>Fe₂O₄</td>
<td>0.39</td>
</tr>
<tr>
<td>NaF</td>
<td>3.52</td>
<td>NaF</td>
<td>0.45</td>
<td>Fe₂(SO₄)₃</td>
<td>2.35</td>
<td>Fe₂(SO₄)₃</td>
<td>1.19</td>
</tr>
<tr>
<td>AgNO₃</td>
<td>3.51</td>
<td>AgNO₃</td>
<td>1.86</td>
<td>NaH₂PO₄</td>
<td>2.28</td>
<td>NaH₂PO₄</td>
<td>0.28</td>
</tr>
<tr>
<td>CaF</td>
<td>3.51</td>
<td>CaF</td>
<td>0.42</td>
<td>Na₂SiF₆</td>
<td>2.26</td>
<td>Na₂SiF₆</td>
<td>0.28</td>
</tr>
<tr>
<td>CoSO₄</td>
<td>3.50</td>
<td>CoSO₄</td>
<td>0.88</td>
<td>AlF₃</td>
<td>2.18</td>
<td>AlF₃</td>
<td>0.89</td>
</tr>
<tr>
<td>CuO</td>
<td>3.45</td>
<td>CuO</td>
<td>0.66</td>
<td>MnCl₂</td>
<td>2.17</td>
<td>MnCl₂</td>
<td>0.91</td>
</tr>
<tr>
<td>AlF₃</td>
<td>3.42</td>
<td>AlF₃</td>
<td>0.44</td>
<td>Mn(NO₃)₂</td>
<td>2.14</td>
<td>Mn(NO₃)₂</td>
<td>0.62</td>
</tr>
<tr>
<td>NiAcetate</td>
<td>3.42</td>
<td>NiAcetate</td>
<td>1.95</td>
<td>H₃BO₃</td>
<td>1.93</td>
<td>H₃BO₃</td>
<td>0.54</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.40</td>
<td>Fe₂O₃</td>
<td>1.33</td>
<td>Cu</td>
<td>1.93</td>
<td>Cu</td>
<td>0.54</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>3.39</td>
<td>NH₄NO₃</td>
<td>1.30</td>
<td>FeAlum</td>
<td>1.74</td>
<td>FeAlum</td>
<td>0.86</td>
</tr>
<tr>
<td>Mo Acid</td>
<td>3.38</td>
<td>Mo Acid</td>
<td>1.28</td>
<td>MnSO₄</td>
<td>1.66</td>
<td>MnSO₄</td>
<td>0.19</td>
</tr>
<tr>
<td>NaN₂O₅</td>
<td>3.37</td>
<td>NaN₂O₅</td>
<td>0.27</td>
<td>Cu₂O</td>
<td>1.53</td>
<td>Cu₂O</td>
<td>0.31</td>
</tr>
<tr>
<td>PbCl₂</td>
<td>3.30</td>
<td>PbCl₂</td>
<td>2.08</td>
<td>PbAcetate</td>
<td>1.50</td>
<td>PbAcetate</td>
<td>1.30</td>
</tr>
<tr>
<td>Mg(NO₃)₂</td>
<td>3.30</td>
<td>Mg(NO₃)₂</td>
<td>1.60</td>
<td>CoCO₃</td>
<td>1.26</td>
<td>CoCO₃</td>
<td>0.00</td>
</tr>
<tr>
<td>MnCO₃</td>
<td>3.27</td>
<td>MnCO₃</td>
<td>0.41</td>
<td>CuCl₂</td>
<td>1.09</td>
<td>CuCl₂</td>
<td>0.00</td>
</tr>
<tr>
<td>MgAcetate</td>
<td>3.27</td>
<td>MgAcetate</td>
<td>1.61</td>
<td>Cu(NO₃)₂</td>
<td>1.06</td>
<td>Cu(NO₃)₂</td>
<td>0.00</td>
</tr>
<tr>
<td>Fe(III) Acetate</td>
<td>3.25</td>
<td>Fe(III) Acetate</td>
<td>1.30</td>
<td>ZnSiF₆</td>
<td>0.54</td>
<td>ZnSiF₆</td>
<td>0.00</td>
</tr>
<tr>
<td>Ca Acetate</td>
<td>3.24</td>
<td>Ca Acetate</td>
<td>1.23</td>
<td>Wood control</td>
<td>0.48</td>
<td>Wood control</td>
<td>0.48</td>
</tr>
<tr>
<td>Ni(NO₃)₂</td>
<td>3.11</td>
<td>Ni(NO₃)₂</td>
<td>1.44</td>
<td>MnF</td>
<td>0.47</td>
<td>MnF</td>
<td>0.00</td>
</tr>
<tr>
<td>LiOH</td>
<td>3.08</td>
<td>LiOH</td>
<td>0.56</td>
<td>ZrF</td>
<td>0.10</td>
<td>ZrF</td>
<td>0.00</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>3.08</td>
<td>MgSO₄</td>
<td>0.98</td>
<td>ZnF</td>
<td>0.02</td>
<td>ZnF</td>
<td>0.00</td>
</tr>
<tr>
<td>LiF</td>
<td>3.04</td>
<td>LiF</td>
<td>0.29</td>
<td>CuCl</td>
<td>0.00</td>
<td>CuCl</td>
<td>0.00</td>
</tr>
<tr>
<td>Li₂SO₄</td>
<td>3.02</td>
<td>Li₂SO₄</td>
<td>0.51</td>
<td>CuCO₃</td>
<td>0.00</td>
<td>CuCO₃</td>
<td>0.00</td>
</tr>
<tr>
<td>Cr₂(SO₄)₃</td>
<td>3.02</td>
<td>Cr₂(SO₄)₃</td>
<td>0.69</td>
<td>CuSO₄</td>
<td>0.00</td>
<td>CuSO₄</td>
<td>0.00</td>
</tr>
<tr>
<td>Pott. Hydr.</td>
<td>2.97</td>
<td>Pott. Hydr.</td>
<td>0.52</td>
<td>FeIII Citrate</td>
<td>0.00</td>
<td>FeIII Citrate</td>
<td>0.00</td>
</tr>
<tr>
<td>Thalate</td>
<td>2.95</td>
<td>Thalate</td>
<td>0.52</td>
<td>KNa Tartrate</td>
<td>0.00</td>
<td>KNa Tartrate</td>
<td>0.00</td>
</tr>
<tr>
<td>(Ni₄)₂(SO₄)</td>
<td>2.95</td>
<td>(Ni₄)₂(SO₄)</td>
<td>0.41</td>
<td>NaCIT</td>
<td>0.00</td>
<td>NaCIT</td>
<td>0.00</td>
</tr>
<tr>
<td>Ni₄(H₂O)₃</td>
<td>2.95</td>
<td>Ni₄(H₂O)₃</td>
<td>0.77</td>
<td>PbO</td>
<td>0.00</td>
<td>PbO</td>
<td>0.00</td>
</tr>
<tr>
<td>NiSO₄</td>
<td>2.92</td>
<td>NiSO₄</td>
<td>0.84</td>
<td>ZnBr₂</td>
<td>0.00</td>
<td>ZnBr₂</td>
<td>0.00</td>
</tr>
<tr>
<td>Pb(NO₃)₂</td>
<td>2.84</td>
<td>Pb(NO₃)₂</td>
<td>0.48</td>
<td>ZnCl₂</td>
<td>0.00</td>
<td>ZnCl₂</td>
<td>0.00</td>
</tr>
<tr>
<td>VoSO₄</td>
<td>2.69</td>
<td>VoSO₄</td>
<td>0.80</td>
<td>ZnCO₃</td>
<td>0.00</td>
<td>ZnCO₃</td>
<td>0.00</td>
</tr>
<tr>
<td>BaAcetateO₃</td>
<td>2.68</td>
<td>BaAcetateO₃</td>
<td>0.35</td>
<td>Na₂HPO₄</td>
<td>0.22</td>
<td>Na₂HPO₄</td>
<td>0.22</td>
</tr>
</tbody>
</table>

9.4.2 Effects of cations and anions on cement hydration

The effects of the presence of particular cations and anions on the hydration of portland cement are illustrated in Figure 9.1 (for cement only) and in Figure 9.2 (for cement with wood). These illustrate the variability among compounds grouped by anion caused by different cations. The cation component of the compound is indicated on the x-axis and its anion component is indicated in the legend. The chlorides of most cations, in particular those of Sn⁴⁺, Al³⁺, Fe³⁺ and Ba²⁺ were the strongest accelerators of cement hydration both with and without wood. Although the chlorides of Mg²⁺ and Ni²⁺ did not stand out as being very strong accelerators of pure cement, they significantly increased the hydration rate of cement containing A. mangium heartwood. Similarly, several compounds in nitrate form (including Co(NO₃)₂ and Fe(NO₃)₃) were not strong accelerators of pure
cement, but they significantly improved hydration of cement containing heartwood. Possible reasons for this are examined in Section 9.4.5.2.

Figure 9.1 Average hydration rates of cement containing compounds denoted by their cation (x-axis) and anion (legend) content; hydration rate for cement containing no additive is denoted by line.

Figure 9.2 Average hydration rates of cement and wood mixtures containing compounds denoted by their cation (x-axis) and anion (legend) content; hydration rate for cement containing no additive is denoted by line.
Chlorides and nitrates of cations such as Cu\(^{+}\), Cu\(^{2+}\), Mn\(^{2+}\) and Pb\(^{2+}\) were strong inhibitors of cement hydration. Note also that the sulphate of Fe\(^{3+}\) and acetate of Ba\(^{2+}\) also inhibited cement hydration, indicating significant interactive effects between cation and anion combination in their effects on cement hydration. The presence of cations Cu\(^{+}\), Cu\(^{2+}\), Mn\(^{2+}\) and Zn\(^{2+}\) and Pb\(^{2+}\) retarded or greatly delayed cement setting within the 24-hour time-frame. These ions retard cement hydration reactions by rapidly forming an amorphous precipitate of insoluble hydroxides, e.g. Zn(OH)\(_2\), and insoluble complexes involving silicates, metal ions and calcium which temporarily blocks access to water by newly hydrating C–S–H grains (Kantro 1975, Thomas et al. 1981, Arligiuic et al. 1982, Taylor and Fuessle 1994, Yousof et al. 1995). Cement hydration resumes after sufficient accumulation of Ca\(^{2+}\) and OH\(^{-}\) ions in the pore solution of the cement paste. This involves the reconfiguration of the amorphous hydroxide into a more crystalline structure, which is incorporated into the hydrating silicate phases (Arliguie and Grandet 1990).

8.4.3 Factors affecting compound efficacy

Figures 9.3 and 9.4 illustrate the distribution of different compounds according to their effect on the hydration of pure cement and cement containing heartwood strands. Their effects on \(T_{\text{max}}\) (Figure 9.3) and hydration rate (Figure 9.4) are graphed for pure cement + compound (x-axis) and the wood + cement + compound mix (y-axis). The results clearly show that the most effective compounds for ameliorating the inhibitory effects of *A. mangium* heartwood were also those that produced the largest increases in maximum hydration temperature and rate of hydration in pure cement.

Figures 9.3 and 9.4 also show an interactive effect between the efficacy of certain compounds and the presence/absence of wood. Compounds in quadrat 1 (shown in Figure 9.3) increased \(T_{\text{max}}\) and hydration rate in both pure cement and cement containing wood. Almost all compounds that increased the maximum temperature and rate of hydration in the wood–cement mix accelerated the hydration of pure cement as well (Figure 9.4). There were some compounds, however, that significantly improved the hydration of pure cement, for example AlK(SO\(_4\))\(_3\) as shown in Figure 9.3, but had little effect on the hydration of cement containing wood.

Compounds in quadrat 2 in Figure 9.3 had their positive effects on the hydration of pure cement inhibited by the presence of inhibitory *A. mangium* heartwood. Compounds in quadrat 2 which included NaCl, Na\(_2\)SO\(_4\) and KBr accelerate cement hydration to some degree (Lea 1971), but their effects were not strong enough to counteract the inhibitory effects of the wood. Of those compounds that reduced \(T_{\text{max}}\) and hydration rate of pure cement (quadrats 3 and 4), some had a beneficial effect on the hydration of cement containing wood. Compounds in quadrats 3 and 4 tended to contain inhibitory cations such as Cu\(^{+}\), Cu\(^{2+}\), Pb\(^{2+}\), Co\(^{2+}\), Zn\(^{2+}\) and Mn\(^{2+}\), or were organic...
acids such as citrates and tartrates. Compounds in quadrat 4 may have interacted chemically with the inhibitory polyphenols in *A. mangium* heartwood, with an overall positive effect on the hydration of wood-cement mixes, as also shown in Table 9.3.

![Figure 9.3](image1.png)

**Figure 9.3** $T_{\text{max}}$ for cement containing compound only vs $T_{\text{max}}$ for cement containing compound plus wood wool. $T_{\text{max}}$ for pure cement (cement control) and for cement containing wood only (wood control) indicated by lines.

![Figure 9.4](image2.png)

**Figure 9.4** Hydration rate for cement containing compound only vs hydration rate for cement containing compound plus wood wool. Hydration rate for pure cement (cement control) and for cement containing wood only (wood control) indicated by lines.
A fifth group of compounds (enclosure 5 in Figure 9.3) had little effect on $T_{\text{max}}$ of cement on its own, but increased the temperature and hydration rate attained in cement containing heartwood. These included nitrates and acetates of $\text{Al}^{3+}$, $\text{Ni}^{2+}$, $\text{Ag}^+$, $\text{Fe}^{3+}$ and $\text{Co}^{2+}$, compounds that had little or no accelerating effect on the hydration of pure cement, as also shown on Figure 9.1. All these compounds did, however, result in the formation of precipitate with $A. \text{mangium}$ heartwood tannins in alkaline medium.

These findings suggest that the formation of insoluble polyphenol-metallic complexes between free cationic species and reactive hydroxyl sites on heartwood polyphenols contributes to ameliorating the inhibitory effects of $A. \text{mangium}$ heartwood on cement hydration. The results indicate that chlorides and nitrates containing cations with a higher positive charge (such as $\text{Sn}^{4+}$, $\text{Zr}^{4+}$, $\text{Fe}^{3+}$ and $\text{Al}^{3+}$) are the most effective additives. Cost would preclude the use of zirconium compounds, but accelerators based on tin, iron or aluminium may be far better suited than CaCl$_2$ for use in wood–cement composites containing $A. \text{mangium}$ and possibly other tropical hardwoods that contain high levels of heartwood polyphenolic extractives. These findings support those of previous studies, which have found compounds containing aluminium to be more effective than CaCl$_2$ for ameliorating the inhibitory effects of hardwoods used in the manufacture of wood–cement composites. For example, AlCl$_3$ was more effective than MgCl$_2$, FeCl$_3$ and CaCl$_2$ for the manufacture of wood–cement composites from the inhibitory, tannin-containing wood of Shorea spp. (Kayahara et al. 1979), and Al$_2$(SO$_4$)$_3$ was the most effective additive for manufacturing WWCB from pre-soaked $A. \text{mangium}$ wood (Soriano et al. 1997). In these studies, however, reasons as to why this might be the case were not considered.

9.4.4 Effect of accelerators on the wood-cement interface

The possible importance of a chemical interaction between an accelerator and the inhibitory heartwood polyphenols is highlighted by comparing the wood-cement interface produced by adding a compound that did not precipitate heartwood polyphenols (CaCl$_2$) and one that did (Cr$_2$O$_3$). CaCl$_2$ is a compound that is among the most effective cement setting accelerators for pure cement, but it did not appear to interact significantly with heartwood polyphenols, whereas Cr$_2$O$_3$ is a compound that did not greatly accelerate cement setting but did precipitate $A. \text{mangium}$ heartwood polyphenols. Scanning Electron Microscopy (SEM) was used to examine the morphology of the set cement adjacent to a heartwood strand after either CaCl$_2$ or Cr$_2$O$_3$ were added in 0.1M concentration to wood-cement hydration samples. The effect of adding CaCl$_2$, which actually produced a higher hydration rate than Cr$_2$O$_3$ (Table 9.1), was varied; in some cases allowing setting to form zones which reproduced the wood surface (such as can be seen in Plate 9.1...
(a) and (b)) and in others showing frequent zones of poorly set cement that did not reproduce the wood surface (Plate 9.1 (c)).

Plates 9.1 (a) to (c) Appearance of cement at the wood-cement interface produced by adding CaCl₂ 0.1M, (d) and (e) adding Cr₂O₃ 0.1M to the hydrating wood-cement mix.
In contrast, the addition of \( \text{Cr}_2\text{O}_3 \) produced a more consistent mould of the wood surface, indicating stronger setting of cement adjacent to strands of inhibitory *A. mangium* heartwood (Plates 9.1 (d) and (e)). Although \( \text{CaCl}_2 \) has a greater accelerating effect on cement hydration than \( \text{Cr}_2\text{O}_3 \), its effects appear to have been inhibited at the wood-cement interface. This could adversely affect the strength of bonding between wood and cement in a composite such as WWCB, particularly as the cement content is much lower than in a wood-cement hydration sample. In contrast, the \( \text{Cr}_2\text{O}_3 \) present in the cement paste is likely to have chemically interacted with inhibitory polyphenols in and on the wood surface allowing less impeded cement setting adjacent to the wood. The performance of \( \text{CaCl}_2 \) and other selected accelerators on the properties of WWCBs made from untreated *A. mangium* wood is covered in Chapter 10.

### 9.4.5 Interaction with heartwood polyphenols

As demonstrated here, chemical interaction between a cement additive and inhibitory heartwood polyphenols may contribute significantly to its efficacy in ameliorating the inhibition of cement hydration by *A. mangium* heartwood, enabling hydration to take place at the wood-cement interface. Water-soluble and alkali-soluble heartwood tannins normally have deleterious effects on cement hydration, as has been demonstrated experimentally by Sandermann and Brendel (1956) and Miller and Moslemi (1991a). These studies indicate that the addition of tannins at a concentration of more than about 0.2% will effectively inhibit cement hydration.

Condensed tannins can be abundant in the heartwood and bark of acacias (Sherry 1971, Hillis 1987). Their molecules contain \( \alpha \)-dihydroxyphenyl groups which have excellent chelation affinity with free metal ions, including \( \text{Cu}^{2+} \) and \( \text{Zn}^{2+} \) (McDonald *et al.* 1996, Scalbert *et al.* 1998, Yamaguchi and Okuda 1998), \( \text{Fe}^{3+} \) and \( \text{Al}^{3+} \) (Kennedy and Powell 1985a, b, Yoneda and Nakatsubo 1998). In our study, solutions containing free cations, or more likely cationic hydrated and \( \alpha \)-lated species based on \( \text{Sn}^{4+}, \text{Al}^{3+}, \text{Fe}^{3+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+} \) and \( \text{Pb}^{2+} \), all formed strong precipitates with the dark-coloured polyphenols leached from *A. mangium* heartwood in alkaline solution, leaving a light yellowish or clear solution behind. Some examples of these are shown in Plate 9.2.

The interactions between a cement hydration accelerator such as \( \text{SnCl}_4 \) or \( \text{FeCl}_3 \), its aqueous dissolution products and dissolved polyphenols of various kinds, including teracacidin, are poorly understood, however the following discussion and review of literature provides some idea of the complexity and of possible processes that may be involved. To assist understanding of the discussion, some information on the structures of acacia heartwood polyphenols and the possible mechanisms by which these might interrupt cement hydration is presented first.
Plate 9.2 Examples of insoluble complexes formed with *A. mangium* heartwood polyphenols, showing heavy precipitation by SnCl\(_4\), Al\(_2\)(SO\(_4\))\(_3\), FeCl\(_3\) and CuCl\(_2\), very light precipitation by CaCl\(_2\) and no precipitation by MgCl\(_2\) or water control.

**9.4.5.1 Acacia heartwood extractives and their effect on cement hydration**

The hot-water-soluble heartwood extractive content in *A. mangium* can be up to 10%, whereas the alkali-soluble (1% NaOH) content is 15% (Jegasethwaran 1989, Peh *et al.* 1982, Khoo *et al.* 1991). The cold-water-soluble extractives content of *A. mangium* can vary from 5% (Cabangon and Evans 2002) to 12.7% (Cabangon *et al.* 2002b). The extractive content of *A. mangium* is relatively low, however, compared to the heartwood extractive contents of up to 27% (hot-water-soluble) and 41% (NaOH-soluble) for certain eucalypts such as messmate stringybark (*Eucalyptus obliqua* L'Hérit) (Hillis 1987). The bulk of *A. mangium* heartwood extractives (over 95%) are soluble in water, and none of the catechins (proanthocyanidins) are found in the water-insoluble fraction (Lange and Hashim 2001). In several hardwoods, including teak and acacias, the concentration of water-soluble heartwood extractives increases from the pith to the outer boundary of the heartwood (Hillis 1960, 1962, 1985, 1987). This is also true for *A. mangium* (Lange and Hashim 2001).

There is only one published paper (Tachi *et al.* 1989) that has investigated how specific acacia (in this case *A. mangium*) heartwood polyphenols might affect cement hydration. These authors were the first to elucidate the polyphenolic composition of *A. mangium* heartwood in order to find out which polyphenols were responsible for the strong inhibitory effect of the heartwood on cement
hydration. They first fractionated various components of the methanol-soluble heartwood extract and tested their effects individually on the hydration of portland cement. Within the combined ethyl acetate- and n-butanol-soluble fraction, the most inhibitory component (A-50) contained two related compounds, teracacidin and iso-teracacidin, as low-molecular-weight monomers in very small quantities.

Teracacidin was first identified and isolated from the heartwood of an arid zone acacia, *Acacia orites*, by Clark-Lewis *et al.* (1961). It is one of four distinctive acacia heartwood leucoanthocyanidins (flavan-3,4-diols) that distinguish the broad morphological subdivisions within the genus (Clark-Lewis and Dainis 1967, Tindale and Roux 1969, Clark-Lewis and Porter 1972). The most common of these is mollicacidin which was first isolated from the heartwood of *Acacia meanresii* de Wild. (formerly *Acacia mollissima* Willd.) by Keppler (1957), and is the 'signature' flavonol pattern for the bipinnate acacias (subsection Botrycephaleae), which comprise the bulk of Australian acacias (Tindale and Roux 1969). Mollicacidin and the closely associated (but rare) guibourtacidin are shown in Figure 9.5(a). Teracacidin is also relatively rare within the genus *Acacia*, but is closely related to the other very common acacia heartwood flavonoid, melacacidin which was first found in blackwood (*Acacia melanoxylon* Roxb.) by King and Bottomly (1953, 1954). These are shown in Figure 9.5(b). Melacacidin is the 'signature' flavonol pattern of the phylloide acacias belonging to the sections Plurinerves and Juliflorae (Tindale and Roux 1969, Clarke-Lewis and Porter 1972).

Unlike mollicacidin and gibourtacidin, the A-ring (left pyran rings in Figure 9.5(a) and (b)) of teracacidin and melacacidin is a catechol (1,2-benzenediol or o-dihydroxyphenyl) unit. Tachi *et al.* (1989) and Yasuda *et al.* (1992) suggested that it is this catechol component that is responsible for

\[
\begin{align*}
\text{(a)} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} \\
\text{HO} & \quad \text{R} & \quad \text{OH} & \quad \text{R} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{(b)} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH} \\
\text{HO} & \quad \text{R} & \quad \text{OH} & \quad \text{R} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]

Figures 9.5  Flavonol structures for the acacia heartwood polyphenols, (a) (+)-mollicacidin (R = OH) and gibourtacidin (R = H); and (b) (--)-teracacidin (R = H) and (--)-melacacidin (R = OH). (From Tindale and Roux 1969).
the observed inhibitory effects of teracacidin and melacacidin on cement hydration. The twin or vicinal hydroxyl groups on catechol units were suggested as being responsible for bi-dentate chelation of Ca\(^{2+}\) ions in cement paste. In the cases of melacacidin and dihydroquercetin (which was shown by Sandermann et al. (1960) to be highly inhibitory of cement hydration), there is a catechol unit on the B-ring (right pyran ring) as well.

The number and positioning of hydroxyl groups in flavonoid aromatic compounds is believed to be important in determining their ability to retard cement hydration. However the exact mechanism by which flavonoids retard cement hydration is unclear (Double 1983), and the subject has received scant attention in the literature. Simple hydroxylated phenolic admixtures have been classified in terms of their ability to retard cement hydration, shown in Figure 9.6. It can be seen that the inhibitory effect of the compounds increases with increasing number of neighbouring (or vicinal) hydroxyl groups. Twin hydroxyl functional groups are believed to interfere with the diffusion of Ca\(^{2+}\) ions in cement paste and the formation of Ca(OH)\(_2\). Ca\(^{2+}\), Al\(^{3+}\) and Fe\(^{3+}\) ions in cement paste may be adsorbed onto reactive sites on the flavonoid as another mechanism by which cement hydration may be disrupted (Double 1983).

![Figure 9.6 Retarding power of aromatics (phenolics) commonly found in heartwood extractives (from Double 1983).](image)

However, it is also possible that adjacent hydroxyl groups on flavonoids chelate with Ca\(^{2+}\) ions via bi-dentate or more complex configurations to form larger organic molecules and insoluble precipitates around Ca(OH)\(_2\), silicate and aluminate phase hydrate nuclei (Double 1983). Adsorption and chelation phenomena induced by reactive groups in heartwood polyphenols may
also alter the charge chemistry on the surface of newly hydrating cement grains, inhibiting the precipitation of Ca(OH)₂ and the hydration of silicate and aluminate phases in portland cement paste.

These theories are further complicated by the fact that flavonoids are readily chemically altered in the alkaline environment of cement. Recent research indicates that, in alkaline solutions (pH 12) at ambient temperature, catechin-based flavonoids undergo structural rearrangement, i.e. epimerisation at C2 on the pyran ring, with an intermediate opening of the pyran ring (Hashida and Ohara 2002). How this might influence the hydration of the various phases of portland cement appears to be unknown.

Catechol groups may disrupt cement hydration reactions by other mechanisms such as interaction with ions such as Al³⁺ and Fe³⁺, and possibly silicates. Iron and aluminium are important constituents of the tricalcium-aluminate (C₃A) and calcium-aluminoferite (C₄AF) phases of portland cement. In the presence of an inhibitory admixture (such as sucrose), which scavenges Ca²⁺ ions from cement suspension, high levels of soluble hydroxoaluminate and hydroxoferrite ions will be generated (Thomas and Birchall 1983), which may interact with catechol. Catechol may also react with silica in cement paste, affecting the normal precipitation of C-S-H gel matrix (Double 1983). Complexes between silica and catechol are known to form in alkaline solution, which results in the deterioration of glass via the solubilisation of silica when the glass is exposed to dissolved organic substances (Ernsberger 1959, Bacon and Raggon 1959). However, there are no detailed studies to confirm whether catechol or tri-hydroxylated phenolics complex with SiO₂, or metal ions other than Ca²⁺, or whether such reactions prevent the growth of portlandite and the silicate, aluminate and aluminoferrite phases of portland cement.

9.4.5.2 Interactions between acacia heartwood polyphenols and accelerators

Heartwood polyphenols extracted from A. mangium were observed to chemically interact with the metallic constituents of cement-setting accelerators including SnCl₂ and FeCl₃, resulting in the coloured precipitates formed in alkali shown in Plate 9.2; however the processes by which this occurred are also far from clear. Catechol- and catechin-based condensed tannins react with metals such as Al³⁺ and Fe³⁺ in neutral conditions to form stable complexes that are sparingly soluble in water (Kipton et al. 1966, Kennedy and Powell 1985a, Bodini et al. 1999). This mechanism is believed to be responsible for the dissolution and translocation of these ions from their oxides and hydroxides as part of the podzolisation process in soils. In alkali, such complexes are insoluble and cause discoloration of paper pulps (Ni et al. 1999). Very stable complexes are formed via bidentate chelation between catechol (dihydroxy) units in heartwood polyphenols and transition metals such as Fe³⁺ (Kipton et al. 1982, Kennedy and Powell 1985b), as shown in Figure 9.7.
However this model may not adequately explain the amorphous precipitates in alkaline solution observed here. Explanation for the precipitates is complicated by possible specificity as to which part of the flavonoid is actively involved in metal chelation.

Slabbert (1992) and Yoneda and Nakatsubo (1998) assert that it is the distinctive phenolic hydroxylation pattern of the B-ring of flavonoids that determines the metal-chelating capacity of tannins, with 3',4',5'-trihydroxylated B-rings having the highest affinity for metals, followed by 3',4'-dihydroxy, then 4'-monohydroxy B-rings with low chelation capacity. The A-ring of flavonoids is considered by Slabbert (1992) and Yoneda and Nakatsubo (1998) to be of little importance in polyphenol-metal chelation reactions. However, the behaviour of flavonoids with a catechol unit on the A-ring, such as teracacidin or melacacidin, was not discussed by these authors.

![Catechol group](image)

$2\text{Fe}^{3+} + 1,2\text{-diphenol} \rightarrow 2\text{Fe}^{2+} + \text{quinone} + 2\text{H}^+$

Figure 9.7 Schematic diagram of bi-dentate chelation of catechol units by Fe$^{3+}$ proposed by Kennedy and Powell (1985b).

![Teracacidin](image)

Figure 9.8 Schematic diagram of Teracacidin as determined by Clark-Lewis et al. (1961).

The acacia heartwood flavonoids, mollicacidin and melacacidin, are characterised by a 3',4'-dihydroxy B-ring (see Figures 9.5 (a) and (b)), and may therefore link together by the bi-dentate chelation model proposed above. However, teracacidin itself, shown in Figure 9.8, does not neatly fit this proposed model. Unlike mollicacidin and melacacidin, teracacidin contains a 4'-
monohydroxy B-ring (phenol unit), casting uncertainty on the model of bi-dentate chelation of the B-ring proposed by Slabbert (1992) and Yoneda and Nakatubo (1998). Nevertheless, one of the characteristic chemical properties of phenols is their facile oxidation by almost any oxidant, affording a complex mixture of polymer products in neutral or basic conditions (Mihailovic and Cekovic 1971, Sheldon and Kochi 1981). As such, the majority of heartwood phenolics already exist in a polymerized form resulting from oxidation (Hillis 1987), although flavan-3,4-diols such as teracacidin can co-exist as stable constituents (Coetzee et al. 1999).

The question of whether teracacidin monomers co-exist with larger quantities of polymeric, intractable phenolic material (condensed tannins), which could be responsible for the formation of the heavy precipitates observed here, is open to question. Unlike the more common acacia flavonoid mollicacidin, teracacidin appears not to be associated with large quantities of polymeric condensed tannin (Tindale and Roux 1969). Accordingly, the entire methanol-soluble extract from A. mangium was found by Tachi et al. (1989) to contain only very small quantities of higher molecular weight (polymerised) substances. This is in contrast to the large quantities of polymeric condensed tannin that was reported to accompany teracacidin in an arid zone acacia (Acacia sparsiflora Maiden) by Clark-Lewis and Dainis (1967).

Nevertheless, during the course of wood conversion and exposure to cement and accelerators, changes to the original polyphenolic constituents of A. mangium heartwood are likely to have occurred. In alkaline media (such as cement paste), further oxidation of mono- and polyhydric phenols by O₂ gives rise to dimers, trimers and intractable, dark coloured, complex mixtures of poorly defined products (Mihailovic and Cekovic 1971), which are likely to have constituted the bulk of the leachate extracted from A. mangium heartwood in this study. Addition of strong metal oxidants such as ferric and stannic ions and colloids are also catalysts for radical-induced linkages of mono- and polyhydric phenols (Sheldon and Kochi 1981). Solutions containing electrolytes such as SnCl₂ or FeCl₃ are also quite acidic (pH 4 or less), and therefore the heartwood flavonoids are also likely to be altered by self-condensation (Bentley 1960), particularly if the compound is added directly to the wood. Leucoanthocyanidins of flavan-3,4-diol configuration (of which teracacidin is one) are acid-sensitive, with many forming insoluble self-condensation polymer products (phlobophenes) even under comparatively mild conditions of pH and temperature (Hathaway 1962, Hillis 1962, Haslam 1966, 1982).

The observed heavy precipitation of the A. mangium heartwood extract here suggests that any remaining teracacidin monomers are likely to be accompanied by much larger quantities of polymeric oxidation products resulting from exposure to alkali and accelerators that were effectively bound up in a complex matrix induced by the addition of a metal oxidant.
Tannin-metal co-ordination models are further complicated by the fact that salts such as SnCl₄ and FeCl₃ dissolve in acid, neutral and alkali to form complex, transitory mixtures of poorly defined colloids or octahedral structures, and polymers (Sargensen 2002 pers. Comm.). These are positively charged hydroxo- and oxo- species and free chloride ions, for example:

\[
\text{SnCl}_4 + H_2O, OH^- \rightarrow [\text{SnCl}(H_2O)_5]^{3+}3\text{Cl}^-, [\text{SnCl}_2(H_2O)_3]^{2+}2\text{Cl}^-, [\text{SnClOH}(H_2O)_4]^{2+}2\text{Cl}^-
\]

\[
\text{FeCl}_3 + H_2O, OH^- \rightarrow [\text{FeCl}(H_2O)_5]^{2+}2\text{Cl}^-, [\text{FeOH(OH}_2)_6]^{2+}2\text{Cl}^-, [\text{FeCl}(H_2O)_6\text{OH}]^{+}\text{Cl}^-, [\text{Fe(OH)}_3(H_2O)_4]^{+}\text{Cl}^-
\]

Metals of higher charge result in complexes of greater stability, and if a metal exists in two different oxidation states, then the more highly charged state nearly always forms more stable complexes than does the lower oxidation state (Sharpe 1981). This is consistent with the finding that chlorides and nitrates of Zr⁴⁺, Sn⁴⁺, Al³⁺ and Fe³⁺ were more effective at neutralising the effects of A. mangium heartwood polyphenols on cement hydration than those of Na⁺, K⁺ or Ca²⁺. The oxidation state of tin was found in this study to be a significant determinant of its utility and effectiveness; whereby SnCl₄ was a far more effective additive than SnCl₂. SnCl₄ when first dissolved in water forms an acidic solution with the predominant tin species present as octahedral [SnCl₆]²⁻, and although SnCl₄ is soluble in water it eventually hydrolyses to a hydrous Sn⁴⁺ oxide precipitate (Donaldson and Grimes 1998). Sn⁴⁺ compounds are preferable as an additive in this case for the reasons outlined by Donaldson and Grimes (1998); these being that (a) the ⁴⁺ oxidation state of tin is more stable than the ²⁻ state and is much slower to hydrolyse in aqueous solution, (b) Sn⁴⁺ is the most effective complexing agent since all of its valence shell electrons are involved in bonding, and (c) exposure of dissolved SnCl₂ to alkali can result in spontaneous disproportionation to metallic tin.

The above discussion indicates that the simple models of catechol chelation by free cations, such as that proposed by Kennedy and Powell (1985b) therefore do not fully explain our observations. Research by Wroblewski and Brown (1979) suggests that chelation of polyphenols such as dihydroquercetin could result in the formation of chains or sheet-like structures. However, the precipitates formed here appeared to have a quite amorphous structure. Positively charged three-dimensional structures formed as the accelerator dissociates in water or hydroxide are also capable of co-ordinating polyphenols in various different configurations to form complex, amorphous matrices (Sargensen 2002 pers. Comm.), perhaps more consistent with the cloudy precipitates formed here.

There is also evidence to suggest that in certain instances precipitation of heartwood polyphenols may not be a necessary precursor to counteracting their inhibition of cement hydration. This is illustrated by the unusual behaviour of MgCl₂, an accelerator that does not directly precipitate
tannins from *A. mangium* but is nonetheless capable of counteracting the inhibitory effects of teracacidin and other inhibitory polyphenols with vicinal hydroxyl groups on the hydration of portland cement. Work by Tachi *et al.* (1989) has demonstrated that 2% MgCl₂, unlike the same quantity of CaCl₂, is a powerful agent for neutralising inhibitory teracacidin in *A. mangium* heartwood. Since MgCl₂ forms no insoluble precipitates with *A. mangium* heartwood polyphenols, the chemical interaction between MgCl₂ and inhibitory heartwood phenolics, and its possible neutralising effect, is even less clear. Yasuda *et al.* (1992) have studied the possible mechanisms of interaction of MgCl₂ with catechol and catechol-based inhibitory polyphenols from acacia (*A. melanoxylon*) and sugi (*Cryptomeria japonica*) heartwood in an attempt to explain its observed beneficial effects on the hydration of portland cement in the presence of tannin-containing woods. Yasuda *et al.* (1992) have speculated that, unlike Ca²⁺ ions, the smaller Mg²⁺ ions (or more likely hydroxo-colloids of Mg) are preferentially adsorbed onto or 'complexed with' reactive hydrating C₃A and C₄AF phases shortly after mixing with water. Experiments showed that in the presence of MgCl₂ added catechol was rapidly removed from the cement paste and adsorbed onto C₃A and C₄AF particles, leaving C₃S free to hydrate with the aid of free Ca²⁺ ions. More detail on the abovementioned phases and hydration reactions of portland cement can be found in Appendix 2 (pp. 407-436).

'Scavenging' of catechol (and catechol-containing inhibitory heartwood polyphenols) was suggested by Yasuda *et al.* (1992) to be facilitated via interaction (chelation) with adsorbed Mg colloids acting as a bridging agent. Mg²⁺ is expected to be more effective in this regard than Ca²⁺ since the stability of complexes with non-transition metal ions of a given charge normally increases with decreasing size of the cation (Sharpe 1981). A similar mechanism was forwarded by Yasuda *et al.* (1992) to explain the positive effects of other accelerators such FeCl₃ on the hydration of cement containing catechol-based polyphenols, however the authors did not discuss the role of direct precipitation of the polyphenols by FeCl₃, as observed here. Their experiments also do not appear to have examined the ability of MgCl₂ solution to directly precipitate catechol or catechol-based polyphenols; however it seems likely that MgCl₂ has a different mechanism by which the effects of inhibitory heartwood polyphenols on cement hydration are neutralised in situ once mixed in with cement paste.

Except for the case of MgCl₂, the observed precipitation of heartwood polyphenols in or on the surface of wood wool may render them less mobile and hence reduce their ability to diffuse out into the surrounding cement gel and inhibit cement hydration reactions. Secondly, precipitated complexes of polyphenols bound at their reactive sites may no longer have free hydroxyl groups that chemically interfere with diffusion of Ca²⁺ ions, Ca(OH)₂ formation and the hydration of calcium silicates in cement paste. These theories go some way towards explaining why the
chlorides and nitrates of Sn\(^{4+}\), Zr\(^{4+}\), Al\(^{3+}\) and Fe\(^{3+}\) were significantly better than CaCl\(_2\) at neutralising the inhibitory effects of \(A.\) mangium heartwood on cement hydration.

From the results it can be postulated that an additive or additive mix that contains small amounts of accelerators such as CaCl\(_2\) or MgCl\(_2\) and cations such as Al\(^{3+}\), Sn\(^{4+}\) or Fe\(^{3+}\) may have considerable synergistic effects and could potentially enable WWCBs and other wood-cement composites to be manufactured from untreated \(A.\) mangium wood. This is investigated in Chapter 10 where selected additives from this study were tested in the manufacture of WWCB from \(A.\) mangium wood wool.

9.5 Conclusions

Inorganic compounds that were capable of precipitating the phenolic constituents of \(A.\) mangium heartwood and accelerating cement hydration were generally more effective at strengthening cement hydration in the presence of \(A.\) mangium heartwood than compounds that simply accelerated cement hydration. The most effective compounds in ameliorating the inhibitory effect of \(A.\) mangium heartwood on cement hydration were soluble in cold water and comprised mainly chlorides and nitrates of metals with high positive charges such as Sn\(^{4+}\), Zr\(^{4+}\), Al\(^{3+}\), and Fe\(^{3+}\).

Certain compounds that precipitated the phenolic constituents of \(A.\) mangium heartwood but lacked the ability to strongly accelerate cement hydration still managed to significantly increase maximum hydration temperature and hydration rate attained in wood–cement mixes compared to cement containing heartwood only. These compounds contained cations or colloids based on Cr\(^{3+}\), Ni\(^{2+}\), Ag\(^+\), Fe\(^{3+}\) and Co\(^{2+}\), and were capable of forming alkali-insoluble complexes with \(A.\) mangium heartwood polyphenols.

The possible importance of direct chemical interaction with inhibitory heartwood polyphenols was investigated further by examining the wood-cement interface using scanning electron microscopy. The ability of the cement to set and mould to the wood surface was greatly enhanced by adding a compound such as Cr\(_2\)O\(_3\), which was not a strong cement-setting accelerator but was capable of precipitating heartwood polyphenols in alkaline media. Cement setting at the wood surface was still impeded after the addition of CaCl\(_2\), which is normally a strong accelerator of cement hydration but does not have the capacity to form stable insoluble complexes with the inhibitory constituents of \(A.\) mangium heartwood. The results suggest that inhibitory heartwood tannins still managed to interfere with the normal action of CaCl\(_2\) where the cement came in contact with the wood surface. This problem may hamper the performance of CaCl\(_2\) in producing adequately consolidated wood-cement composites from \(A.\) mangium, as others have also found (Tachi et al. 1988, Eusebio et al. 2002b).
The unusual case of MgCl₂, which was among the top 6 compounds which improved the compatibility of inhibitory A. mangium heartwood on cement hydration but did not complex leached polyphenols, was discussed. A few previous studies have noted the difference between MgCl₂ and CaCl₂ and have suggested that colloidal Mg²⁺ may act as a catalyst for the adsorption of inhibitory catechol-based polyphenols onto reactive aluminate phases that begin to hydrate immediately, removing them from the cement paste and allowing the C3S phase to hydrate normally.

A discussion of the structures of acacia heartwood polyphenols suggested that the presence of catechol groups might be responsible for their inhibitory effects on cement hydration. The scant information available on this subject meant it was unclear as to exactly how cement hydration reactions might be affected. Discussion of the literature indicated that the different positions of the catechol groups on acacia heartwood flavonoids could influence their ability to interact with metal ions in both cement paste and in cement-setting accelerators.

The findings from this study suggest that the inhibitory effect of A. mangium heartwood on cement hydration can be largely blocked by the addition of an inorganic compound that both accelerates cement hydration and forms insoluble complexes with the heartwood tannins. Additives containing a cost-effective accelerator such as CaCl₂ or MgCl₂ and higher charge cations such as Al³⁺, Sn⁴⁺ or Fe³⁺ could potentially enable wood-cement composites to be manufactured from fresh A. mangium wood and possibly other tropical hardwoods. The performance of MgCl₂ and CaCl₂ in the manufacture of low cement-content WWCBs from untreated A. mangium wood is examined in Chapter 10. They are compared with compounds such as SnCl₄, FeCl₃ and AlCl₃, which are capable of complexing heartwood tannins and accelerating cement hydration, and therefore have the potential to improve the properties of WWCBs manufactured from A. mangium wood.
Chapter 10 Manufacture of WWCBs from A. mangium using simple inorganic accelerators.

10.1 Introduction

The use of a cement-setting accelerator is the simplest and most commonly used method to ameliorate the inhibitory effects of wood on cement hydration during the manufacture of cement-bonded composites (Wei et al. 2000a, Wei and Tomita 2001). Cement-setting accelerators are particularly effective in improving the strength properties of composites with low cement content such as WWCB (Sorfa 1984), and resistance to moisture-induced swelling in wood-cement composites (Kayahara et al. 1979, Wei et al. 2000a). In Chapter 9, laboratory-scale cement hydration tests were used to assess a wide range of chemical additives for their ability to increase the strength of hydration of cement containing A. mangium heartwood. The most effective of these significantly increased the hydration rate of cement containing the heartwood, and most also formed insoluble precipitates with leached heartwood tannins in alkaline solution. However, the performance of a chemical additive in a cement hydration test with a very high cement:wood ratio that runs over 24 hours may not necessarily translate into the desired strength increase in wood-cement composites such as WWCB, which have a low cement:wood ratio. The effectiveness of the different additives therefore needs to be verified by the manufacture of test boards containing the accelerators in practical quantities.

In this study a selection of the most effective accelerators identified in the hydration tests in Chapter 9 were tested for their ability to improve the mechanical properties of WWCB made from shredded, untreated A. mangium wood wool. The compounds used included some that formed insoluble metal-polyphenol complexes; i.e. SnCl₄, FeCl₃, and the chloride, nitrate and sulphate of Al³⁺, in accordance with the hypothesis that this action would translate into improved bonding between A. mangium wood wool and cement. Other compounds tested included CaCl₂, MgCl₂, Ca(NO₃)₂, SrCl₂, Na₂SiO₃ and a chloride-based commercial admixture known as 'Pozzolith™'. These are well-known accelerators and are commonly used in the manufacture of wood-cement composites for their ability to accelerate cement hydration, but they do not form metal-polyphenol complexes. Compounds such as Ca(NO₂)₂, Al(NO₃)₃, Na₂SiO₃, were selected for their lower corrosiveness compared with most chloride-based cement-setting accelerators (Rosenberg et al. 1977, Ramachandran 1994). The corrosion potential of WWCBs containing different quantities of accelerators was tested using four different types of commonly used iron-based nail fastenings.

Previous studies that have used accelerators during the manufacture of WWCBs from A. mangium include Soriano et al. (1997), Cabangon et al. (1998) and Eusebio et al. (2002a); these have always used pre-soaked wood wool, and even then with variable results, which are discussed
later in this Chapter. This is the first study that has attempted to use simple cement-setting accelerators with untreated wood wool from an incompatible tropical hardwood species (*A. mangium*) with the aim of eliminating the need to pre-soak the wood wool.

10.2 Aims and objectives

The aim of this study was to manufacture medium-density WWCBs from untreated *A. mangium* wood wool that meet quality standards by using small amounts of selected simple inorganic compounds. Specific objectives were to:

1. Manufacture WWCBs of acceptable mechanical strength and water resistance using *A. mangium* wood wool (which has had no prior treatments such as pre-soaking or long-term storage) using small amounts of simple inorganic accelerators, and to compare these WWCBs with similar boards made from pre-soaked wood wool.

2. Test the corrosive potential of WWCBs containing different types of accelerators in different concentrations, and assess whether it is possible to achieve the above-mentioned objective using less corrosive additives.

10.3 Materials and methods

10.3.1 Preparation of wood wool from billets

Two *A. mangium* trees measuring approximately 12 m in height were obtained in June 2000 from a 12-year-old provenance trial located at Kuranda in North Queensland (location shown in Chapter 4). Tree 1 was 33 cm DBHOB from PNG-N (Kini province, seedlot 16938) and Tree 2 was 40 cm DBHOB from PNG-SE (Boite province, seedlot 16992). Both trees contained approximately 75% heartwood. The trees were felled and cut into logs measuring 1 m or 50 cm, colour-coded (by tree) and shipped to Canberra where they were debarked and cross-cut into 46-cm-long billets for immediate conversion into wood wool strands. This was done at WoodTex Pty Ltd as described in Chapter 3. The shredded wood wool was bagged, returned to Canberra and immediately spread out to dry indoors for about 2 weeks.

Half of the total quantity of wood wool was then pre-soaked in water at ambient temperature to remove the soluble inhibitory constituents from the wood. This was done by filling 70-L plastic bins with approximately 2 kg of air-dried wood wool and adding luke-warm (25-30°C) water to the wood wool to completely submerge it. Luke-warm water was used because results in Chapter 8 showed that cold water may not remove enough extractives to enable the manufacture of well consolidated WWCB from *A. mangium*. The wood wool was lightly weighed down with small
weights to keep it submerged for 24 h, as shown in Plate 10.1 (a). The leachate was then poured off and the wood wool rinsed once with clean water, drained and spread out to dry under cover for two weeks. This process was repeated until approximately 20 kg of wood wool per tree had been pre-soaked and dried. Prior to board manufacture, the wood wool was screened by sifting it through a grille measuring 40 x 50 mm (Plate 10.1 (b)) to remove fines shorter than about 10 mm. Screened wood wool was then weighed into batches of 504 g (for one board) and stored in open bags.

10.3.2 Additives used and their preparation

The additives and concentrations used to make WWCBs from unsoaked and soaked *A. mangium* wood wool are shown by the dots in Table 10.1 below.

Table 10.1 Compounds used and their molar concentrations.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conc. (M)</th>
<th>Tree 1</th>
<th>Tree 1 (s)</th>
<th>Tree 2</th>
<th>Tree 2 (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂</td>
<td>0.05</td>
<td>-</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>-</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>MgCl₂ (MC)</td>
<td>0.05</td>
<td>-</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>0.05</td>
<td>-</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>FeCl₃ (FC)</td>
<td>0.025</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>SnCl₄ (SC)</td>
<td>0.025</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>0.05</td>
<td>-</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>-</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Al₂(SO₄)₃ (AS)</td>
<td>0.05</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>Al(NO₃)₃ (AN)</td>
<td>0.05</td>
<td>-</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>-</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>Na₂SiO₃</td>
<td>0.1</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>-</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>Ca(NO₂)₂</td>
<td>0.05</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>Pozzolith*</td>
<td>10 mL</td>
<td>-</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>-</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>SC + MC</td>
<td>0.05 + 0.05</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>FC + MC</td>
<td>0.05 + 0.05</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>AS + MC</td>
<td>0.05 + 0.05</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>AN + MC</td>
<td>0.05 + 0.05</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>SC + MC</td>
<td>0.025 + 0.05</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>FC + MC</td>
<td>0.025 + 0.05</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>*</td>
</tr>
</tbody>
</table>

*Pozzolith is a CaCl₂-based solution containing polymers to enhance cement strength. (s) denotes soaked wood wool.
In most cases two concentrations, 0.05 M and 0.1 M, were used for unsoaked wood. Exceptions to this were compounds known to have no effect at 0.05 M, including CaCl$_2$, MgCl$_2$, Na$_2$SiO$_3$ and SrCl$_2$. In the case of other accelerators such as SnCl$_4$ and FeCl$_3$, 0.1 M was too strong for use with pre-soaked wood wool. Instances where a particular compound and concentration was not used is indicated by a hyphen in Table 10.1.

10.3.3 Manufacture of WWCBs

Medium-density WWCBs (target 700-900 kg/m$^3$) were manufactured from shredded, air-dried $A.~mangium$ wood wool to examine the effects of the addition of water-soluble inorganic salts on the mechanical properties of boards. Boards were manufactured using a wood-cement ratio of just under 1:1, as recommended by Soriano et al. (1997). Each board contained 504 g of wood wool, 508 g of portland cement ASTM Type 1 (Blue Circle Southern Cement Batch No. 23MA01), and 523 g of water to which each additive was added at a specified concentration, either 0.05 or 0.1 M and in some cases 0.025, 0.2, 0.4 or 0.6 M. The solution containing the pre-dissolved accelerator was first sprinkled through the wood wool to wet all strands. Pre-spraying or mixing wood wool with a small amount of accelerator solution is preferable to pre-dipping, since the accumulation of leached inhibitory wood constituents will reduce the effectiveness of the stock solution (Sandermann 1971, Simatupang et al. 1977). The treated wood wool was then left for 2 to 3 minutes to allow any reactions with wood constituents such as heartwood polyphenols to take place. The cement powder was then sprinkled through the wet wood wool in stages interspersed with hand mixing to evenly coat all strands with cement, as shown in Plate 10.1 (c). The mix was then transferred to a formply mould measuring 300 x 380 mm placed on a rectangular sheet of melamine-coated formply measuring 340 x 420 x 17 mm. The mix was evenly spread and flattened using a wooden block to form a mat as shown in Plate 10.1 (d). The mould was removed and another piece of formply was placed on top of the mat. Two wooden spacing rods measuring 12 x 12 x 300 mm were placed at either end between the formply sheets to ensure that final pressed board thickness was 12 mm. The resulting assemblage was pre-pressed while the mat for the next board was mixed, and the process was repeated to produce a sandwich of two mats between three sheets of formply. This stack of mats was then placed between two steel plates measuring 340 x 470 x 15 mm and pressed at ambient temperature to 20 000 psi using a PHI hydraulic operated press (Plate 10.1 (e)). The compressed mats were kept under pressure for 24 h by bolting the two steel plates together using four 8 mm thick bolts, an assemblage that could then be removed from the press. After 24 h the boards were de-clamped, stacked and conditioned for 10 weeks at 20 ± 1°C and 65 ± 5% r.h. to allow the cement to cure and gain strength. Between 2 and 4 boards were manufactured per day and a total of 100 boards were manufactured over a period of about 50 days.
(a) pre-soaking wood wool  
(b) sifting wood wool to remove fines  
(c) coating the wood wool with cement  
(d) distributing the WWCB mat  
(d) PHI platen press with clamp jig to right  
(e) sample board with test sample on left  

Plates 10.1 (a) to (e) Laboratory WWCB manufacturing process.
10.3.4 Determination of board mechanical properties

Each conditioned board measuring 340 x 320 x 12 mm was sawn into five test samples measuring 230 x 50 mm using a large bandsaw. In the absence of a standard test method for medium-density WWCBs, the size of the test pieces used to determine board flexural properties was adapted from the Philippine Standard for 12 mm Particleboard (1976). Samples 1 and 3 were tested for MOR and MOE in the dry condition. Samples 2 and 4 were tested for MOR and MOE in the wet condition, after they had been immersed in water at ambient temperature (23°C) for a period of 24 h. Prior to soaking, the samples were weighed and their thickness measured at three points along their length using a Mitutoyo digital caliper. These measurements were used to determine the basic density of pieces 2 and 4 (see Section 10.3.5). After soaking, the samples were drained on paper towels for 20 min to remove excess water. The thickness and weight of each sample were re-measured, and the absorption of water (WA %) and thickness swelling (TS %) of samples were calculated and expressed as percentage of original sample weight and thickness, respectively. Three-point flexural tests were carried out using the Instron 4505 Universal Testing Machine, using a span of 18 mm, cross-head and bearer diameter of 25 mm and loading speed of 5 mm/min (test jig shown in Chapter 7).

10.3.5 Experimental design and statistical analysis

The experiment was designed to compare the effects on board mechanical properties of 2 treatments: (i) pre-soaking or not pre-soaking the wood wool in water prior to manufacture (2 levels); and (ii) additive type/concentration (A/C) combination (34 levels). One or more different concentrations were used for each of the 16 additives tested. Boards covering the 34 additive/concentration combinations for wood wool from Tree 1 (unsoaked) were made first (in a randomised order) followed by all 34 randomised combinations for Tree 2 (soaked), Tree 2 (unsoaked) and finally Tree 1 (soaked). One board was made for each A/C combination from each Tree/Soaking (T/S) combination. After conditioning, each board was cut into 5 sections, two of which were tested dry (pieces 1 and 3) and two (pieces 2 and 4) tested in the wet condition. The resulting split-plot design accounted for variation at 3 levels: variation between T/S combinations, variation between boards, and variation between sections.

Sample density was only measured on those sections used in the wet tests. The values determined from the wet test sections for each board were therefore randomly assigned to the dry test sections from the same board. For all response variables except water absorption, analysis of the residual plots showed greater variation among the samples from boards containing unsoaked wood wool compared with samples from boards containing pre-soaked wood wool. In general, while samples from boards containing pre-soaked wood wool had higher responses than those from
boards containing unsoaked wood wool for response variables, there was no evidence of an increase in variation with response variable for WWCBs made from pre-soaked or unsoaked wood wool which would suggest transforming the response variables. Therefore, unlike some experiments presented in previous Chapters, the analysis here allowed for the different levels of variation in the data sets for boards made from soaked and unsoaked wood wool.

Mixed linear models were used to analyse the results, specifically the effects of pre-soaking the wood wool and addition of accelerators on board properties. Board density was treated as a covariate and the three levels of variation (above) as random effects. Fixed effect terms were retained in the model if Wald tests showed them to be significant at the 5% level. Significant results are plotted graphically and bars representing the least significant difference (p ≤ 0.05) are included on graphs to facilitate comparison of means.

10.3.6 Effect of accelerators on wood wool strength

The effects on strand strength of exposure to selected accelerator solutions at the concentrations used in the manufacture of boards were tested using wood wool strands from poplar (*Populus deltoides* L.). Poplar was used instead of *A. mangium* wood wool because the *A. mangium* wood wool was not straight grained and was highly variable in thickness compared with poplar wood wool. In contrast poplar strands were thinner and more uniform and hence could be tested for tensile strength using a purpose-designed filament test jig. Straight-grained strands of poplar ranging between 100 and 200 µm in thickness that were kink- and damage-free were selected from bales of commercially produced wood wool. Strands were divided into batches of six, numbered from 1 to 6 and allocated to one of 11 selected accelerator/concentration combinations. The thickness of each strand was measured using a digital micrometer (Lorentzen & Wettre) shown in Plate 10.2 (a). Strands were then conditioned in a conditioning room for four weeks at 20 ± 1°C and 65 ± 5% r.h. to 12% MC. The central 20-mm portion of each strand was immersed in a 10-mL-capacity beaker containing the accelerator solution for three min, air dried for three days and placed back in the conditioning room at 20 ± 1°C and 65 ± 5% RH for another four weeks until ready for testing. Accelerators tested included Al₂(SO₄)₃, FeCl₃ and SnCl₄ at 0.05 and 0.1 M, CaCl₂ and MgCl₂ at 0.1 and 0.2 M, and Na₂SiO₃ at 0.4 M.

Conditioned strands were tested for tensile strength using a 10-mm filament and strand testing jig mounted on the Instron 4505 Universal Testing Machine, as shown in Plate 10.2(b). The span was fixed at 100 mm, loading speed was 5 mm/min, and strands were tested to failure. Maximum load at breaking point (N), stress to breakage (MPa) and energy to breakage (J), i.e. the area under the load-displacement line, were determined and averaged for each of the six replicates. Only stress was plotted and discussed since all response variables were strongly correlated with each other.
Plates 10.2 (a) Strand thickness micrometer and (b) tensile test jig used to determine the tensile properties of wood wool strands exposed to different kinds of cement set accelerators.

10.3.7 Assessment of nail corrosion

The remaining fifth portion from each WWCB was used to test the effects of board composition on the corrosion of four different types of readily available iron-based nails. Four nails of each type were nailed into each test piece. The nail types were:

1. ordinary wood nails (Otter brand bullet head bright 25 mm x 1.8 mm);
2. wood tacks (Otter brand cut tacks blued 20 x 1.6 mm);
3. hardboard nails (Otter brand hardboard zinc plated 25 x 1.6 mm); and
4. fibre-cement nails (Otter brand fibre-cement galvanised 25 x 2 mm).

Each test piece was drawn up into 4 sections, into which one of each nail type was hammered until it reached the bottom of the board, leaving approximately 6 mm of nail head exposed. Examples of the embedded nails can be seen in Plates 10.4 (a) to (c), which show nails after exposure to corrosion. The weight of each nail and its position in the test piece was recorded prior to nailing. The test pieces containing the nails were then cut into two halves, one half to be tested in
a highly corrosive environment in which samples were subjected to periodic wetting and the other in a humid but less corrosive environment protected from direct sources of moisture such as rain. The two types of test pieces were placed in shallow 8-L-capacity plastic tubs in which they were suspended on stiff polypropylene mesh above a shallow bath of water in the bottom of the tub, as shown in Plate 10.3.

The sealed tubs were placed in a controlled temperature room maintained at 30°C to create a environment of high relative humidity around the test pieces in order to simulate the humid conditions found in the tropics. The samples in the high or 'wet' corrosion environment were sprayed with distilled water every two weeks to simulate periodic wetting by rain. After 18 months of exposure, the samples were carefully removed from the tubs to avoid disturbing the friable deposits of rust products on the nails. Since it was not possible to remove the nails for re-weighing without significant damage, breakage and disturbance of the rust deposits, the nails were instead given a non-destructive visual assessment of the accumulation of rust. Each nail was given a score between 0 (no change in nail surface) and 5 (heavily encrusted or broken off). An accumulated score for the two nails of each type was determined for each sample and used to generate an average corrosion index between 0 and 10 for each board in the 'wet' and 'dry' corrosion environments. For the purpose of statistical analysis, the accumulated scores for each nail were treated as continuous variables. The analysis assessed the effects of four factors: 'compound', 'concentration', 'environment' and 'nail type', and a composite factor ('compound/concentration') which incorporated data for all concentrations of each compound.

Plate 10.3 Sealable tub containing water, elevated mesh and corrosion test samples.
10.4 Results and discussion

The type of additive used and its concentration ('treatment'), and whether unsoaked or pre-soaked wood wool was used, significantly affected the mechanical properties of WWCBs manufactured from *A. mangium* wood wool, as shown in Table 10.2. There was also a significant interaction ($p < 0.001$) between 'treatment' and soaking on the density and strength properties of boards when tested in the dry condition.

Table 10.2 Chi-squared probabilities (p-values) for significance of effects of additive/concentration ('Treatment') and pre-soaking wood wool ('Soaking') on board mechanical properties.

<table>
<thead>
<tr>
<th></th>
<th>MOR</th>
<th>WMOR</th>
<th>MOE</th>
<th>WMOE</th>
<th>TS</th>
<th>WA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Soaking</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Treat x Soaking</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Basic Density*</td>
<td>0.162</td>
<td>&lt;0.001</td>
<td>0.579</td>
<td>&lt;0.001</td>
<td>0.1036</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>

*Based on analysis of co-variance testing for any further variation explained by basic density

10.4.1 Density and strength properties of boards containing unsoaked wood wool and single compounds

The addition of different accelerators at different concentrations to WWCBs made from unsoaked *A. mangium* wood wool had a highly significant effect ($p < 0.001$) on board consolidation (density) and strength properties. The bending strength (MOR) and stiffness (MOE) of cement-bonded wood composite boards are strongly correlated with board density (Badejo 1988, Wolfe and Gjinolli 1997); and for the WWCBs manufactured here board density (as influenced by treatment) largely determined their strength properties, as shown in Figure 10.1. No boards below 620 to 640 kg/m$^3$ were above the minimum MOR of 6.75 MPa required by the Philippine National Standard for non-structural 12-mm medium-density WWCB (PNS/CTP 07: 1990). The Japanese Industrial Standard for 12-mm-thick particleboard (JIS-A 5908: 1994) requires a minimum MOR of 7 MPa. The majority of boards over 700 kg/m$^3$ in density met or exceeded these requirements and no boards under 800 kg/m$^3$ were below 7 MPa in MOR (Figure 10.1).

Figures 10.2 (a) and (b) show the average basic density of boards manufactured from unsoaked and soaked *A. mangium* wood wool using different accelerators at (a) 0.05 M and (b) 0.1 M solution strength, respectively. At 0.05 M strength (Figure 10.2 (a)), only boards containing SnCl$_4$ were comparable in density to their counterparts made from pre-soaked wood wool. At 0.1 M concentration both SnCl$_4$ and FeCl$_3$ resulted in well-consolidated boards of higher density (>700 kg/m$^3$) when unsoaked wood wool was used to manufacture boards, as shown in Figure 10.2(b). Boards containing these accelerators and unsoaked wood wool attained similar high average density (>720 kg/m$^3$) to boards containing pre-soaked wood wool and conventional accelerators such as
CaCl₂ or 'Pozzolith' (Figure 10.2(b)). The density of boards containing Ca²⁺ and Sr²⁺-based accelerators and unsoaked wood wool was low (<500 kg/m³), regardless of concentration used.

Figure 10.1 Modulus of Rupture (MOR) v Basic Density for all boards manufactured. Lines show minimum MOR (7 MPa) specified in JIS-A 5908, and corresponding minimum board density (640 kg/m³), below which no boards met this standard.

Figures 10.2 Average basic density of boards manufactured from unsoaked and soaked A. mangium wood wool with accelerators at (a) 0.05 M and (b) 0.1 M strength.
In terms of bending strength (MOR) of boards made from unsoaked wood wool shown in Figures 10.3 (a) and (b); only two compounds—FeCl₃ and SnCl₄—were effective in enhancing MOR to a level that exceeded the PNS/CTP 07 (1990) standard for non-structural 12 mm WWCB of 6.75 MPa, and even the more stringent ISO 8335 (1987) for cement-bonded particleboard of 9 MPa. When used at 0.1 M strength, both FeCl₃ and SnCl₄ were effective in strengthening boards made from unsoaked *A. mangium* wood wool. Such boards averaged 10.9 and 10.8 MPa in MOR, respectively, (Figure 10.3(b)). At 0.05 M concentration (Figure 10.3(a)), only the use of SnCl₄ (equivalent to 1.8% of cement weight) resulted in boards of above-standard strength (MOR = 11.6 MPa). At this lower concentration the use of FeCl₃ resulted in average MOR of only 4.7 MPa. All other compounds added at 0.1 M concentration failed to produce boards of acceptable strength from unsoaked wood wool even though in some cases (AlCl₃ and Al₂(SO₄)₃) board density was only slightly below 700 kg/m³. This suggests that, despite moderate to good cement consolidation in the boards, the bond strength developed between the wood and cement may have been lower.

In terms of stiffness (MOE), boards made from unsoaked wood wool and containing SnCl₄ were strongest (MOE = 2284 MPa for 0.05 M and 2256 MPa for 0.1 M addition), as shown in Figures 10.4 (a) and (b), respectively. At 0.1 M, boards containing FeCl₃ attained an average MOE of 2178 MPa. MOE values for boards containing all other accelerators were significantly lower (p < 0.001), below 800 MPa for 0.05 M and below 1200 MPa for 0.1 M addition.
The strength properties of boards made from unsoaked *A. mangium* wood wool and containing small amounts of SnCl₄ and FeCl₃ were higher than those achieved in other studies that have attempted to manufacture WWCBs with a similar wood:cement ratio from *A. mangium* wood using cement-setting accelerators, even when pre-soaked wood wool was used. In a study by Soriano *et al.* (1997), MOR of boards made from pre-soaked *A. mangium* and containing 3% CaCl₂ or Al₂(SO₄)₃ was about 6 MPa. In a study by Eusebio *et al.* (2000b) MOR of boards made from pre-soaked wood wool and the same two accelerators at 3% w/w cement reached 8 MPa, but had low MOE of about 1500 MPa. Cabangon *et al.* (1998) manufactured boards from pre-soaked wood wool and CaCl₂, Al₂(SO₄)₃ or FeCl₃. The MOR of these boards varied between 1.5 and 2 MPa, figures that are remarkably low considering that pre-soaked wood wool was used. The boards manufactured in the study by Cabangon *et al.* (1998) also had unusually high water absorption, between 145 and 155% of board dry weight. In a study by Lynch (1997) WWCBs were manufactured using pre-soaked wood wool and 3.1% CaCl₂. Average MOR for these boards was 8.5 MPa and average MOE was 700 MPa, but for reasons that were not explained the MOE of the boards was very low.

The results from this study accord well with the hypothesis advanced in Chapter 9 whereby only cement-setting accelerators with the ability to chemically interact with heartwood polyphenols by forming insoluble complexes are likely to be effective in low concentrations in improving the properties of wood-cement composites made from tropical hardwoods like *A. mangium*, which
contain inhibitory heartwood polyphenols. Boards containing accelerators with no ‘complexing’ capacity, such as SrCl₂, CaCl₂ and Pozzolith, failed to consolidate even after the solution concentration was doubled to 0.2 M. The inability of CaCl₂ to produce consistently adequate setting of the cement directly in contact with the wood surface of *A. mangium* heartwood was shown using scanning electron microscopy in Chapter 9, and is likely to have contributed to the poor bonding and consolidation of WWCBs containing CaCl₂. Lee and Short (1989) have found that the efficacy of CaCl₂ at improving the properties of WWCB is extremely variable, depending on the type of wood used to make boards. CaCl₂ was found to be effective in the case of sweetgum (*Liquidambar styraciflua* L.), and ineffective in the case of red oak (*Quercus falcate* Michx.) where oak tannin or quercetin was the primary cause of low compatibility. Tachi *et al.* (1988) and Subiyanto and Firmanti (1998) have also found CaCl₂ to be ineffective at counteracting the inhibitory effects of heartwood polyphenols (including teracacidin) during the manufacture of wood-cement composites from untreated *A. mangium* wood.

10.4.2 The effect of using pre-soaked wood wool and single compounds on board properties

The wood of *A. mangium* is widely considered to be unsuitable for the manufacture of wood-cement composites without some form of pre-treatment (Rahim and Ong 1983, Jegasethwaran 1989, Tachi *et al.* 1988, 1989). Soaking in water at ambient temperature is effective at enhancing its compatibility, although it has been found to be necessary to soak *A. mangium* wood wool in tepid water for at least 6 h to facilitate the manufacture of WWCBs of acceptable quality even with the aid of accelerators (Soriano *et al.* 1997, Cabangon *et al.* 1998, Eusebio *et al.* 2000b). Some researchers suggest 24 hours is necessary (for example Sulastiningsih *et al.* 1990).

In this study the use of pre-soaked wood wool had a highly significant (*p < 0.001*) effect on board mechanical properties. As shown in Figures 10.2 (a) and (b), the use of wood wool that had been pre-soaked for 24 h usually resulted in boards with basic density above 750 kg/m³; above the minimum of 600 kg/m³ for 12-mm-thick WWCBs specified in the Philippine Standard PNS/CTP 07 (1990). Boards reached an average MOR of 8 MPa without the use of accelerators; however many accelerators, particularly CaCl₂, further improved board strength even when added at the low concentration of 0.05 M, as shown in Figure 10.3(b). Boards containing 0.1 M CaCl₂ and pre-soaked wood wool attained an average MOR of almost 15 MPa, well above the minimum of 9 MPa specified by ISO 8335 for higher density and higher cement-content CBP products. Where pre-soaked wood wool was used, a 0.05 M solution concentration of accelerator was sufficient to manufacture boards of acceptable density and strength, as shown in Figures 10.2 (b) and 10.3 (b). However, even when pre-soaked wood wool was used no single compound either at 0.05 or 0.1 M resulted in boards exceeding the minimum MOE of 3000 MPa specified in ISO 8335 for CBP.
Although the addition of accelerators and/or the use of pre-soaked wood wool produced boards with MOR similar or higher than that of CBP, the much lower cement content of the boards is likely to have reduced their MOE to below that of CBP, despite the addition of cement-setting accelerators. When using pre-soaked wood wool for board manufacture the addition of many of the accelerators, including SnCl₄ and Al₂(SO₄)₃, became unnecessary and resulted in little improvement in board strength. Provided the wood is relatively free of inhibitory heartwood tannins simple, inexpensive accelerators based on CaCl₂ can be among the most effective compounds for improving board strength properties. Some of the accelerator compounds, including CaCl₂ and Pozzolith, FeCl₃ and AlCl₃, increased board MOR by up to 50% compared to boards containing no accelerator. Work by Cabangon et al. (1998) also showed that pre-soaked A. mangium wood wool responded particularly well to conventional cement-setting accelerators (CaCl₂, Al₂(SO₄)₃ and FeCl₃) producing consistently stronger boards than similarly treated eucalypt (E. pellita) or poplar (P. euramerica) wood.

10.4.3 Dimensional stability of WWCBs

The effects of different accelerators on board thickness swelling (TS) are shown in Figures 10.5 (a) and (b) for 0.05 M and 0.1 M levels, respectively. The water absorption (WA) of WWCBs is shown in Figures 10.6 (a) and (b).

Figures 10.5 Average thickness swelling of boards manufactured from unsoaked and soaked A. mangium wood wool with accelerators at (a) 0.05 M and (b) 0.1 M strength.
At 0.05 M, only SnCl₂ reduced TS to below 5% when unsoaked wood wool was used. While most accelerators added at 0.1 M strength resulted in moderate to good dimensional stability of boards, only the addition of SnCl₄ and FeCl₃ reduced thickness swelling to 5% or below as specified in JIS-A 5908. These boards also absorbed the lowest quantity of water during immersion, less than 35% of their weight. ISO 8335 specifies a maximum TS of 2% after immersion in water for 24 h; however, this specification was intended for composites with high cement content, such as CBP, rather than WWCB. In contrast, moderately well consolidated boards such as those containing Al(NO₃)₃ and Ca(NO₂)₂ swelled by over 10% and absorbed water to over 50% of their weight, suggesting poor bonding between the wood and cement, and hence, reduced resistance to the deleterious effects of water.

Boards made from pre-soaked wood wool had good dimensional stability even when the level of accelerator addition was 0.05 M. All accelerator types reduced TS to below 5% (Figure 10.5 (a)) and WA to below 35% (Figure 10.6 (b)). However, there were only isolated instances where WWCBs were below the maximum TS of 2% specified for higher cement-content CBPs by ISO 8335, even when accelerators were added at 0.1 M strength. These are discussed in Section 10.4.5. In contrast to expectations, the WA values for boards containing pre-soaked wood wool with the higher levels of accelerators, specifically CaCl₂ and SrCl₂, were slightly higher, for unknown reasons.
10.4.4 Strength loss upon wetting

The ability of accelerators either individually or in combinations to consolidate the cement matrix was critical to achieving adequate board densification (greater than about 640 kg/m$^3$), which in turn resulted in higher strength and resistance to water. The effect of immersion in water for 24 h on the MOR of boards is shown in Figures 10.7 for boards containing compounds at concentrations of (a) 0.05 M and (b) 0.1 M.

![Figure 10.7](image-url)

Figures 10.7 Average wet MOR of boards manufactured from unsoaked and soaked *A. mangium* wood wool with accelerators at (a) 0.05 M and (b) 0.1 M strength.

All boards containing pre-soaked wood wool and an accelerator retained an average MOR above the minimum of 5.5 MPa specified in ISO 8336 (no minimum wet MOE is specified). No minimum wet MOR or wet MOE is specified in either JIS-A 5908 or PNS/CTP 07 for CBP or WWCBs. In contrast, the wet MOR of boards containing unsoaked wood wool was below 5.5 MPa. The use of unsoaked wood wool appears to have made boards more susceptible to water-induced deterioration of bonding between wood and cement despite good dry bond strength. The possible migration of extractives to the wood-cement interface caused by water during board soaking has been suggested by Eusebio *et al.* (2000b) as a possible explanation as to why exposure to water adversely affects board strength in WWCBs. Almost regardless of the dry strength of boards, most of them suffered losses in dry MOR of around 50% after exposure to water for 24 h.

Improvements in the resistance of boards to water-induced deterioration in strength through the use of additive combinations are examined in Section 10.4.5 below.
10.4.5 The effects of additive combinations

The effects of using small amounts of four compounds (Al₂(SO₄)₃, Al(NO₃)₃, FeCl₃ and SnCl₄), either on their own or mixed with 0.05 M MgCl₂ (i.e. 1% w/w cement) on the mechanical properties of boards containing unsoaked wood wool are shown in Figures 10.8 (a) for MOR and (b) for MOE. The effects of these same combinations on MOR and MOE of boards made from pre-soaked wood wool are shown in Figures 10.9 (a) and (b). Other board properties, including MOR after 24 h exposure to water, thickness swelling and water absorption are shown in Table 10.3.

Significant (p < 0.001) increases in the strength of boards made from unsoaked wood wool could be achieved by using 0.05 M MgCl₂ mixed with either 0.05 M Al₂(SO₄)₃ or 0.025 M SnCl₄. These boards were stronger than those containing these same compounds used individually at similar concentrations. With Al₂(SO₄)₃ the average board MOR increased from 4 MPa to 8.5 MPa, and with SnCl₄ from 3.5 MPa to 10.5 MPa. However no beneficial effect on strength was obtained by increasing the concentration of SnCl₄ to 0.05 M, possibly because board strength was already high after the addition of 0.05 M SnCl₄ on its own. The results suggest that 0.025 M SnCl₄ may have been sufficient to neutralise enough inhibitory extractives from the wood wool to enable a relatively small amount of supplementary MgCl₂ to further accelerate the hydration and consolidation of the cement binder.

In contrast to SnCl₄, the same effect could not be achieved by combining a small amount of FeCl₃ (either 0.025 or 0.05 M) with MgCl₂. SnCl₄ has been found in this study to be a more effective accelerator than FeCl₃, particularly at low concentrations, and therefore could have had a greater synergistic effect with MgCl₂ that was particularly effective at neutralising the inhibitory effects of A. mangium wood on the hydration of cement. Whether the same effect could be achieved by supplementing a compound such as SnCl₄ with CaCl₂ is unknown and would certainly be worthy of further investigation. As discussed in Chapter 9 MgCl₂, unlike CaCl₂, is also capable of chemically neutralising the effects on cement hydration of catechol-based heartwood polyphenols, which helps explain its beneficial effect in additive mixtures.

Na₂SiO₃ has been used in combination with other cement setting accelerators to significantly enhance the properties of cement-bonded wood composites. It is possible that this compound would also have worked well in combination with many of the accelerators used in this study. Na₂SiO₃ was to be tested as a mixture with other accelerators in this study except that Na₂SiO₃ could not be mixed with other accelerators such as SnCl₄ or FeCl₃ without the formation of a precipitate and subsequent difficulty adding the active ingredients in soluble form to the wood wool prior to adding cement. It might be worthwhile adding Na₂SiO₃ after another accelerator (such as SnCl₄, MgCl₂ or FeCl₃) has been added to the wood wool, as part of a two-step process.
The effect of supplementing individual accelerators with 0.05 M MgCl$_2$ on the strength of boards made from pre-soaked wood wool was broadly similar to that observed for boards made from unsoaked wood wool. Strength properties of boards containing 0.05 M SnCl$_2$ plus 0.05 M MgCl$_2$ were significantly higher than if either of these compounds were added on their own. The
effect of supplementing $\text{Al}_2(\text{SO}_4)_3$ with 0.05 M $\text{MgCl}_2$ was also positive, but less pronounced. Doubling the quantity of $\text{SnCl}_4$ added to pre-soaked wood wool resulted in a decrease in board strength; however this did not occur if $\text{SnCl}_4$ was mixed with $\text{MgCl}_2$. MOR was significantly increased by supplementation with $\text{MgCl}_2$ in this case, but the effect was not much greater than that produced by adding 0.025 M $\text{SnCl}_4$ or $\text{FeCl}_3$, and was less than that obtained through adding $\text{CaCl}_2$. Note, however, that in certain instances where pre-soaked wood wool was used, boards met the minimum MOE of 3000 MPa specified in ISO 8335 for high cement-content CBP. Average MOE for boards containing the combinations $\text{SnCl}_4$ at 0.05 M + $\text{MgCl}_2$ at 0.05 M and $\text{Al(NO}_3)_3$ at 0.5 M + $\text{MgCl}_2$ at 0.05 M were 3178 and 3109 MPa, respectively. This is an important finding which supports the suggestion of Sorfa (1984) that small amounts of selected accelerators can greatly improve the properties of low-cement-content composites such as WWCB, potentially giving lower-density panels similar mechanical properties (MOR and MOE) to composites that contain much higher quantities of portland cement, such as CBP.

Table 10.3 shows the average values for wet MOR, TS and WA of boards containing unsoaked and pre-soaked wood wool with the above-mentioned additive combinations and with only the single compounds. Instances where boards met the ISO 8335 Standard for wet MOR and TS are shaded in blue.

Table 10.3 Wet MOR, Thickness Swelling and Water Absorption of boards made from unsoaked and pre-soaked wood wool.

<table>
<thead>
<tr>
<th>Boards made from unsoaked wood wool</th>
<th>Wet MOR (MPa)</th>
<th>Thickness Swelling (%)</th>
<th>Water Absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Single comp.</td>
<td>+1% $\text{MgCl}_2$</td>
<td>Single comp.</td>
</tr>
<tr>
<td>$\text{MgCl}_2$</td>
<td>--</td>
<td>1.6</td>
<td>--</td>
</tr>
<tr>
<td>$\text{FeCl}_3$ 0.025</td>
<td>1.7</td>
<td>2.29</td>
<td>10.6</td>
</tr>
<tr>
<td>$\text{FeCl}_3$ 0.05</td>
<td>2.1</td>
<td>2.73</td>
<td>5.9</td>
</tr>
<tr>
<td>$\text{SnCl}_4$ 0.025</td>
<td>2.2</td>
<td>5.53</td>
<td>11.5</td>
</tr>
<tr>
<td>$\text{SnCl}_4$ 0.05</td>
<td>4.7</td>
<td>5.32</td>
<td>3.8</td>
</tr>
<tr>
<td>$\text{Al}_2(\text{SO}_4)_3$</td>
<td>2.1</td>
<td>3.80</td>
<td>9.3</td>
</tr>
<tr>
<td>$\text{Al(NO}_3)_3$</td>
<td>0.9</td>
<td>2.28</td>
<td>13.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Boards made from pre-soaked wood wool</th>
<th>Wet MOR (MPa)</th>
<th>Thickness Swelling (%)</th>
<th>Water Absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>4.7</td>
<td>--</td>
<td>5.6</td>
</tr>
<tr>
<td>$\text{MgCl}_2$</td>
<td>5.6</td>
<td>5.1</td>
<td>2.8</td>
</tr>
<tr>
<td>$\text{FeCl}_3$ 0.025</td>
<td>6.9</td>
<td>7.1</td>
<td>2.6</td>
</tr>
<tr>
<td>$\text{FeCl}_3$ 0.05</td>
<td>6.2</td>
<td>7.7</td>
<td>2.9</td>
</tr>
<tr>
<td>$\text{SnCl}_4$ 0.025</td>
<td>8.1</td>
<td>10.0</td>
<td>1.6</td>
</tr>
<tr>
<td>$\text{SnCl}_4$ 0.05</td>
<td>5.1</td>
<td>9.7</td>
<td>2.0</td>
</tr>
<tr>
<td>$\text{Al}_2(\text{SO}_4)_3$</td>
<td>5.4</td>
<td>6.9</td>
<td>3.7</td>
</tr>
<tr>
<td>$\text{Al(NO}_3)_3$</td>
<td>6.4</td>
<td>9.2</td>
<td>4.2</td>
</tr>
</tbody>
</table>

LSD 1.9 2.6 7.0

Blue shading denotes cases conforming to ISO 8335 for wet MOR and TS.

In Section 10.4.4 it was shown that the addition of single compounds at either 0.05 M or 0.1 M strength to boards made from unsoaked wood wool was insufficient to prevent large strength losses
when boards were exposed to water. However, combining selected additives with MgCl₂ often resulted in better retention of board strength after wetting, particularly in the case of additive combinations containing SnCl₄.

It can be seen in Table 10.3 that combining 0.025 M SnCl₄ with 0.05 M MgCl₂ produced boards with a residual MOR in excess of 5.5 MPa after they were exposed to water for 24 h. Combining a small quantity of SnCl₄ with MgCl₂ appears to have improved the resistance of wood-cement boards to deterioration by water. As can be seen from Table 10.3, the combination of SnCl₄ at 0.025 M and MgCl₂ at 0.05 M also significantly increased the dimensional stability of boards, reducing average TS from 11.5% for boards containing SnCl₄ (0.025 M) on its own to 2.7 % if SnCl₄ was used in combination with MgCl₂. In fact the TS of boards made from pre-soaked wood wool with SnCl₄ at 0.025 or 0.05 M plus 0.05 M MgCl₂ was below 2%, meeting the stringent requirement for CBP in ISO 8335 but at much lower cement content.

Water absorption was also reduced from over 50% to 31%. Note, however, that the same effect was not observed if 0.025 M FeCl₃ was combined with MgCl₂. Combining Al₂(SO₄)₃ with MgCl₂ also had a beneficial effect on the resistance of boards to water.

As shown earlier, the addition of most compounds resulted in boards retaining a wet MOR of 5.5 MPa or above as specified by ISO 8335. However, boards containing pre-soaked wood wool and combinations of SnCl₄ or Al(NO₃)₃ with MgCl₂ retained a higher average wet MOR (> 9 MPa) than did other boards containing pre-soaked wood wool. This suggests that certain combinations of additives could enable the production of WWCBs with a higher resistance to water.

10.4.6 Further enhancement of board properties

The properties of WWCBs made from unsoaked A. mangium wood could be further enhanced by increasing the level of addition of certain compounds that were relatively ineffective when used in small quantities. Unlike either CaCl₂ or SnCl₄, higher quantities of accelerators such as MgCl₂ and Na₂SiO₃ added to unsoaked A. mangium wood wool significantly improved board consolidation and strength over time, as shown in Figure 10.10. The addition of 0.2 M MgCl₂ (4.5% w/w cement) resulted in an average board MOR of 11.0 MPa, a significant increase from the 3.8 MPa obtained when 0.1 M MgCl₂ was added. Residual MOR after exposure to water for 24 h was also above 5.5 MPa, suggesting that higher quantities of MgCl₂ could produce better resistance to deterioration by water, even if inhibitory heartwood polyphenols are retained in the wood. The findings for MgCl₂ accord well with the findings of Tachi et al. (1988) and Yasuda et al. (1992) which showed that MgCl₂, unlike CaCl₂, was a powerful agent for neutralising the inhibitory effects of acacia heartwood polyphenols, as discussed in Chapter 9.
Increased board strength could also be obtained by adding increasingly large quantities of Na$_2$SiO$_3$. The addition of 0.4 M (8.4% w/w cement) and 0.6 M (12.6%) of Na$_2$SiO$_3$ resulted in boards with average MOR of 14.5 MPa and 17 MPa, respectively. Corresponding values for the MOE of these boards were 2876 and 3229 MPa, significantly higher than for any other boards made from unsoaked wood wool. Research by Melnikova and Bulnaeva (1995) showed that the addition of Na$_2$SiO$_3$, Al$_2$(SO$_4$)$_3$ and technical lignosulphonate (a retarder) to WWCBs resulted in increased density and fortification of the usually porous interface between the wood surface and cement, which greatly enhanced the strength of the composites after curing.

However, this same effect could not be achieved by adding larger amounts of SnCl$_4$, because of the deterioration in strand strength (which is discussed in Section 10.4.7 and is shown in Figure 10.11). MgCl$_2$ and Na$_2$SiO$_3$ are agents that, when used in larger quantities, accelerate cement setting and also improve cement strength and bonding in wood-cement boards over time. They are therefore commonly used in the manufacture of CBPs, often in combination, to counteract the inhibitory effects of untreated wood particles on cement hydration (Eusebio et al. 1995, Nagadomi et al. 1996). The results from this study indicate that these accelerators could also be very useful in the manufacture of WWCBs from inhibitory tropical hardwoods like *A. mangium*.

![Figure 10.10](image-url)  
**Figure 10.10** Effect of concentration of different accelerators on dry and wet MOR of WWCBs made from unsoaked *A. mangium* wood wool.
10.4.7 Effect of accelerators on strand strength

Figure 10.11 shows the effect of selected accelerator compounds at different concentrations on the tensile properties of poplar wood wool strands. FeCl$_3$ at 0.1 M and SnCl$_4$ at 0.05 and 0.1 M significantly (p = 0.004) reduced strand strength. In contrast, other accelerators such as Na$_2$SiO$_3$ and MgCl$_2$, even when used at higher concentrations, did not significantly reduce wood wool strength.

The solutions of SnCl$_4$ and FeCl$_3$ were strongly acidic (pH < 2.5 to 3) which was likely to have caused the pronounced deterioration in strand strength observed here. This may explain why increasing the content of SnCl$_4$ in WWCBs from 0.05 M to 0.1 M resulted in no further increase in board strength (Figures 10.3 (a) and (b)). MOR of boards containing SnCl$_4$ at 0.05 and 0.1 M and FeCl$_3$ at 0.1 M were all between 10 and 11 MPa, whereas the addition of a very high quantity of Na$_2$SiO$_3$ (>10% w/w cement) resulted in boards that exceeded 15 MPa in bending. The deleterious effects of SnCl$_4$ and FeCl$_3$ at 0.1 M on strand strength suggests that, if addition is above about 0.05 M, the benefits of improved cement hydration and bonding with wood strands may be offset by significant weakening of the reinforcing strands. Another study (Kayahara et al. 1979) also showed that the strength of WWCBs can be adversely affected by the addition of acidic accelerators (in their case AlCl$_3$) above a concentration of 3%. Exposure of wood to acids or alkalis (outside the pH range 3-10) has highly deleterious effects on its strength (Kollmann 1951, Gobie 1954, Thompson 1968). The results here suggest that the addition of acidic accelerators should be minimised and preferably supplemented with a larger quantity of a more benign compound such as MgCl$_2$ or Na$_2$SiO$_3$ to further enhance composite strength if required.

![Graph showing the effect of different accelerators and concentrations on the tensile strength of wood wool strands.](image)

$p = 0.004$

Figure 10.11 Effect of different accelerators and concentrations on the tensile strength of wood wool strands.
10.4.8 Relating cement hydration data to WWCB strength properties

Despite the large number of studies that have tested the compatibility of wood with cement using cement hydration tests, few of these have attempted to relate the cement hydration indices obtained from such tests to the strength properties of different types of wood-cement composite panels. A few studies have compiled results from both hydration tests and properties of composite boards to produce predictive models for the strength properties of CBPs based on hydration exotherms (Osinski and Potter 1997, Ma et al. 2002a). Lee and Hong (1986) found a close linear correlation between maximum hydration temperature \( T_{\text{max}} \) of wood flour-cement mixtures and the compressive strength of cylindrical casts containing the wood flour, but no correlation with hydration time. Wei et al. (2000a) found good correlations between the effects of a wide range of different wood species on the hydration of cement and their performance in CBPs. As discussed in Chapter 2, Lee et al. (1987) showed that the very high cement:wood ratios used in laboratory tests for wood-cement compatibility can mask the effects of species and treatments (particularly additives) on properties of cement-bonded boards, and that such tests are therefore a poor predictor of actual species/treatment suitability for commercial production of boards. Wood-cement hydration tests also do not account for the potential effects of accelerators on the final strength of wood-cement composites or the variable reinforcing capacity of wood elements in different shapes and sizes. Nevertheless, Wei et al. (2000b) found a good correlation between \( T_{\text{max}} \) generated in birch wood flour-cement mixes containing different accelerators with the strength properties of CBPs containing those compounds. Ma et al. (2002a) used total energy released during hydration (area beneath the time-temperature curve) to predict MOR and MOE of CBPs containing different additives.

Figure 10.12 shows the correlation between the hydration rate (a function of both temperature and time) generated in wood-cement mixes containing wood wool of A. mangium heartwood and accelerators at 0.1 M concentration from Chapter 9 and the MOR of boards containing A. mangium wood wool and the same accelerators added at 0.1 M concentration. As expected there was a significant \( (p < 0.001) \) positive correlation between the effect of the accelerator on cement setting over a 24-h period and its effect on the strength of WWCBs. However there was also high variation between different types of accelerator. For example, compounds above the regression line, such as \( \text{Na}_2\text{SiO}_3 \), \( \text{Al}_2(\text{SO}_4)_3 \), and \( \text{FeCl}_3 \), all imparted higher board strength properties than might be predicted by a regression model based purely on their effects on the hydration rate of a wood-cement mix.

Both \( \text{Na}_2\text{SiO}_3 \) and \( \text{Al}_2(\text{SO}_4)_3 \) are commonly used in the manufacture of CBPs and fibreboards because of their proven ability to strengthen the composite matrix over the curing period and during service (Goldberg et al. 1987, Simatupang et al. 1989, Kühne and Meier 1990, Chew et al. 1992, Eusebio et al. 1995, Nagadomi et al. 1996a-c). \( \text{Na}_2\text{SiO}_3 \) is usually added in liquid form and, being
deliquescent, it is believed to contribute water to ongoing hydration of the cement matrix over time. The strongly hydrated Al₂(SO₄)₃·9H₂O may produce a similar effect. These effects on hydration and matrix consolidation occur in the days, weeks and months after initial cement setting and are therefore not detected in the exothermic reaction monitored over a 24 h time frame. The ongoing effects of compounds such as Na₂SiO₃ on matrix consolidation and board strength over time were therefore not accounted for in the results generated by the wood-cement compatibility tests undertaken in Chapter 9.

![Figure 10.12](image)

Figure 10.12 Relationship between hydration rate attained in cement hydration test samples containing accelerators at 0.01 M concentration and the strength (MOR) of boards manufactured using the same accelerators and concentration.

In contrast, the addition of other aluminium-based compounds such as Al(NO₃)₃ and AlCl₃, as well as CaCl₂, SrCl₂ and MgCl₂, at the relatively low concentration of 0.1 M resulted in lower board strength properties than might be predicted on the basis of their effect on cement hydration. In these cases, results based solely on hydration rate (R) appear to have overestimated the potential effects of these compounds on the properties of WWCBs made from untreated A. mangium wood. One possible cause of this discrepancy is that the cement:wood ratio in hydration test samples is necessarily much higher (20:1) than that present in WWCB (1:1). In the cement hydration study the compounds were mixed with the cement before adding the heartwood strands to ensure complete and uniform addition, and this may have enabled compounds such as CaCl₂, MgCl₂ and SrCl₂ to accelerate cement hydration in zones not directly in contact with wood wool strands.

When manufacturing WWCBs it is necessary to coat the strands with the aqueous compound solution and then evenly coat the strands with a thin layer of cement powder. It is likely that unless
the chemical reacts immediately with inhibitory compounds in and on the surface of the wood wool they may still leach out and retard normal cement setting. This may have happened when small quantities of 'non-complexing' compounds such as CaCl₂, MgCl₂ and SrCl₂ were used in the manufacture of boards from unsoaked *A. mangium* wood wool.

However, the relatively poor performance of Al(NO₃)₃ and AlCl₃ in WWCBs manufactured in this study was not expected since these compounds also formed insoluble complexes with *A. mangium* heartwood polyphenols in the hydration study. Previous studies have shown that aluminium-based compounds can enhance the properties of wood-cement composites made from tannin-containing woods. It is possible that the concentration of the aluminium compounds (0.1 M) used here was not sufficient to fully counteract the inhibitory effects of heartwood polyphenols on cement hydration in WWCBs. Research by Yasuda *et al.* (1992) using inhibitory polyphenols with vicinal hydroxyl groups (from the heartwood of sugi) also found that AlCl₃ was only mildly effective in reducing its inhibitory potential, compared with MgCl₂. Their results accord with the findings here, so the same may also be true for inhibitory polyphenols from *A. mangium* heartwood. This particular accelerator may therefore not be suitable for the manufacture of wood-cement composites from woods such as *A. mangium*.

The results from this study suggest that, as a general guide, an accelerator should increase hydration rate in cement containing an inhibitory wood such as the heartwood of *A. mangium* to above about 4°C/h (which is at or above the rate of hydration produced by a hydration sample of the same size containing pure cement) if it is to be an effective additive for WWCB containing untreated wood wool.

10.4.9 Effects of WWCBs containing accelerators on deterioration of metal fastenings

Very few studies have assessed the effects of chloride-containing accelerators incorporated in wood-cement composites on the corrosion of metal fastenings. This is despite the fact that the problem of potential chloride-induced corrosion of metal contacts and fastenings is addressed in both the German (DIN 1101, 1989) and British (BS 1105, 1984) standards for WWCBs by specifying a maximum chloride content. In the German standard (DIN 1101 1987) the chloride ions leached by hot water from WWCB must not exceed 0.35% of the board mass. Despite these regulations, it has been claimed by Ye *et al.* (2002) that the use of CaCl₂ in CBPs does not affect the corrosion of metal fastenings.

Table 10.4 shows the effects of the factors 'compound/concentration', 'nail type', and 'corrosion environment' on the accumulation of oxides on iron-based nails embedded in WWCBs exposed to a wet or dry environment. 'Compound/concentration', 'nail type' and 'corrosion environment' had highly significant effects on the accumulation of oxides on nails. Most of the variation, however,
was accounted for by 'corrosion environment' (wet or dry) and 'nail type', as indicated by their large variance components (Wald statistic), rather than accelerator type.

Table 10.4 Chi-squared probabilities (p-values) for effects of factors on the accumulation of rust oxides on nails embedded in WWCBs made from A. mangium containing different accelerators.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Wald Statistic</th>
<th>Chi-square probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>compound/concentration</td>
<td>48.43</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>corrosion environment</td>
<td>231.86</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>nail type</td>
<td>338.82</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>comp. x corrosion environment</td>
<td>42.71</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>comp. x nail type</td>
<td>205.48</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>corr. environment x nail type</td>
<td>50.05</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>comp. x nail type x corr. environment</td>
<td>50.05</td>
<td>N.S.</td>
</tr>
</tbody>
</table>

There were also significant two-way interactions, but no lower order interaction between, all three factors. Figure 10.13 shows the interaction between compound and environment, averaged across nail type. The results show that the chloride-based accelerators did not corrode nails any more than other accelerators in the dry environment. However, chloride-based accelerators did, as expected, have significantly greater adverse effects on nails than the non-chloride accelerators in the wet environment. Note that there was a base-level average accumulation of oxides on nails (an effect largely confined to the two types of zinc-coated nails) through being in contact with the alkaline cement board. This was reduced, but not significantly, by the use of compounds such as Ca(NO$_2$)$_2$, a base-metal nitrite known to be a corrosion inhibitor (Rosenberg et al. 1977, Ramachandran 1996).

Figure 10.13 Average accumulation index for each accelerator in the wet and dry environments. Accumulation index derived from summation of visual scores for oxide accumulation on each nail type.
The four types of commonly available nails reacted very differently to the presence of different accelerators in WWCBs. Figure 10.14 shows the interaction between nail type and compound (averaged across environment) on corrosion. The interaction between nail type and environment (averaged across compound) on corrosion is shown in Figure 10.15. Both types of zinc-coated nails (zinc-plated and galvanised) had consistently high accumulation indices for rust oxides, between about 6 and 10, regardless of compound type (Figure 10.14) or corrosion environment (Figure 10.15). In contrast, the alkaline conditions of the WWCBs did not adversely affect the ordinary nails. However, both the zinc-coated nail types reacted strongly with the alkali and/or accelerators in the boards, causing the accumulation of oxide products over exposed nail surfaces. The galvanised nails were sold specifically for the fastening of fibre-cement boards, but still appeared to react strongly with alkali regardless of the moisture conditions. Where the fibre-cement nails were in contact with boards containing chloride the galvanising had been eaten away beneath the accumulated oxides leaving the core of the nail exposed to further rusting.

![Figure 10.14](image)

**Figure 10.14** The effects of different accelerators contained in WWCBs on the accumulation of oxides on four different kinds of nails.
Figure 10.15 The effect of corrosion environment (dry or wet) on oxide accumulation on different nail types exposed to cement-setting accelerators in WWCBs.

Contrary to expectation, the ordinary (and least expensive) wood nails showed the lowest levels of accumulation of rust oxides, particularly in the drier environment. However, in the wet environment all the chloride-based accelerators, especially SnCl₄ and AlCl₃, produced far more severe rusting. In contrast, the non-chloride accelerators such as Al₂(SO₄)₃, Al(NO₃)₃ and Ca(NO₂)₂ did not cause severe deterioration of the normal nails, even during periodic wetting. The efficacy of nitrite-based compounds at reducing corrosion of ferrous-based inclusions within cement and concrete structures is not conclusive. A study by Collepardi et al. (1990) showed that adding NaNO₂ (thought to be a corrosion inhibitor) actually exacerbated the corrosion of steel reinforcements in cracked concrete exposed to sea water.

The cut tacks and the zinc-plated and galvanised nails were generally more susceptible to the accumulation of rust oxides and deterioration by accelerators, both chloride and non-chloride (Figures 10.14 and 10.15). The appearance of each nail type with different levels of rust can be seen in Plates 10.4 (a) to (c). All chloride-containing compounds except SrCl₂ also severely rusted the cut tacks in the wet environment. Due to the small size of these nails, several had rusted through completely, as can be seen in Plate 10.4 (b). Contrary to expectations, this nail type was particularly susceptible to corrosion by MgCl₂ and additive combinations containing MgCl₂.

The results indicate that the presence of even relatively small amounts of chloride-based accelerators can still severely damage most nail types (even galvanised nails designed for use in cement-bonded composite products) over a relatively short period of time in a wet environment. In regular concreting applications, free chloride resulting from the addition of chloride-based
accelerators is gradually transformed into an immobile bound form over time. For example 0.6% free Cl\(^-\) takes 28 days to be ‘neutralized’ (Pauri et al. 1990). The behaviour of free Cl\(^-\) ions present in a cement-bonded wood composite product such as WWCB and the confounding effect of the wood content are completely unknown. It is possible that all free Cl\(^-\) ions are not transferred to a completely bound form in WWCBs, and may remain in the wood and allow corrosion to occur on fastenings once the composite gets wet.

Plates 10.4 Examples of exposed nails given an accumulation rating of 0 (L) to 5 (R) for (a) ordinary wood nails, (b) cut tacks, (c) zinc-plated nails and (d) galvanised fibre-cement nails.
In the case of the cut tacks, zinc-plated and galvanised nails, all of the accelerators that facilitated the production of strong boards from unsoaked *A. mangium* wood caused severe corrosion of nails, especially in the wet environment. The normal nails were the most resistant to rusting and oxide accumulation in general, but were still highly susceptible to corrosion by chlorides in the wet environment. The results accord with the general paradox that most additives that accelerate cement setting (such as chlorides and nitrates) also promote corrosion and those capable of inhibiting corrosion (such as tannins) often retard cement hydration (Thomas 1987). In light of these findings, careful selection of nail or fastening type will be necessary for WWCBs that contain accelerators, particularly chloride-based ones, and construction techniques should emphasise the protection of embedded fastenings from moisture.

### 10.5 Conclusions

The aim of the research presented in this Chapter was to manufacture well consolidated medium-density WWCBs from untreated *A. mangium* wood with the aid of selected cement-setting accelerators identified in Chapter 9 as being potentially beneficial in counteracting the inhibitory effects of the heartwood on cement setting. The results indicate that only a few accelerators used in low quantities sufficiently counteracted the inhibitory effects of *A. mangium* heartwood on cement hydration as to enable the manufacture of well-consolidated WWCBs from unsoaked wood-wool of *A. mangium*. The results accord well with the hypothesis that chemical interaction with inhibitory heartwood polyphenols may be necessary if the additive is to be effective at low concentrations at ameliorating the effect of the heartwood on cement setting. Such accelerators included SnCl$_4$ and FeCl$_3$, which were effective when used at approximately 2% of cement weight. This could allow (for the first time) the manufacture of medium-density WWCBs from *A. mangium* wood that has not been pre-soaked or pre-treated in any way.

Additives containing CaCl$_2$, a common, usually effective, and inexpensive cement-setting accelerator were ineffective in improving the properties of WWCBs made from unsoaked wood wool. MgCl$_2$, while only mildly effective on its own at low concentration, has the potential to form a powerful combination with other additives that are also relatively ineffective on their own, for example 1% SnCl$_4$ or 2% Al$_2$(SO$_4$)$_3$. Acidic accelerators, including SnCl$_4$ and FeCl$_3$, significantly reduced the tensile strength of wood wool strands, which is likely to have an adverse effect on the strength properties of WWCBs if these accelerators are added at higher concentrations. Unlike CaCl$_2$ and SnCl$_4$ selected compounds, i.e. MgCl$_2$ and Na$_2$SiO$_3$, were effective when added in larger quantities for improving the density, strength and moisture resistance of WWCBs made from unsoaked wood wool. These are significant findings which could be beneficial to small-scale manufacturers of WWCBs in countries like the Philippines as they could eliminate the need to add
expensive acidic and corrosive accelerators during the manufacture of WWCB from *A. mangium* (where pre-soaking of wood wool is impractical).

Many of the accelerators tested significantly improved the mechanical properties of WWCBs made from pre-soaked wood wool. This was particularly the case for the chloride-based accelerators, SnCl₄ (in very small quantities), CaCl₂, FeCl₃ and AlCl₃. The ability of additives (individually or in combinations) to enhance the density of the cement matrix was critical to achieving higher board strength and resistance to water. Adding MgCl₂ also imparted good resistance to water. Good strength and resistance to water are important properties of building materials in tropical climates, and the results here indicate that the judicial application of small quantities of cement-setting accelerators by manufacturers could significantly improve the quality and durability of low-cement content WWCBs made even from inhibitory hardwoods such as tropical acacias.

As expected, there was a significant positive correlation between the ability of a compound to accelerate cement setting in the presence of inhibitory *A. mangium* heartwood and its ability to strengthen WWCBs made from untreated *A. mangium* wood wool. However, there were some discrepancies between different compounds, for example CaCl₂, SrCl₂ and Al₂(SO₄)₃, all of which had the same effect on cement hydration rate but differed significantly in their ability to produce WWCBs of acceptable quality. This is most likely to have been caused by differences between cement hydration tests and WWCB manufacture, in particular the different time frames over which samples are assessed, and different wood:cerement ratios. Results obtained from cement hydration tests are therefore only a general guide to the potential ability of chemical additives to improve the strength of wood-cement composites made from inhibitory wood species. Compounds obviously must also be tested by manufacturing wood-cement composite panels under realistic conditions to obtain a true measure of their efficacy.

Another important (but often neglected) feature of wood-cement composite panels containing accelerators is their potential to corrode nails or other metal fastenings. Four nail types, including galvanised nails designed especially for cement-bonded boards were embedded in WWCBs containing different accelerators. As expected, the chloride-based accelerators caused severe deterioration of nails particularly when board samples were exposed to moisture. However, contrary to expectations, the zinc-plated and galvanised nail types reacted strongly with accelerators and/or cement and accumulated a heavy coating of oxides, whereas the ordinary wood nails underwent minimal change, particularly in the drier environment. Less corrosive WWCBs could be made from untreated *A. mangium* wood using non-chloride containing compounds such as Na₂SiO₃ and Al₂(SO₄)₃, provided they are used in greater quantities.
Overall, the study shows that, contrary to previous findings, medium-density WWCBs with acceptable properties can be manufactured from untreated A. mangium wood and possibly other tropical acacia woods through the addition of relatively small quantities of selected cement-setting accelerators provided they can also both interact chemically with inhibitory heartwood polyphenols and accelerate cement hydration. In fact low-cement-content medium-density WWCBs can be produced that possess similar mechanical properties to cement-bonded particleboard, which contains more than three times the quantity of cement and is around twice the density. The results from this study demonstrate that wood wool-based cement composites with satisfactory properties can be manufactured using lower quantities of cement and wood species that are deemed to be ‘incompatible’ with cement. Such composites are likely to be better suited to developing countries where wood from planted tree species such as A. mangium may be in plentiful supply, and building material cost and simplicity of manufacture are important considerations.
Chapter 11 General summary, conclusions and suggestions for further research

11.1 Summary and conclusions of this thesis

11.1.1 Background to the research

The aim of this thesis was to examine the suitability of a wide range of Australian acacias and eucalypts for the manufacture of low-cost wood-cement composites, and to overcome impediments to the utilisation of these woods for this purpose. Principal objectives included the development of methods of overcoming the inhibitory effect A. mangium wood on the hydration of cement, and of utilising eucalypt wood, particularly mallee eucalypts, for the manufacture of wood-cement composites. Factors hindering the use of acacias and eucalypts for the manufacture of wood-cement composites both in Australia and in many developing countries were identified in the Literature review (Chapter 2). These included a lack of knowledge about the types and properties of wood-cement composites and problems encountered during their manufacture and use as building materials caused by highly variable wood-cement compatibility. The latter was confounded by the lack of a reliable and standardised method for testing wood-cement compatibility and the difficulty of clearly linking the results from wood-cement compatibility tests to the properties of wood-cement composites, particularly WWCB. The review of the literature found that many previous studies demonstrated limited understanding of the chemistry of cement and its hydration, and of how wood chemical constituents interfere with cement hydration. This has also hampered efforts to maximise the quality of cement-bonded wood composites made from acacia or eucalypt wood. There was, however, considerable information about cement hydration and how sugars interfere with cement minerals in the cement-specific literature, which was detailed in Appendix 2. Far less information was available on how other wood extractives, such as heartwood polyphenols, interfere with cement hydration. A dearth of information on the compatibility of most acacia and eucalypt species with cement was also identified as a significant obstacle to the use of these woods for the manufacture of wood-cement composites.

11.1.2 Establishment of methodology for wood-cement compatibility testing

A review of previous studies indicated that there was wide variation in the methodology used to assess wood-cement compatibility (Chapter 2). Data from different studies could not, therefore, be directly compared, and it was hypothesised that many of the results were not relevant to the manufacture of wood-cement composites in practice. A scientifically-based methodology for testing wood-cement compatibility was first described by Sanderman and Kohler (1964). Their method involved combining ground-up wood flour, cement and water at fixed ratios and measuring the
maximum hydration temperature attained and the time taken for setting to occur. This method, or versions of it, have been almost universally adopted for testing a very wide range of wood species for their compatibility with portland cement. Results from such tests have often been used to estimate whether a wood species is suitable for the manufacture of wood-cement composites, including WWCB. The validity of this was questioned, forming the basis for the experiments described in Chapter 3, which examined the relevance of 'established' methods of testing wood samples for their compatibility with portland cement.

In Chapter 3 the question of whether the 'standard' wood-cement hydration test based on wood flour could reliably predict the compatibility of eucalypt and acacia wood (in wood wool form) with cement was examined. It was found that different species rankings were obtained according to whether the hydration test used wood flour or wood wool. It was correctly hypothesised and determined by experimentation that significantly altering the geometry and condition of test samples, for example by fine grinding, significantly altered the effect of the wood on the hydration of portland cement. Hence, hydration tests based on wood flour are unable to reliably predict the compatibility of wood in wood wool or flake form with cement, and are clearly unsuitable for estimating how a wood species will perform as a raw material for the manufacture of WWCB. An alternative method was developed to more reliably estimate the effects of eucalypt and acacia in wood wool form on the hydration of cement. This involved finely slicing green or dry wood through the tangential-longitudinal plane into flakes of the same thickness as wood wool (0.3 to 0.6 mm) using a framers guillotine. Wood in this form had a similar effect on the hydration of portland cement to that of wood wool. Furthermore it was possible to prepare such samples from small increment cores obtained from standing trees with out loss of material. This methodology facilitated subsequent experimentation (Chapters 4 and 5) involving the screening of a large range of acacia and eucalypt species for their compatibility with portland cement. The methodology was also more suitable for the preparation of samples from cores, wedges or small-diameter discs.

11.1.3 Compatibility of acacias and eucalypts with portland cement

In Chapter 4 results from wood-cement compatibility testing of commercially important tropical acacia and eucalypt species were presented. Trees were sampled non-destructively by coring. *A. mangium* was the most intensively sampled species (70 trees from seven different provenance/site groups). The overall aim of the work was to determine if there were any significant differences in the compatibility of wood obtained from different provenances or trees. It was hoped that certain families or even provenances of *A. mangium* with higher natural compatibility with cement might be identified as part of a strategy to improve the suitability of this species for the manufacture of wood-cement composites. There were no trees from *A. mangium* that were 'compatible' with
cement; all of the wood samples from this species when mixed with cement resulted in a hydration rate that was less than half that of pure cement. There were also no significant differences in the wood-cement compatibility of samples obtained from trees of different provenances. Wood samples from all three acacia species, *A. mangium*, *A. aulacocarpa* and *A. crassicarpa* were classified as 'incompatible' with portland cement; however, pre-soaking the wood flakes in water at room temperature for 24 hours significantly improved compatibility of all samples. Contrary to initial expectations variation in compatibility did not correlate with heartwood content of the sampled *A. mangium* trees. However there was a strong negative effect on compatibility caused by hot-water-soluble extractive content of the heartwood in the sample. Without the ability to identify any tropical acacia trees with high natural compatibility with cement, alternative methods of improving their suitability for the manufacture of wood-cement composites needed to be found. These were investigated later in Chapters 8, 9 and 10.

In contrast to the acacias, the wood samples from the two eucalypt species tested, *E. pellita* and *E. urophylla*, were of high compatibility with cement, and pre-soaking the wood flakes had little effect on compatibility. The wood from many of the eucalypt trees sampled was potentially suitable for the manufacture of wood-cement composites without any wood pre-treatment.

To address the dearth of information on wood-cement compatibility of acacias and eucalypts identified in Chapter 2, a wide range of temperate species of Australian acacias and eucalypts were tested and ranked for their compatibility with portland cement in Chapters 5 and 6. In Chapter 5 the wood-cement compatibility of temperate acacia and eucalypt species grown in controlled field trials in the Australian Capital Territory was reported. As with the tropical species, the eucalypts as a group were found to be far more compatible with portland cement than the acacias. Most of the temperate acacias were 'incompatible' with cement. Even after removal of extractives by hot water, several acacia species became only 'moderately' compatible with cement (hydration rate between 1.5 and 2°C/h). Such species are unsuitable for the manufacture of wood-cement composites unless a more effective wood pre-treatment can be developed. Although the heartwood content of acacia species had little effect on their compatibility with cement, the hot-water-soluble extractive content was negatively correlated with compatibility, a trend similar to that found in the tropical species (Chapter 4). Among the temperate acacia species, both the sapwood and heartwood were found to be incompatible with cement.

There was much greater variation in the compatibility of temperate eucalypts with cement than was the case for the temperate acacias. Approximately one third of the eucalypt species tested were classified as 'incompatible', one third 'moderately compatible', and one third 'compatible' with cement. The sapwood rather than the heartwood of temperate eucalypts adversely affected wood-cement compatibility. Accordingly, there was a significant positive correlation between heartwood
content and hydration rate for the temperate eucalypts. The review of literature showed that previous attempts to use eucalypts for wood-cement composites produced mixed or poor results. Species examined previously included E. camaldulensis, E. grandis and E. tereticornis, all of which are important plantation species in many countries. In this study E. camaldulensis was found to be 'incompatible' with cement, whereas E. grandis was of moderate to good compatibility. Some other commercially important species of eucalypt, including E. regnans and E. obliqua, were among the most compatible of the eucalypt species tested, suggesting that there may be considerable merit in testing young trees from such species for their suitability for conversion into composites such as WWCB or wood-cement flakeboards. Certain fast-growing temperate acacia species (such as A. mearnsii) may also be suitable provided the wood is pre-soaked in water first to remove inhibitory extractives. Further information is required on the ease of conversion of such woods to wood wool or flakes and the effects of the species on composite properties.

Large quantities of small-diameter, low-grade mallee wood residues are likely to be generated by farm plantations in Western Australia as a result of selectively removing the leaves for the production of mallee eucalypt leaf oils. In Chapter 6 the compatibility of selected oil mallee eucalypt species with cement was assessed as a first step towards determining the potential suitability of such residues for the manufacture of wood-cement composite panels. The five mallee species tested were of 'moderate' compatibility with cement (hydration rate between 1.5 and 2°C/h), and similar in compatibility to that of samples of flaked radiata pine, a species that is used for the commercial manufacture of WWCB in Australia. The inclusion of bark in mallee eucalypt wood samples did not significantly reduce its compatibility with cement, except for one species, E. loxophleba ssp. lissophloia. The bark from this species was highly incompatible with cement, possibly because it contained highly inhibitory extractives that interfered with cement hydration.

Three potentially important oil-producing species of Western Australian melaleuca were also tested for their compatibility with cement. In contrast to the mallee wood, melaleuca wood (which consisted entirely of sapwood) was highly incompatible with cement, possibly because of its high soluble carbohydrate content. Melaleuca wood had a particularly deleterious effect on the time taken for the cement to set, sometimes delaying setting by up to 22 hours. The setting time for pure cement is about 9 hours. The wood of one species, M. uncinata, was so incompatible that supplementing the wood with bark significantly improved its compatibility with cement. The low compatibility of melaleuca wood with cement could be readily overcome by simply pre-soaking the wood in cold water. Unlike the wood of tropical and temperate acacias, melaleuca wood attained a high compatibility ranking (hydration rate >2.5°C/h) after pre-soaking in cold water for 24 hours, indicating that this may be a simple and effective pre-treatment to facilitate the use of melaleuca wood for the manufacture of wood-cement composites. There was insufficient sample material
available to allow the manufacture and testing of wood-cement composites made from melaleuca wood.

Residues obtained from the chipping of small-diameter mallee eucalypt stems were used to manufacture cement-bonded boards. Although the boards consolidated well, their strength properties were low, < 2 MPa in bending strength, and therefore they clearly did not meet minimum standards for strength of wood-cement boards. In contrast, boards made from radiata pine particleboard flakes were between 5 and 6 MPa in bending strength. The inclusion of bark from the mallee eucalypt in boards did not significantly reduce their strength (except in the case of *E. loxophleba*); however, it adversely affected the resistance of boards to water. The poor properties of boards made from the mallee eucalypt residues were thought to have been caused by the small size and inappropriate geometry of the chips produced by the conventional farm-based chipper-shredder used to process stems.

11.1.4 Improving the quality of wood-cement composites made from mallee eucalypt wood

Ways of improving the suitability of eucalypt wood (particularly mallee wastes) for the manufacture of wood-cement composites were investigated in Chapter 7. Alternative methods of converting small diameter stem-wood into particles and flakes were investigated with a view to producing better quality wood-cement composites from mallee eucalypt residues. Cement-bonded composite boards made from mallee were compared with similar boards made from commercial timber species grown in Western Australia, including maritime pine, radiata pine and Tasmanian bluegum (low- and high-density wood). The mallee stems were too small to be debarked or converted into wood wool strands using conventional wood processing equipment. Flaking of the partially dried stems (with bark on) using a knife mill, however, produced a good range of flake sizes from 70 mm down to fine particles. Fortunately, most of the bark was reduced to fines that could be removed from the larger flakes by sieving. Flakeboards manufactured from all species (especially the pines and bluegum) were of good quality compared to the CBPs that were manufactured and assessed in Chapter 6. Board properties were further improved by the addition of accelerators (*CaCl₂* and *MgCl₂*), as expected. Boards made from mallee flakes and those produced from dense, slow-grown bluegum were just below the minimum requirement of 9 MPa in bending required by ISO 8335 for cement-bonded boards. This was despite the fact that accelerators were added during board manufacture. The weaker boards produced from mallee and high-density bluegum wood were likely to have arisen from the highly variable and high average flake thickness produced by flaking the higher density, small-diameter stems in a knife mill which was designed to flake softwood timber. In contrast, the strength properties of boards manufactured from pine and low-density, fast-grown, bluegum wood exceeded the ISO standard. The average MOR of boards
made from low-density bluegum and containing MgCl\textsubscript{2} was 15 MPa. These findings indicate that wood density can greatly affect the properties of wood-cement composites through its effects on the conversion of wood to particles or flakes.

Accordingly, the use of large thin flakes conferred significantly greater strength properties to cement-bonded boards than did small particles such as those used in the manufacture of conventional resin-bonded particleboard. Board sensitivity to moisture was, however, reduced by the use of small particles. These findings accord with those of other researchers, for example Warden \textit{et al.} (2002). Contrary to expectations, however, curing of boards at elevated temperature (65°C) reduced board properties, possibly because it rapidly reduced the water content of the composite, preventing the cement from curing properly. Further research is needed to find ways of optimising the curing of cement-bonded flakeboards to reduce curing time without compromising board properties.

Although the small-diameter mallee wood could not be converted to wood wool and tested in the manufacture of WWCB on a commercial scale, the plantation bluegum, radiata pine and maritime pine were used to produce low-density (~350 kg/m\textsuperscript{3}) WWCB insulating panels in a commercial fabrication plant. Contrary to expectations, the bluegum timber appeared to be very well suited to the manufacture of low-density WWCB, and the boards that were produced were more resistant to impact loading than boards of similar strength and density made from pine wood wool. This may be explained by the higher strength wood wool strands from bluegum timber compared to those from radiata pine.

11.1.5 Improving the compatibility of \textit{A. mangium} with cement and its suitability for the manufacture of wood-cement composites

The third major objective of this study was to overcome the inhibitory effect of \textit{A. mangium} wood on the hydration of cement. \textit{A. mangium} has been found in previous studies to perform poorly in wood-cement composites unless inhibitory heartwood constituents are removed by pre-soaking the wood in water and/or cement-setting accelerators are added during composite manufacture. In some studies WWCBs of acceptable quality could not be produced, even when such treatments were applied (for example Cabangon \textit{et al.} 1997, Soriano \textit{et al.} 1997, Eusebio \textit{et al.} 2002b). This is despite the fact that the wood is easily converted into good quality wood wool. \textit{A. mangium} is now an important plantation species in South-East Asia, and it would be highly beneficial if effective methods of improving its compatibility with cement could be developed. Various strategies were examined as a means of improving the compatibility of \textit{A. mangium} wood with cement and its suitability for the manufacture of WWCBs. First, a wide range of trees from the species was
screened (Chapter 4) to determine whether there is sufficient natural variation in the compatibility of its wood to allow for the selection and propagation of trees to produce wood that is better suited to the manufacture of WWCBs. Despite considerable variation in wood-cement compatibility among trees, there were no ‘compatible’ wood samples identified, and heartwood extractive content appeared to play an important role in determining the wood-cement compatibility among trees of this species. In light of these findings, subsequent experimentation (Chapters 8 to 10) focussed on strategies to neutralise the inhibitory effects of the heartwood of *A. mangium* on cement hydration.

In Chapter 8 a range of wood pre-treatments designed to improve the compatibility of *A. mangium* heartwood with cement was assessed. These included; removal of extractives using various solvents at different temperatures, exposure of wood to heat, sunlight or electrical plasma, and coating wood strands with water-repellent substances. The removal of inhibitory extractives from *A. mangium* heartwood using water or dilute alkali was the most effective means of increasing its compatibility with cement. It was found that water temperature greatly influenced the amount of extractives removed from *A. mangium* heartwood, and hence its compatibility with cement. Pre-soaking wood in tepid water (> 25°C) removed sufficient extractives to significantly increase the compatibility of *A. mangium* heartwood with cement. Although pre-soaking in tepid water was an effective pre-treatment, in practice it requires large amounts of fresh water, time, space and labour, as well as an environmentally friendly means of disposing of the leachate. Hence alternative pre-treatments were also examined. Dipping the heartwood strands momentarily in cement-setting accelerators, including CaCl₂, FeCl₃ and SnCl₄, was found to be almost as effective as pre-soaking them in water at 23°C for 12 to 24 hours. While dipping the strands in CaCl₂ had little effect, dipping in FeCl₃ or SnCl₄ greatly increased the compatibility of *A. mangium* heartwood strands with cement. These two pre-treatments were as effective as pre-soaking in hot water (80 to 100°C) for 1 to 6 hours, and did not require the use of prolonged soaking in hot water nor the need to dispose of extractive-laden leachate. Treatments that exposed heartwood strands to heat, plasma or UV radiation had little effect on their compatibility with cement, since they did not appear to remove or chemically alter the heartwood extractives responsible for inhibiting cement hydration. Pre-coating strands with simple water-repellent substances, including oils and waxes, was also relatively ineffective. These also did not remove or chemically modify the heartwood extractives and the water-repellent coating may have been degraded by the alkali generated by the cement paste.

Following on from the findings of Chapter 8, a much wider range of chemical additives was tested for their ability to improve the compatibility of *A. mangium* heartwood with cement in Chapter 9. Compounds were added to wood-cement mixes containing *A. mangium* heartwood strands and were ranked according to their ability to increase the rate of hydration of portland cement. Fifteen out of a total of 137 additives tested increased hydration rate of cement containing
heartwood to more than 2°C/h and reduced setting time to less than 10 hours (almost half that of control samples containing no added chemical). Most of the effective compounds significantly increased the hydration rate of pure portland cement (containing no heartwood) and also chemically interacted with the alkali-soluble heartwood polyphenols in *A. mangium* that are responsible for inhibiting cement hydration. The mechanism by which the inorganic compounds and/or their dissolution products interact with heartwood polyphenols appears to be complex and not comprehensively or readily explained by the literature. The most promising and readily available compounds were chlorides of Sn⁺, Al³⁺, Fe³⁺ and Mg²⁺. These were subsequently selected and used in the manufacture of WWCBs from untreated *A. mangium* wood wool (Chapter 10).

Experimentation described in Chapter 10 showed that it was be possible to manufacture good quality WWCBs from fresh, unsoaked *A. mangium* wood wool by adding relatively small quantities (1-2% w/w cement) of SnCl₄ or FeCl₃. The maximum bending strength of boards containing these compounds was 11 MPa. This finding is noteworthy because previous studies have not been able to manufacture well consolidated WWCBs from fresh *A. mangium* wood. In comparison, CaCl₂, a commonly used cement-setting accelerator, was ineffective in improving the properties of WWCBs made from untreated *A. mangium* wood. SnCl₄ and FeCl₃ are, however, highly corrosive to ferrous-based fixings and, being acidic, were also found to adversely affect the strength of wood wool strands. To overcome the second problem, MgCl₂ and Na₂SiO₃ were also tested as additives and were found to be effective if used at higher quantities (over about 5% of cement weight). Board strength could be increased to 17 MPa if 12% Na₂SiO₃ was added. Combining small quantities of SnCl₄ or Al₂(SO₄)₃ with MgCl₂ was also very effective in facilitating the production of well consolidated and strong boards.

All of the 31 accelerator/concentration combinations tested improved the properties of boards when pre-soaked wood wool was used to manufacture WWCBs, indicating that heartwood extractives in *A. mangium* interfered with many of the compounds, including CaCl₂, preventing them from accelerating or strengthening cement hydration.

The study also provided an opportunity to determine whether the results from wood-cement hydration tests can accurately predict how cement-setting accelerators might perform in wood-cement composites. As expected, there was a significant positive correlation between the hydration rate produced by a compound in cement containing *A. mangium* heartwood and its effect on the strength of WWCBs made from fresh *A. mangium* wood. However, certain compounds (such as CaCl₂ and SrCl₂) performed worse in WWCBs than expected from the results of the hydration tests, whereas compounds such as Al₂(SO₄)₃ performed better than expected, since all three compounds resulted in a similar hydration rate in the wood-cement hydration tests presented in Chapter 8. This finding demonstrates that wood-cement hydration tests (which necessarily employ a much higher
cement:wood ratio than that used in wood-cement composites) only provide a general indication of the potential performance of wood species and chemical additives in wood-cement composites.

The only accelerators capable of producing well consolidated WWCBs from unsoaked *A. mangium* wood when used in small quantities were chlorides. Not surprisingly, boards containing these types of additives were highly corrosive to ferrous-based nail fastenings, particularly in wet conditions. Contrary to expectations, common uncoated steel nails were more resistant to oxidation and corrosion by a wide range of accelerators than zinc-coated nails. Galvanised nails, which are designed specifically for cement-based products, were not immune to corrosion when exposed to WWCBs containing chloride-based accelerators. Thus it was recommended that the use of chloride-based accelerators in WWCBs should be kept to a minimum, and replaced or supplemented by larger amounts of less corrosive compounds such as Na₂SiO₃.

Despite the high dry strength of several of the WWCBs made from untreated *A. mangium* and cement containing accelerators, they still lost approximately half their strength after exposure to water for 24 hours. The high wood content and relatively low resistance to water of WWCBs is responsible for their poor performance when exposed to water. Further research is required to develop manufacturing techniques or board surface treatments that improve the water resistance of WWCBs. Some suggestions for improving the water resistance of WWCBs are made in Section 11.2.2.

### 11.2 Specific and general suggestions for further research

#### 11.2.1 Extensions of findings from this research

Several of the findings reported in this thesis are worthy of further investigation. Results presented in Chapter 4 indicated that there is considerable variation in the hot-water-soluble extractive content of heartwood from different *A. mangium* trees. Since this trait is closely linked with the compatibility of the wood with cement, a worthwhile avenue of further investigation would be to undertake wider sampling of heartwood extractive contents from *A. mangium* trees to determine the extent of genetic and/or environmental control of the trait. Review of literature for other commercial tree species indicates that heartwood extractive composition and quantity are under strong genetic control. Therefore it may be possible to select and grow short-rotation trees of a species such as *A. mangium* that contain a lower heartwood tannin content and whose wood is better suited to the manufacture of wood-cement composites. It should be noted, however, that *A. mangium* has very low genetic diversity compared with other important plantation tree species such as *E. camaldulensis* (Moran et al. 1989, Harwood and Williams 1992).

Further research into the quality of WWCB or other cement-bonded composites from the tropical eucalypts *E. pellita* and *E. urophylla* would also be useful, since these woods have a high
289
natural compatibility with cement. Results presented in Chapter 7 showed that E. bicostata was well
suited to the manufacture of cement-bonded flakeboards and low-density WWCBs. The enhanced
impact strength of WWCBs made from this species was probably due to the higher strength of the
wood wool strands and better mat compaction. Wood from low-density, fast-grown E. bicostata is
known to be difficult to convert to solid timber products, but it may potentially be highly suitable
for the manufacture of higher density, semi-structural flakeboards or WWCBs for building
purposes. This would be a worthwhile avenue for further investigation. Reasons for the poor
compatibility of other eucalypts such as E. camaldulensis with cement (identified as problematic in
both this and previous studies) also deserve further attention.
The use of selected cement-setting accelerators was found to be a solution to the problem of
manufacturing good quality WWCB from fresh A. mangium wood wool, thereby removing the need
to pre-soak the wood in water. This method may be applicable in the case of numerous other
inhibitory tannin-containing wood species; however, this would need to be verified by further
experimentation. It was noted in Chapter 2 that acidic substances in wood, such as tannic acids, can
be deleterious to the long-term bonding and durability of wood-cement composites (Frazer 1977,
Blankenho m et al. 1994). Before recommending such a manufacturing technique for the
manufacture of WWCBs, the effect of leaving tannins in the wood and the addition of acidic
acclerators such as SnC1 4 or FeCh would need to be determined over the service life of the
composite in various environments by subsequent experimentation.
There was no plausible explanation in the literature for the complex chemical interactions
between A. mangium heartwood polyphenols and additives such as SnC14 and MgCh. This area
certainly warrants further investigation. It is not known why certain compounds that also form
strong complexes with A. mangium heartwood polyphenols, including Ah(NO 3) 3 and AlCh, were
relatively ineffective in improving WWCB properties whereas certain non-complexing compounds,
. such as MgCh and Na2 SiO 3 , were more effective, particularly when used in higher quantities. A
possible mechanism by which MgCh is able to overcome the inhibitory effects of acacia heartwood
polyphenols on cement hydration was found in the literature (Yasuda et al. 1992); however, this
subject area would benefit from further study.
The incorporation of carefully selected chemical additives during the manufacture of cementbonded boards would be beneficial in enabling the use of a wide range of incompatible lower
density wood species that are easily machined into good-quality wood wool or flakes. The quality
of wood wool or flakes produced from the parent wood can still critically affect composite strength,
even if wood-cement compatibility problems are overcome. The potential of wood from other
readily available, fast-grown acacias such as A. aulacocarpa or A. mearnsii for the manufacture of
wood-cement composites deserves to be examined further, since it has been demonstrated here that


it is possible to overcome the problems posed by wood-cement incompatibility during board manufacture using relatively simple techniques.

During the course of experimentation undertaken in this thesis, a few additional noteworthy results were obtained. In Chapter 3 it was shown that reducing compatible woods (such as poplar) to finely ground ball-milled flour made the wood highly incompatible with cement. Such a phenomenon has been observed previously and requires further investigation to explain the physico-chemical basis for this effect. Another interesting but unexpected result was the extreme incompatibility of the bark of *Eucalyptus loxophleba* ssp. *lissophloia* with cement. A chromatography study may elucidate the presence of a different type of bark polyphenol that sets this species apart taxonomically from other mallee species. Ground-up waste bark from this species or an extract from it could make a cheap and useful cement retarder or plasticiser. The bark from this species may have other potential applications, for example as a source of chemicals for tannin-based adhesives.

11.2.2 *General suggestions for improving acacia and eucalypt wood suitability for wood-cement composites*

The range of wood-cement composite materials available today provides many options for the conversion of fast-grown, low-grade timber or waste lignocellulosic materials into value-added composite products. The scientific and patent literature discussed in Chapter 2 and throughout the thesis indicates that there are many inventive and novel ways of overcoming the inherent problem of poor wood-cement compatibility that has historically hindered the manufacture of wood-cement composites from a wide range of wood species. Relatively few of these innovations have had a commercial impact, possibly because they increase the cost of manufacturing boards or have undesirable side effects on the properties of the composites. Taking into account weight, cost and energy considerations for portland cement, there is an ongoing need to balance cement content in wood-cement composites with board strength properties, water resistance and long-term durability. Hence manipulation of flake size (thickness, length and width) and orientation within boards was identified as a significant but simple strategy for improving the properties of wood-cement composites, as demonstrated for mallee eucalypt wood in Chapters 6 and 7.

From the point of view of minimising the cement content and hence the cost and weight of wood-cement composite panels, the manufacture of medium- and/or high-density WWCB may be a viable option. In the case of many types of woody wastes, for example mallee stems, the production of wood wool is not technically possible because the wood is too small in diameter, too knotty or crooked, or is already in the form of small chips. The only conversion options for such material are flakes, particles, fibres or crushed strands.
A review of the literature clearly indicated that, despite their advantages in terms of strength and fire-resistance, there are still several problems preventing the wide-spread use of cement-bonded particulate composites such as CBP. CBPs currently have a much higher cement content to compensate for the lower reinforcing capacity of small particles and higher water absorption caused by the finer form and higher surface area of the wood aggregate. Current production economics and technology of CBPs make them uncompetitive with other building materials, including common conventional wood composites such as particleboard and MDF. The high cement content of CBP also makes it more susceptible to carbonation and dimensional instability with changes in humidity, resulting in cracking and deterioration over time, particularly in dry climates.

The results presented in Chapters 6 and 7, and other research available on cement-bonded flakeboards, suggest that conversion of wood to flakes or strands rather than particles might be a better option for manufacturing wood-cement composites, particularly in the case of less compatible wood species. Flakes and strands not only allow for reductions in cement content, but also improve mechanical reinforcement of the composite by the wood elements. Close examination of the literature on cement-bonded wood flakeboards revealed that such products had been first developed by Elmondorf in the early 1960s, but were never fully commercialised. Board properties were greatly increased by the mechanical orientation of flakes (particularly in the surface layers); however such products seem to have been forgotten until relatively recently. This early research showed that flakes should be of sufficient size and geometry to facilitate mechanical orientation, allowing multi-layered cross-ply mat structures that further increase the strength properties of wood-cement composite panels. More recent studies by Ma et al. (2002) and Kuroki et al. (2002) highlight the benefits of using large oriented flakes in cement-bonded boards. Recent research by Warden et al. (2002) also indicates that there is potential for plantation eucalypt wood to be used to manufacture such boards.

A variety of other relatively simple methods exist that could be employed to further increase the strength and water resistance of wood-cement composites made from flaked wood residues. In this regard, the pre-treatment of the flakes to ameliorate inhibitory extractives in wood may be among the most effective. For example the treatments patented by Gamage (1996) and Walter and Walter-Gurzeler (1991) discussed in Chapter 7 appear to have considerable potential. Research involving such pre-treatments would be a logical extension of the research undertaken here on utilising mallee waste in wood-cement composites, and could also be relevant to the use of other wood residues or agricultural wastes in pre-fabricated cement-bonded panels.

The positive effects of the partial substitution of portland cement with siliceous pozzolans (such as fly ash or RHA) on the water resistance of wood-cement composites and their longer term durability outdoors suggests good potential for their use as part of the matrix in wood-cement
composites. This may be particularly useful in composites containing bark. The choice of wood species used may significantly influence the efficacy of portland cement substitutes, as discussed in Chapter 2. There is an obvious need for further research with different wood types, additives and processing techniques to overcome these problems.

In view of energy and cost-of-production considerations of portland cement-bonded wood composites, the potential for the almost complete replacement of portland cement with a recyclable waste product such as blast furnace slag should not be overlooked. The literature indicates that alkali-activated slag-based binders are far less susceptible to the effects of inhibitory polysaccharides and polyphenols contained in most acacias and many eucalypts. On the other hand, the processing of boards using this kind of binder is more complicated than is the case for conventional cement-based composites. Slag-based binders have never been tested with Australian wood species and would constitute a worthwhile area for further research.

Finally, more trial houses and buildings using mineral-bonded wood composites should be promoted in Australia and elsewhere, comparing these with the cost and long-term performance of other building materials in a realistic setting. Although cement-bonded fibreboard is used for construction in Australia, there is apparently only one trial house made (partially) from wood-cement composites such as WWCB. This model house indicates that 50-mm WWCB panelling is cost-effective with considerably higher insulating capacity than other more traditional forms of cladding, including weatherboard and fibre-cement sheets. The national forest products research organisation (FPRDI) in the Philippines has for a number of years had on display model houses made from products such as WWCB and cement-bonded boards made from waste sludge from the paper industry to monitor the long-term performance of the structure, its panels and fastenings in realistic climatic conditions. The construction of additional buildings containing WWCB, CBP or cement-bonded flakeboards in Australia may promote greater public awareness of the benefits and versatility of such composite materials, leading to greater investment in further research, development and ultimately the manufacture of this class of building materials.
REFERENCES


Hse, S.J. Branham and C. Chow, Taiwan Forestry Research Institute (TFRI) Extension Series No. 96, pp. 554-564.


Collepardi, M. (1994). Superplasticizers and air-entraining agents: state of the art and future needs. *American Concrete Institute SP-144 (Concrete Technology)*: 399-416.


Harwood, C.E.; Applegate, G.; Robson, K. and Williams, E.R. (1993). Early growth of provenances and progenies in Acacia mangium seed production areas in North Queensland,


Searle, S.D. (2000). *Black wattle (Acacia mearnsii) for farm forestry*. Department of Natural Resources and Environment (DNRE), Melbourne, 18 pp.


Use of Acacias for Wood-Cement Composites

K.E. Semple and P.D. Evans

Abstract

Composites of cement and wood-wool are widely used for building construction in many developing countries. They are simple to manufacture and can utilise relatively small diameter pulp logs and logging residues. Wood from the extensive acacia plantations in South East Asia may be suitable for the manufacture of wood-cement composites, but to date there have been relatively few studies that have examined their feasibility. In this paper the use of acacias in wood-cement composites is reviewed, and preliminary findings on the compatibility of some commonly planted tropical and temperate acacias with cement are presented. These results are compared with those using coniferous wood species of very high and very low compatibility with cement, and with an important tropical eucalypt species. Heartwood samples from the tropical acacias were less compatible with cement than those of the temperate acacia species in that they greatly inhibited cement setting. The sapwood samples of the tropical acacias were generally compatible with cement, whereas those of the temperate species were not. Acacia heartwood (and sapwood of some species) probably contains soluble compounds which chemically inhibit the setting of cement. To overcome these effects, pre-soaking of wood-wool (to remove inhibitory compounds) and/or the use of cement hardening accelerators are often required to manufacture wood-wood cement panels from acacias. Other possible means of improving the compatibility of acacia wood with cement are: selecting and growing acacias which contain less heartwood, and whose wood is more compatible with cement; using younger trees which contain less heartwood; and using a cement substitute (rice-hull ash) which may be less susceptible to the inhibitory compounds present in acacia heartwood.

Australian acacias are widely planted throughout Southeast Asia, because of their ability to colonise and grow rapidly on low-nutrient and weed-infested sites, and to produce large volumes of wood, mainly for use as pulp and fuelwood (Gunn and Midgley 1991).

Wood-wood cement composite panels are widely used in many developing countries as a low cost building material. They can be fabricated locally using pulp-quality wood and logging residues, cement and water. The panels are resistant to termites, decay, water and fire, and they have good machining, nailing, and sound-proofing characteristics. Acacia plantation wood could potentially be used by wood-wool cement panel industries, but to date there have been few studies of the compatibility of acacia wood with cement and of the manufacture of wood-cement composite panels from acacias.

A range of low molecular weight chemical compounds in wood constrain the use of many wood species for wood-cement composites. Such compounds include soluble carbohydrates, sugars and extraitives which may be leached from the wood in the alkaline environment of cement, inhibiting the cement-setting process and resulting in boards of inferior strength and durability (Biblis and Lo 1968). Methods of ameliorating the effects of these extraneous components on cement include:

- extraction of wood to remove inhibitory compounds;
- storage or ponding of wood allowing microorganisms to metabolise sugars;
- the use of rapid-hardening cements or cement-hardening accelerators such as calcium chloride and aluminium sulfate; and
- adding rice-hull ash or fly ash to the cement to make it less susceptible to the inhibitory effects of soluble wood components.

1 Department of Forestry, The Australian National University, Canberra, 2600, Australia
This paper reviews the suitability of acacias for wood-cement composites and presents some preliminary results on the compatibility of a range of important tropical and temperate acacias with cement. These results are compared with:

- two wood species known for their high compatibility with cement (Picea abies (L.) Karst. and Pinus radiata D. Don.);
- one species known for its extreme incompatibility (Larix europaea D.C.); and
- an important plantation eucalypt species, Eucalyptus pellita F. Muell.

Possible ways of ameliorating the inhibitory effects of acacia wood on cement-setting are discussed.

**Literature Review**

**Wood-cement products using acacia wood**

Sadun and Ibrahim (1990) found that cement-bonded particle boards could be made to Malaysian standard (MS 934, 1986) using four-year-old Acacia mangium Willd. at a wood-cement ratio of 1:3 without chemical additives. Board properties could be improved by adding 0.6% and 0.4% lime and reducing the wood-cement ratio to 1.25. Cement-bonded particle boards with satisfactory mechanical properties were made using various sized flakes of Acacia mearnsii de Wild. and Portland cement, apparently without the use of accelerators (Teixeira and Pereira 1987).

Flawes and Chittenden (1967) found that A. mearnsii could be used to make commercial quality wood-wool cement boards, providing that the wood-wool was soaked in a 1% calcium chloride solution before mixing with cement. Calcium chloride and other mineral salts, if added to the wood, cause rapid setting of cement around wood surfaces before water-soluble components can migrate from the wood and inhibit cement setting (Pazner 1978). A 3% solution was recommended to obtain boards with reduced surface friability. Salastirinsih et al. (1990) found that it was necessary to soak A. mangle wood-wool in cold water for 24 hours before making wood-wool cement boards. The addition of calcium chloride and calcium hydroxide further improved board properties.

Based on the pulling force required to remove test sticks set in cement in a laboratory study, Rahimi and Ong (1983) rated A. mangium as unsuitable for use in wood-cement composites. Its bonding strength was only moderately improved by preliminary soaking with aluminium sulfate or calcium chloride.

**Extractives in acacia wood and their effects on Portland cement**

Yasin and Qureshi (1989) suggested that the amount of hot-water-soluble extractives in wood species is a good indicator of their compatibility with cement. This suggestion was based on the finding that the strength of wood-cement particle boards was inversely proportional to the extractive content of the wood used. Boards made from Acacia nilotica (L.) Delile, with an extractive content of 7.8%, had only moderate strength, whereas Populus alba L. with the lowest extractive content (2.4%) produced the strongest boards.

Other studies suggest that in the case of acacias, the level of extractives may not be indicative of the cement-inhibiting characteristics of the wood. The amount and chemical nature of extractives varies greatly between species, and no one single compound can account for variation in wood-cement compatibility; Hachimi and Moslemi (1989) found that A. mearnsii was highly incompatible with cement, even though its wood was relatively low in hot-water-soluble extractives. Thus its extractive content was only 7.8% compared with other equaly incompatible species, Quercus suber L. and Sipo tenaceissimo L., which had higher extractive contents (>12%). This suggests that the chemical composition of extractives plays a major role in influencing the compatibility of wood with cement; Hachimi and Moslemi found that extractive content itself could explain only 50% of the variation observed in wood-cement compatibility. They identified a threshold level of extractives (7%) above and below which woods were classified as either 'incompatible' or 'compatible' with cement, respectively.

Tachi et al. (1989) found that A. mangium had a similar hot-water-extractive content to other three species: Alhizia falcararia (L.) Fosberg, Eucalyptus delegatensis Bl. and Gmelina arborea L. However, it inhibited cement hydration significantly. They subsequently isolated and identified two teracyclidine-type flavonoids which had a similar effect. They suggested that other highly inhibitory compounds were also likely to be present in the heartwood of A. mangium.

**Materials and Methods**

Wood flour was prepared for 11 wood species:

temperate acacias A. dealbata Link, A. melanoxylon R.Br., A. aurantiaca; Eucalyptus pellita (six-year-old Papua New Guinea/South West Provenance grown at Atherton District, Queensland, Australia); and the coniferous species Picea abies, Larix europaea, and Pinus radiata (18-year-old Monterey Provenance grown at Piers Creek, Australian Capital Territory, Australia).

Wood blocks were reduced to matchstick-sized pieces using a hatchet, and coarsely ground in a 'junior' laboratory mill to particles approximately 1 mm in diameter. These were then further ground in a Wiley mill to 20–40 mesh size. Heartwood and sapwood flour was prepared separately for all acacias and E. pellita, but no sapwood was available for A. dealbata. In the coniferous species, the heartwood and sapwood could not be differentiated. Wood flour was stored in open jars in a conditioning room at 20 ± 1°C and 65 ± 5% relative humidity for at least one week until ready for use. Just before use, a separate sample was taken for each flour to determine its equilibrium moisture content.

Two 15 g (even dry basis) samples of wood flour from the heartwood and sapwood of each species (except A. dealbata) were used. Each sample was placed in a sealable Dalgety polythene bag and evenly mixed with 200 g of fresh, dry, Portland cement (Blue Circle Southern brand, batch 199/97). Distilled water (90.5 ml) at 20°C was then added to the wood and cement, and the slurry was hand-kneaded for 2–3 minutes until evenly mixed. Two control samples containing only cement and 80 ml of water were similarly prepared. The amounts of cement, wood-flour and water used in the experiment accord with the recommendations of Weatherwax and Turkov (1964).

Immediately after mixing a sample, the tip of a temperature thermocouple (Type J) was tamped to the bag and enclosed within the body of the cement mix by folding and then securing the bag and contents around it. The bag was then placed in a polystyrene cup and sealed within a large thermos flask (Figure 1). A cement hydration temperature measuring apparatus capable of measuring the heat of hydration of six wood-cement mixtures over a 23-hour period recorded temperatures at 15-minute intervals. The curves were smoothed by progressive averaging and plotting of every three readings. All experiments were undertaken in a conditioning room at 20 ± 1°C and 65 ± 5% humidity. The ratio of area under each hydration curve from 0–23 hours to that of the cement control, the C₄ factor, was used to assess the compatibility of the different wood species with cement (Hachmi et al., 1990).

---

**Results and Discussion**

The effects on cement hydration of both compatible woods (A. mangium sapwood and P. abies) and incompatible woods (A. mangium heartwood and L. europaea) are shown in Figure 2. Cement containing wood-flour from incompatible wood species showed only a slight initial temperature rise within the first two hours, with no further exothermic reaction over the test period of 23 hours. Compatible wood types did not prevent cement hydration, although the maximum hydration temperature (T_max) compared with pure cement was reduced and the time taken to reach T_max was greater than that for pure cement. Both T_max, itself and the time to reach T_max, influence the cement hydration curve shape and hence the C₄ factor compatibility index (Hachmi et al., 1990).

Compatibility indices (i.e. C₄ factor) of E. pellita, of the acacia species sapwood and heartwood (separately), and of the coniferous species sapwood and heartwood (combined) are shown in Table 1. Hachmi and Mesléri (1989) divided wood species into three compatibility groupings across the range of C₄ factor values:

- incompatible (<25%),
- moderately compatible (25–60%), and
- compatible (>60%).
Using this classification, the sapwood of all the tropical acacias (except *A. aulacocarpa*) and that of *E. pellita* could be classed as compatible (Table 1).

The sapwood of *A. crassicarpa* had the highest compatibility index (CAₘₐₙₙ = 81.9%) whereas *A. aulacocarpa* sapwood was only moderately compatible (CAₘₙₙ = 66.4%). The sapwood samples of the temperate acacias (*A. melanoxylon* and *A. mearnsii*) were incompatible (Cᵢ = 23.6% and 21.4% respectively).

The heartwood samples of the tropical acacias were incompatible with CAₘₙₙ factors ranging from 21.1% for *A. aulacocarpa* to 27.7% for *A. auriculiformis* (Table 1). The heartwood of the temperate species (*A. dealbata*, *A. melanoxylon* and *A. mearnsii*) and that of *E. pellita* was moderately compatible with CAₘₙₙ values only slightly above 28%. The heartwood of *A. dealbata* had the highest compatibility (CAₘₙₙ = 38.3%) of all the acacia heartwood specimens tested.

The results for the sapwood of the tropical acacias were promising relating them to the wood species of high compatibility (*P. abyss* and *P. radiata*) and low compatibility (*L. europae*) (Table 1). They indicate a relatively high compatibility with cement, not markedly lower than that of *P. abyss* or *P. radiata*, particularly in the cases of *A. crassicarpa* and *A. mangium*. The results for the heartwood of the tropical acacias and the sapwood of the temperate species were notable in that they showed the wood to be almost as incompatible with cement as *Larix* sp. which are among the most incompatible wood species ever tested (Hofstraed et al. 1984). (It has not been determined whether the inhibitory extractive compounds in the heartwood of tropical acacias tested here are the same as those identified in *A. mangium* by Tachi et al. 1989.)

Table 1. CAₘₙₙ factors for sapwood and heartwood of acacia species, *E. pellita*, and coniferous wood species.

<table>
<thead>
<tr>
<th>Wood species</th>
<th>Sap CAₘₙₙ (%)</th>
<th>Heart CAₘₙₙ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>A. aulacocarpa</em></td>
<td>66.4</td>
<td>21.1</td>
</tr>
<tr>
<td><em>A. auriculiformis</em></td>
<td>72.9</td>
<td>27.7</td>
</tr>
<tr>
<td><em>A. crassicarpa</em></td>
<td>81.9</td>
<td>21.8</td>
</tr>
<tr>
<td><em>A. dealbata</em></td>
<td>—</td>
<td>38.3</td>
</tr>
<tr>
<td><em>A. mangium</em></td>
<td>80.8</td>
<td>23.9</td>
</tr>
<tr>
<td><em>A. mearnsii</em></td>
<td>21.4</td>
<td>29.4</td>
</tr>
<tr>
<td><em>A. melanoxylon</em></td>
<td>23.6</td>
<td>30.1</td>
</tr>
<tr>
<td><em>E. pellita</em></td>
<td>71.2</td>
<td>28.4</td>
</tr>
<tr>
<td><em>P. abyss</em></td>
<td>91.2</td>
<td>—</td>
</tr>
<tr>
<td><em>P. radiata</em></td>
<td>91.4</td>
<td>—</td>
</tr>
<tr>
<td><em>L. europae</em></td>
<td>18.3</td>
<td>—</td>
</tr>
<tr>
<td>GPC control</td>
<td>100.0</td>
<td>—</td>
</tr>
</tbody>
</table>

Figure 2. Typical cement hydration curves for compatible (*A. mangium* sapwood and *P. abyss*) and incompatible (*A. mangium* heartwood and *L. europae*) woods compared with pure cement (GPC).
The results for the tropical acacias suggest that the proportion of heartwood and sapwood used in manufacturing wood-cement composites will greatly affect the setting, curing and properties of panels. Most previous research has found that acacia wood requires either soaking (Sulistrijingsh et al. 1990), a high cement:wood ratio (Studt and Ibrahim 1990), or cement-hardening accelerators (Flavell and Chithenden 1967) for successful use in wood-cement composites. All of these measures add extra cost to panel production, so other more cost-effective methods of improving the compatibility of acacia wood with cement are required.

Identifying and selecting acacia species and trees which contain less heartwood at a given age, or which develop heartwood at a later age, may be one method of increasing the suitability of acacia wood for the manufacture of wood-cement composites. Bhunishuman et al. (1962) found significant heartwood variation among provenances and families of five-year-old A. mangium trees. Families from the Orombo River, Papua New Guinea, had the least heartwood while those from Captain Billy, Queenslands, had the most. Further investigations will aim to confirm such findings, and examine whether families of A. mangium which form less heartwood at a given age, or possess few inhibitory extractives, are more compatible with cement and therefore better suited to the manufacture of wood-cement composites. Other options may include the manufacture of wood-cement composites from younger trees which contain less heartwood, and the use of alternative inorganic binders, such as rice-hull ash, which may be less susceptible to the inhibitory compounds in acacia heartwood.

Conclusion

The sapwood samples of the tropical acacia species A. mangium, A. crassicarpa, A. auriculiformis, and that of Eucalyptus pellita, were either 'compatible' or 'moderately compatible' with cement; sapwoods of the temperate species A. melanoxylon and A. mearnsii were incompatible. The heartwood samples of all the acacias and of E. pellita were generally incompatible with cement; however, the heartwood of the temperate acacia species, especially A. dealbata, was less inhibitory than that of the tropical species. Future work will focus on ways of overcoming the incompatibility of tropical acacia wood with cement. Soaking and/or the use of accelerators are currently required in the manufacture of wood-cement panels from acacias, and methods for reducing or eliminating the need for such treatments deserve investigation. Such alternatives include selection of acacias which contain less heartwood and whose wood is more compatible with cement, and the use of cement-rice hull ash mixtures as more effective binders.

Acknowledgment

The financial support provided by the Australian Centre for International Agricultural Research (ACIAR) is gratefully acknowledged.

References


Compatibility of some Australian acacias with Portland cement

K. L. Semple, P. D. Evans
Department of Forestry, The Australian National University, Canberra, 0200, Australia

Subject The compatibility of the wood of several acacia species with Portland cement was measured and compared with that of spruce and larch, two species known respectively for their high and low compatibility with cement.

Methods and materials Wood flour (20-40 mesh) was prepared using a Wiley mill for the tropical acacias Acacia mangium Willd., A. auriculiformis (L.) K. Benth., A. dealbata Link, A. melanoxylon R. Br. and A. mearnsii de Wild., the temperate acacias A. dealbata Link, A. melanoxylon R. Br. and A. mearnsii de Wild., the temperate acacias A. dealbata Link, A. melanoxylon R. Br. and A. mearnsii de Wild., the temperate acacias


Results 1. Wood-cement mixtures containing acacia heartwood or L. europea wood flour remained soft, failing to set within the test period of 23 hours and resulting CA-factors were below 40%. Heartwood from all of the acacias was therefore incompatible with cement, with CA-factors for the tropical acacia species ranging from 21.1% in A. dealbata to 27.7% in A. auriculiformis (Table 1). Maximum hydration temperatures for the heartwood of the tropical acacia species varied from 29.9 °C for A. crassicarpa to 33.0 °C for A. auriculiformis. The CA-factor values for A. auriculiformis, A. crassicarpa and A. mangium were only slightly higher than that found for L. europea wood which is noted for its extreme incompatibility with cement. The heartwood samples from the temperate acacias (A. dealbata, A. mearnsii and A. melanoxylon) were only slightly more compatible than the tropical acacia species.

2. The sapwood samples from all of the tropical acacias were compatible with cement, with Tm, values of 33.0 to 55.2 °C and CA-factor values varying from 66.3 to 81.9% (Table 1). However, the sapwood samples from the temperate acacia species were incompatible with cement (Tm, = 30.5 °C and CA = 21.4% and 23.6% for A. mearnsii and A. melanoxylon respectively).

3. The proportion of heartwood and sapwood in tropical acacia wood is likely to influence the curing and the properties of wood-cement composite panels made from such species. These results suggest that soluble compounds in the heartwood of the acacia species and the sapwood of the temperate acacia species inhibit cement hydration and setting.

References

Table 1. Tm, and CA-factors for acacia sapwood and heartwood, coniferous wood species and cement control

<table>
<thead>
<tr>
<th>Wood species</th>
<th>Sapwood</th>
<th>Heartwood</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tm, (°C)</td>
<td>CA-factor (%)</td>
</tr>
<tr>
<td>A. dealbata</td>
<td>55.2</td>
<td>66.4</td>
</tr>
<tr>
<td>A. auriculiformis</td>
<td>53.0</td>
<td>72.9</td>
</tr>
<tr>
<td>A. crassicarpa</td>
<td>34.5</td>
<td>81.9</td>
</tr>
<tr>
<td>A. dealbata</td>
<td></td>
<td>36.5</td>
</tr>
<tr>
<td>A. mangium</td>
<td>53.2</td>
<td>80.8</td>
</tr>
<tr>
<td>A. melanoxylon</td>
<td>30.5</td>
<td>23.6</td>
</tr>
<tr>
<td>L. europea</td>
<td></td>
<td>28.2</td>
</tr>
<tr>
<td>P. davisii</td>
<td>60.3</td>
<td>91.1</td>
</tr>
<tr>
<td>Cement control</td>
<td></td>
<td>66.3</td>
</tr>
</tbody>
</table>

Financial support from the Australian Centre for International Agricultural Research (ACIAR) is gratefully acknowledged.
Selected wood characteristics of tropical acacia and eucalypt species growing in provenance trials in north Queensland, Australia

K.E. SIMPLE1, R.B. CUNNINGHAM1 and P.D. EVANS1

1Department of Forestry, The Australian National University, Canberra, Australia
2Statistical Consulting Unit, The Australian National University, Canberra, Australia

SUMMARY

This study examined tree size (DBHOB), % heartwood and wood density of three important acacia and two eucalypt species growing in provenance trials in north Queensland, Australia. The wood density of Acacia mangium was significantly lower than that of A. auriculata and A. crassicarpa, but there were no significant differences in DBHOB or % heartwood between the three acacia species. Provenances of A. mangium varied significantly in DBHOB and wood density, and for this species there was a significant positive correlation between DBHOB and % heartwood. The Papua New Guinea (PNG) provenances of A. mangium were larger in diameter than the Queensland provenances, and the PNG-N provenance had the highest wood density. Eucalyptus grandis trees were significantly larger in diameter and had a higher % heartwood than those of E. pelli. However, there was no significant difference in the wood density of the two eucalypt species. Significant provenance variation in DBHOB and % heartwood existed in E. pelli; however, unlike A. mangium, there was no distinct relationship between DBHOB and % heartwood.

Keywords: Acacia mangium, Eucalyptus pelli, provenance trials, % heartwood, REML, wood density.

INTRODUCTION

Several tropical acacia and eucalypt species have rapidly established themselves as important commercial plantation species in South-East Asia. Brown salwood (A. mangium Willd.) is the most widely planted and documented tropical acacia species. Both red mahogany (E. pelli F. Muell.) and Timor mountain gum (E. sprucei S.T. Blake) have been planted for industrial wood and reafforestation in only a few countries, but they have the potential to be much more widely grown in the humid and sub-humid tropics (Doran and Turnbull 1997). These tropical acacias and eucalypts are of interest, especially in South-East Asia, for their capacity to colonise and grow rapidly on degraded, low-nutrient and weed infested sites and produce large volumes of wood, mainly for use as pulp and forwood (Gan and Midgley 1991). In countries such as Indonesia and Malaysia, tropical acacia species (especially A. mangium) typically have much faster early growth (first six years) than most eucalypt species (Kurinichu et al. 1996, Turvey 1995). For example, species and provenance trials in south Kalimantan, Indonesia found early mean annual increment (MAI) of up to 26 m³ ha⁻¹ y⁻¹ in A. mangium compared with 3.1 m³ ha⁻¹ y⁻¹ in E. pelli (Obano et al. 1995).

Information on provenance variation in wood characteristics of even widely planted species like A. mangium is scarce (Awang and Bhumihannon 1993). There has been a few studies of wood density and % heartwood in A. mangium and E. pelli (e.g. Pipatitwattanaakis 1989, Liang and Gan 1991, Bhumihannon et al. 1992, Clark and Hicks 1996), but similar information for other plantation grown tropical acacias is not available. Furthermore, no attempts have been made previously to relate % heartwood to tree size.

This study examined species and provenance differences in tree size (DBHOB), % heartwood and wood density in the stems of three acacia and two eucalypt species growing in provenance trials in north Queensland, Australia. The relationship of DBHOB to % heartwood was also examined in A. mangium and E. pelli. These same species are being tested as part of a larger study of their potential as raw material for wood-wool cement board and other wood-cement composites. The results are therefore discussed with special reference to wood-suitability for these types of products.

MATERIALS AND METHODS

Sampling

Three acacia and two eucalypt species planted at different sites in north Queensland, Australia were sampled for tree size (DBHOB), wood density and heartwood content. The species were brown salwood (A. mangium Willd.), brush ironbark wattle (A. auriculata F.Muell. ex Benth.), Northern...
wattle (A. crassicarpa Conm. ex Berth.), red mahogany (E. pellita F. Muell.) and Tinaroo mountain gum (E. urophylla S.T. Blake). Details of species, provenances, sites and planting dates are given in Table 1. Ten trees from each of the 16 species/provenance/site groups (160 trees in total) were sampled through January, February and early March 1998. Two cores per tree were extracted; 320 cores in total.

The locations, altitudes and site types for the planting sites are summarised in Table 2. Kuranda and Karri are located on the Atherton Tablelands, Mission and Ellenton are coastal lowland sites in the Cardwell district. Etna is a coastal lowland site, with fertile krasnozem soils producing very rapid growth of the E. pellita and E. urophylla trees planted there (Dickinson and Sun 1995). Mean annual temperatures range from 18.4 to 26.6°C for the Cardwell district lowland sites, and from 15.9 to 23.6°C on the Atherton Tablelands site (Steele and Nikes 1967). These districts experience a distinct dry season (<40 mm rainfall) of around four months.

<table>
<thead>
<tr>
<th>Species</th>
<th>Provenance</th>
<th>Site</th>
<th>Planting date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acacia mangium</td>
<td>PNG-N</td>
<td>Kuranda</td>
<td>1991</td>
</tr>
<tr>
<td>Acacia mangium</td>
<td>PNG-N</td>
<td>Mission</td>
<td>1991</td>
</tr>
<tr>
<td>Acacia mangium</td>
<td>PNG</td>
<td>Kuranda</td>
<td>1991</td>
</tr>
<tr>
<td>Acacia mangium</td>
<td>PNG-SW</td>
<td>Kuranda</td>
<td>1991</td>
</tr>
<tr>
<td>Acacia mangium</td>
<td>QCR</td>
<td>Mission</td>
<td>1991</td>
</tr>
<tr>
<td>Acacia mangium</td>
<td>PNG-SW</td>
<td>Kuranda</td>
<td>1991</td>
</tr>
<tr>
<td>Acacia mangium</td>
<td>PNG-SW</td>
<td>Mission</td>
<td>1991</td>
</tr>
<tr>
<td>Acacia crassarapa</td>
<td>PNG-SW</td>
<td>Mission</td>
<td>1991</td>
</tr>
<tr>
<td>Eucalyptus pellita</td>
<td>L1</td>
<td>L1</td>
<td>1992</td>
</tr>
<tr>
<td>Eucalyptus pellita</td>
<td>L1</td>
<td>L1</td>
<td>1992</td>
</tr>
<tr>
<td>Eucalyptus pellita</td>
<td>PNG-SW</td>
<td>L1</td>
<td>1992</td>
</tr>
<tr>
<td>Eucalyptus pellita</td>
<td>PNG-SW</td>
<td>Ellenton</td>
<td>1991</td>
</tr>
<tr>
<td>Eucalyptus pellita</td>
<td>PNG-Kinrow</td>
<td>L1</td>
<td>1991</td>
</tr>
<tr>
<td>Eucalyptus monophylla</td>
<td>PNG-Wetar</td>
<td>L1</td>
<td>1991</td>
</tr>
</tbody>
</table>

Provenance locations:
- PNG-SW: PNG south of Fly River west of long. 142°E.
- PNG: PNG east of Fly River east of long. 142°E.
- PNG: Pin North Queensland (type York north of lat. 13°S).
- QCR: Queensland Cairns Region (lat. 15° to 19°S).
- PNG-Kinrow: Lat. 8°25'S, Long. 141°W/1; Alt. 45 m. Within bounds of PNG-SW.

Table 2. Location, altitude and soil type of planting sites in north Queensland

<table>
<thead>
<tr>
<th>Site</th>
<th>Lat (S)</th>
<th>Long (E)</th>
<th>Alt. (m)</th>
<th>Mean annual rainfall (mm)</th>
<th>Soil type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Damper</td>
<td>18°24'</td>
<td>146°06'</td>
<td>20</td>
<td>2110</td>
<td>yellowwood soil</td>
</tr>
<tr>
<td>Ellenton</td>
<td>18°24'</td>
<td>146°06'</td>
<td>20</td>
<td>1955</td>
<td>yellowwood soil</td>
</tr>
<tr>
<td>Etna</td>
<td>17°33'</td>
<td>145°54'</td>
<td>750</td>
<td>1500</td>
<td>basaltic clay loam</td>
</tr>
<tr>
<td>Kuranda</td>
<td>16°45'</td>
<td>145°50'</td>
<td>380</td>
<td>1150</td>
<td>red podolic soil</td>
</tr>
<tr>
<td>Mission</td>
<td>18°38'</td>
<td>145°52'</td>
<td>90</td>
<td>1650</td>
<td>grey clay soil</td>
</tr>
</tbody>
</table>

Not all species and provenances were represented at all sites. Some species and provenance combinations were present at more than one site. These were A. mangium (PNG-N and PNG) and A. crassarapa (PNG-SW) at both Kuranda and Mission, and E. pellita (L1) at Kuranda and Ellenton. In addition, the acacia and eucalyptus provenance trials were established at different experiments and therefore experienced different establishment and thinning histories. The acacias were all established at an initial spacing of 3 x 1.8 m (1850 stems ha⁻¹) then thinned to 925 stems ha⁻¹ at 2 years (Harwood et al. 1993). E. pellita and E. urophylla were planted at 1100 stems ha⁻¹ at even spacing then thinned at 1 and 2 years to 770 and 400 stems, respectively (Dickinson and Sun 1995). These differences were taken into account during subsequent analysis and interpretation of data from the two trials.

Core extraction and storage

Two 12 mm diameter cores were extracted from each tree at right angles to each other using a Tanaka mounted corer fitted with a P+T Trecor™ coring head. The cores were extracted from trees at a height of 1.3 m from ground. Clear areas of the bole were sampled and knots and other defects were avoided. The DBHOD (cm) of each tree was recorded. Following extraction, cores were placed in labelled, labelled with species, provenance, family number, location and exact site of extraction. These were kept in an ice-box in the field and subsequently kept frozen (-10°C) to minimize drying and mould growth prior to measuring wood characteristics.

Heartwood content and green volume

The heartwood content of each core was determined by measuring the entire core length and the length of the heartwood portion (which in all species was visually distinct) using...
Minuwている50 cm vernier calipers. Heartwood percentage was calculated by considering the core length and heartwood length as diameters of two circles, and calculating the heartwood and total stem areas, from which heartwood content (in %) was derived. The average % heartwood for each tree was obtained by averaging measurements from the two cores.

**Basic wood density**

After thawing, each green core was weighed and its volume determined using an Archimedean method (Haygreen and Bowyer 1982). The water into which the cores were immersed contained 2 ml of surfactant to reduce the incidence of entrapped air bubbles around the wood. The weight of the water displaced by the core was recorded. The specific gravity of water at room temperature was taken as 1; therefore the weight of water displaced was equated with core volume in cm³. An average % moisture content (MC) was derived for each core by cutting slivers 1 mm in thickness at intervals of approximately 10 mm along the core. The green weight of the slivers was measured immediately after they were cut from the core. The slivers were oven-dried at 105°C for 24 h and then reweighed. The MC was used to estimate the core’s dry weight for calculation of basic wood density. Estimation of oven-dry weight was used because further experimentation required the use of most of the green wood from the cores.

**Statistical analysis**

Only three of all the species x provenance combinations in our data were replicated at different sites. These were provenances of *A. mangium* from FNQ and PNG/N and *A. auriculiformis* from PNG/EW, which were replicated at Kuranda and Mareton (Table 1). Our data are also clearly not balanced for species and provenance. For example, the *E. urophylla* FNQ/Mareton combination is unique and only *A. mangium* and *E. pellita* were sampled from multiple provenances. Therefore, the structure of our data necessitated the use of statistical procedures that were appropriate for the analysis of unbalanced data. Statistical analysis proceeded in two stages. Firstly, a combined mixed linear model analysis of all data was completed, with species and provenance assumed to be fixed effects and site and tree (replicates) as random effects. Note that there is only one degree of freedom for estimating the species x provenance interaction. Secondly, mixed linear model analysis was undertaken for *A. mangium* and *E. pellita* separately in order to reduce the effects of confounding between species and provenance on our interpretation of results. For all analyses, estimates were by weighted least squares following estimation of variance components by Restricted Maximum Likelihood (REML) (Paterson and Thompson 1971, Searle et al. 1992). This methodology was chosen because it is particularly suitable and efficient for modeling unbalanced data with both fixed and random effects. All data analysis was performed using Glimstat (Lawes Agricultural Trust 1994). The change in deviance statistic was used to measure the importance of fixed effects (species and provenance), which is referred to an appropriate $X^2$ distribution to obtain significance levels (p-values). DBHOB was transformed by log, (ln), although back-transformed averages are referred to and discussed in the Results and Discussion section. Provenance comparisons of % heartwood from regression modelling of DBHOB and % heartwood were based on adjusted data sets from which the effects of variation in DBHOB on % heartwood had been removed.

**RESULTS AND DISCUSSION**

**Species differences in DBHOB, % heartwood and wood density**

There were significant (p<0.001) effects of species and provenance on DBHOB, % heartwood and wood density. There was no evidence of additional variation due to sites and there was no significant interaction between provenance and species. Averages for DBHOB, % heartwood and wood density for each acacia species, adjusted for provenance differences, are shown in Figure 1.
No significant differences in DBHOB were found between the three acacia species, whose average DBHOB ranged from 21.7 cm in A. auriculiformis to 26.5 cm in A. mangium (Figure 1(a)). Furthermore, there were no significant differences in % heartwood among the three acacia species (Figure 1(b)), whose % heartwood ranged from 52.8% in A. mangium to 41.5% in A. auriculiformis. A. mangium had a significantly lower wood density than A. crassicarpa and A. auriculiformis (Figure 1(c)). These results accord with those in the literature. A. mangium is classed as a light hardwood with a density of 420-483 kg m⁻³ (Razali and Hamami 1993) whereas the densities of naturally occurring A. crassicarpa and A. auriculiformis exceed 550 kg m⁻³ (Edswell 1978).

The low density of A. mangium wood has an important bearing on its suitability as a pulp species. A. mangium compares favourably with eucalypt wood in pulp and paper quality, but its high % heartwood (500 to 600 kg m⁻³) for bleaching grade hardwood pulps for fine papers. Hence it has been suggested that A. mangium needs to be preferentially selected for higher density to improve its pulping characteristics (Balotico and Clark 1998). However, A. crassicarpa, which had similar density to A. auriculiformis (Figure 1(c)), has relatively low pulp yield and is also difficult to bleach to required brightness without fibre damage and loss compared to A. mangium. However, A. crassicarpa, which had similar density to A. auriculiformis (Figure 1(c)), has relatively low pulp yield and is also difficult to bleach to required brightness (Clark et al. 1991). Therefore, it appears that wood density should not be used as the sole criterion for assessing the suitability of tropical acacias for pulp and paper manufacture.

E. urophylla trees were significantly larger (DBHOB = 28.9 cm) than those of E. pellita (17.8 cm), possibly because they were only sampled at the high quality Eros site (Figure 2(a)). However, this difference in tree size between E. urophylla and E. pellita accords with the results from several species trials in South-East Asia, where E. urophylla has consistently outperformed E. pellita in terms of height and diameter (Nuryanto 1996, Pegg and Wang 1994, Phinyupin et al. 1996).

Figure 2(b) indicates that differences in % heartwood of the two eucalyptus species followed a similar trend to that of DBHOB. Thus E. urophylla had significantly higher % heartwood (52.8%) than E. pellita (36.0%). A previous study found lower heartwood contents of 25 to 29% in 5-year-old E. pellita grown in Kerala, India (Bhat et al. 1987). This discrepancy may be explained by the positive correlation between tree age and heartwood content in eucalyptus.

Wood density data for E. pellita and E. urophylla from other studies are summarised in Table 3. The data from Clark and Hicks (1996) are from the same plantations sampled in this study, and therefore their results may be compared directly with those obtained here (Figure 2(c)). The average wood density of E. pellita and E. urophylla at Eros have increased by 9% and 11%, respectively, from when they were last sampled in 1996 at age 5 years. The density of E. pellita wood here (Figure 2(c)) is considerably higher than that of five-year-old trees grown in Kerala, India. Our results suggest that E. urophylla has lower wood density than E. pellita, in accordance with its established reputation for having a lower wood density than most eucalypt species in natural stands ranging between 540 and 570 kg m⁻³ (Doran and Turnbull 1997).
Provenance differences in *A. mangium*

There were significant differences in DBHOB (p=0.001) and wood density (p=0.005) between provenances of *A. mangium* (Figure 3).

![Graph](image)

**Figure 3.** Provenance means for (a) DBHOB and (b) wood density for *A. mangium* from separate mixed model analysis

Trees from the PNG provenances were significantly larger (DBHOB of 24.1, 27.8 and 24.8 cm for PNG-N, SE and SW respectively) than those from the two Queensland provenances (Figure 3(a)). The trees from QCR provenance had the lowest DBHOB of 20.2 cm even though they were one year older than those of the other provenances. The provenance trials sampled here were also assessed for height (16-17 months after planting by Harwood *et al.* (1993). The trees were then around 3.5 to 4 m in height. Harwood *et al.* (1993) found highly significant differences at the provenance level for stem height, with the PNG provenances performing better than the Queensland provenances. They also found no significant provenance x site interaction for 44 families of PNG provenance planted at both Kuranda and Moreton. Findings here for the now older trees accord with those of Harwood *et al.* (1993).

PNG-N and QCR provenances were significantly higher in wood density (averaging 475 kg m⁻³ and 462.8 kg m⁻³, respectively) than PNG (416.9 kg) and PNG-SW (427.6 kg) (Figure 3(b)). In contrast to our findings, measurements of trees in 6-year-old provenance trials of *A. mangium* at Lad Krating, Thailand, found no significant provenance variation in wood density (Pipawatwanakul 1989). These results were derived from trees grown in warmer, wetter climates in South-East Asia whose wood density might be expected to be somewhat lower than the trees in this study. Much faster growth rates occur in South-East Asia, because of more favourable site and climatic conditions, than in Queensland (Harwood *et al.* 1993). The better sites and faster growth rates may have had a masking effect on any genetic variability in wood density.

A study using PIODYN, which is an indirect method of estimating wood density in living trees, showed PNG provenances of *A. mangium* grown in Sarawak, Malaysia, to be lower in density than others (Liang & Gue 1991). This same study also found density to be significantly influenced by site and growth rate, with larger diameter trees grown at better sites having higher wood density. In contrast, our study found that trees from PNG-N had the highest wood density, although provenances from PNG were not consistently higher or lower in density than those from Queensland provenances. Furthermore, there was no strong link between tree size and wood density. The reasons for these discrepancies are not known and further information on site-provenance/density relationships for the commercial tropical acacia species is needed.

Provenance differences in *E. pellita*

For *E. pellita*, there were strong effects of provenance on DBHOB (p=0.056) and % heartwood (p=0.002), but not on wood density. Adjusted averages for DBHOB and % heartwood are shown in Figure 4.

The trees of PNG-Kirris provenance grown in favourable conditions at Elton were significantly larger (24.3 cm DBHOB) than trees of all other provenances (Figure 4(a)). However, the relative influence of site on this observation is unknown because this provenance was only represented at Elton. Unlike *A. mangium*, PNG provenances of *E. pellita*
were not larger in DBHOB than the Queensland provenance. The smallest trees came from FNQ and PNG-SW provenances (17.4 and 16.5 cm DBHOB respectively) which may in the case of PNG-SW be explained by the fact that they were a year younger than those of FNQ and PNG-HJ at Ellerbeck. Trials of Queensland and PNG provenances of E.pellita on Melville Island, Northern Territory, and in Sarawak, Malaysia, have found the early performance (survival, height and diameter growth) of the PNG provenances to be superior to those of Queensland provenances (Harwood et al. 1997). However the authors found this trend to be less clear in the provenance trials at Cardwell (Kairi and Damper) in Queensland, a finding which our results support.

E.ellita from PNG-Kiriwo had significantly higher % heartwood (56.4%) than all other provenances (Figure 4(b)). The other provenances varied little in % heartwood. FNQ had the lowest (27.8%), which may have been influenced by the effect of provenance on tree size, since trees from the FNQ provenance were very small.

Although not significant, the fast-growing PNG-Kiriwo provenance had the lowest wood density of 487.4 kg m\(^{-3}\). The slower growing FNQ and PNG-SW provenances both had relatively high wood density (556.3 and 602.2 kg m\(^{-3}\) respectively).  

**Relationship between DBHOB and % heartwood**

There were positive relationships between DBHOB and % heartwood across provenances of A. mangium (Figure 5). The slope of the relationship between DBHOB and % heartwood was the same for all provenances, but intercepts varied (Figure 5). Overall, differences in the % heartwood of A. mangium provenances were not significantly different with the exception of PNG-SW, which had a higher % heartwood than the other provenances at any nominal value of DBHOB. For example, at an average DBHOB of 24.5 cm, trees from PNG-SW provenance had % heartwood content of 56.2% whereas comparable figures for PNG-N and PNG-SE were 43.8% and 45.1% respectively.

![Figure 5](image_url)

**Figure 5**  % heartwood vs. DBHOB for all provenances of A. mangium

In *Pinus*, heartwood proportion has been found to be strongly negatively correlated with crown size and vigour and hence inversely proportional to growth rate (Hillers 1987). In contrast, % heartwood was found to be greater in fast-grown European larch (*Larix decidua* Mill.) trees from vigorous lowland provenances of Switzerland than in slow-growing high altitude provenances (Kalmundan 1993). Our findings, for the effect of growth rate on % heartwood in *A. mangium* accord with results for *Larix*, but appear to contradict the trend in *Pinus*. Further data is needed to construct an adequate model of the relationship between heartwood proportion and crown and stem size, and hence growth rate, in tropical forest species.

In contrast with *mangium*, no clear relationship between DBHOB and % heartwood was found for provenances of *E. ellita*.
pellita. Hillis (1987) states that the width and ring number of the sapwood in eucalypt over 15 years of age remains practically unchanged throughout the rest of the tree's life. Heartwood proportion would therefore steadily increase in a predictable fashion with tree age and size in the tree mixture. As the trees in this study get older, a clearer relationship between tree diameter and % heartwood may emerge.

Utilisation in wood-cement composites

Previous studies (Rahim and Ong 1983, Tachi et al. 1986, 1990, Sulastiningih et al. 1990) have shown that the heartwood of A. mangium is incompatible with Portland cement and hence unsuitable for use in wood-cement composites without prior removal of extractives which inhibit cement setting and/or the use of chemical cement-setting accelerators. The heartwood of E. pellita is less inhibitory of cement hydration than that of A. mangium (Semple and Evans 1998, Semple et al. 1999). There are no data on the compatibility of E. umbratilis wood with cement, although its heartwood has a low extractive content (Doran and Turnbull 1997) which may be advantageous for wood-cement composites.

Semple and Evans (1998) found that heartwood flour of A. anacardifolia and A. crassicarpa was also highly incompatible with Portland cement. However, the sapwood of these tropical acacias and of A. mangium was compatible. The proportion of heartwood in such species may therefore be expected to influence their suitability for use in wood-cement composites. Accordingly, this feature of acacia wood may be worthy of further consideration during the selection and breeding of tropical acacias for use in wood-cement composites.

A. mangium forms heartwood before its second year of growth (Marson 1996). This study found some evidence of a provenance effect on % heartwood in A. mangium (Figure 5). This suggests that it may be possible to grow provenances of A. mangium that form less heartwood for wood-cement composites. However, the strong positive correlation between % heartwood and tree diameter suggests there may be a conflict between maximising growth rate and wood volume and minimising heartwood content, and that early harvesting may be a more practical means of reducing average heartwood content in A. mangium trees.

CONCLUSIONS

1. Tropical acacia species varied in wood density, but not in tree size (DBHOB) or % heartwood. The wood density of A. mangium was significantly lower than that of A. anacardifolia and A. crassicarpa. PNG provenances of A. mangium were superior in terms of DBHOB to those of Queensland provenances. The PNG-N provenance had higher density wood than other provenances, which could be important given the need for increased wood density in A. mangium to improve its suitability for the production of bleaching-grade pulp.

2. E. umbratilis trees were significantly larger and had a higher % heartwood than those of E. pellita, but there was no significant difference in the wood density of the two eucalypt species. E. pellita displayed significant provenance differences in DBHOB and % heartwood, but not wood density. PNG-Kiriwo provenance of E. pellita grown at 18 yrs were largest in diameter and had the highest % heartwood, however no distinct trend emerged showing PNG provenances to out-perform the Queensland provenance.

3. There was a positive correlation between DBHOB and % heartwood in A. mangium, which is of significance for the use of A. mangium for wood-cement composites and possibly other wood products.

ACKNOWLEDGEMENTS

The trees sampled in this study were obtained from provenance trials established by CSIRO and managed by Queensland Department of Primary Industry. The Australian Centre for International Agricultural Research (ACIAR) provided financial support for the research. Thanks are extended to Dr Mike Siet for comments on the manuscript and to Mr Noel Semple and Dr Ann Gibson for editorial assistance.

REFERENCES


LAWES AGRICULTURAL TRUST. 1994. Grait - a general statistical program 5 Release (3.1). Lawes Rothamstede Experimental Station, UK.


Cement Hydration Tests Using Wood Flour may not Predict the Suitability of Acacia mangium and Eucalyptus pellita for the Manufacture of Wood-Wool Cement Boards

By K.J. Scumble, R.B. Cunningham, and P.D. Evans

1 Department of Forestry, The Australian National University, Canberra, Australia
2 Statistical Consulting Unit, The Australian National University, Canberra, Australia

Summary

Wood-wool cement boards (WWCBs) are manufactured in many tropical countries where have extensive eucalypt and acacia plantations. Wood from such plantations could act as a potential raw material for WWCBs, but the suitability of most tropical eucalypts and acacias for the manufacture of such products is unknown. This study was undertaken to assess whether the standard laboratory test for wood-cement compatibility, which measures heat of hydration in wood flour-cement mixtures, is an appropriate method for screening tropical eucalypts and acacias for their compatibility with cement and suitability for the manufacture of WWCBs. Wood samples from a tropical eucalypt (E. pellita) and a tropical acacia (A. mangium) were tested in two forms, i.e. flour and wood, for their compatibility (expressed by maximum hydration temperature and C_r factor) with Portland cement. Factors significantly influenced the effect of the wood on cement hydration, resulting in a different species compatibility ranking for flour and wood. As the heattwood content of wood-wool cement hydration test samples increased, T_m and C_r factor increased whereas the opposite occurred for those containing wood flour. Tests using wood flour ranked E. pellita as being more compatible with cement than A. mangium whereas the ranking was reversed when wood-wood was used. Furthermore, at low wood levels the compatibility of samples containing wood-wood or wood flour with cement was similar whereas at high wood levels, samples containing wood-wood were much more compatible with cement than those containing wood flour.

Laboratory tests designed to screen eucalypts and acacias for their compatibility with cement should use wood in a coarser form with a lower surface-to-volume ratio than flour. Caution should be exercised if using results from wood flour-cement hydration tests to estimate the suitability of wood species for the manufacture of WWCBs or possibly other wood-cement composites.

Introduction

Wood-wool cement boards (WWCBs) are manufactured in many tropical countries where have extensive eucalypt and acacia plantations. Wood from such plantations could act as a potential raw material for WWCBs, but the suitability of most tropical eucalypts and acacias for the manufacture of WWCBs and other wood-cement composites is unknown. The first step in determining their suitability is to screen them for their compatibility with cement. This is necessary because many wood species contain extractives which inhibit cement hydration and such species are considered to be unsuitable for use in wood-cement composites (Kanik et al. 1969). Howe,ver, the suitability of many wood species contains extractives which inhibit cement hydration and such species are considered to be unsuitable for use in wood-cement composites (Sandermann et al. 1969; Biddle and Lu 1988; Zhong and Mostofi 1985).

Laboratory screening tests of the compatibility of wood with cement generally measure the exothermic reaction (heat of hydration) over time when wood flour is mixed with cement and water. Wood species have been classified on the basis of maximum hydration temperature (Sandermann and Kohler 1964) and other reaction parameters such as time to reach maximum temperature, rate of hydration increase and area under the hydration curve (e.g. Hofstrand et al. 1984; Hachmi et al. 1990). It has been generally assumed in the literature that using wood flour is relevant to the compatibility of strands or particles of wood (as used in wood-cement composites) with cement. The compactness of wood flour has been shown to influence its compatibility with cement (Weatherwax and Tarkow 1964), however, little consideration has been given as to whether screening tests using wood flour correlate with the compatibility of wood-wood with cement. The most obvious factor which might confound the relationship between the results of cement compatibility tests undertaken using wood flour and the suitability of wood for WWCBs in practice is that wood flour has a larger surface-to-volume ratio than wood. This could determine the ease with which extractives may be leached from wood, which is likely to influence its compatibility with cement.

In this study wood flour and wood-wood from brown saw-wood (Acacia mangium Willd.), red mahogany (Eucalyptus pellita F. Muell.) and black poplar (Populus x can-

Heftekongring / Vol. 53 / 1995 / No. 3
© Copyright 1996 Walter de Gruyter - Berlin - New York
Materials and Methods

Preparation of wood

The tree species used in the experiment were: *Aniba mangium* (SWIDEN BARK PINE), *Eucalyptus globulus* (EUCALYPT WOOD PINE) and *Pseudosyringa vacciniana* (unknown origin). *A. mangium* and *E. globulus* were chosen because of their importance as plantation species in Southeast Asia. *Pseudosyringa vacciniana* is used to make WWBCs in Australia and was selected as a control. Six-year-old *E. globulus* and *A. mangium* trees, two for each species, growing in a wood orchard in Atherton (Queensland) were felled and cross-cut. The billets were shredded into wood-wool measuring 3mm in width and about 0.4-0.6mm in thickness at Woodtec Pty Ltd (Bendigo, Victoria) using a 1975 Van Ellen shredder. The *P. vacciniana* was obtained as shredded wood, in two batches, cut from an unknown number of 30-year-old trees. The wood-wool was air dried at 23°C for 24 hours and then stored under cover at room temperature (20°C).

Wood-wool from *A. mangium* and *E. globulus* was separated into sapwood and heartwood on the basis of the distinct colour difference between sapwood and heartwood in both species. *P. vacciniana* does not form a visually distinct heartwood (Hillis 1987), thus separation of sapwood and heartwood in this species was not possible. Wood-wool was then cut into pieces measuring about 3cm in length using scissors and placed in open bags in a conditioning room at 20 ± 1°C and 3 ± 0.5% r.h., for two weeks.

When possible, wood flour was prepared from blocks of air-dried heartwood and sapwood, reducing them to matchstick-sized pieces using a hurkett and grinding in a ‘Junior’ laboratory mill to produce particles measuring approximately 1 mm in diameter. These were then further ground in a Wiley mill (Arthur H. Thomas Co.) to 30–40 mesh size. Wood of *P. vacciniana* and the sapwood from one of the trees of both *A. mangium* and *E. globulus* was unavailable in solid form and was ground as described above from wood-wool. The wood flour was stored in a conditioning room at 20 ± 1°C and 3 ± 0.5% r.h., for two weeks.

The following amounts of sapwood and heartwood flour and wood for each species were weighed out (seven-dry weight basis) and placed in separate containers: 5g three-level, 2.4V wood, 15g medium level 1 (2% wood), 15g medium level 2 (7% wood) and 2g (high level 9% wood). Within each of the wood levels, three categories of heartwood content were used: 50%, 10% and 50% and 100%, resulting in 48 different samples for each species. Once weighed, the wood samples were kept in the conditioning room at 20 ± 1°C and 3 ± 0.5% r.h. immediately, after mixing, the tip of a temperature thermometer (Type K) was taped to the outside of the sample bag and enclosed within the body of the wood-wool mix by folding the bag in two and securing the folded bag with adhesive tape. The bag was then placed in a polyethylene cup and sealed inside a 1 l capacity thermos-flask. This process was carried out over the six wood species. A constant temperature-humidity apparatus, similar to that used by Jaffe and Simpson (1993), was used to measure the heat of hydration of the six wood-wool cement samples over 24 hours. Temperatures were recorded at 15 minute intervals and the curves were plotted by taking the progressive averages of every three successive readings. Maximum heat of hydration temperature ($T_{max}$) was recorded and a wood-wool compatibility index, $C$-factor (Hill and Simpson, 1990), was calculated. The $C$-factor is the ratio of the areas under the wood sample-cement and cement only hydration curves, expressed as a percentage. All experiments were undertaken in a conditioning room maintained at 20 ± 1°C and 3 ± 0.5% r.h.

Experimental design and statistical analysis

The experimental design used factorial principles, investigating the effects of four fixed factors on wood-wool compatibility, i.e. wood form (flour or wood), species, heartwood content and wood level, and also various random factors, including those associated with replicates obtained from different trees. A total of 28 days was required to test all of the samples. The factors of greatest interest were the effects of wood form and species on compatibility so these factors were randomized within each day of six-sample run. The level of randomization was for wood level and 9 heartwood with one combination of these two factors tested each day. Wood from the first tree (or block in the case of *P. vacciniana*) of each species was tested over the first 14 days, followed by the second and third blocks over the next 14 days. Every 7th day 4 control cement samples were measured comprising a total of 4 cement runs over the entire experiment. The main effects of and interactions between each of the four factors for $T_{max}$ and $C$-factor were tested for significance using an appropriate multi-factorial ANOVA model at the 5% significance level. Before the final analysis, diagnostic checks on the normality and variance of the data were undertaken. The factorial design of the experiment allowed data to be averaged across non-significant (p > 0.05) effects thereby giving the experiment greater precision. Significant results are plotted graphically and bars representing the least significant difference (p < 0.05) are included on graphs to facilitate comparison of means.

Results and Discussion

The wood form (flour or wood) and wood level used in cement hydration tests had highly significant (p < 0.005) effects on maximum hydration temperature ($T_{max}$) and $C$-factor (Table 1). More importantly, wood form interacted strongly with heartwood content, species and wood level (Table 1), producing different results and interpretations of wood-wool compatibility from tests using wood flour compared to those used wood-wool.

The effect of wood form on wood-wool compatibility can be seen clearly in Figure 1, which shows the interaction between wood form and heartwood content, averaged across species, on $T_{max}$ and $C$-factor. As the heartwood content of wood-wool cement hydration test samples increased $T_{max}$ and $C$-factor increased, whereas the opposite occurred in those containing wood flour (Fig. 1). Heartwood extractions which inhibit cement hydration may be readily leached from wood flour and this could explain why decreases in wood-wool compatibility were observed to occur as the heartwood content increased.
Table 1. Significant main effects and interactions between factors

<table>
<thead>
<tr>
<th>Effects and interactions</th>
<th>F-probability (p) for $T_{max}$</th>
<th>F-probability (p) for $C_\nu$ factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood form</td>
<td>&lt; 0.001 (s)</td>
<td>&lt; 0.001 (s)</td>
</tr>
<tr>
<td>Wood level</td>
<td>0.005 (s)</td>
<td>0.001 (s)</td>
</tr>
<tr>
<td>9% Heart wood form</td>
<td>0.002 (s)</td>
<td>0.005 (s)</td>
</tr>
<tr>
<td>Species + Wood form</td>
<td>0.011 (s)</td>
<td>0.007 (s)</td>
</tr>
<tr>
<td>Wood level + Wood form</td>
<td>&lt; 0.001 (s)</td>
<td>&lt; 0.001 (s)</td>
</tr>
<tr>
<td>9% Heart + Species</td>
<td>0.017 (s)</td>
<td>0.007 (s)</td>
</tr>
</tbody>
</table>

Wood content of the wood flour increased. In contrast, wood flour has a much lower surface-to-volume ratio than wood flour and, therefore, the ease with which extractives are removed from wood flour may be lower than for wood flour. Furthermore, the extractives in heartwood may be less susceptible to leaching in the aqueous environment of cement because heartwood is less permeable than sapwood; this may in part explain the observation (Fig. 1) that as the 9% heartwood in wood flour increased, wood-cement compatibility increased.

The form of the wood used in the cement hydration tests also influenced the "perceived" compatibility of the different wood species with cement. Tests using wood flour ranked E. pellita as being more compatible with cement than A. manganium whereas the ranking was reversed when wood-wool was used (Fig. 2). For example, average $C_\nu$-factors for E. pellita and A. manganium flour were 64.5 and 56.5% respectively whereas for wood-wood they were 72.4 and 77.5% (Fig. 2). These compared with P. cunnninghamii wood at 65.4 and 70.8% for flour and wood respectively. The leachability of extractives from wood flour and wood-wood may help explain the observed switch in species compatibility ranking between the two wood forms. Heartwood of A. manganium is known to contain a variety of condensed tannin (flavonoid) extractives which strongly inhibit cement hydration (Tachi et al. 1989). Such extractives may be easily leached from wood flour but less readily from wood-wood, and hence it is not surprising that tests using wood flour ranked A. manganium as the least compatible of the wood species tested. The reduced compatibility of E. pellita wood in wood form may tentatively suggest wood structure-related differences in the leachability of inhibitory compounds from solid wood of different species.

As expected, wood form interacted significantly (p < 0.001) with wood level (Fig. 3), whereby compatibility with cement decreased markedly with increasing levels of wood flour and less so for wood-wood. The smaller particle size in wood flour would result in a greater increase in the ratio of surface area-to-weight with increasing wood level compared with wood wood, thus affecting wood-cement compatibility to a greater extent.

Finally, figure 4 shows a significant interaction between species and heartwood content whereby wood-cement compi-
Table 2. Average $T_{max}$ for wood form and wood level of E. pellita, A. mangium and P. x euramericana by heartwood content and wood level.

<table>
<thead>
<tr>
<th></th>
<th>Heartwood*</th>
<th>Floor</th>
<th>Wood</th>
<th>Plum</th>
<th>Wood</th>
<th>Plum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>50%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Floor</td>
<td>Wood</td>
<td>Floor</td>
<td>Wood</td>
<td>Floor</td>
</tr>
<tr>
<td>Low</td>
<td>63.3</td>
<td>64.9</td>
<td>63.1</td>
<td>63.5</td>
<td>60.7</td>
<td>62.3</td>
</tr>
<tr>
<td>M1</td>
<td>57.8</td>
<td>57.6</td>
<td>63.8</td>
<td>55.1</td>
<td>47.4</td>
<td>53.1</td>
</tr>
<tr>
<td>M2</td>
<td>53.8</td>
<td>52.3</td>
<td>48.2</td>
<td>54.1</td>
<td>35.2</td>
<td>49.4</td>
</tr>
<tr>
<td>High</td>
<td>42.9</td>
<td>46.2</td>
<td>33.2</td>
<td>40.6</td>
<td>24.2</td>
<td>43.6</td>
</tr>
<tr>
<td>Average</td>
<td>54.6</td>
<td>55.8</td>
<td>48.9</td>
<td>53.4</td>
<td>44.4</td>
<td>52.6</td>
</tr>
</tbody>
</table>

* 0% heartwood = sapwood. 50% heartwood = 50% heartwood/50% sapwood.

Fig. 3. Interaction between wood level and wood form for $T_{max}$ and $C_{factor}$; data averaged across species and heartwood content.

Fig. 4. Interaction between heartwood content and species for $T_{max}$ and $C_{factor}$; data averaged across wood form and wood level.

Compatibility increased in E. pellita and decreased in A. mangium with increasing heartwood content. The trend in A. mangium was due to the high average compatibility of sapwood regarding form. In contrast to the extreme incompatibility of the heartwood in flour form for reasons already discussed. Explanations for the pattern observed in E. pellita are less

Holzforschung / Vol. 55 / 1999 / No. 3
Table 3. Average C-factor for wood flour and wood-wool of 4. *f. pellic*., 4. *mangium* and 4. *x. cunninghamii* by 3 heartwood content and wood level

<table>
<thead>
<tr>
<th>Species</th>
<th>0% heartwood</th>
<th>50% heartwood</th>
<th>100% heartwood</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0% heartwood</td>
<td>50% heartwood</td>
<td>100% heartwood</td>
</tr>
<tr>
<td>Low</td>
<td>93.3</td>
<td>93.3</td>
<td>85.4</td>
</tr>
<tr>
<td>M1</td>
<td>79.6</td>
<td>79.6</td>
<td>72.9</td>
</tr>
<tr>
<td>M2</td>
<td>62.3</td>
<td>62.3</td>
<td>69.0</td>
</tr>
<tr>
<td>High</td>
<td>43.3</td>
<td>43.3</td>
<td>50.1</td>
</tr>
<tr>
<td>Average</td>
<td>67.8</td>
<td>67.8</td>
<td>56.1</td>
</tr>
<tr>
<td>E. pellic</td>
<td>93.1</td>
<td>93.1</td>
<td>91.0</td>
</tr>
<tr>
<td>M1</td>
<td>74.6</td>
<td>74.6</td>
<td>72.9</td>
</tr>
<tr>
<td>M2</td>
<td>53.3</td>
<td>53.3</td>
<td>49.2</td>
</tr>
<tr>
<td>High</td>
<td>38.3</td>
<td>38.3</td>
<td>30.0</td>
</tr>
<tr>
<td>Average</td>
<td>64.5</td>
<td>64.5</td>
<td>54.1</td>
</tr>
<tr>
<td>P. x cunningham</td>
<td>91.8</td>
<td>91.8</td>
<td>85.7</td>
</tr>
<tr>
<td>M1</td>
<td>74.2</td>
<td>74.2</td>
<td>72.9</td>
</tr>
<tr>
<td>M2</td>
<td>53.6</td>
<td>53.6</td>
<td>49.2</td>
</tr>
<tr>
<td>High</td>
<td>38.0</td>
<td>38.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Average</td>
<td>65.4</td>
<td>65.4</td>
<td>54.1</td>
</tr>
</tbody>
</table>

* 0% heartwood = sapwood; 50% heartwood = 50% heartwood/50% sapwood.

Conclusions

Cement hydration tests using wood flour do not accurately predict the compatibility of wood-wool of either *A. mangium* or *E. pellic* with cement. Further research is needed to develop a more accurate method of screening acacia and eucalypt wood species for their compatibility with cement. Following the development of such a method, a greater range of acacia and eucalypt need to be tested for their compatibility with cement and potential suitability for use in wood-cement composites.

Acknowledgements

The authors thank the Australian Centre for International Agricultural Research for financial support, Queensland Department of Primary Industries for supplying wood samples, Mr John Woods and staff at Woodco Pty Ltd for processing wood into wood-wool and Mr Noel Sempio and Dr Anne Gibson for editorial assistance.

References


Received January 13th 1988

K.E. Sempie and P.D. Evans
Department of Forestry
The Australian National University
Canberra, 0200
Australia

R. B. Cunnings
Statistical Consulting Unit
The Australian National University
Canberra, 0200
Australia
ADVERSE EFFECTS OF HEARTWOOD ON THE MECHANICAL PROPERTIES OF WOOD-WOOL CEMENT BOARDS MANUFACTURED FROM RADIATA PINE WOOD

Kate Semple
Graduate student

and

Philip D. Evans†
Reader
Department of Forestry
The Australian National University
Canberra, ACT 0200, Australia
(Received April 1999)

ABSTRACT

Wood-wool cement boards (WWCBs) that are manufactured commercially in Australia from radiata pine occasionally contain localized areas in which there is poor bonding between wood and cement. The cause of this defect, which leads to the rejection of boards before they are sold, is not known, but it has been suggested that it may be due to the use of blue-stained wood or heartwood in the manufacture of boards. In this study, both wood types were tested for their effects on the hydration of Portland cement and the mechanical properties of WWCBs. Blue-stained sapwood slightly retarded the hydration of cement but had no significant \( P < 0.05 \) effect on the mechanical properties of boards. In contrast, heartwood severely retarded cement hydration, and boards made from heartwood had little structural integrity. The appearance of such boards resembled the defective portions of commercially produced boards, and therefore it can be concluded that the defect arises from the inhibitory effect of heartwood on cement hydration. The problem could be eliminated by processing logs from young radiata pine trees, less than 12–15 years old, which will contain little or no heartwood.

Keywords: *Pinus radiata*, wood-wool cement board, heartwood, mechanical properties.

INTRODUCTION

Wood-wool cement board (WWCB) is an in-organic-bonded panel product manufactured from strands of wood (excelsior) and Portland cement (Moslemi 1989). In Australia, WWCB was manufactured originally from black poplar (*Populus euramerica* L. De Wit) wood from plantations that were established for the Australian match industry, but radiata pine (*Pinus radiata* D. Don) wood obtained from forest thinning operations is now the preferred wood species (Woolley 1998). In general, radiata pine wood has proved to be an excellent raw material for the manufacture of WWCB, and the boards made from radiata pine are widely used in Australia in non-structural applications such as ceiling panels and soundproofing barriers alongside highways. However, occasionally boards manufactured from radiata pine contain localized areas in which there is poor bonding between wood and cement. The cause of this defect, which leads to the rejection of boards before they are sold, is not known; but it has been suggested that it may be due to the use of heartwood or wood with severe blue-stain in the manufacture of boards.

There have been no reports of the effect of radiata pine heartwood on the properties of WWCB, but abietic acid, which is one of a number of resin acids that constitute 71% of extractives in radiata pine heartwood (Uprichard 1991), has been shown to inhibit the setting of
cement (Miller and Mosleml 1991a). In addition, previous studies have also shown that the heartwood of other Pinus species, for example loblolly pine (Pinus taeda L.) (Weather wax and Tarkow 1964, 1967) and jack pine (Pinus contorta Dougl. ex Loud.) (Miller and Moslemi 1991b), inhibits the setting of cement to a greater extent than sapwood. The colonization of wood by blue-stain fungi has a positive effect on the compatibility of wood with cement (Davis 1966; Biblis and Lo 1968; Raczkowski et al. 1983) because the fungi metabolize low molecular weight polysaccharides that retard the setting of cement (Sandermann and Brandel 1956; Bruere 1966). In contrast, decayed wood, which contains sugars resulting from the enzymic degradation of cellulose and hemicelluloses, strongly inhibits the setting of cement (Weather wax and Tarkow 1964, 1967; Simatupang 1966; Meiier 1990).

The aim of this study was to determine the water use of radiata pine heartwood or severely blue-stained sapwood could lead to the production of defective wood-wool cement boards and, secondly, if they do, to suggest practical solutions to eliminate the problem.

MATERIALS AND METHODS
Sampling and preparation of wood raw materials

Heartwood and sapwood wood-wool was obtained from 14-year-old radiata pine trees growing in plantation at Hepburn Springs in Central Victoria. Trees were felled, debarked, and converted into ten billets 20–25 cm in diameter and 46 cm in length. Billets were air-dried for 9 months and converted into wood-wool, measuring 0.3 x 3 x 460 mm, using a van Ellen shredder at WoodTex Pty Ltd in Bendigo, Victoria. Heartwood and sapwood wood-wool from each billet was separated during shredding and packed into separate bags. Further screening of heartwood and sapwood, based on the color of the two wood types, was then undertaken to obtain samples containing only heartwood or only sapwood. Two batches of wood-wool severely affected by blue-stain fungi were also obtained from WoodTex Pty Ltd in Bendigo, Victoria. Wood-wool for extractive content and cement compatibility testing was cut into short (2–3 cm) lengths using scissors and then placed in a conditioning room maintained at 20 ± 1°C and 65 ± 5% RH for 2 weeks. Wood-wool for the manufacture of experimental panels was similarly conditioned without cutting.

Wood extraction and determination of extractive content

The extractive content of the wood-wool was determined as follows: 20-g samples of chopped heartwood and sapwood wood-wool from each billet were ground separately to 10-mesh size using a Wiley mill; 5 g of the resulting wood flour was added to a preweighed oven-dry cellulose extraction thimble (Whatman brand 19 x 90 mm), which was then immediately reweighed. This was placed in a 100-ml Soxhlet extraction apparatus and refluxed with 250 mL of ethanol (4), acetone (1), and toluene (1) for 4 h. After extraction the thimble was drained of excess solvent, oven-dried overnight at 105°C, and reweighed. Duplicate extractive content determinations were undertaken for each sample. The moisture content of air-dry samples was determined separately to enable calculation of extractive content on an oven-dry wood basis. Extracted heartwood wood-wool was also tested for its compatibility with cement. Extraction of wood-wool followed the procedure described above, except that 15 g of chopped wood-wool was placed in the Soxhlet extraction apparatus, rather than a cellulose extraction thimble, and the wood-wool was air-dried after removal from the Soxhlet.

Measurement of wood-cement compatibility

Duplicate samples of blue-stain-affected sapwood, extracted heartwood, and unextracted heartwood and sapwood from the ten billets were assessed for their compatibility with Portland cement using a method that measures the heat of hydration evolved by a mixture of
wood cement and water under standard conditions. Then 100 g of fresh, dry cement (Blue Circle Southern Brand; batch no. 131/98) was placed in a sealable "Dal grip" polythene bag and evenly mixed with 41.5 g of distilled water at 20°C for 1 to 2 min to form a slurry. A 5-g sample of wood-wool was then added and thoroughly mixed with the slurry. The cement controls (containing no wood) used 40 mL of water. Immediately after mixing the cement and wood, the tip of a temperature thermocouple (Type J) was taped to the bag and enclosed within the body of the cement-wood mixture by folding and then securing the bag and contents around it. A cement hydration temperature measuring apparatus (Moslemi and Lim 1984; Irle and Simpson 1993) capable of measuring the heat of hydration of six wood-cement mixtures over a 23-h period was used to record temperatures at 15-min intervals. The curves were smoothed by progressive averaging and plotting of every three readings. All experiments were undertaken in a conditioning room at 20 ± 1°C and 65 ± 5% RH. Previous studies of the suitability of wood species or type for use in wood-cement composites have generally ranked them according to their effect on the maximum hydration temperature (Tmax) attained by a wood-cement mixture (Sandermann et al. 1960; Sandermann and Kohler 1964; Weatherwax and Tarkow 1964) or the time taken to reach Tmax (Weatherwax and Tarkow 1964; Biblis and Lo 1968). Hachmi et al. (1990) developed a wood-cement compatibility index (Ca factor) based on the ratio of the area under the hydration curve of a wood-cement mixture to that of a cement control, which they suggested was the best method of assessing the hydration behavior of any lignocellulosic material with cement. To enable our results to be compared with those of previous studies, Tmax, time taken to reach Tmax, and Ca-factor were calculated for each hydration sample, and hydration rate (Tmax-Tmin/Time) was also used as an additional quantitative index of wood-cement compatibility. The Tmax component of hydration rate was defined as the minimum temperature attained during the first 5 h of hydration.

**Manufacture of WWCBs and mechanical testing of boards**

WWCBs were made from heartwood and sapwood wood-wool obtained from each billet, i.e., 10 boards each for sapwood and heartwood. Two boards were also made from the batches of blue-stained sapwood. A cement:wood ratio of just over 3:1 was used in accordance with commercial practice (Woolley 1998). One-hundred-fifty g of wood and 500 g of cement (Blue Circle Southern Brand; batch no. 247MA98) were used for the manufacture of each board. The wood-wool was placed in a netted bag, which was momentarily submerged in a bucket of clean tap water at 20°C before it was drained for 2 min. This imparted an average of 400 g of water to the wood-wool. The wet wood-wool was placed in a large plastic bowl, cement was progressively sprinkled through it, and wood-wool and cement were mixed by hand over a period of 10 min.

The resulting quantity of cement-coated wood-wool was placed on a 12-mm-thick plywood sheet within a hardwood frame that measured 25 × 310 × 240 mm. A second plywood sheet was then placed on top of the frame and the resulting assembly was pre-pressed. Wood-wool and cement mixture for a second board were prepared, and the first board assembly was removed from the press. A second frame was placed on top of the assembly, and the process of making the first board was then repeated. A third plywood sheet was then placed on top of the second board, and the two boards were pressed using a PHI platens press (model no. PW220g-X4A) for 24 h at 140 kPa. The platen were manually closed using a lever-operated hydraulic oil pump. After 24 h, the boards were removed from the press, labelled, and placed in a conditioning room at 20 ± 1°C and 65 ± 5% rh. to cure for 28 days. This is the minimum time recommended for cement...
type GP (formerly Type A/Type 1) to reach its maximum strength. Two samples measuring 50 × 23 mm were cut from each board, and their dimensions (width and thickness) were recorded using Mitutoyo digital callipers. The modulus of rupture (MOR) of board samples was determined using a three-point bending cell attached to an H.T.E. (Hounsfield) testing machine using a span length of 100 mm, cross-head speed of 6 mm/min and cross-head and bearer diameters of 5 mm. The results from the experimental boards were compared with measured MOR for two commercial WWCBs of the same cement-wood ratio, density, and thickness.

Statistical analysis

Matched data sets for heartwood and sapwood of each of the ten billets (Tmax, hydration time, hydration rate, Cα-factor, and board MOR) were compared by paired t-tests (one-tail, P < 0.05 significance level). The data sets were checked for normality prior to statistical analysis. A least significant difference (LSD, P < 0.05) bar is included on the graph depicting the mechanical properties of WWCBs in order to facilitate comparisons of means.

RESULTS AND DISCUSSION

Cement compatibility and board mechanical properties

Radiata pine sapwood was significantly (P < 0.001) more compatible with Portland cement than heartwood. Hence, Tmax, hydration rate, and Cα-factor (Table 1) were all significantly higher for sapwood than for heartwood, and wood-cement mixtures containing sapwood reached their maximum hydration temperature more quickly than those containing heartwood (Table 1). These results accord with previous studies that have shown that the heartwood of Pinus species inhibits the setting of cement to a greater extent than sapwood (Weatherwax and Tarkow 1964, 1967; Miller and Moslemi 1991b). As expected, the average extractive content of radiata pine heartwood (4.3%) was greater than that of sapwood (1.2%), although there was considerable variation in the extractive content of heartwood wood-wool samples obtained from different billets, ranging from 1.2% to 8.8%. Removal of heartwood extractives resulted in considerable improvement in the compatibility of the wood-wool with cement (Table 1).

![Graph of Modulus of Rupture (MPa) vs Wood Type](image)

**Fig. 1.** Average modulus of rupture (MOR) for WWCBs made from sapwood, blue-stained sapwood, and heartwood compared to MOR of a commercially manufactured board.

**Table 1.** Average cement compatibility indices and extractive contents for sapwood, heartwood, and blue-stained sapwood.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Tmax (°C)</th>
<th>Time (h)</th>
<th>Hidration Rate (%)</th>
<th>Cα-Factor (%)</th>
<th>Extractive Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sapwood</td>
<td>50.7 (2.1)*</td>
<td>10.9 (0.6)</td>
<td>2.25 (0.25)</td>
<td>89.5 (7.6)</td>
<td>1.2 (0.4)</td>
</tr>
<tr>
<td>Heartwood</td>
<td>45.8 (3.0)</td>
<td>15.9 (1.2)</td>
<td>1.36 (0.31)</td>
<td>72.0 (11.8)</td>
<td>4.3 (2.5)</td>
</tr>
<tr>
<td>Blue-stained sapwood</td>
<td>42.0 (4.5)</td>
<td>10.7 (0.7)</td>
<td>1.79 (0.03)</td>
<td>70.7 (14.7)</td>
<td>—</td>
</tr>
<tr>
<td>Extracted heartwood</td>
<td>48.0 (0.8)</td>
<td>12.5 (0.1)</td>
<td>1.70 (0.04)</td>
<td>86.4 (1.3)</td>
<td>—</td>
</tr>
<tr>
<td>Neat cement</td>
<td>55.5 (0.4)</td>
<td>9.2 (0.2)</td>
<td>2.03 (0.03)</td>
<td>100 (0.0)</td>
<td>—</td>
</tr>
</tbody>
</table>

* Standard deviation in parentheses.
Results in Table 1 suggest that blue-stained wood was less compatible with cement than sapwood, in contrast to previous studies that have found that blue-stained wood has a positive effect on the setting of cement (Davis 1966; Biblis and Lo 1968; Raczkowski et al. 1983). The blue-stained wood tested here was obtained from radiata pine billets that had been stored outside for 9 months. It is possible that during this prolonged storage period the billets were colonized by decay fungi as well as blue-stain fungi. Since decayed wood strongly inhibits the setting of cement (Weatherwax and Tarkow 1964), this may explain why the blue-stained wood tested here inhibited rather than accelerated cement hydration. In accord with this suggestion, Meier (1990) noted that the beneficial effects of long-term storage of wood on cement hydration may sometimes be masked by attack of the wood by decay fungi.

Differences in the properties of boards containing sapwood or heartwood were apparent during the process of manufacturing them. Boards made from sapwood were dry and stiff as soon as they were removed from the press, whereas those made from heartwood were damp and spongy. Boards made from radiata pine heartwood were significantly ($P < 0.05$) weaker in bending than those made from sapwood or blue-stained sapwood (Fig. 1). The MOR of boards manufactured from blue-stained sapwood, which was obtained by testing four samples cut from two boards, was slightly lower, but not statistically different ($P > 0.05$) from that of boards made from sapwood. The MOR of
boards made from blue-stained sapwood was higher, but not statistically different from the average MOR of the commercial board samples (2 MPa).

The results of this study clearly show that radiata pine heartwood inhibits cement hydration and is highly unsuitable for the manufacture of WWCB. The appearance of the WWCB specimens manufactured from radiata pine heartwood (Fig. 2) bears a strong resemblance to the defect (Fig. 3) characterized by poor bonding between wood and cement that is occasionally found in commercially produced WWCBs made from radiata pine.

Radiata pine heartwood extractives are composed of resin acids (71%), fatty acid esters (11%), fatty acids (2%), phenols (6%), and unsaponifiables (10%) (Uprichard 1991). Resin acids and fatty acid esters have been shown to interfere with the hydration of cement and reduce bonding between cement and wood (Steward 1986; Miller and Moslemi 1991a). Furthermore, the heartwoods of loblolly and lodgepole pine, which contain similar types of extractives to those found in radiata pine heartwood (Erdtman 1952), also inhibit the setting of cement to a greater extent than sapwood (Weatherwax and Tarkow 1964, 1967; Miller and Moslemi 1991b). Therefore it can be concluded that the defect in commercially produced radiata pine WWCB, which is characterized by poor bonding between wood and cement and leads to the rejection of boards at the plant level, is caused largely by the inhibitory effects of heartwood on cement hydration.

Minimizing the effects of heartwood

Heartwood usually begins to form in radiata pine between 12 and 15 years of age (Bamber
and Burley 1983), and there is a strong negative correlation between growth rate and site productivity and heartwood volume (Bamber 1976; Hillis 1987). In order to minimize any deleterious effects of radiata pine heartwood on the properties of WWCB, wood from fast-grown young trees (<15 years old) should be used for the manufacture of WWCBs. If radiata pine wood for use by WWCB plants is derived from forest thinning operations, care should be taken to ensure that first thinnings (<15 years) are used as these generally contain little or no heartwood. In contrast, logs from long-delayed first thinnings (past 15 years) and later thinning operations should not be used for the manufacture of WWCB as they will contain considerably more heartwood.

ACKNOWLEDGMENTS

The authors acknowledge financial and material support provided by the Australian Centre for International Agricultural Research (ACIAR), Mr. John Woolley, Manager, WoodTex Australia Pty Ltd, and Blue Circle Southern Cement Ltd (Australasia).

REFERENCES


Compatibility of 8 temperate Australian Eucalyptus species with Portland cement

K. E. Semple, P. D. Evans (Sen)
Department of Forestry, The Australian National University, Canberra, 0200, Australia

R. B. Cunningham
Statistical Consulting Unit, The Australian National University, Canberra, 0200, Australia

Subject Few of the over 800 species of Eucalyptus have been screened for their compatibility with Portland cement and suitability for the manufacture of wood-cement composites. The compatibility with Portland cement of 8 temperate species of Eucalyptus native to SE Australia was measured, and the effects of sapwood content and of extractive removal on wood-cement compatibility were assessed.

Methods and materials Wood from 8 species of Eucalyptus: E. globulus ssp. bicostata, E. smithii, E. nitens, E. oreades, E. macrocarpa, E. kenshamii, E. macarthurii and E. karri (E. marginata) was sampled from two different sites; Kowen and Uriarra, near Canberra, Australia. The trees were 15 years old and at each site, 6 trees per species were sampled. From each tree a disk, approximately 1.5 cm in thickness, was cut from breast height (1.3 m). Disks were air-dried, proportion of sapwood determined and two 1.5 cm wedges cut from opposite sides of the disk. The wedges were sliced tangentially into slivers 0.3 cm in thickness, conditioned to 12% MC and 5 g of slivers tested for compatibility with Portland cement, expressed using hydration rate (R, °C/h; Sandermann and Kohler 1964). The effect of water soaking (23 °C for 24 h) on wood-cement compatibility was also assessed. Statistical analysis used a general linear mixed

Fig. 1a-d a Hydration rate (°C/h) for unsoaked wood by species; b effect of soaking on compatibility; c site x soaking interaction on compatibility; and d average % sapwood content by species and site.
model with species and soaking as fixed effects, and random effects arising from site, plot and tree. Variance components analysis was used to assess interactive effects of site and % sapwood on the compatibility of the species with cement. Significant results are presented graphically and an error bar (Least Significant Difference, LSD) is included on each graph to facilitate comparison of means.

Results 1. The wood of all 8 species of Eucalyptus reduced the normal hydration rate of Portland cement, but there were significant (p = 0.004) differences between species (Fig. 1a). E. badgensis and E. smithii had the highest compatibility (R = 1.27 and 1.19 °C/h respectively) whereas E. microcarpa and E. benthamii had the lowest compatibility (R = 0.88 and 1.01 °C/h respectively).

2. Soaking of the eucalypt wood in water at ambient temperature significantly (p < 0.001) improved wood-cement compatibility (Fig. 1b) by removing most of the extraneous substances responsible for inhibiting cement hydration.

3. Wood from Kowen was significantly lower (p < 0.001) in average compatibility than that from Uriarra (Fig. 1c) possibly because it contained a greater proportion of sapwood (Fig. 1d) which contains polysaccharides and phenolic extractives that inhibit the hydration of Portland cement (Fischer et al, 1974). Some phenolic extractives are insoluble in cold water, perhaps accounting for the slightly reduced compatibility of wood from Kowen even after soaking (Fig. 1c).

References:
Sandermann W, Kohler R (1964) Holzforschung 18: 53-59
The suitability of five Western Australian mallee eucalypt species for wood–cement composites

K.E. Semple a,b, R. B. Cunningham a, P.D. Evans a

a Department of Forestry, The Australian National University, Canberra, Australia
b Statistical Consulting Unit, The Australian National University, Canberra, Australia
c Centre for Advanced Wood Processing, The University of British Columbia, Vancouver, Canada

Abstract

There are currently around 10,000 ha of mallee eucalypt plantations in Western Australia that have been established primarily for the production of eucalypt leaf oils. Planting rates are projected to increase dramatically in future. The financial viability of these plantations is dependent upon finding a commercial outlet for the small diameter wood and bark residues, which may constitute up to half of the harvested material. The potential for such residues to be utilised in cement-bonded wood composite panels was investigated here. The woody residues of five species of mallee eucalypt, as expected, inhibited the hydration reaction of Portland cement, but not to such an extent as to make the wood unsuitable for cement composites. The bark of one of the species, E. laevisulphata spp. lissuphloia, inhibited the setting of Portland cement to such an extent that the residue of this species (with bark present) was unsuitable for use in wood–cement composites. Three out of the five mallee eucalypt species retained relatively good compatibility with cement even when bark was present in the residues. The flexural properties (MOR and MOE) of cement-bonded panels manufactured from chipped mallee eucalypt residues were low in comparison to similar boards made from radiata pine, probably because of the smaller particle size and lower aspect ratio of the eucalypt wood residues. Boards made from E. polyalata, E. torata and E. kochii spp. plenisulphata were stronger and more resistant to water than those made from E. angustissima and E. laevisulphata spp. lissuphloia. On the basis of our findings, opportunities and challenges for the commercial utilisation of mallee eucalypt wood for wood–cement composites are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Oil mallee; Eucalyptus; Radiata pine; Particleboard; Portland cement

1. Introduction

Rising water tables in the wheat belt of Western Australia (WA) due to extensive clearing of native vegetation over the last 100 years is transferring salts from ancient marine sediments to the upper soil horizons with devastating effects on agricul-
tural productivity. Almost 105 or 1.8 million ha of wheat belt soils are now affected to some extent by salinity (Government of Western Australia, 1996). This is forecasted to increase to 50% over the next 50 years unless large-scale revegetation of affected areas is undertaken (Ferdowsian et al., 1996). To help rectify the problem, an ambitious program to establish large-scale tree plantations has been put in place and it is projected that by the year 2020, 800,000 ha of tree crops (mainly eucalypts) will have been planted on farmland (Shea and Hewett, 1997). It is hoped that such plantations will ameliorate rising water tables and accompanying soil salinity as well as providing income for farmers through the sale of eucalypt wood and leaf oils (Shea et al., 1994; Berry, 1997, Shea, 1998). Around 45 species of eucalypts and acacias are currently being tested for their ability to grow on salt affected land (Shea, 1998). Preliminary results suggest that mallee eucalypts, which are hardy, lignotuberosous, multi-stemmed trees adapted to the semi-arid zones of Eastern and Western Australia, are well suited for planting on salt-affected sites, and have the potential to generate significant volumes of wood and essential leaf oils (Wildy et al., 2000). Five species in Eucalyptus polybractea R.T. Baker, E. angustissima F. Muell sp. angustissima, E. kochii Maiden and Blakely sp. pleiosoma (Gardner) Brooker, E. hartii Johnson & Hill and E. laeviphraxe (Beath) show promise and are being assessed for their commercial potential.

Oil-mallees contain high concentrations of essential leaf oils (> 2.5% of leaf fresh weight), of which cineole (eucalyptol) is the most abundant and important component (Milthorpe et al., 1998). E. polybractea is the premier source of high grade cineole oils (1.8-cineole is the principle active constituent of medicinal oils) in Australia today (Boland et al., 1991). Leaf oil is the main commercial product derived from mallee plantations in Australia, but commerce is currently limited to niche markets in high quality pharmaceutical oils rather than the larger market for general purpose eucalyptus oil which is supplied at lower cost by China (McKelvie et al., 1994). In future Australia could potentially supply very large markets for ‘new generation’ industrial solvents based on eucalyptus oil (Wildy et al., 2000). The yields and chemical composition of oils (where known) from the leaves of each of the mallee eucalypt species examined in this paper are shown in Table 1.

Mallee eucalypt trees coppice prolifically and harvesting on a continuous basis could take place as frequently as every 1–2 years (Shea, 1998). However, cineole yields from mallee leaves are highest in older leaves around 5 years of age (Eastham et al., 1993). Later harvest of trees is therefore the preferred option, which would result in the generation of large quantities of woody biomass left over after stripping the leaves for distillation. Economic analysis indicates that the financial viability of oil production from mallee plantations depends on farmers finding a commercial outlet for the woody residues (Bartle et al., 1996). Around 3 tonnes/ha/year of clean dry woodchips can be produced at most sites after a 3–5 year rotation (Bartle, 2001), so, plantations of oil-mallee eucalypts could potentially generate around 13 million cubic metres of woody biomass annually in WA (Shea, 1998). A preferred option for disposing of the woody residue is by chipping, making a ready source of fuel for distillation, electricity generation and carbonisation into activated charcoal products (Evans, 1997; Fung, 1999), and raw material for the manufacture of

<table>
<thead>
<tr>
<th>Species</th>
<th>% Oil yield</th>
<th>Primary constituents</th>
<th>Source: Boland et al. (1991)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E. angustissima</td>
<td>No data</td>
<td>No data</td>
<td></td>
</tr>
<tr>
<td>E. hartii</td>
<td>2.1–4.5</td>
<td>1.8-cineole (75–83%)</td>
<td></td>
</tr>
<tr>
<td>E. kochii</td>
<td>1.2–3.7</td>
<td>1.8-cineole (83–94%), 9-p-cymene</td>
<td></td>
</tr>
<tr>
<td>E. laeviphraxe</td>
<td>2.4</td>
<td>1.8-cineole (97%), 9-p-cymene, 4-methyleen-3-ylo acetate</td>
<td></td>
</tr>
<tr>
<td>E. polybractea</td>
<td>0.75</td>
<td>1.8-cineole (92%)</td>
<td></td>
</tr>
</tbody>
</table>
wood-based composites (Bartle, 2001). There is however, no information on the suitability of mallee eucalypt residues for the manufacture of wood-based composites. This paper deals specifically with potential utilisation of chipped mallee wood and bark residues from five oil-mallee species for the manufacture of cement-bonded composite panels.

The first step in assessing the suitability of different wood species for use in cement-bonded composites involves testing whether the wood significantly inhibits the hydration reaction of Portland cement (Sandermann and Kohler, 1984). The wood and bark residues of mallee eucalypt species were first tested to determine their effect on the hydration of Portland cement. By themselves cement hydration tests are insufficient to fully assess whether wood is suitable for the manufacture of cement-bonded composites. Therefore cement-bonded particleboards (CBPs) were manufactured in the laboratory from chipped residues of different mallee species and tested for their physical properties. Results were compared with those obtained from testing CBPs manufactured from radiata pine (Pinus radiata D. Don), a species that is suitable for the manufacture of wood-cement composites (Simple and Evans, 2000).

2. Materials and methods

2.1. Field trial establishment and locations

The six mallee eucalypt field trials sampled here were located in South Western Australia. At each site, the species and subspcies (nine in total) were planted in randomised plots of 44 trees at 1.5 × 2 m² spacing across three blocks (replicates). The trials were established in June and July 1993. Prior to planting, the sites were ploughed to around 600 mm depth, and depending on type and severity of weeds the sites were treated with between 1 and 3 l/ha of Roundup® (glyphosate) and/or Gesotop® (simazine) herbicide. At the beginning of 1995, one block at each site was harvested using a chainsaw to 10 cm above ground level, allowing coppice to regenerate, which was 2.3 years old when harvested for sampling in this study. Of the total number of species represented in field trials, only five (E. polybractea, E. Kochii ssp. plenissima, E. angustissima ssp. angustissima, E. horstii and E. leucophleba ssp. discoidea) had shown sufficient growth across all sites included in this study.

2.2. Wood sampling

Wood was sampled from the field trials in April-May 1999 from two of the blocks at each site, one containing the 2.5-year-old coppice and the other containing 6-year-old seedling trees. Due to cyclone damage at Carnarvon in 1998, insufficient material was available for sampling at this site, so trees at five sites, Kalannie, Trayning, Beverly, Newdegate and Esperance were sampled. One site (Newdegate) had only 2.5-year-old coppice available for sampling. Two trees were cut at random from each block. The trunks were removed and the stems divided into two portions, one of which was stripped of bark. The wood was then air dried for around 2 weeks before the barked and de-barked portions of each tree were chipped separately using an MTD-model Chipper-Shredder. The residues were then separated by sieving into four size classes (< 3.9, 2.4–3.9, 1.7–2.4 and < 1.7 mm). The 1.7–2.4 mm fraction from each tree (with and without bark) was retrieved and kept in a conditioning room maintained at 20 ± 1 °C and 65 ± 5% r.h. for 3 weeks. This size class was used to examine the effect of mallee eucalypt wood on the hydration of cement. Two 5 g samples—one with bark and one without—for each tree were placed in open-topped plastic tubes. Samples were again kept in the conditioning room until use. Two samples of commercial radiata pine particleboard flakes were also prepared and tested in the same manner for their compatibility with cement.

2.3. Measurement of cement hydration temperature and compatibility indices

One hundred grams of Portland cement Type I (ASTM Type A) Blue Circle Southern brand, batch no. 172MA99 was thoroughly mixed with water at 20 °C in a sealable polyethylene bag for
2 min. The amount of water used was fixed at 0.4 ml/g of cement plus an extra 0.7 ml/g of wood (oven dry basis) in accordance with the recommendations of Hashmi et al. (1990). The wood sample was then evenly mixed into the cement slurry. Cement control samples (containing no wood) contained 100 g of cement and 40 ml of water.

Immediately after mixing, the tip of a temperature thermocouple (Type J) was taped to the outside of the sample bag and enclosed within the body of the wood–cement mix by folding the bag and contents around it and securing the folded bag with adhesive tape. The bag was then placed in a polystyrene cup and sealed inside a 1-L capacity thermos flask. This process was carried out for six samples. All experiments were undertaken in a controlled temperature room maintained at 20 ± 1 °C. A cement hydration temperature logging apparatus, similar to that used by Irl and Simpson (1993), was used to measure the heat of hydration of the six wood–cement samples over 23 h. Temperatures were recorded at 15-min intervals and the curves were smoothed by plotting the progressive averages of every three successive readings. Maximum heat of hydration temperature (T_max °C) and time taken to reach T_max were recorded, and two wood–cement compatibility indices, C_x factor (Hashmi et al., 1990), and hydration rate (R = T_max − T_min/Time) were calculated. The C_x factor is the ratio of the areas under the wood–cement sample and control (cement only) hydration curves, expressed as a percentage. The T_min component of hydration rate is the minimum temperature attained during the first 5 h of hydration. Residues from mallee eucalypt species were classified as compatible, moderately compatible or incompatible with cement based on the extent to which they retarded cement hydration (Sandermann and Kohler, 1964).

2.4. Manufacture of cement-bonded particleboards in the laboratory

CBPs were manufactured from chipped and screened mallee eucalypt residues. Sampling was insufficient to allow the manufacture of boards from residues obtained from each site and tree age class. Therefore, for each species, the 2.4–3.9 mm (large) and 1.7–2.4 mm (small) size fractions were combined in the proportions 65 and 35% across site and age class, respectively, to produce bulk samples each weighing approximately 100 g, sufficient for the manufacture of two boards (replicates). This was done separately for residue with and without bark. The small size (< 10–50 mm diameter) of mallee eucalypt stems restricts the options for converting the wood into engineered wood particles which maximise the strength of particleboards (Maloney, 1977). Hence, it was important to compare the mechanical properties of CBP made from chipped mallee eucalypt residues with those of boards made from commercially produced radiata pine particleboard flakes. The manufacture of boards followed the methodology of Yasin and Qureshi (1990) and Sudin and Ibrahim (1999). The boards contained one part wood (325 g) to two parts Portland cement (650 g), 13 g of CaCl_2 (2% w/w cement) and 250 g of water. The wood residue for each board was first sprayed evenly with the dilute aqueous solution of CaCl_2 and cement was sprinkled through the wet wood particles. The cement and wood was mixed thoroughly by hand and then immediately transferred to a steel mould measuring 240 × 300 mm^2 placed on a rectangular sheet of plywood measuring 340 × 420 × 17 mm^3. The mat was evenly spread and flattened using a wooden block, the mould removed and another piece of plywood placed on top of the mat. Two wooden spacing rods measuring 12 × 12 × 300 mm^3 were placed at either end of the two plywood sheets to ensure that pressed board thickness was 12 mm. The resulting assemblage was pre-pressed to reduce its height while the mat for the next board was mixed. This process was repeated to produce a sandwich of 3 mats. This stack of mats was placed between two steel plates measuring 340 × 470 × 15 mm^3 and pressed at approximately 60 kN using a PHI 101.6 mm RAM hydraulic press. The pressed mats were kept under compression for 24 h by bolting the two steel plates together using four 8 mm thick bolts. After 24 h the boards were de-clamped, stacked vertically and conditioned for 28 days at 20 ± 1 °C and 65 ± 5% r.h. to allow the cement to cure and
gain strength. In addition to the 20 boards made
from mallee residue, 2 boards were manufactured
in exactly the same manner from commercial radi-
data pine particleboard flakes obtained from Carter
Holt Harvey Pains in Tumut, NSW. During the
manufacture of mallee eucalypt boards, replicate
1 of all species and bark content combinations
were manufactured in random order over the first
4 days, followed by replicate 2 over the next 4
days.

2.5. Determination of board mechanical properties

Conditioned boards measuring 240 x 100 x 12
mm³ were sawn into 4 test samples measuring
230 x 50 mm². Samples 1 and 3 were tested for
modulus of rupture (MOR, MPa) and modulus of
elasticity (Young’s modulus-MOE, MPa) in the
dry condition. Samples 2 and 4 were tested for
MOR and MOE in the wet condition, after they
were soaked in water at ambient temperature
(23 °C) for 24 h. Before soaking, the samples
were weighed and their thickness measured at
three points along their length using a Mitutoyo
digital micrometer. After soaking, the samples
were drained on paper towels for 15 min to
remove excess water. The sample thickness and
weight of samples was re-measured and the per-
centage absorption of water and thickness
swelling (TS) of samples was calculated (expressed
as % of original weight and thickness, respect-
ively). Three-point flexural testing was carried
out using an Instron Universal Testing Machine,
with a span of 18 mm, cross-head and bearer
diameter of 25 mm and loading speed of 5 mm/
min.

2.6. Experimental design and statistical analyses

The design of the experiment that examined the
effect of mallee eucalypt wood and bark residues
on the hydration of cement reflected the nesting of
species/age class plots within sites (locations), and
the availability of wood from 2 trees (replicates)
per species and plot. At each location, there were
three plots, each containing trees of a different
age-class. Therefore it was not possible to repli-
cate each age-class at the site level as the two trees
from each species age class plot were taken from
within the same plot. During assessment of the
effect of wood and bark residues on cement hy-
dration, each daily run of 6 cement hydration
samples contained 3 species age class combina-
tions and samples ‘with’ and ‘without’ bark. Ev-
ery 10 successive hydration samples contained all
species/age class combinations randomised for
one tree and site. All site, species, age class and
bark combinations were assayed for the first tree
followed by all of those for the second.

For the analysis of the cement hydration data,
the main effects of, and interactions between, each
of the four factors, species, site, age class and
bark content for $T_{max}$, time to $T_{max}$, hydration
rate and $C_v$-factor were tested for significance
using an appropriate multi-factorial ANOVA
model at the 5% significance level. Of the four
wood–cement compatibility indices, calculated
from hydration data, hydration rate is graphed as
it is a function of both maximum hydration tem-
perature and time taken to reach $T_{max}$.

For the experiment that compared the mechani-
cal properties of CBPs made from mallee eucalypt
residues with those of boards made from radiata
pine, the effects of species and bark content, and
at the experimental level, of test condition (dry or
wet) on the mechanical properties (MOR, MOE,
TS and WA) of boards were tested for signifi-
cance using a mixed-model ANOVA. In the cases
of MOR and MOE, logarithmic transformation
($\ln$) of the data was undertaken before analysis
and the results plotted on the log scale, however
actual values are presented and cited in the discus-
sion. Significant results are plotted graphically
and bars representing the least significant differ-
ence ($P \leq 0.05$) are included on graphs to facil-
itate comparison of means.

3. Results

3.1. Effect of wood and bark residues on cement
hydration

Fig. 1 illustrates the effects of mallee eucalypt
wood residues on the hydration exotherm of Port-
land cement. The addition of the residues to
cement clearly reduced maximum hydration temperature attained ($T_{\text{max}}$), hydration rate ($\text{C}_H\text{r} / \text{h}$) and $C_a$-factor and increased time to $T_{\text{max}}$. Residues containing bark were generally less compatible with cement than bark-free residues. Furthermore, the extent to which the mallee eucalypt wood and bark residues retarded the hydration of Portland cement varied with species (Fig. 1 and Tables 2 and 3).

$E. kochii$ had the highest average compatibility in terms of three of the wood—cement compatibility indices ($T_{\text{max}} = 45.5 \degree C, R = 1.8 \degree C/h$, $C_a = 70.8\%)$, while $E. angustissima$ had the lowest ($T_{\text{max}} = 42.6 \degree C, R = 1.5 \degree C/h$, $C_a = 39.9\%)$ (Table 3). The compatibility indices of the remaining three mallee eucalypt species were similar (Table 3), and despite the differences in compatibility between species, all of them could be rated as having moderate to good compatibility with cement. The compatibility indices for radiata pine were, however, higher than those of the mallee eucalypt species (Table 3).

The presence of bark in mallee eucalypt wood samples significantly ($P < 0.001$) reduced the hydration indices of wood—cement mixtures (Table 3). This effect is clearly illustrated in Fig. 2 which shows the interactive effect of species and bark on rate of hydration in residue—cement mixtures. The bark of $E. laxocephala$ in particular, severely retarded the hydration of cement (Table 3). The bark of $E. angustissima$ also inhibited cement hydration but not to the same extent as for $E. laxocephala$. The adverse effect of bark was less pronounced for $E. horistes$, $E. kochii$ ssp. plenistima and $E. polybractea$ and these species all retained relatively high compatibility with cement even when bark was present (Table 3).

The wood properties of trees often vary depending on their geographic location, and woody material examined here was obtained from trees growing at five different sites throughout the wheat belt zone of WA. There was, however, no significant influence of the geographic origin of the wood residues on their ability to retard cement hydration. There was however a significant interactive effect ($F = 0.04$) of tree age and bark on cement hydration ($T_{\text{max}}$, hydration rate and $C_a$-factor) (Table 2). This may have occurred because there was a greater proportion of bark present in the younger coppice trees which led to bark-containing samples from young trees having a greater inhibitory effect on cement hydration.

### Table 2

Analysis of variance for main effects and interactions between factors on cement hydration reaction indices

<table>
<thead>
<tr>
<th>Site</th>
<th>Time</th>
<th>Rate</th>
<th>$C_a$-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Age</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>Species</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>Age x species</td>
<td>$P &lt; 0.001$</td>
<td>$P &lt; 0.001$</td>
<td>$P &lt; 0.001$</td>
</tr>
<tr>
<td>Bark</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>Age x bark</td>
<td>$P = 0.04$</td>
<td>$P &lt; 0.001$</td>
<td>$P &lt; 0.001$</td>
</tr>
<tr>
<td>Species x bark</td>
<td>$P &lt; 0.001$</td>
<td>$P &lt; 0.001$</td>
<td>$P &lt; 0.001$</td>
</tr>
<tr>
<td>Age x species x bark</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
</tbody>
</table>
Table 3
Cement compatibility indices of mallee eucalypt wood species (with and without bark) and radiata pine

<table>
<thead>
<tr>
<th>Species</th>
<th>E. cornu</th>
<th>E. horizontis</th>
<th>E. leucocoryne</th>
<th>E. polbractea</th>
<th>E. radiata</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No bark</td>
<td>Bark</td>
<td>No bark</td>
<td>No bark</td>
<td>No bark</td>
</tr>
<tr>
<td>Tmax (°C)</td>
<td>42.6</td>
<td>39.9</td>
<td>43.5</td>
<td>43.9</td>
<td>44.0</td>
</tr>
<tr>
<td>Time-Tmax (%)</td>
<td>14.3</td>
<td>16.1</td>
<td>12.2</td>
<td>14.6</td>
<td>13.3</td>
</tr>
<tr>
<td>Rate (%/h)</td>
<td>1.5</td>
<td>1.2</td>
<td>1.8</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>C4/ factor (%)</td>
<td>59.9</td>
<td>50.7</td>
<td>70.8</td>
<td>66.5</td>
<td>64.8</td>
</tr>
</tbody>
</table>

Indices for cement control were 55.1 °C, 9.6 h, 3.4 °C/h and 100%.

3.2. Mechanical properties of cement-bonded particleboard mechanical properties

The mechanical properties (MOR and MOE) of CBPs were significantly (*P = 0.005*) affected by both mallee eucalypt species and by whether board samples were tested in the dry or wet condition. These effects are illustrated in Fig. 3(a) and (b). The presence of bark in boards slightly reduced their mechanical properties however this effect was not significant (*P > 0.05*). E. horizontis, E. Kochii, E. pinnata, and E. polybractea produced the strongest boards (Dry MOR = 1.29, 1.44, and 1.48 MPa, respectively) as shown in Fig. 3(a), in accord with the relatively high compatibility of these species with cement. In comparison, boards containing radiata pine flakes averaged 5.72 MPa in bending. The strength properties, particularly MOR, of boards made from radiata pine were not significantly affected by immersion of samples in water for 24 h prior to testing (Fig. 3(a)). In contrast, boards made from E. loxopleba and E. angustissima had the lowest strength (Dry MOR = 0.69 and 0.96 MPa, respectively) and were most affected by exposure to water. These species were clearly less suitable for the manufacture of wood-cement composites than the other mallee eucalyptus.

TS and water absorption of boards were not significantly affected by species (Fig. 4(a) and (b)), however when bark was present in the residue, water absorption of boards increased from an average of 26.1–31.0% and TS from 4.7 to 6.5%. In comparison, water absorption and TS of radiata pine boards containing no bark were 22 and 2%, respectively.

4. Discussion

4.1. Cement hydration

Of the 300 species of Eucalyptus (Boland et al., 1984) described to date few have had their wood tested for compatibility with Portland cement, and even fewer fully assessed for their suitability for the manufacture of cement-bonded composites. Selected species of Eucalyptus, mainly sub-tropical and tropical species of importance in developing countries, have been tested for compatibility with Portland cement with varied re-
results. *E. gomphocephala* DC wood flour was reported to be of intermediate compatibility ($C_a = 54\%$) by Hachmi and Moslemi (1989). Wood particles from 3 to 4 year old *E. saligna* Smith plantation thinnings were found to have low to moderate compatibility with cement by Mansanares et al. (1991). Compatibility improved slightly for wood from older trees. Mature wood from important native Western Australian species *E. diversicolor* F. Muell. (Karri) and *E. marginata* Donn ex Smith (Jarrah) gave poor results in wood flour–cement hydration tests (Sandermann and Kohler, 1964). Reports on the suitability of one of the most important commercial eucalypt species in the Asia/Pacific region, *E. camaldulensis* Dehnh., are variable. *E. camaldulensis* has been recommended as suitable for the manufacture of wood–cement board based on results from hydration studies using wood flour (Jain et al., 1989) and wood flour–cement compressive strength tests (Shukla et al., 1984). *E. camaldulensis* wood flour was also classed as compatible with cement ($C_a = 69\%$) by Hachmi and Moslemi (1989). The aforementioned studies derived compatibility information from hydration tests using finely ground wood flour that does not simulate the effects of larger wood flakes on cement hydration (Semple et al., 1999) and makes meaningful comparisons with our results difficult.

Recently we screened a range of temperate eucalypts for their compatibility with cement (Semple et al., 2000). Wood was tested in the form of flakes rather than particles, and employed the same proportions of wood, cement and water used here. Species included *E. globulus* sp. bicostata, *E. smithii* R. Baker, *E. nitens* (Deane & Maiden), *E. viminalis* Labill., *E. macarthurii* Deane & Maiden, *E. benthamii* (L. Johnson & Balfell), *E. bagaudiana* Beuzv. & Welch and *E. kurtzoffiana* (Maiden & Cambage). Hydration rates for these species were between 0.88 and 1.27 °C/h, a lower range of values than those obtained for the mallee eucalypts tested here.

The finding that the bark of three of the five mallee species had little effect on the compatibility of woody residue with cement may be of some practical benefit since it may eliminate the need to completely segregate wood and bark when manufacturing CBPs. This contrasts with many other timber species such as *picea* (Pimus sp.) which have bark that inhibits the setting of Portland cement more strongly than the wood itself (Yoshimoto and Minami, 1976). In the case of *E. leucoplaea*, however, bark would need to be separated.
from the wood before board manufacture due to its highly inhibitory effect on cement hydration. The proportion of bark by volume in *E. loxophleba* was not higher than in the other species, suggesting the presence in its bark of certain compounds, not found in the other species, which strongly inhibit the setting of Portland cement. Unless a reliable and cost-effective method of either removing all the bark from *E. loxophleba* or ameliorating the inhibitory effects of its bark on cement hydration was developed, then this species would be highly unsuitable for use in wood–cement composites.

Studies of the suitability of eucalypts for cement bonded composites have found site to be an important factor affecting the properties of the composites. For example, the compatibility of *E. deugdapha* Blume with cement and strength of wood–wool cement boards made from *E. deugdapha* were affected significantly by where the trees were grown in Indonesia (Pariboer and Suwandi Kliwon, 1977). Our recent study of the compatibility of temperate eucalypt species with cement (Semple et al., 2000) also found a significant effect of site on wood–cement compatibility. The trees grown on poorer sites were smaller with a greater proportion of sapwood which retards cement hydration to a greater extent than heartwood. The lack of variation in sapwood/heartwood content in the mallee eucalypt trees sampled here may account for our observation that trees showed similar compatibility with cement irrespective of where they were grown. The lack of site specificity in wood compatibility with cement would be favourable to the use of mallee residues for CBP, which would require large volumes of biomass from different areas. However, running counter to this is the fact that some of the more favourable species may not grow well in some areas.

4.2. Strength properties of cement-bonded particleboards

It is clear that flexural properties of boards made from the available mallee eucalypt residues were low (≈1 MPa MOR and ≈500 MPa MOE) compared with those of boards made from commercially produced radiata pine wood flakes (MOR = 5.72 MPa, MOE = 2850 MPa), and of commercially produced CBPs whose flexural properties range from 8 to 15 MPa in stiffness and 4000–6000 MPa in elastic modulus (Dinwoodie, 1978; Moslemi, 1989). This is despite the

\[
\begin{align*}
\text{MOR} & = 5.72 \text{ MPa} \\
\text{MOE} & = 2850 \text{ MPa}
\end{align*}
\]

Fig. 4. Effect of bark in residue on average (a) water absorption and (b) TS of CBPs manufactured from mallee eucalypt residues; results averaged across species, site and age class.
fact that the compatibility of radiata pine and mallee eucalypt wood with cement was not statistically different. The relatively good compatibility of the mallee eucalypt wood residues with cement (particularly those of E. polychroma and E. kochii ssp. pinicola) may have been largely confounded by the unfavourable geometry of particles generated from in-field chipping. The chipped mallee residues consisted of small particles with a much lower aspect ratio than the radiata pine wood flakes. This probably accounts for the lower strength properties of the mallee eucalypt boards, as there is a strong correlation between the aspect ratio of wood flakes used in particleboards and the mechanical properties of the boards (Fisher, 1972; Maloney, 1977). Tachi et al. (1988) also attributed poor strength properties of CBP made from E. delegatensis compared with those of other species to unfavourable particle geometry.

The conversion of small diameter mallee residue into particles with a greater aspect ratio would be desirable; however, smaller particles from mallee residue may be suitable as surface material for particleboards whose central layer contains larger sized material from different wood species. Alternatively, small mallee eucalypt stems may be better suited to conversion into wood–cement composites composed of longitudinally split or shredded strands such as those used in Scriber (Hutchings and Leicester, 1988), or sliced strand timber (Miyatake and Fujii, 1997).

Although the presence of bark did not significantly affect compatibility of woody residues from three of the five mallee eucalypt species with cement or reduce the flexural properties of CBPs, it did increase the water absorption capacity and swelling of boards. This effect is likely to have been due to the increased water absorption capacity of bark compared with the woody material. These findings suggest that the use of CBPs made from residues containing bark may be best suited to interior applications. CBPs made using residues from species of lower compatibility (E. loxopleba and E. angustissima) were also more susceptible to deterioration of flexural properties upon exposure to water (Fig. 3(a) and (b)). This was probably because the cement binder was weaker and more easily penetrated by water and disrupted by swelling of wood particles.

5. Conclusions

The wood from five leaf-oil producing species of mallee eucalypt had moderate to good compatibility with Portland cement. The presence of bark resulted in E. loxopleba and to a lesser extent E. angustissima residues being incompatible with cement and unsuitable for use in wood–cement composites. Geographic location of trees and their age exerted little influence on the compatibility of wood residues with cement, although the higher proportion of bark in the younger (2.5-year-old) material may have slightly reduced its compatibility with cement. Flexural properties of CBPs made from mallee eucalypt wood residue were significantly influenced by species, but not the presence of bark. Water absorption and swelling of boards, although unaffected by species, increased significantly when bark was present. Although well consolidated boards could be manufactured from the residue of most species, the boards had poor mechanical properties compared to commercially produced CBPs or those made from radiata pine. The small particle size and aspect ratio of chipped residues is believed to have been the primary cause of low mechanical strength of the boards. This highlights the need to find alternative methods of preparing residues for the manufacture of CBP and possibly other types of composites.

Acknowledgements

The authors thank the Rural Industries Research and Development Corporation (RIRDC) Joint Venture Agroforestry Program for financial assistance, and Dr Syd Shea and Mr John Bartle of the Department of Conservation and Land Management (CALM), for initiating the project and providing financial and in-kind support. We also thank Mr Andrew McCarthy of CALM, Western Australia for collecting and chipping mallee eucalypt residues.
References


Government of Western Australia 1996. Salinity: a situation statement for Western Australia. Agriculture Western Australia, CALM, Department of Environmental Protection, Waters and Rivers Commission, Perth, pp. 44.


Screening Inorganic Additives for Ameliorating the Inhibition of Hydration of Portland Cement by the Heartwood of Acacia mangium

Kate E. Semple¹ and Philip D. Evans²

Abstract
The suitability of Acacia mangium for the manufacture of cement-bonded wood composites is adversely affected by the presence of heartwood tannins — water soluble polyphenolic extractives that strongly inhibit the hydration of Portland cement. Once the inhibitory extractives have been removed from the wood by soaking it in fresh water, wood-cement composites such as wood-wool cement boards (WWCBs) can be manufactured from A. mangium. However, if a sufficient supply of fresh water is not consistently available, alternative strategies are needed to ameliorate the effect of polyphenols in A. mangium wood on cement hydration. Certain compounds such as calcium chloride are commonly used in the manufacture of wood-cement composites to reduce the inhibitory effect of heartwood extractives on the hydration of cement. It is well known that calcium chloride achieves this effect by accelerating the hydration of cement. This alone is not sufficient to overcome the inhibition of cement hydration caused by heartwood polyphenols in species like A. mangium. Compounds that accelerate cement hydration and also chelate or chemically modify polyphenols to prevent them from interfering with cement hydration may be more effective than calcium chloride at improving the compatibility of A. mangium wood with cement. This study used laboratory-scale cement hydration tests to screen a wide range of soluble and insoluble inorganic additives to identify those most effective at strengthening the hydration of Portland cement. The ability of compounds to form insoluble chelates with inhibitory heartwood polyphenols from A. mangium was tested, as was their capacity to strengthen the hydration of cement containing A. mangium heartwood. The results showed that compounds with the ability to strongly accelerate cement hydration and form insoluble chelates with inhibitory heartwood tannins were the most effective at reducing the inhibitory effect of A. mangium heartwood on cement hydration. Most of the compounds were chlorides and nitrates, including SnCl₄, AlCl₃, (NH₄)₃Ce(NO₃)₃, and FeCl₃. These compounds accelerate cement hydration and also contain cations such as Sn⁺, Al³⁺ and Fe⁺⁺ which can strongly chelate heartwood tannins in A. mangium. Accordingly, these compounds were more effective than calcium chloride (CaCl₂) which, although it accelerated cement hydration, did not form insoluble chelates with heartwood tannins. The treatment of wood with compounds that can accelerate cement hydration and chelate heartwood extractives may facilitate the manufacture of wood—cement composites from fresh A. mangium wood, a goal that hitherto has not been possible to achieve using conventional cement-hardening additives.

¹ANU Forestry, The Australian National University, ACT 0200, Australia. Email: Kate.Semple@anu.edu.au
²Centre for Advanced Wood Processing, University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada. Email: ph.evans@interchange.ubc.ca

Wood—wool cement boards (WWCBs) are becoming an important building material in several tropical countries because of their low cost and ease of manufacture, good mechanical and insulation properties, modular construction capabili-
ties, and good resistance to biodeterioration and fire (Pablo 1989; Ramirez-Carretti et al. 1998). Extensive planting of acacia and eucalypt species in the Asia-Pacific region in recent decades (Vereecke 1993) could provide an abundant supply of wood for the manufacture of WWCBs. Acacia mangium Wild., is one of the most successful of the species introduced into South-East Asia, and it has therefore generated considerable interest as a possible raw material for WWCB manufacturing industries in countries such as the Philippines. However, water-soluble and alkali-soluble polyphenolic substances present in the heartwood of A. mangium severely retard the normal course of cement hydration (Tachi et al. 1989), resulting in poor bonding in wood–cement composites. This is a major impediment to the use of A. mangium as a raw material for WWCB manufacture. Inhibitory polyphenols in A. mangium heartwood are water soluble (Tachi et al. 1988) and therefore can be easily removed by soaking wood in water for 12 to 24 h, but in dry regions and in some seasons there can be insufficient fresh water available for soaking wood-wool. Therefore it is important to develop alternative methods of improving the compatibility of A. mangium with cement so that this species can be used for WWCBs in countries where it is widely planted and readily available.

Certain inorganic compounds are commonly used during the manufacture of wood–cement composites to reduce the inhibitory effect of heartwood extractives on the hydration of cement (Zhengian and Moslemi 1985). Calcium chloride (CaCl₂) in particular has been successfully used to improve the strength properties of WWCB (Kayahara et al. 1979; Lee and Short 1989; Serrano et al. 1998). It is well known that CaCl₂ achieves this effect by accelerating the hydration of cement particularly the tri-calcium silicate phase (C₃S), reducing setting time, and, in some cases, increasing maximum hydration temperature (Lea 1971; Ramachandran 1994). This alone is not sufficient to overcome the severe inhibition of cement hydration caused by heartwood polyphenols in species like A. mangium. Compounds that accelerate cement hydration and also chelate or chemically modify polyphenols to prevent them from interfering with cement hydration may be more effective than CaCl₂ in improving the compatibility of A. mangium wood with cement. This study screened a wide range of soluble and insoluble inorganic chemical additives for their ability to accelerate the hydration of cement and also chelate heartwood polyphenols in A. mangium. The aim was simply to determine whether compounds that possessed both attributes were more effective than CaCl₂, in ameliorating the inhibitory effects of A. mangium heartwood on cement hydration.

**Materials and Methods**

**Wood sample collection and preparation**

Wood-wool was obtained from two eight-year-old Brown Salwood (Acacia mangium Wild.) trees grown in provenance trials at Dampier (18°24′S 146°06′E, altitude 20 m a.s.l.) in North Queensland, Australia. Two end-matched logs, 1.15 m long, were removed from the felled trees and two end-matched billets measuring 0.46 m were cut from the middle of each log. The eight billets were shredded in the green condition into wood-wool strands measuring 0.3 mm × 3 mm × 460 mm at Woodtex in Bendigo, Victoria, keeping the wood-wool from the two trees separate. The wood-wool was air dried under cover for about two weeks and grab-samples (approx. 100 g) were then randomly taken for sorting to isolate and retain strands of pure heartwood. The heartwood strands were cut into pieces approximately 50 mm in length using scissors and stored for at least two weeks in a conditioning room maintained at 20 ± 1°C and 65 ± 5% RH, until needed.

**Compounds and their preparation**

In total, 127 inorganic compounds were studied. These comprised chlorides, sulphates, nitrates, acetates, oxides, carbonates and fluorides of the cations Al, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr and Zn. Several miscellaneous compounds including citrates, tartrates, bromides and oxalates of Na and K were also tested. The solubility in water of each compound was checked (Wcalt 1970) to determine whether to add each one to cement as a solid or liquid. The water-soluble compounds were dissolved in distilled water at room temperature to 0.1 M strength in 250 mL volumetric flasks. Four 40 mL aliquots of each compound solution were poured into separate 50 mL capacity vials for addition to
cement hydration samples; two for addition to wood–cement samples and two for addition to samples containing cement only. The two vials to be added to wood–cement samples were prepared with an extra 0.7 mL of distilled water per g of wood used, in accordance with the recommendations of Hachmi et al. (1990). The insoluble compounds were pulverised to remove lumps, using a mortar and pestle, and four equal amounts were weighed out into four 5 mL capacity vials for addition as dry powder to cement hydration samples. The amount of each compound used in a hydration test corresponded to the amount that would be present in 40 mL of a 0.1 M solution if the compound were soluble in water. This ensured consistency in concentration of additives across soluble and insoluble compounds.

Measurement of cement hydration exotherms

Each aliquot of the compounds was added to 100 g of fresh dry Portland cement Type I (Blue Circle Southern brand, batch no. 090MA99) in a sealable ‘Dal grip’ polyethylene bag and thoroughly mixed by hand kneading for about 2 min at 20°C. Insoluble compounds were added as a dry powder to 100 g of dry cement in a ‘Dal grip’ bag and evenly mixed through the cement, after which distilled water was added to mix the cement slurry as described above. For samples containing only neat cement or cement plus compound but no wood, 40 mL of distilled water or compound solution was added. For each cement sample to which wood was to be added, 43.5 mL of distilled water or compound solution was first added and mixed. Then 5 g of chopped A. mangium heartwood-wool was added and massaged though the cement slurry until evenly coated. Immediately after the mixing of a cement hydration sample, the tip of a temperature thermocouple (Type J) was taped to the outside of the sample bag and enclosed within the body of the cement or wood–cement mix by folding the bag and contents around it. The folded bag was then secured with adhesive tape, placed in a polystyrene cup and sealed inside a 1 L capacity thermos flask. This process was carried out for six samples. A cement hydration temperature-logging apparatus, similar to that used by Irie and Simpson (1993), was used to measure the heat of hydration of the six wood–cement samples over 23 h. Temperatures were recorded at 15 min intervals. The curves were smoothed by plotting the progressive average of each three successive readings. Maximum heat of hydration temperature (T) and time taken to reach T (t) were recorded, and two wood–cement compatibility indices, Cα-factor (Hachmi et al. 1990), and hydration rate (R) = (TMT MAX t0) were calculated. The Cα-factor is the ratio of the areas under the hydration curves of a wood–cement sample and the control (cement only), expressed as a percentage. The component of hydration is the minimum temperature attained during the first 5 h of hydration. All experiments were done in a controlled temperature room maintained at 20 ± 1°C.

Experimental design and execution

In addition to the two cement control (cement only) and two wood–cement control samples, 137 compounds were tested with two replicates for neat cement and two replicates (trees) for wood–cement samples. The experimental design contained a nested structure of cement and cement + wood hydration samples within the compounds stratum. In each daily six-replicate run of hydration samples, three compounds were tested at random. For each compound, two matched samples were run, one with cement + compound and the other with cement + wood. All compounds were run in random order for replicate 1 (cement) and wood from tree 1 (cement + wood) over the first 46 days followed by replicate 2 and wood from tree 2, again randomised by compound over the next 46 days.

Compounds were ranked in order of their efficacy in improving the strength (expressed as TMAX and hydration rate) of the exothermic reaction of cement: containing the inhibitory heartwood-wool of A. mangium. Compounds were also assessed for their effects on the normal course of hydration of Portland cement by comparing the hydration exotherms TMAX and hydration rate of cement containing compound mixtures with those of cement alone. Average hydration rates in wood–cement mixes generated by compounds grouped by anion/cation content
are shown in Figs 1 and 2. For each compound the \( T_{\text{h**}} \) and hydration rate of the wood-cement mix were graphed against those obtained for samples containing cement and compound only (Figs 3 and 4).

**Determination of polyphenol–metallic complexes**

Freshly mixed cement slurry is highly alkaline (pH 11) and it increases in alkalinity with time as calcium hydroxide is produced (Lea 1971; Taylor 1997). This has a strong leaching effect on wood and will dissolve and remove more than just the water soluble heartwood extractives (Goldstein 1984). Therefore, sodium hydroxide was used to obtain a leachate containing alkali-soluble inhibitory polyphenols from *A. mangium* heartwood. To obtain the heartwood leachate, 10 g of chopped *A. mangium* heartwood woold was placed in a beaker containing 300 mL of alkali solution at pH 11.5-12 (0.01 M NaOH) and soaked in a waterbath for 6 h at 35°C. After the soaking, the wood-woold was removed and the leachate was filtered under vacuum through a 40 mm diameter sintered glass crucible (frt no. 3) to remove any sludge and solids such as wood fibre. Then 100 mL of the dark leachate was diluted with 150 mL of 0.01 M NaOH to produce a transparent brown liquid in which any insoluble precipitate, if formed, could be clearly seen. A small amount (1 mL) of solution containing the soluble compound was added to 7 mL of dilute alkali leachate in a glass vial to test its ability to form an insoluble precipitate with heartwood polyphenols in alkaline medium. The strength and colour of any precipitate and the time it took to form were noted. To illustrate the effect of complexes formed with heartwood polyphenols in the extract, 10 drops of selected compound solutions were added to larger quantities of dilute extract in 25 mL test-tube bottles (Plate 1).

**Results and Discussion**

Several of the 137 compounds tested markedly strengthened the hydration of cement containing inhibitory *A. mangium* heartwood-woold. Around 50 of the compounds raised the average \( T_{\text{h**}} \) and hydration rate of cement containing wood-woold from 31°C and 0.5°C h\(^{-1}\), respectively, to over 37°C and 21°C h\(^{-1}\). The 20 compounds that resulted in the greatest increase in hydration rate for cement containing inhibitory wood-woold are listed in Table 1. Of these, nine compounds were chlorides, seven were nitrates and two were chromium salts. In a study by Zhengtian and Moslemi (1985), 30 compounds, mainly chlorides and sulphates, were tested for their effects on the hydration of Portland cement containing Western Larch (*Larix occidentalis*) heartwood flour. Western Larch is one of the least compatible wood species with cement (Sanderman and Kohler 1964; Hofstrand et al. 1984). The most effective compounds for ameliorating cement inhibition identified by Zhengtian and Moslemi (1985) were the chlorides SnCl\(_4\), FeCl\(_3\), AlCl\(_3\), and CaCl\(_2\). Our findings accord well with theirs, despite the fact that these workers used a softwood that does not contain tannin polyphenols. They did not test the effect of their additives on neat cement and therefore could not gauge the accelerating effect of each compound.

In our study, CaCl\(_2\) performed well as an accelerator in the presence of inhibitory wood-woold of *A. mangium*, but it was not as effective as the chlorides of Sn\(^{4+}\), Al\(^{3+}\), Fe\(^{3+}\), Mg\(^{2+}\), Ba\(^{2+}\), Ni\(^{2+}\) and Sr\(^{2+}\) (Table 1). Here SnCl\(_4\), AlCl\(_3\), and FeCl\(_3\) were ranked 1st, 2nd and 4th respectively, whereas CaCl\(_2\) was ranked 11th. CaCl\(_2\), a by-product of sodium carbonate manufacture, has long been favoured as a cement setting accelerator due to its low cost, availability and predictability (Lea 1971; Taylor and Fusselo 1994; Taylor 1997). The anion–cation combination in CaCl\(_2\) acts as an accelerator mainly on the tricalcium silicate (C\(_3\)S) phase in Portland cement and is one of the most effective anion–cation combinations for use in neat cement (Ramachandran 1994). Our findings suggest that several other inorganic salts may be better suited than CaCl\(_2\) for use in wood-cement composites. Other studies have also found alternative compounds to be more effective than CaCl\(_2\) for ameliorating the inhibitory effects of certain woods used in the manufacture of wood-cement composites. For example, AlCl\(_3\) was found to be the most effective chloride compared with MgCl\(_2\), FeCl\(_3\), and CaCl\(_2\), for the manufacture of wood-cement composites from the inhibitory wood of *Shorea spp.* (Kayahara et al. 1979). Also, Soriano et al. (1997) found that Al\(_2(SO_4)_3\) was a
Table 1. Top 20 compounds by hydration rate of wood-cement mix, with corresponding maximum hydration temperature and time.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hydration rate (°C h)</th>
<th>Max. temp. (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrCl₂</td>
<td>5.5</td>
<td>59.9</td>
<td>6.9</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>4.5</td>
<td>55.6</td>
<td>6.9</td>
</tr>
<tr>
<td>(Ni)₂(C₂H₄N₂)₃</td>
<td>4.3</td>
<td>55.5</td>
<td>5.2</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>3.6</td>
<td>51.5</td>
<td>8.1</td>
</tr>
<tr>
<td>ZnNO₂</td>
<td>3.5</td>
<td>54.6</td>
<td>7.2</td>
</tr>
<tr>
<td>Al(NO₃)₃</td>
<td>2.9</td>
<td>48.4</td>
<td>6.3</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>2.8</td>
<td>48.9</td>
<td>9.5</td>
</tr>
<tr>
<td>BaCl₂</td>
<td>2.6</td>
<td>47.2</td>
<td>9.4</td>
</tr>
<tr>
<td>NiCl₂</td>
<td>2.5</td>
<td>46.6</td>
<td>9.2</td>
</tr>
<tr>
<td>SrCl₂</td>
<td>2.4</td>
<td>47.1</td>
<td>10.0</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>2.3</td>
<td>45.4</td>
<td>9.9</td>
</tr>
<tr>
<td>Al₂(SO₄)₃</td>
<td>2.2</td>
<td>48.5</td>
<td>8.9</td>
</tr>
<tr>
<td>Fe(NO₃)₃</td>
<td>2.1</td>
<td>47.3</td>
<td>8.9</td>
</tr>
<tr>
<td>PbCl₂</td>
<td>2.1</td>
<td>46.0</td>
<td>23.9</td>
</tr>
<tr>
<td>Na₂CrO₂</td>
<td>2.0</td>
<td>47.8</td>
<td>11.4</td>
</tr>
<tr>
<td>Ni₃(C₂H₃O₂)₂</td>
<td>1.9</td>
<td>46.6</td>
<td>11.0</td>
</tr>
<tr>
<td>Cu(NO₃)₂</td>
<td>1.9</td>
<td>44.2</td>
<td>13.9</td>
</tr>
<tr>
<td>Ag(NO₃)₂</td>
<td>1.9</td>
<td>47.4</td>
<td>11.6</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>1.8</td>
<td>45.7</td>
<td>11.4</td>
</tr>
<tr>
<td>Ba(NO₃)₂</td>
<td>1.8</td>
<td>43.4</td>
<td>10.4</td>
</tr>
<tr>
<td>Wood control</td>
<td>0.5</td>
<td>31.0</td>
<td>18.5</td>
</tr>
</tbody>
</table>

more effective additive than CaCl₂ or waterglass (sodium silicate, Na₂O.3SiO₂) for manufacturing WWCB from A. mangium wood.

The effects of the presence of particular cations on the hydration of Portland cement are illustrated in Fig. 1. The addition of compounds containing Al³⁺, Ba²⁺, Ca²⁺, Cr³⁺, K⁺, Li⁺, Na⁺ and Sr²⁺ generally had an accelerating effect on the hydration of neat cement. In the cases of K⁺ and Na⁺, this did not translate into any beneficial effect on the low hydration rate (0.5°C h⁻¹) of cement caused by the presence of inhibitory heartwood. The hydration rate of cement containing heartwood was doubled by the addition of compounds containing Al³⁺, Ba²⁺, Ca²⁺, Cr³⁺, Fe²⁺, Mg²⁺, Li⁺, Ni²⁺, Pb²⁺ and Sr²⁺, even though some of these (such as Co²⁺ and Ni²⁺) had relatively little effect on the hydration of neat cement. The presence of Pb²⁺ greatly delayed cement setting. The addition of compounds containing Cr³⁺, Mn³⁺ and Zn²⁺ retarded the hydration of neat cement and did not increase the hydration rate of cement containing A. mangium heartwood. Such heavy metal ions are thought to retard cement hydration reactions by forming a sheath of insoluble hydroxide and silicate complexes of metal-calcium in the alkaline cement paste, which blocks access to water by newly hydrating C-S-H grains (Taylor and Fuescel 1994; Yousof et al. 1995).

The general effectiveness of the chlorides, nitrates and acetates as groups in ameliorating the inhibitory effects of the wood is shown schematically in Fig. 2. There was high variation within these groups that was caused by the effects of the cations shown in Fig. 1. The compounds in the more effective groups; i.e. chlorides, nitrates and acetates, were all added as solutions. Compounds added mainly as insoluble powders, i.e. oxides, carbonates and fluorides, were not effective in increasing the hydration rate of cement containing wood; in fact the addition of most carbonates and fluorides adversely affected the hydration of Portland cement. Addition of the higher molecular-weight organic acids, citrate and tartrate, completely retarded cement setting (Fig. 2).
Figure 1. Average hydration rates of neat cement and cement containing *A. mangium* heartwood, for compounds grouped by cation content. Rates for neat cement and for cement containing wood-wool are indicated by lines.

Figure 2. Average hydration rates of cement and cement containing *A. mangium* heartwood, for compounds grouped by anion content. Rates for neat cement and for cement containing wood-wool are indicated by lines.

The hydration rates produced by individual compounds are shown for neat cement (Fig. 3) and for cement containing heartwood of *A. mangium* (Fig. 4). These figures illustrate the variability among compounds, grouped by anion, caused by various cations. The cation component of the compound is indicated on the x-axis and its anion component is indicated in the legend. Again, the efficacy of chlorides and nitrates is apparent, but there were also significant interactive effects between cation and anion components. For example, chlorides of compatible cations such as Al³⁺ and Fe²⁺ produced highest hydration rates of all anion groups, whereas incompatible cations such as Cu²⁺ and Zn²⁺ were most inhibitory when added as chlorides. This effect can be most clearly seen in Fig. 3. Note the low variability in the effect of cations when added in the insoluble oxide form.

Figures 5 and 6 illustrate the distribution of effects of all compounds. Their effects on *T*₅₈₅
Figure 5. $T_{\text{MAX}}$ for cement containing compound only vs. $T_{\text{MAX}}$ for cement containing compound plus wood-wool, showing four quadrants: $T_{\text{MAX}}$ for neat cement (cement control) and for cement containing wood only (wood control) indicated by lines.

Figure 6. Hydration rate for cement containing compound only vs. hydration rate for cement containing compound plus wood-wool. Rate for neat cement (cement control) and for cement containing wood only (wood control) indicated by lines.

(Fig. 5) and hydration rate (Fig. 6) are graphed for neat cement + compound (x-axis) and the wood + cement + compound mix (y-axis). The results indicate that the most effective compounds for ameliorating the inhibitory effects of *A. mangium* heartwood were also those which produced the greatest increases in maximum hydration temperature and rate of hydration of neat cement.

Figures 5 and 6 suggest an interactive effect between the efficacy of certain compounds and the presence or absence of wood. Compounds in quadrant 1 (see Fig. 5) increased $T_{\text{MAX}}$ and hydration rate in both the neat cement and cement + wood samples. Almost all compounds that increased the rate of hydration in the wood-cement mix increased that of neat cement as well (Fig. 6). Compounds in quadrant 2 had their positive effects on the hydration of neat cement nullified by the presence of inhibitory *A. mangium* heartwood. Such compounds included NaCl, Na$_2$SO$_4$, and KIBr; these are compounds that when added in small amounts accelerate cement hydration to some degree (Lea 1971) but whose action does not appear to be strong enough to counteract the inhibitory effects of the wood. Additives in quadrant 3 were clearly inhibitors of cement hydration, and comprised compounds containing Cu$^{2+}$, Pb$^{2+}$, Co$^{2+}$, Zn$^{2+}$ and Mn$^{2+}$ or citrates and tartrates. A fifth group of compounds (enclosed on Fig. 5) had little effect on maximum hydration temperature of cement on its own, but increased the temperature attained in cement containing heartwood. These included nitrates and acetates of Al$^{3+}$, Ni$^{2+}$, Ag$^{+}$, Fe$^{3+}$ and Co$^{2+}$, compounds that also had no strong accelerating effect on the hydration rate of neat cement. An alternative mechanism to that of simply accelerating cement hydration reactions is needed to explain how such compounds can ameliorate the inhibitory effects of unextracted *A. mangium* heartwood on cement hydration. One possibility alluded to in the introduction is that the formation of insoluble organo-metallic complexes (chelates) between free cations and reactive sites on heartwood polyphenols may contribute significantly to neutralising their inhibitory effects, allowing cement hydration reactions to proceed.

**Organometallic complexes**

Heartwood tannins have deleterious effects on cement hydration, as has been demonstrated experimentally by Sandermann and Brendel (1956) and Miller and Moslemi (1991). These studies indicate that the addition of more than about 0.2% will effectively inhibit cement hydration. However, certain cations in cement accelerators may be capable of neutralising their inhibitory effects on cement hydration reactions by chelating phenolic groups in the tannins, resulting in the formation of insoluble complexes.

Condensed tannins can be abundant in the heartwood and bark of acacias (Sherry 1971; Hillis 1987). Their molecules have a dihydroxyphenyl groups which have excellent chelation affinity...
Plate 1. Effect of addition of accelerator compound solution to dilute alkali-soluble extract from *A. mangium* heartwood.

![Diagram](image)

Figure 7. Schematic structure for teracacidin

with metal ions including Cu$^{2+}$ (Scalbert et al. 1998; Yamaguchi and Okuda 1998), Fe$^{3+}$ and Al$^{3+}$ (Yoneda and Nakatsubo 1998; Ni et al. 1999). In our study, soluble solutions containing the cations Sn$^{4+}$, Al$^{3+}$, Fe$^{3+}$ and Ni$^{2+}$ all formed insoluble complexes with the coloured polyphenols leached from *A. mangium* heartwood in alkaline solution as shown in Plate 1, leaving a light coloured solution behind. Solutions containing the inhibitory cations Cu$^{2+}$ and Pb$^{2+}$ also immediately produced heavy precipitates, whereas Co$^{3+}$ and Mn$^{2+}$ formed lighter precipitates. Note in Plate 1 the very small precipitate formed with Ca$^{2+}$ and no evidence of complex formation with Mg$^{2+}$.

A compound known as teracacidin (Clark-Lewis et al. 1961) shown in Fig. 7, was first isolated from the heartwood of *A. mangium* and shown to be highly inhibitory to cement hydration (Tachi et al. 1989). Teracacidin is one of four distinct types of heartwood polyphenols in the leucoanthocyanidin series that characterise different taxonomic groupings within the genus *Acacia* (Tindale and Roux 1969; Clark-Lewis and Porter 1972). These are flavan-3,4-diols which differ from each other in their phenolic hydroxylation patterns.

Teracacidin differs from other leucoanthocyanidins in that it contains only a 4'-monohydroxy B-ring, unlike mollicacidin and melacacidin which are characterised by a 3',4'-dihydroxylated B-ring. This dihydroxy configuration on the flavonoid B-ring of condensed tannins is a catechol unit and is the main group involved in metal chelation (Slabbert 1992). According to Slabbert (1992) and Yoneda and Nakatsubo (1998) it is the distinctive phenolic hydroxylation pattern of the B-ring that determines the metal chelating capacity of tannins, with 3',4',5'-trihydroxylated B-rings having the highest affinity for metals followed by 3',4'-dihydroxy
then 4'-mono-hydroxy B-rings with low chelating capacity. Chelate formation between catechol units and a transition metal such as Fe\(^{3+}\) is shown in Fig. 8 (Powell and Taylor 1992; Kennedy and Powell 1993). It was suggested to be of little importance in tannin-metal chelating reactions (Slabbert 1992; Yoneda and Nakatsubo 1998). If this is correct, it would seem unlikely that teracacinid can be effectively chelated since it contains only 1 hydroxyl group (\(\text{OH}\)) on the B-ring (Fig. 7). It is also known that acidic conditions are optimal for the formation of tannin-metal complexes (McDonald et al. 1996). Despite this, the extract from A. mangium in our study formed strong complexes in alkaline conditions. Teracacinid has been found to be accompanied by much larger quantities of apparently polymeric, intractable phenolic material (condensed tannins) in the heartwood of certain other acacia species such as A. sparsiflora (Clarke-Lewis and Dainis 1967), but no studies are available to confirm this to be the case in A. mangium. It is therefore unclear at this stage whether the teracacinid component in our A. mangium heartwood extract was being chelated by cations such as Sn\(^{4+}\), Al\(^{3+}\) or Fe\(^{3+}\) or was similarly associated with larger quantities of other inhibitory tannins that were preferentially chelated. This question requires further investigation.

The formation of polyphenol–metallic complexes in or on the surface of wood-wool may render them less mobile and hence reduce their ability to diffuse out into the surrounding cement paste and inhibit cement hydration reactions. Chelated polyphenols, without free hydroxyl groups, may also be unable to chemically interfere with diffusion of Ca\(^{2+}\) ions, Ca(OH)\(_2\) production and the hydration of calcium silicates in cement paste. Such actions may have contributed to the chlorides and nitrates of Al\(^{3+}\) and Fe\(^{3+}\) being significantly better than CaCl\(_2\) at neutralising the effects of A. mangium heartwood on cement hydration. It was difficult to determine the relative contribution of chelation of inhibitory polyphenols to ameliorating incompatibility of the heartwood, considering the strong accelerating effect of these chlorides on the hydration of neat cement. However, as shown in Fig. 1, several compounds containing Fe\(^{3+}\), Co\(^{2+}\) and Ni\(^{2+}\) had little effect on the hydration of neat cement, but their addition resulted in a two-fold increase in hydration rate of cement containing wood-wool. This provides some evidence that chelation and immobilisation of inhibitory heartwood polyphenols may play an important role in reducing their inhibitory effects. An additive mix that contains small amounts of both an accelerator (such as CaCl\(_2\)) and an accelerator or chelating agent (containing such ions as Al\(^{3+}\), Sn\(^{4+}\) or Fe\(^{3+}\)) may have considerable synergistic effects and potentially enable WPCB to be manufactured from A. mangium without the need for complete removal of extractives.

**Conclusion**

A wide range of inorganic additives were screened for their effects on the hydration of Portland cement and their potential to ameliorate the low compatibility of A. mangium heartwood with cement. Many compounds were found to be more effective than CaCl\(_2\), the most well known and widely used cement setting accelerator. These compounds were all soluble in cold water and comprised mainly chlorides and nitrates, including SnCl\(_2\), AlCl\(_3\), (NH\(_4\))\(_2\)Ce(NO\(_3\))\(_6\) and FeCl\(_3\). The most effective compounds produced a strong accelerating effect on the hydration of neat Portland cement. They also contained cations that formed insoluble chelates when the compound solution was added to alkali soluble A. mangium heartwood extract.

The latter effect may also contribute to ameliorating the effect of inhibitory A. mangium heartwood polyphenols on cement hydration. In support of this suggestion it was found that several compounds that did not strongly accelerate cement hydration partially neutralised the inhibitory effects of A. mangium heartwood on cement hydration, resulting in an increase in maximum hydration temperature attained in wood-cement mixes. These compounds often contained cations such as Ni\(^{2+}\), Al\(^{3+}\), Fe\(^{3+}\) and Co\(^{2+}\) — transition metals that can, like Al\(^{3+}\) and Fe\(^{3+}\), form insoluble complexes or chelates with inhibitory acacia heartwood polyphenols. Additives that could not be added in soluble form, mainly oxides, carbonates and fluorides, were ineffective at ameliorating the inhibitory effects of heartwood on cement hydration. Compounds containing heavy metals.
such as Zn\(^{2+}\), Pb\(^{2+}\), Cu\(^{2+}\), and organic acids such as citrate and tartrate strongly inhibited the hydration of Portland cement and were unsuitable as additives.

The results from this study suggest there may be merit in testing additives that combine a strong accelerating effect with the ability to form insoluble complexes with inhibitory heartwood tannins during the manufacture of WWCB from A. mangium wood. If such compounds are successful then they could provide a useful alternative to the current method of soaking wood-wool in water, which is used to ameliorate the inhibitory effect of A. mangium heartwood on cement hydration.

Acknowledgements

Financial assistance for the work was provided by the Australian Centre for International Agricultural Research (ACIAR). The authors also thank Dr Lee Wellings, Research School of Chemistry, and Dr Nick Welham, Research School of Physical Sciences, ANU, for advice and assistance in obtaining compounds. Thanks also to Mr Bob Parkin, Blue Circle Southern Cement Industries-Australasia, for provision of cement.

References


The use of Cement Hydration Tests to Predict the Suitability of Acacia mangium and Eucalyptus pellita for the Manufacture of Wood-Wool Cement Boards

By K.E. Semple¹, R.B. Cunningham² and P.D. Evans¹

¹Department of Forestry, The Australian National University, Canberra, Australia
²Statistical Consulting Unit, The Australian National University, Canberra, Australia

Summary

Wood-wool cement boards (WWCBs) are manufactured in many tropical countries which have extensive eucalypt and acacia plantations. Wood from such plantations could act as a potential raw material for WWCBs, but the suitability of most tropical eucalypts and acacias for the manufacture of such products is unknown. This study was undertaken to assess whether the standard laboratory test for wood-cement compatibility, which measures heat of hydration in wood flour-cement mixtures, is an appropriate method for screening tropical eucalypts and acacias for their compatibility with cement and suitability for the manufacture of WWCBs. Wood samples from a tropical eucalypt (E. pellita) and a tropical acacia (A. mangium) were tested in two forms, i.e. flour and wool, for their compatibility (expressed by maximum hydration temperature and CA-factor) with Portland cement. Form significantly influenced the effect of the wood on cement hydration, resulting in a different species compatibility ranking for flour and wool. As the heartwood content of wood-wool-cement hydration test samples increased, $T_{\text{max}}$ and CA-factor increased whereas the opposite occurred for those containing wood flour. Tests using wood flour ranked E. pellita as being more compatible with cement than A. mangium whereas the ranking was reversed when wood-wool was used. Furthermore at low wood levels the compatibility of samples containing wood-wool or wood flour with cement was similar whereas at high wood levels, samples containing wood-wool were much more compatible with cement than those containing wood flour. Laboratory tests designed to screen eucalypts and acacias for their compatibility with cement should use wood in a coarser form with a lower surface-to-volume ratio than flour. Caution should be exercised if using results from wood flour-cement hydration tests to estimate the suitability of wood species for the manufacture of WWCBs and possibly other wood-cement composites.
Introduction

Wood-wood cement boards (WWCBs) are widely used in many tropical countries because of their low cost and ease of manufacture, excellent mechanical and insulation properties and resistance to moisture, fire, termites and fungi (Pablo 1989). In recent years, extensive eucalypt and acacia plantations have been established in the Asia-Pacific region (Verhe 1963) and wood from such plantations is a potential raw material for use in WWCBs. However, the suitability of most tropical eucalypts and acacias for the manufacture of WWCBs and other wood-cement composites is unknown. The first step in determining their suitability is to screen them for their compatibility with cement. It is therefore necessary to determine first whether results from current methods of wood-cement compatibility testing (which use wood flour) will accurately represent the compatibility of tropical acacia and eucalypt wood-wood with cement.

In this study wood flour and wood-wood from brown salwood (Acacia mangium Willd.), red mahogany (Eucalyptus polita F. Müell.) and black poplar (Populus × euramericana (Dode) Guinier) were compared for compatibility with Portland cement. The aim was to determine the effect, if any, of wood form (flour or wood) on the reaction of the wood with cement in order to assess whether standard tests for wood-cement compatibility using wood flour might be used to screen eucalypt and acacia species as suitable raw material for the manufacture of WWCBs.

Wood-cement compatibility testing

Wood species vary greatly in their compatibility with cement and suitability as raw materials for wood-cement composites. It is time consuming to manufacture wood-cement composites in the laboratory and then test their mechanical and physical properties. Therefore a preliminary, rapid, screening test which measures the compatibility of wood with cement is usually used when assessing the suitability of wood species for use as wood-cement composites. The most commonly used screening test measures, under controlled conditions, the exothermic reaction (heat of hydration) over time when wood flour is mixed with cement and water. Wood species are then classified on the basis of maximum hydration temperature (Sandermann and Kohler 1964) and other reaction parameters such as time taken to reach maximum temperature, rate of temperature increase and area under the hydration curve (e.g., Hofstrand et al. 1984; Hachimi et al. 1990). Alternative tests measure the compressive strength of cylindrical plugs of wood-cement blocks (Lee and Hong 1986; Blankenhom 1994) or the pulling force required to remove test sticks of different wood species set in cement (Rahim and Ong 1983).

The most comprehensive evaluation of the compatibility of different wood species with cement was undertaken by Sandermann and Kohler (1964). They measured the maximum hydration temperature of 99 species from 43 families. Types and amounts of water and alkali soluble chemical constituents in wood are believed to adversely affect its compatibility with cement (Hachimi and Mosler 1989, Miller and Mosler 1991). Such compounds include heartwood polyphenols, simple sugars, sugar acids and hemicelluloses (Sandermann et al. 1960; Biblis and Lo 1968; Fischer et al. 1974; Simayupang 1986; Zhengjian and Mosler 1986). Other important factors include the form and particle size of wood (Weatherwax and Tarkow 1964) and the wood:cement ratio (Lee et al. 1986), both of which vary greatly among different types of wood-cement composite. Compatibility may vary greatly between heartwood and sapwood and even between trees of the same species.

There is still no standard method for conducting cement-wood hydration tests nor standard indices expressing compatibility, making meaningful comparisons between different estimates difficult. Early recommendations made by Weatherwax and Tarkow (1964) using 15 g (oven-dry basis) wood and 200 g cement have been adopted by numerous subsequent researchers although there are variations on the amount of wood used. For example 20 g of wood was used by Sandermann and Kohler (1964) and 10 g by Sudin and Irvahin (1989). The correct balance of wood:cement in these tests is crucial for meaningful results; very low wood:cement ratios may mask subtle differences in wood sample-cement hydration behaviour (Lee et al. 1987).
In varying the amount of wood, the amount of water added to the wood-cement mix also varies. Weatherwax and Tarkow (1964) used 90.5 g of water for their wood-cement mixtures and 80 g for control samples, a practice used by most subsequent workers. This equates to 0.4 g water per g of wood and an extra 1 g per g of wood. Sandermann and Kohler (1964) used 20 g wood, 200 g cement and 100 g water, also equating to an extra 1 g water per g wood added. However, Sudin and Ibrahim (1989) used 10 g wood, 200 g cement and 80 g water for their hydration tests. Hashmi et al. (1990) confirmed that 0.4 g of water per g of pure cement optimised cement hydration, but recommended that an extra 0.7 g of water per g of wood (oven-dry basis) should be added. The authors stressed that excess water would dilute the mineral constituents of cement, reducing its maximum hydration temperature and increasing its setting time.

The coarseness of wood flour has a marked influence on its compatibility with cement (Weatherwax and Tarkow 1964). The most common size used in previous studies is 20 or 20/40 mesh although in some cases, finer flour of 40 to 60 or 60 mesh was used (e.g. Weatherwax and Tarkow 1964, Miller and Moslemi 1991). It has been generally assumed in the literature that tests using wood flour are relevant to the compatibility of sawdust, flakes and larger particles of wood (as used in wood-cement composites) with cement. There are no published examples of the use of wood-wood in cement hydration tests. The question therefore arises as to whether the use of wood flour in laboratory cement hydration tests can provide a reliable estimate of how wood-wood will affect cement hydration.

The most obvious factor which might confound the relationship between the results of cement compatibility tests undertaken using wood flour and the suitability of wood for WCWs is that wood flour has a larger surface-to-volume ratio than wood-wood. This could determine the ease with which extractives are leached from wood, which is likely to influence its compatibility with cement. Wood flour is prepared from dry wood blocks whereas wood-wood is usually shredded from green billets and then air-dried. This may cause differences in the distribution of soluble carbohydrates of the sapwood (Miller and Moslemi 1991), Hachem and Campbell (1989), further complicating comparisons between wood flour and wood-wood in compatibility with cement.

Materials and Methods

Preparation of wood

The tree species used in the experiment were: Acacia mangium (PNG/Irian Jaya Prov.), Eucalyptus pellita (PNG/SW Prov.) and Populus x euramericana (unknown origin). A. mangium and E. pellita were chosen because of their importance as plantation species in Southeast Asia. Populus x euramericana is used to make WCWs in Australia and was selected as a control. Six-year-old E. pellita and A. mangium trees, two for each species, growing in a seed orchard in Atherton, Queensland were felled and cross-cut. The billets were shredded into wood-wood measuring 3 mm in width and about 0.4-0.6 mm in thickness at Woodtex Pty Ltd (Bendigo, Victoria) using a 1972 Van Elten shredder. The P. x euramericana was obtained as shredded wood, in two bales, cut from an unknown number of 30-year-old trees. The wood-wood was air dried at 23°C for 24 hours and then stored under cover at room temperature (≈20°C).

Wood-wood from A. mangium and E. pellita was separated into sapwood and heartwood on the basis of the distinct colour difference between sapwood and heartwood in both species. P. x euramericana does not form a visually distinct heartwood (Hillis 1987), thus separation of sapwood and heartwood in this species was not possible. Wood-wood was then cut into pieces measuring about 3 cm in length using scissors and placed in open bags in a conditioning room at 20 ± 1°C and 65 ± 5% r.h. for two weeks.

When possible, wood flour was prepared from blocks of air-dried heartwood and sapwood, reducing them to match-stick sized pieces using a hatchet and grinding in a 'Junior' laboratory mill to produce particles measuring approximately 1 mm in diameter. These were then further ground in a Wiley mill (Arthur H. Thomas Co.) to 20-40 mesh size. Wood of P. x euramericana

K. E. Sempie, et al. 

379
and the sapwood from one of the trees of both A. mangium and E. pellita was unavailable in solid form and was ground as described above from wood-wool. The wood flour was stored in a conditioning room at 20 ± 1°C and 65 ± 5% r.h. for two weeks.

The following amounts of sapwood and heartwood flour and wool for each species were weighed out (oven-dry weight basis) and placed in separate containers: 5 g (low level; 2.4% wood), 10 g (medium level 1, 4.8% wood), 15 g (medium level 2, 7% wood) and 20 g (high level, 9% wood). Within each of the wood levels, three categories of heartwood content were used: 0%, 50% and 100%, resulting in 48 different samples for each species. Once weighed, the wood samples were kept in the conditioning room at 20 ± 1°C and 65 ± 5% r.h.

**Measurement of cement hydration temperature and compatibility index**

Flour or wool samples were evenly mixed with an aqueous slurry of 200 g of fresh Portland cement Type I (Blue Circle Southern brand, batch no. 99997) at 20°C in a scalable 'Dalglip' polyethylene bag by hand kneading for around 2 minutes. The amount of water used varied according to the amount of flour or wool being tested. This was fixed at 0.4 mL per g of cement plus an extra 0.7 mL per g of wood (oven dry basis) in accordance with the recommendations of Hachimi et al. (1990). Cement control samples contained 200 g of cement and 80 g of water.

Immediately after mixing, the tip of a temperature thermocouple (Type J) was taped to the outside of the sample bag and enclosed within the body of the wood-cement mix by folding the bag and contents around it and securing the folded bag with adhesive tape. The bag was then placed in a polystyrene cup and sealed inside a 1 L capacity thermos flask. This process was carried out for six samples. A cement hydration temperature logging apparatus, similar to that used by Ile and Simpson (1993), was used to measure the heat of hydration of the six wood-cement samples over 23 hours. Temperatures were recorded at 15-minute intervals and the curves were smoothed by plotting the progressive averages of every three successive readings.

Maximum heat of hydration temperature (T_max) was recorded and a wood-cement compatibility index, C_w-factor (Hachimi et al. 1990), was calculated. The C_w-factor is the ratio of the areas under the wood sample-cement and control (cement only) hydration curves, expressed as a percentage. All experiments were undertaken in a conditioning room maintained at 20 ± 1°C and 65 ± 5% r.h.

**Experimental design and statistical analysis**

The experimental design used factorial principles, investigating the effects of four fixed factors on wood-cement compatibility, i.e. wood form (flour or wool), species, heartwood content and wood level, and also various random effects, including those associated with replicates obtained from different trees. A total of 28 days was required to test all of the samples. The factors of greatest interest were the effects of wood form and species on compatibility so these factors were randomised within each daily six-sample run. The next level of randomisation was for wood level and % heartwood with one combination of these two factors tested each day. Wood from the first tree (or bale in the case of P. x euramericana) of each species was tested over the first 14 days, followed by the second tree/bale over the next 14 days. Every 7th day 4 cement control samples were measured comprising a total of 4 control runs over the entire experiment.

The main effects of and interactions between each of the four factors for T_max and C_w-factor were tested for significance using an appropriate multi-factorial ANOVA model at the 5% significance level. Before the final analysis, diagnostic checks on the normality and variance of the data were undertaken. The factorial design of the experiment allowed data to be averaged across non-significant (p>0.05) effects thereby giving the experiment greater precision. Significant results are plotted graphically and bars representing the least significant difference (p<0.05) are included on graphs to facilitate comparison of means.
Results and Discussion

The wood form (flour or wool) and wood level used in cement hydration tests had highly significant (p<0.005) effects on maximum hydration temperature (T_max) and CA-factor (Table 1). More importantly, wood form interacted strongly with heartwood content, species and wood level (Table 1), producing different results and interpretations of wood-cement compatibility from tests using wood flour compared with those which used wood-wool.

Table 1. Significant main effects and interactions between factors.

<table>
<thead>
<tr>
<th>Effects and interactions</th>
<th>F-probability (p) for T_max</th>
<th>F-probability (p) for CA_factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>wood form</td>
<td>&lt;0.001 (s)</td>
<td>&lt;0.001 (s)</td>
</tr>
<tr>
<td>wood level</td>
<td>0.005 (s)</td>
<td>&lt;0.001 (s)</td>
</tr>
<tr>
<td>%heart*wood form</td>
<td>0.002 (s)</td>
<td>0.005 (s)</td>
</tr>
<tr>
<td>species*wood form</td>
<td>0.011 (s)</td>
<td>0.055 (ns)</td>
</tr>
<tr>
<td>wood level*wood form</td>
<td>&lt;0.001 (s)</td>
<td>&lt;0.001 (s)</td>
</tr>
<tr>
<td>%heart*species</td>
<td>0.017 (s)</td>
<td>0.007 (s)</td>
</tr>
</tbody>
</table>

The effect of wood form on wood-cement compatibility can be seen clearly in Figure 1, which shows the interaction between wood form and heartwood content, averaged across species, on T_max and CA-factor. As the heartwood content of wood-wool in cement hydration test samples increased T_max and CA-factor increased, whereas the opposite occurred in those containing wood flour (Fig. 1). Heartwood extractives which inhibit cement hydration may be readily leached from wood flour and this could explain why decreases in wood-cement compatibility were observed to occur as the heartwood content of the wood flour increased. In contrast, wood-wool has a much lower surface-to-volume ratio than wood flour and therefore the ease with which extractives are removed from wood-wool may be lower than for wood flour. Furthermore, the extractives in heartwood may be less susceptible to leaching in the aqueous environment of cement because heartwood is less permeable than sapwood; this may in part explain the observation (Fig. 1) that as the % heartwood in wood-wool increased, wood-cement compatibility increased.

![Figure 1](image-url)
The form of the wood used in the cement hydration tests also influenced the "perceived" compatibility of the different wood species with cement. Tests using wood flour ranked *E. pellita* as being more compatible with cement than *A. mangium* whereas the ranking was reversed when wood-wool was used (Fig. 2). For example, average CA factors for *E. pellita* and *A. mangium* flour were 64.5 and 56.5% respectively whereas for wood-wool they were 72.4 and 77.5% (Fig. 2). These compared with *P. euramericana* wood at 65.4 and 79.8% for flour and wool respectively. The leachability of extractives from wood flour and wood-wool may help explain the observed switch in species compatibility ranking between the two wood forms. Heartwood of *A. mangium* is known to contain a variety of condensed tannins (flavonoid) extractives which strongly inhibit cement hydration (Tachi et al. 1989). Such extractives may be easily leached from wood flour but less readily from wood-wool, and hence it is not surprising that tests using wood flour ranked *A. mangium* as the least compatible of the wood species tested. The reduced compatibility of *E. pellita* wood in wool form may tentatively suggest wood structure-related differences in the leachability of inhibitory compounds from solid wood of different species.

![Figure 2](image.png)

**Fig. 2.** Interaction between species and wood form for $T_{\text{max}}$ and $C_A$ factor; data averaged across heartwood content and wood level.

As expected, wood form interacted significantly ($p<0.001$) with wood level (Table 3 and Fig. 3), whereby compatibility with cement decreased markedly with increasing levels of wood flour and less so for wood-wool. The smaller particle size in wood flour would result in a greater increase in the ratio of surface area-to-weight with increasing wood level compared with wood-wool, thus affecting wood-cement compatibility to a greater extent.

Finally, Figure 4 shows a significant interaction between species and heartwood content whereby wood-cement compatibility increased in *E. pellita* and decreased in *A. mangium* with increasing heartwood content. The trend in *A. mangium* was due to the high average compatibility of sapwood regardless of form, in contrast to the extreme incompatibility of the heartwood in flour form for reasons already discussed. Explanations for the pattern observed in *E. pellita* are less straightforward. Reduced levels or reduced leachability of inhibitory extractives in the heartwood and/or depression of sapwood compatibility by the presence and leachability of inhibitory substances in the sapwood. High levels of soluble carbohydrates and sugars in and on the surface of sapwood can greatly reduce its compatibility with cement (Biblis and Lo 1968; Fischer et al. 1974), however this possibility could not be directly related to the findings of this study without further investigation.
Overall, the results for A. mangium and E. pellita suggest that cement hydration tests using wood flour do not accurately predict the compatibility of wood-wool with cement for these species. Findings suggest that cement hydration tests using wood flour may underestimate the compatibility of species such as A. mangium whose inhibitory heartwood extractives may not be as easily leached from wood-wool to retard cement hydration. The greatly altered geometry of wood flour may also mask differences between wood species in structure, permeability and extractive leachability of wood in wool, larger particle or flake form. Accordingly, cement
The Use of Cement Hydration Tests

Hydration tests designed to screen wood species for their compatibility with cement should use coarse wood samples with a lower surface-to-volume ratio than wood flour. The extent to which our findings are relevant to other wood species is not known; however, they suggest that suitability estimates of wood species for WWCBs and possibly other wood-cement composites based on screening tests which use wood flour should be viewed with caution.

Conclusions

Cement hydration tests using wood flour do not accurately predict the compatibility of wood-wool of either A. mangles or E. pellita with cement. Further research is needed to develop a more accurate method of screening acacia and eucalypt wood species for their compatibility with cement. Following the development of such a method, a greater range of acacias and eucalypts need to be tested for their compatibility with cement and potential suitability for use in wood-cement composites.

Acknowledgements

The authors thank the Australian Centre for International Agricultural Research for financial support, Queensland Department of Primary Industries for supplying wood samples, Mr John Woolley and staff at Woodtex Pty Ltd for processing wood into wood-wool and Mr Noel Semple and Dr Anne Gibson for editorial assistance.

References


Postal Addresses

K.E. Semple and P.D. Evans
Department of Forestry, The Australian National University, Canberra, 0200, Australia.

R.B. Cunningham
Statistical Consulting Unit, The Australian National University, Canberra, G200, Australia.
THE MANUFACTURE OF CEMENT-BONDED FLAKE-BOARDS FROM
WESTERN AUSTRALIAN MALLEE, BLUE GUM AND COMMERCIAL
PINE SPECIES

K.E. Semple¹ and P.D. Evans²

¹Graduate Student, Forestry Program, The Australian National University, Canberra ACT 0200
Australia.
Email: Kate.Semple@anu.edu.au
²Professor and Director, Centre for Advanced Wood Processing, University of British Columbia,
Vancouver, B.C. Canada V6T 1Z4.

Keywords: Mallee, Pinus, Eucalyptus, cement composites, accelerators

ABSTRACT

Mallee eucalypt (E. horistes/E. polybractea), blue gum (Eucalyptus bicostata), maritime pine (Pinus pinaster) and radiata pine (Pinus radiata) form the bulk of the tree plantation estate in Western Australia. Blue gum and the two pine species are primarily grown to produce pulp and paper and sawn timber, respectively, whereas mallees are increasingly being planted to arrest the deterioration of land by salinity and to increase farm incomes through the production of pharmaceutical oils from leaves. There is a pressing need, however, to utilize waste mallee wood and bark residues produced during the harvesting of leaves to make the overall cultivation of mallee profitable. Wood from mallee eucalypt, blue gum and pine species was compared for their potential suitability for the manufacture of cement-bonded flake-boards. The aim was to determine which species would be best suited to the manufacture of wood-cement flake-boards and to identify the optimum method of flake pre-treatment for each wood type. Wood flake pre-treatments included soaking flakes in cold or hot water and the addition of common cement setting accelerators (CaCl₂ and MgCl₂). In the case of the mallee eucalypt and blue gum wood, pre-soaking and/or addition of cement accelerator was necessary to improve board strength properties. Board flexural properties were adversely affected by increasing thickness of flakes that resulted from the processing of denser mallee and blue gum wood. The findings of this study are designed to provide preliminary guidelines for the establishment of small to medium-scale industries manufacturing cement-bonded wood composite panels from residues arising from the processing of mallee and other low value wood from commercial timber species grown in Western Australia.

INTRODUCTION

Severe land degradation arising from increasing soil salinity on farmland in the low rainfall wheat belt of Western Australia (WA) has led to an ambitious program of tree crop development to arrest the problem. It is projected that by the year 2020, 800, 000 hectares of trees will have been established on such land, with the potential to ameliorate soil salinity problems and generate around 13 million cubic meters of woody biomass annually (Shea 1998). Several species of mallee eucalypts endemic to WA have been found to be particularly well suited for planting on these low rainfall sites. Mallees are shrub-like, multi-stemmed eucalypts adapted to the arid and semi-arid zones of Australia. Some species such as E. polybractea R.T. Baker contain high quantities of eucalyptus leaf oils that are distilled for medicinal use and as solvents. There are currently around 10, 000 ha of mallee eucalypt plantations in WA, with projections for sharp increases in planting rates (Bartle pers. comm. 1999). To create incentives
Symposium on Bio-Based Composites

for farmers to plant more trees and gain adequate returns from them, markets for leaf oil and the woody residues will need to expand.

Leaf oil will be the primary commercial product derived from mallee plantations. Economic analysis, however, has shown that the financial viability of oil production depends on farmers also finding commercial outlets for the waste wood and bark residues left over after harvesting leaves for distillation (Bartle et al. 1996). According to Bartle (2001), the option currently being explored which is expected to consume much of the material is conversion to chips and subsequent use as biomass energy for power generation and activated charcoal. However, the potential of wood and bark residues for the manufacture of a much wider range of products including composite panels and paper products also needs to be investigated. There is very little information available about the suitability of this material for the manufacture of wood-based composite panels, in particular cement-bonded composite panels.

Previous work (Semple et al. 2002) indicated that chipped wood and bark residues of several mallee species of commercial interest was of moderate to good compatibility with Portland cement, with only one notable exception. A pilot study on the manufacture of cement-bonded boards showed that in-field chipping of the stems did not produce the correct particle size and geometry required to maximize the strength properties of cement-bonded panels. The same study also found that the presence of mallee bark did not adversely affect the strength properties of wood-cement boards, but it did reduce their resistance to water. Mallee stem wood residues, being very small in diameter (<5-10 cm) contain a high proportion of bark (up to 50%) that may prove impractical to remove using conventional log debarking machinery. To produce furnish with more favorable geometry, in this study we converted mallee stems (E. polybractea and E. horistea), into flakes using a knife disk flaker. The resulting flakes were screened which had the beneficial effect of removing much of the bark from the processed wood. We report here on the properties of cement composites made from such flakes and the ability of various wood pre-treatments to improve the mechanical properties of the composites. The properties of cement-bonded composite boards containing mallee flakes are compared with those of similar boards manufactured from other important plantation species in Western Australia including blue gum (E. bicostata), radiata pine (P. radiata) and maritime pine (P. pinaster).

MATERIALS AND METHODS

Log Harvesting

Logs from mallee, blue gum, radiata pine and maritime pine were collected from different sites with similar soil type throughout the wheat-growing zone of south west of Western Australia in June/July 2001. For all species, material from 10 individual trees was sampled and pooled to ensure a good mix of parent material. The mallee trees were grown from seed collected from native stands and were sampled from hedge rows spaced 40 to 50 m apart on pasture land. Being multi stemmed, one large stem (1-2 m long and 7-10 cm in diameter) was harvested at ground level from each of the ten trees from the two mallee species. The stems were cut back to 1 m for shipment. Blue gum and the two pines were sampled from plantations during commercial harvesting operations. From each tree one log measuring 1.2 m was taken from a different height to ensure a mixed sample of wood representing different trees and positions in trees starting at 0.3 m above ground level. The blue gum trees sampled were of two different diameters as a result of harvesting dominant (DBH = 30-45 cm; Blue gum 1) and suppressed trees (DBH = 7-12 cm; Blue gum 2) from the stand.
Preparation Of Wood Flakes

Log samples were converted into flakes and particles using a laboratory disk flaker (Bezner No. 6577) located at the Carter Holt Harvey particleboard factory in Oberon, NSW. The blue gum and pine logs were first debarked by hand using an axe and then cut using a chainsaw into rounds measuring 300 mm in length. These were then further reduced to pieces measuring approx. 200 x 50 x 100 mm using a block splitter prior to flaking. The mallee stems were unable to be debarked practically and were therefore cut into 200 mm long rounds which were flaked with the back on. The knife mill used was 80 cm in diameter and contained 8 separate knife blades set at a 45° angle to cut flakes along the grain. The flakes, the largest of which measured approximately 105 x 45 mm, were then dried in a large oven at 50°C for approx. 48 h to reduce their moisture content to approximately 10%. They were then stored undercover for 4 months. Flakes were screened through a 10 mm sieve to remove fines under 10 x 10 mm. As a result of knife milling and subsequent sieving, approx. 90% of the bark from the mallee was removed with the small particles leaving the large flakes with a minimal content of large fibrous strands of bark.

Manufacture Of Cement-Bonded Flake And Particle Boards

Cement-bonded flake-boards were manufactured according to a randomized block design to test the effects of the following factors on the properties of boards:

• species (mallee, low and high density blue gum, radiata pine and maritime pine) and
• flake pre-treatment (none, cold water soak 24 h, hot water soak 8 h, addition of CaCl₂ or MgCl₂ at 2% w/w cement).

A total of 55 boards measuring 380 x 300 x 15 mm were produced over a period of one month. Boards were manufactured using a wood: cement ratio of 1:3 and a water: cement ratio of 0.5. Cement coated flakes were distributed by hand into a mould measuring 300 x 380 mm placed on a rectangular sheet of formply measuring 340 x 420 x 17 mm. When the mat was fully built up the mould was removed and another piece of formply placed on top of the mat. Two wooden spacing rods measuring 15 x 15 x 300 mm were placed at either end between the two formply sheets to achieve a pressed board thickness of 15 mm. The resulting assemblage was pre-pressed while the mat for the next board was mixed and the process repeated to produce a sandwich of 2 mats between 3 sheets of formply. The stack of mats was placed between two steel plates measuring 340 x 470 x 15 mm and pressed at ambient temperature to 15 kg/cm² using a PhH hydraulic operated press. The pressed mats were kept under pressure for 24 h by bolting the two steel plates together using four 8 mm thick bolts, an assemblage which could then be removed from the press. After 24 h the boards were de-clamped, stacked and conditioned for approx. 10 weeks at 20 ± 1 °C and 65 ± 5% R.H. to allow the composites to cure and gain maximum strength.

After curing all wood-cement boards were cut into 5 samples measuring 50 x 230 mm using a diamond edged rock cutting saw. Samples were kept in a conditioning room at 20°C and 65% r.h. to equalize for 14 days prior to testing board mechanical properties. Mechanical properties evaluated included density, bending strength (Modulus of Rupture) and stiffness or Young's modulus (Modulus of Elasticity). The resistance of boards to water (water absorption and thickness swelling) after immersion for 24 h was also tested.
RESULTS AND DISCUSSION

Mechanical Properties Of Flake-Boards

All flake-boards manufactured in this study exceeded the minimum density of 1000 kg/m³ stipulated by ISO 8335 for cement-bonded boards, ranging in density between 1080 and 1300 kg/m³. Boards made from the mallee eucalypt and small-diameter high density blue gum wood were in the upper range due to the higher bulk density of the parent material. The average MOR and MOE of boards made from mallee flakes compared with those manufactured from the other wood species are shown in Tables 1 and 2. The shading denotes samples that did not meet the standard strength properties of 9 MPa in bending (MOR) and 3000 MPa in stiffness (MOE) for cement bonded boards set out in ISO 8335.

The flexural properties of boards made from mallee flakes failed to meet the standard and were significantly (p<0.001) lower than those of pine or blue gum. While the MOR and MOE of boards made from untreated flakes of low-density blue gum did not meet the standard, presoaking and accelerator addition significantly improved their mechanical properties. In the case of the mallee eucalypt and higher density blue gum, neither cold water soaking nor the addition of accelerators was sufficient to produce boards exceeding 9 MPa in bending (Table 1). However, variation in MOR (shown by standard deviation) indicates that some mallee boards containing CaCl₂ and MgCl₂ met the standard, suggesting that only minor increase in the quantity of accelerator used may be necessary to manufacture boards of acceptable quality from mallee flakes. Note from Table 2 that the average MOE of mallee boards containing either of the two accelerators was above the ISO standard of 3000 MPa.

In contrast, boards made from untreated flakes of the two pines, exceeded the ISO standard. Table 1 indicates that no marked gain in MOR was gained by pre-soaking pine flakes or adding cement set accelerators. However in the case of MOE an almost 20% increase was achieved through the addition of MgCl₂. The best pre-treatment for maritime pine was the addition of CaCl₂ while extractive removal by hot water maximized the mechanical properties of boards made from radiata pine. Previous work by Semple and Evans (2000) indicates that unextracted heartwood of radiata pine is incompatible with cement and has a deleterious effect on the mechanical properties of wood-wool cement board.

Table 1 - Average MOR (MPa) of flake-boards influenced by species and flake treatment (Standard deviation in parentheses).

<table>
<thead>
<tr>
<th>Species</th>
<th>No Treatment</th>
<th>Cold Water</th>
<th>Hot Water</th>
<th>CaCl₂</th>
<th>MgCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>maritime pine</td>
<td>10.5 (2.7)</td>
<td>9.9 (1.5)</td>
<td>11.2 (1.8)</td>
<td>13.8 (2.2)</td>
<td>12.1 (1.7)</td>
</tr>
<tr>
<td>radiata pine</td>
<td>11.1 (2.3)</td>
<td>12.9 (2.2)</td>
<td>13.1 (2.2)</td>
<td>11.9 (1.6)</td>
<td>9.6 (2.2)</td>
</tr>
<tr>
<td>blue gum 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>blue gum 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mallee</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LSD = 3.26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2 - Average MOE (MPa) of flake-boards influenced by species and flake treatment (Standard deviation in parentheses).

<table>
<thead>
<tr>
<th>Species</th>
<th>No Treatment</th>
<th>Cold Water</th>
<th>Hot Water</th>
<th>CaCl₂</th>
<th>MgCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>maritime pine</td>
<td>4112 (751)</td>
<td>4175 (554)</td>
<td>4307 (587)</td>
<td>4870 (349)</td>
<td>4902 (573)</td>
</tr>
<tr>
<td>radiata pine</td>
<td>4493 (1080)</td>
<td>4764 (602)</td>
<td>4792 (536)</td>
<td>4990 (1083)</td>
<td>3879 (1379)</td>
</tr>
<tr>
<td>blue gum 1</td>
<td></td>
<td>3487 (1247)</td>
<td>4330 (621)</td>
<td>4393 (807)</td>
<td>3809 (1101)</td>
</tr>
<tr>
<td>blue gum 2</td>
<td></td>
<td>3510 (2607)</td>
<td>3610 (877)</td>
<td>3538 (951)</td>
<td>3880 (386)</td>
</tr>
<tr>
<td>mallee</td>
<td></td>
<td></td>
<td></td>
<td>3559 (951)</td>
<td>3839 (961)</td>
</tr>
<tr>
<td>LSD = 1037</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The relationship between MOR and MOE of all boards is shown in Fig. 1. There is significant variation in MOE among boards over about 8 MPa in bending, and some boards meeting the standard 9 MPa in bending were below 3000 MPa in stiffness. Localized variation in mat distribution and density arising from hand forming may account for this observation.

![Modulus of Rupture (MPa) vs Modulus of Elasticity (MOE)](image)

The highest average board strength was achieved using low density blue gum (blue gum 1) in the presence of an accelerator, suggesting that this wood type as well as the pines may be very well suited to the manufacture of cement-bonded flakeboard. The strength properties of flake-boards made from mallee were a marked improvement on boards manufactured from chipped mallee wood in our pilot study (Semple et al. 2002), particularly when an accelerator was used. This suggests that flakes are a better material than particles for the manufacture of cement-bonded boards from mallee eucalypt. However it appears that it is necessary to use an accelerator to produce boards of acceptable quality.

The good performance of blue gum (especially the lower density wood) in cement-bonded flake-boards here contrasts with previous reports indicating that eucalypts are unsuitable for the manufacture of cement-bonded composites (e.g. Tachi et al. 1988, Yasin and Quereshi).
1990). Our findings for blue gum, however, are supported by a recent study of the manufacture of cement-bonded composites from eucalypts (Warden et al. 2002). In their study, eight temperate eucalypt species, including blue gum were used to manufacture wood-cement flake-boards and wood-cement particleboards. Wood-cement ratio was 1:3 and water content 0.38, considerably lower than that used here (0.5). CaCl₂ was added at 2% w/w cement to some boards. Boards were between 1200 and 1400 kg/m³ in density after curing, but only boards made from blue gum were above 8 MPa in bending, averaging 10.8 MPa. Greatly reduced board strength among other species was attributed to poor flake geometry (low aspect ratio) and high quantity of fines in the board furnish.

The size and thickness of the flakes, limited mould size and mat forming by hand made it difficult to achieve a high level of homogeneity in flake distribution in this study. Boards with lower homogeneity and greater surface roughness were weaker and failure tended to occur within less compacted zones. Better control of flake thickness and automatic mat formation equipment could overcome this problem, leading to enhanced board flexural properties. Warden et al. (2002) also observed significant variation in the mechanical properties of cement-bonded flake-boards which they attributed to manual mat formation and to the relatively large wood cement element size used to make boards. The lower strength of boards made from mallee and high density blue gum was also likely influenced by their high average and highly variable flake thickness (as shown in Table 3), geometry and reduced compressibility.

<table>
<thead>
<tr>
<th>Species</th>
<th>Basic Density (Kg/m³)</th>
<th>Average Flake Thickness (mm)**</th>
<th>Std. Dev.</th>
<th>Range (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>maritime pine</td>
<td>470</td>
<td>0.36</td>
<td>0.12</td>
<td>0.11-0.85</td>
</tr>
<tr>
<td>radiata pine</td>
<td>395</td>
<td>0.36</td>
<td>0.11</td>
<td>0.12-0.79</td>
</tr>
<tr>
<td>bluegum 1</td>
<td>500</td>
<td>0.30</td>
<td>0.13</td>
<td>0.07-1.15</td>
</tr>
<tr>
<td>bluegum 2</td>
<td>900-950</td>
<td>0.54</td>
<td>0.44</td>
<td>0.12-3.58</td>
</tr>
<tr>
<td>mallee</td>
<td>850</td>
<td>0.60</td>
<td>0.32</td>
<td>0.18-2.72</td>
</tr>
</tbody>
</table>

*Forest Products Commission Data
**Average of 250 flakes/wood type

Milling of mallee and high density blue gum produced flakes of variable thickness ranging from less than 0.15 mm to over 3 mm, which had a tendency to scroll up during drying. This adversely affected mat homogeneity, compression, and evenness of board surfaces. In contrast pine and low density blue gum flakes were thinner (averaging 0.3 to 0.36 mm), less variable in thickness, and remained flat, with the latter tendency to separate into a more fibrous structure. As a result, both pine and low density blue gum flakes produced a more compact mat structure. Adjustment of knife flaker parameters to better suit dense woods and produce thinner, more even, flakes could lead to improved board properties.

**Resistance To Water And Dimensional Stability**

The average bending strengths of boards after soaking in water for 24 h are shown in Table 4. None of the boards made from mallee eucalypt wood met the minimum wet MOR of 5.5 MPa specified in ISO 8335, however all boards made from pine or low-density blue gum met this requirement. Pre-soaking of flakes from high density blue gum or the addition of accelerator (CaCl₂) was necessary to produce boards with adequate residual strength after exposure to water.

---

Table 4 - Average bending strength of boards after soaking in water for 24 h as affected by species

<table>
<thead>
<tr>
<th>Species</th>
<th>MOR (MPa)</th>
<th>Failure mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>maritime pine</td>
<td>2.3</td>
<td>Flake failure</td>
</tr>
<tr>
<td>radiata pine</td>
<td>2.1</td>
<td>Flake failure</td>
</tr>
<tr>
<td>bluegum 1</td>
<td>2.0</td>
<td>Flake failure</td>
</tr>
<tr>
<td>bluegum 2</td>
<td>1.8</td>
<td>Flake failure</td>
</tr>
<tr>
<td>mallee</td>
<td>1.6</td>
<td>Flake failure</td>
</tr>
</tbody>
</table>

*Forest Products Commission Data
ISO 8335 has a fairly stringent maximum thickness swelling of cement bonded particleboards boards of 2% after soaking in water at ambient temperature for 24 h. Thickness swelling of most boards manufactured in this study exceeded this value, but usually not by a wide margin (Table 5). Hot water soaking, CaCl₂ and MgCl₂ pre-treatments were effective in most cases at reducing thickness swelling of boards so that they met the required standard.

Warden et al. 2002 found that the size and shape of wood flakes strongly influenced the thickness swelling of cement-bonded flake-boards. Thickness swelling increased significantly with increasing flake thickness, from 0.3 to 0.9 mm, and decreasing flake length. The use of thicker flakes resulted in less homogeneous boards with a more irregular ‘open’ surface similar to that of boards made from mallee and higher density blue gum. Flake-boards exhibited greater thickness swelling than cement-bonded particleboards possibly due to their rough surface and greater void-space (Warden et al. 2002). Fuwape and Fuwape (1994) attempted to rectify this problem in cement-bonded flake-boards made from spruce (Picea sitchensis) by using sawdust in the top and bottom layers. Such an approach improved dimensional stability, but significantly reduced board bending strength and stiffness.

**Potential Further Improvement Of Board Properties**

Despite the increased thickness swelling of boards composed of flakes rather than particles the use of larger sized wood furnish has a number of advantages. It is a very effective way of reducing carbonation-induced shrinkage in wood-cement composites (Sanderson 1973, Broker and Simatupang 1974). It also provides much greater scope for flake or strand orientation to impart higher flexural properties to boards. The idea of manufacturing cement-bonded boards with orientated flakes is not new and was first developed and patented by El mondorf (1963, 1966) to produce a high strength panel product (termed Embedded Fiber Board) at a fraction of the cost of producing plywood. A pilot plant at Palo Alto, California produced 12 mm thick boards containing flakes measuring 25 and 50 mm in length, a wood-cement-water ratio of 1:2.5:1 and pressed at up to 200 psi (14 kg/cm²) to a target density of between 1000 and 1200 kg/m³. The cement:wood ratio could be varied between 2 and 5 parts cement to balance durability, weather resistance and strength against cost, machinability and handling on building sites. The flexural properties of non-oriented flake-boards were 14.8 MPa for MOR and 2071 MPa for MOE, whereas those of orientated flake-boards were 22.7 MPa and 6560 MPa for MOR and MOE respectively.
The development of resin-bonded OSB (Elmondorf 1965, McNatt et al. 1992, Youngquist 1999) led to a decline in interest in the cement-bonded variety, with its slow production rate, low machinability and ease of handling, and much lower strength-to-weight ratio. However, there is renewed interest in use of wood-cement flake-boards as structural building materials in countries such as China (Zhao 1992, Tu 1995, Xiong 1996) as they possess a favorable combination of properties including strength, resistance to moisture, biodeterioration and fire, and low manufacturing cost. Cement-bonded boards that employ conventional OSB manufacturing technology and combine the high production rate and flexural properties of OSB with high fire resistance have also received renewed interest in the North American construction market (Bach and Kolker 1995). Here a combination of rapid setting magnesite cement, an MDI resin and hot pressing are used to achieve the production rate of OSB. The early work of Elmondorf (1965) demonstrated that mechanical strand orientation can be readily applied in the manufacture of cement-bonded flake-boards, however the moisture present in and on the strans is critical to the success of the process. There must be just enough to bind the cement powder to the strans during mat formation or 'air-felting' but not enough to enable the flakes to clump together.

The other major avenue for improving cement-bonded flakeboard properties including dimensional stability is flake pre-treatment with inorganic and/or organic additives. Novel methods exist for preparing wood flakes for use in wood-cement composites by pre-mixing them with relatively inexpensive minerals. A patent by Walter and Walter-Gurzel (1991) indicates that pre-mineralization of small wood flakes using a 13-15% solution of Al2(SO4)3 followed by a water-based suspension of finely ground kaolin (Al2O3, 2SiO2) significantly improves the performance of wood-cement composites. An Australian patent lodged by Gamage (1997) involving the pre-treatment of sawdust with sodium meta-silicate powder, MgCO3, MgSO4, Polyethylene glycol (PEG) and lime achieves a similar effect. Pre-mineralization methods deserve to be tested on mallee wood and bark residues with the aim of improving board strength and resistance to water.

CONCLUSIONS

Cement-bonded flake-boards are receiving renewed attention as building materials because of their strength properties, resistance to fire, moisture and biodeterioration, and cost effective manufacturing. Flake-boards manufactured from commercial pine and low density blue gum at wood-cement ratio of 1.3 were of good quality. The addition of accelerators (CaCl2 and MgCl2) further improved the properties of boards made from blue gum. Average MOR of boards made from commercial blue gum with MgCl2 was 15 MPa, indicating unusually good potential for this eucalypt species for the manufacture of cement-bonded flake-boards. Thickness swelling of boards made from untreated wood flakes of all species was above 2% the maximum level permitted by ISO 8335, however hot water-extraction of flakes or the use of accelerators improved thickness swelling in most cases. Interestingly, the flake-boards exhibited increasingly high variation in MOE for a given MOR above about 8 MPa. This may have been caused by localized variation in board structure arising from hand formation of mats and variation in flake geometry. Board flexural properties were greatly reduced in the cases where flakes from higher density wood (blue gum 2 and mallee) were used. Addition of accelerators at 2% w/w cement significantly improved the strength of boards made from mallee flakes, but not enough to meet the minimum properties specified in ISO 8335. Adjustment of flake thickness, geometry and alignment, and use of pre-treatment are necessary to further improve the properties of cement-bonded boards manufactured from mallee wastes.
ACKNOWLEDGEMENTS

This project was financed by the Rural Industries Research and Development Corporation (RIRDC) and the Western Australian Department of Conservation and Land Management, Natural Heritage Trust Project No. 973849 through the auspices of Mr John Bartle (Farm Forestry Unit). We are very grateful also to Dr Ryde James (ANU Forestry), and Dr Anne Cowling and Ms Christine Donnelly (ANU Statistical Consulting Unit) for their in-kind support for the project.

REFERENCES


APPENDIX 2 Supplementary information for Chapter 2

1. Portland cement components and hydration reactions

1.1 Origin and components

Modern portland cements are produced by the clinkering of a mix of the following minerals: calcium oxide (CaO) from limestone and coral deposits; silica (SiO₂) from sands and shales; and aluminium oxide (Al₂O₃) and ferric oxide (Fe₂O₃) from ores (Brunauer and Copeland 1964, Lea 1971). These raw materials are crushed, mixed and pre-heated to \( \approx 800^\circ\text{C} \) and then passed through a large rotary kiln where they are cooked at 1300-1500°C for 1-2 minutes. The clinker then falls through cooling grates and is refined with a small amount (3-6%) of gypsum (CaSO₄) in a large water-cooled ball-mill. The final product constitutes around 60% of the original raw material by weight.

The resulting portland cement is a hydraulic inorganic binder activated by water whose principal phases are tricalcium silicate (C₃S, or 'Alite'), \( \beta \)-dicalcium silicate (C₂S, or 'Belite'), tricalcium aluminate (C₃A) and tetracalcium aluminoferrite (C₄AF), with Pentacalcium tricaluminate (C₅A) as a minor constituent. Their approximate proportions in portland cement clinker are given in Table 1 (information from Lea 1971, Brandt 1995, Taylor 1997).

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviated Formula</th>
<th>Proportion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium silicate (C₃S)</td>
<td>3CaO·SiO₂</td>
<td>25-60</td>
</tr>
<tr>
<td>( \beta )-Dicalcium silicate (C₂S)</td>
<td>2CaO·SiO₂</td>
<td>15-20</td>
</tr>
<tr>
<td>Tricalcium aluminate (C₃A)</td>
<td>3CaO·Al₂O₃</td>
<td>4-12</td>
</tr>
<tr>
<td>Tetracalcium aluminoferrite (C₄AF)</td>
<td>4CaO·Al₂O₃·Fe₂O₃</td>
<td>8-12</td>
</tr>
<tr>
<td>Pentacalcium tricaluminate (C₅A)</td>
<td>5CaO·3Al₂O₃</td>
<td>1-2</td>
</tr>
<tr>
<td>Minor constituents</td>
<td></td>
<td>5-8</td>
</tr>
</tbody>
</table>

In practice, these phases do not exist in a pure state; rather they contain small amounts of a wide variety of impurities including magnesium oxide, and sodium, potassium, sulphur, phosphorus, titanium, vanadium, chromium and manganese compounds (Bensted 1983). The quantities of impurities are higher in portland cements that incorporate blast furnace slag, which affects phase reactivity, crystallisation and composition of hydration products. However, descriptions of the reactions of the pure phases in the presence of lime and gypsum gives good approximations of the most important hydration reactions occurring in portland cement (Bensted 1983). The quantities of each phase vary according to manufacturer and type produced; for example C₃S is suggested by Brandt (1995) to be present at between 38 and 60% and C₂S between 15 and 38% of portland...
cement. The proportions of these phases in five types of commonly available portland cement are shown later in Table 2 on p. 26. The proportions of C4AF and C4A can be up to 15 and 18% respectively. Minor constituents of portland cement include gypsum (3-6% of total), added to regulate setting time by preventing flash-set, and aid strength development and volume stability of the matrix (Taylor 1997).

Cement production is one of the most energy intensive of all industrial manufacturing processes, with a primary intensive physical energy requirement of between 6 and 8 GJ/t of portland cement produced (Scheuer and Sprung 1990, Martin et al. 1999). Most of this energy (=90%) is consumed by the high temperature rotary kiln clinkering process. However, a shift from wet and semi-dry to dry clinkering processes, as well as supplementation of fossil fuels, over the last decade has resulted in reductions in primary fuel energy costs of cement production (CANMET and Radian Canada Inc. 1993, Martin et al. 1999, Ruth et al. 2000). However the electrical energy required to pre-grind and blend the raw materials and finely pulverise the clinker is also highly significant, particularly in modern dry clinkering processes (Lowes and Bezant 1990).

Cement production can therefore account for a significant proportion of total energy consumption in developing nations, making this material relatively costly compared with traditional building materials such as wood or rock. Other issues associated with the manufacture and use of portland cement include high CO₂ emissions from combustion and decarbonisation of limestone during clinkering, and the production of nitrous and sulphurous oxides and other particulate pollutants (CANMET and Radian Canada Inc. 1993). Apart from improved energy efficiency in the clinkering process, energy costs of cement production can also be reduced by the partial supplementation of portland cement with pulverised blast furnace slag, oil-shale, fly ash and volcanic pozzolanas (Scheuer and Sprung 1990).

1.2 Principal hydration reactions

The four major components of pure portland cement exist as distinct phases in unhydrated cement clinker, each possessing its own specific reactivity with water and distinct hydration products with different morphological characteristics and contributions to final cement strength (Marchese 1983). The hydration reactions of the major phases are given by Bensted (1983) and Taylor (1997), and relate mainly to reactions occurring during the main period of hydration, i.e. during the first 9 to 24 hours. Notwithstanding cement composition, minor changes in the amount of water available, temperature, pH and foreign materials in the mix significantly affect the hydration process and types of hydrates produced (Brunauer and Copeland 1964, Witt 1966). It is important to note that after initial setting, hydration reactions continue to contribute to the hardening of cement for months and years (Brunauer and Copeland 1964). A good overview of the reactions and
hydration mechanisms of portland cement forms the basis for a better understanding of the effects of admixtures that accelerate or retard cement hydration, and hence these are briefly summarised here from information contained in Benstead (1983).

**Tricalcium and β-dicalcium silicate (C3S and C2S)**

The hydration of C3S and C2S involves a sequence of overlapping reactions of different rates. There is an immediate and short-lived exothermic reaction on contact with water, followed by the induction or 'dormant period of relative inactivity in which an exchange of ionic species occurs between solution and the solid anhydrous C3S particles (Skalny and Young 1989). This diffusion-controlled process leads conditions that herald the main period of hydration generating a heat of hydration of ~500 J/g to form a family of calcium silicate hydrates (C-S-H) and solidified calcium hydroxide (Ca(OH)\(_2\)) known as 'portlandite' (1):

\[
\text{(1)} \quad 2\text{Ca}_3\text{SiO}_4 + 6\text{H}_2\text{O} \rightarrow \text{Ca}_6\text{Si}_2\text{O}_7\cdot 3\text{H}_2\text{O} + 3\text{Ca(OH)}_2
\]

B-C2S hydrates much more slowly than C3S but forms a similar type of C-S-H (2):

\[
\text{(2)} \quad 2\text{Ca}_2\text{SiO}_4 + 4\text{H}_2\text{O} \rightarrow \text{Ca}_6\text{Si}_2\text{O}_7\cdot 3\text{H}_2\text{O} + \text{Ca(OH)}_2
\]

This reaction has a lower heat of hydration (250 J/g) and produces Ca(OH)\(_2\), which facilitates strength development. Ca(OH)\(_2\) can be amorphous as well as in the form of hexagonal crystals during the early stages of cement hydration, but becomes totally crystalline in hardened cement.

C-S-H hydrates from reactions (1) and (2) to form amorphous, poorly crystallised, non-stoichiometric materials of di- and poly-silicates which subsequently form the main binder in hardened portland cement. They are also the main contributors to early compressive strength development. Most of the hydration reaction for C3S occurs within 28 days, but can continue on a very small scale for up to a year, whereas less than half of the C2S hydrates within the first 28 days, and considerable hydration occurs after 1 year. Sulphate from the added gypsum enters the C-S-H phase and contributes to early compressive strength development (Brunauer and Copeland 1964, Benstead 1983, Taylor 1997).

**Tricalcium aluminate (C3A)**

C3A hydrates very rapidly on its own in water with a high heat of hydration (1340 J/g) (3):

\[
\text{(3)} \quad 2\text{Ca}_2\text{Al}_2\text{O}_6 + 2\text{H}_2\text{O} \rightarrow \text{Ca}_9[\text{Al(OH)}_4]_2\cdot 3\text{H}_2\text{O} + 2[\text{Ca}_2\text{Al(OH)}_2\cdot 3\text{H}_2\text{O}]
\]

(C2AH8) (C4AH13)
These initial hydrates, C2AH8 and C4AH13, emerge as unstable hexagonal plates which convert to the more stable 2[Ca3Al(OH)6]2 + 9H2O (C3AH6) which take on cubic form as the hydration temperature rises above 40°C (Stein 1963). At ambient temperature the hexagonal hydrates will persist for over 24 hours (Benstead 1983).

The almost instantaneous hydration of C3A to C4AH13 in the presence of lime requires the addition of gypsum (CaSO4) to portland cement to prevent flash setting and to regulate the timing of the exothermic reaction. In the presence of lime and gypsum in portland cement, C3A undergoes a series of reactions to reach its final hydrate products. Once water is added, two simultaneous reactions take place in an alkaline solution containing Ca2+ and SO4- ionic species generated by the dissolution of some of the CaSO4 and lime. C3A reacts rapidly with Ca(OH)2 and water to form nuclei of the calcium aluminate hydrate C3AH13 (4):

\[
(4) \quad \text{Ca}_3\text{Al}_2\text{O}_6 + \text{Ca}(	ext{OH})_2 + 12\text{H}_2\text{O} \rightarrow 2[\text{Ca}_2\text{Al}((\text{OH})_2)_3\text{H}_2\text{O}]
\]

(C3AH13)

As the C3AH13 is formed, it reacts with the CaSO4 in solution to form a surrounding insoluble sheath known as 'etteringite', with concurrent generation of Ca(OH)2 (5):

\[
(5) \quad 2[\text{Ca}_2\text{Al}((\text{OH})_2)_3\text{H}_2\text{O}] + 3[\text{CaSO}_4\cdot 2\text{H}_2\text{O}] + 14\text{H}_2\text{O} \rightarrow 2[\text{Ca}_6\text{Al}((\text{OH})_6\text{H}((\text{SO}_4))_2\cdot 26\text{H}_2\text{O}]
\]

+Ca(OH)2

This layer of etteringite creates a semipermeable barrier to water, temporarily halting the further rapid development of C3AH13 nuclei until sufficient water diffuses through the etteringite to allow hydration at a more controlled rate. Etteringite exhibits strong crystal morphology, forming hexagonal needles or aligned columns.

Once there is no longer sufficient CaSO4 to continue forming etteringite, the C4AH13 nuclei that had developed from the rapid initial hydration of C3A react with the surrounding etteringite to form a calcium aluminate hydrate monosulphate (6):

\[
(6) \quad \text{Ca}_6\text{Al}((\text{OH})_6\text{H}((\text{SO}_4))_2\cdot 26\text{H}_2\text{O} + 4[\text{Ca}_2\text{Al}((\text{OH})_2)_3\text{H}_2\text{O}] \rightarrow 3[\text{Ca}_4[\text{Al}(\text{OH})_6]]\text{SO}_4\cdot 6\text{H}_2\text{O} + 2\text{Ca}((\text{OH})_2 + 20\text{H}_2\text{O}
\]

This starts to occur after 8 to 16 hours, once the maximum hydration temperature is reached. Any further unreacted C3A hydrates to C4AH13, which in combination with the monosulphate, forms the final solid product from the hydration of C3A. Both the C4AH13 and monosulphate exhibit similar morphological characteristics, crystallising as stacked hexagonal plates to form
columns. Although strongest exothermically, the hydration of C3A contributes little to the strength development of portland cement.

**Calcium aluminoferrite (C4AF)**

C4AF hydrates at a slower rate than C3A, with a lower heat of hydration (420 J/g) and also contributes little to strength development. In the presence of lime and gypsum, the hydration reaction series for C4AF is similar to that of C3A, with nuclei of Fe³⁺-substituted C₄AH₁₃ and ettringite formed, followed by the later formation of Fe³⁺-substituted monosulphate. The three reactions are as follows:

Initial formation of Fe³⁺-substituted C₄AH₁₃ nuclei (7):

\[
(7) \quad \text{Ca}_2\text{AlFeO}_5 + 2\text{Ca(OH)}_2 + 11\text{H}_2\text{O} \longrightarrow 2[\text{Ca}_2\text{Al}_{1/2}\text{Fe}_{1/2}(\text{OH})_7\cdot 3\text{H}_2\text{O}]
\]

Concurrent formation of Fe³⁺-substituted ettringite (8):

\[
(8) \quad \text{Ca}_2\text{AlFeO}_5 + \text{Ca(OH)}_2 + 3[\text{CaSO}_4\cdot 2\text{H}_2\text{O}] + 25\text{H}_2\text{O} \longrightarrow 2\text{Ca}_6[\text{Al}_{12}\text{Fe}_{12}(\text{OH})_6]\text{[(SO}_4)_3\cdot 26\text{H}_2\text{O}]
\]

Formation of Fe³⁺-substituted monosulphate (9):

\[
(9) \quad 4[\text{Ca}_2\text{Al}_{1/2}\text{Fe}_{1/2}(\text{OH})_7\cdot 3\text{H}_2\text{O}] + \text{Ca}_6[\text{Al}_{12}\text{Fe}_{12}(\text{OH})_6]\text{[(SO}_4)_3\cdot 26\text{H}_2\text{O} \longrightarrow 3[\text{Ca}_4(\text{Al}_{12}\text{Fe}_{12}(\text{OH})_6]\text{[(SO}_4)_3\cdot 6\text{H}_2\text{O} + 2\text{Ca(OH)}_2 + 20\text{H}_2\text{O}}
\]

The final hydration products, Fe³⁺-substituted monosulphate and C₄AH₁₃, combine in solid solution with those formed from C3A as they are structurally very similar.

1.3 Mechanisms of hydration

The characteristic hydration curve for pure portland cement, an example of which is shown in Figure 1, is characterised by an initial short period of exothermic hydrate formation followed by a dormant or 'induction' period. Most of the heat evolved during this first short period of hydration is derived from the heat of wetting of the cement powder and hydration of free CaO (Double 1983). The duration of the subsequent dormant or 'induction' period depends on ambient temperature, purity of the mineral phases, particle size, water to solid ratio, and the presence of admixtures such as retardants, fillers or accelerators (Bensted 1983). The dormant period is believed to be primarily caused by the formation of the coating of C-S-H known as 'eterteringite' around newly hydrating clinker particles soon after the addition of water (Double et al. 1978, Jennings and Pratt 1979,
Taylor 1997), although exactly what triggers the end of the dormant period has been subject to much debate.

The mechanisms of hydration of the predominant silicate phases of portland cement have been extensively investigated, giving rise to numerous complex and contradictory theories. The situation is further complicated by the likelihood of different factors controlling hydration rate during different phases of hydration (Double 1983). According to Double (1983) the rate of early hydration is controlled by at least three factors: (i) hydrolysis of anhydrous clinker phases; (ii) nucleation and growth of hydration products; and (iii) diffusion of water and dissolved ions such as Cl− or other anions from admixtures through coatings of hydration products around cement grains.

The initiation and development of the main phase of hydration has been subject to two general schools of thought; theories of 'delayed nucleation' (Young 1972, Young et al. 1973, Tadros et al. 1976a,b) and later theories of 'protective coating' (Bensted 1983, Double 1983, Taylor 1997). The 'delayed nucleation' theories propose that once water is added there is rapid initial hydrolysis and dissolution of C3S particles, which carry a positive surface charge.

![Figure 1 Hydration temperature vs time curve for Ordinary portland Cement type I showing the influence of accelerating/retarding admixtures (from Thomas 1987).](image)

The induction period is initiated by the adsorption of Ca2+ ions onto the silica-rich surface of C3S particles, greatly reducing their further dissolution. The paste becomes supersaturated with Ca2+ and OH− ions as the silicate ions inhibit the growth of Ca(OH)2 crystals. Once this reaches about 1.5 to 2 times the saturation concentration, Ca2+ and OH− ions start to precipitate out of solution and into nuclei that grow and remove further ions from solution, allowing rapid hydration.
of C-S-H to begin. However, according to Double (1983) these theories are not accurate, since crystalline Ca(OH)$_2$ has been detected in cement paste sometimes long before supersaturation by Ca(OH)$_2$ and the end of the induction period (Slegers and Rouxhet 1977), and pre-seeding cement paste with Ca(OH)$_2$ crystals does not significantly accelerate hydration (Odler and Dorr 1979).

In contrast, 'protective coating' theories view the growth of Ca(OH)$_2$ crystals as an effect of renewed hydration after the induction period, rather than the cause (Bensted 1983, Double 1983). One of the major 'protective coating' theories is the osmotic membrane model (Double et al. 1978, Birchall et al. 1978 and 1980, Double 1983). This regards the C-S-H gel coating around cement clinker grains as semi-permeable, allowing water and Ca$^{2+}$, but not silicate ions, to be slowly imbibed up to a point where the surrounding layer is ruptured by osmotic pressure. This terminates the dormant period and renewed hydration can then take place, allowing the growth of secondary silicate phase C-S-H hydration products, which take the form of hollow fibrils. The rate of hydration is therefore determined by the structure, thickness and permeability of C-S-H membranes (Double 1983) whose formation in turn is influenced by cement mineralogy and the presence of admixtures that accelerate or retard hydration (Thomas 1987). A contradictory observation to the proposed osmotic pressure model is that the C-S-H membrane that restricts the hydration of silicate clinker grains is physically disrupted by the nucleation and growth of Ca(OH)$_2$ crystals in and on their surface (Jennings and Pratt 1979, Barnes et al. 1980). It has been suggested that the hollow fibrils formed during the early stages of cement hydration are not secondary silicate phase products, but are composed of ettringite formed before the silicate phases begin to hydrate normally.

The above discussion indicates that the chemical diffusion, adsorption, hydration and product crystallisation processes that occur after portland cement is mixed with water are very complex and may not be definitively explained using a single model.

1.4 The action of accelerating admixtures

The addition of an accelerating admixture such as CaCl$_2$ to portland cement decreases the dormant period of hydration caused by the early formation of ettringite and increases heat evolution during renewed hydration as shown in Figure 2 (Ramachandran 1994).

There have been several theories as to how CaCl$_2$ increases the rate of cement hydration. CaCl$_2$ is thought to act mainly on the C3S phase, since Ca$^{2+}$ and Cl$^-$ ions together are very effective in accelerating the hydration of C3S (Ramachandran 1994). Early theories (e.g. Kleinlogel 1923) suggested that acceleration occurred via the formation of calcium oxychloride or chloroaluminate hydrates, but these were later discounted because stable complexes are only formed in the presence of much higher concentrations of CaCl$_2$ (>18 %) than those that are normally used in cement and cement composites. Later theories (e.g. Rosenberg 1964, Berger et al. 1972, Ramachandran 1981) suggested that CaCl$_2$ acted as a catalyst for hydration reactions rather than undergoing incorporation
into hydrate products; however the mechanism by which this occurs is not clear (Ramachandran 1994).

Figure 2 Influence of different quantities of CaCl$_2$ on the heat evolution characteristics of hydrating C3S (from Ramachandran 1994)

Ramachandran (1971) suggested that Cl$^-$ can exist in various states: as free ions in solution; as a complex on the surface of C3S grains during the dormant period; as a chemi-sorbed layer on C-S-H surfaces; and incorporated within the interlayers and lattice structure of C-S-H. This incorporation of chloride into the C-S-H gel layers produces marked changes in their microstructure and morphology, which in turn changes the capillary porosity distribution and permeability (Young et al. 1973, Young 1974, Le Sueur et al. 1981, Singh and Ojha 1981, Thomas 1987). Numerous studies have found that the C-S-H gel layer formed in the presence of CaCl$_2$ is less compacted and more open and spongy than that found in ordinary portland cement. According to Double (1983) and Thomas (1987) this can effectively reduce the dormant period and increase the rate of hydration by allowing earlier penetration by water followed by more rapid deterioration of the C-S-H gel layer. Osmotic pressure on the C-S-H gel membrane may also be increased by the inwards diffusion of free Cl$^-$ ions (Singh and Ojha 1981). The morphology of C-S-H hydration products has been shown to change from needles to plate-like or crumpled foil-like structures in the presence of CaCl$_2$. This is thought to be due to the adsorption of Cl$^-$ ions on the C-S-H surface and their subsequent incorporation into the lattice structure of hydrated C-S-H (Berger et al. 1972, Collepardi and Marchese 1972, Ramachandran 1994). Cured cement containing CaCl$_2$ has been shown to contain thick, cone-like crystals measuring up to 5 microns in diameter in free spaces (such as wood lumens) by Ahn and Moslemi 1980), which were suggested to provided much greater mechanical
interlocking within the cement and between wood and cement within a wood-cement composite structure.

The effect of adding different admixtures on heat evolution in portland cement is shown in Figure 3 (Double 1983). According to Collepardi et al. (1971) and Kantro (1975) a range of anions in inorganic admixtures can be ranked in order of their accelerating effect on the hydration of C3S:

\[
\text{SO}_4^{2-} > \text{OH}^- > \text{Cl}^- > \text{Br}^- > \Gamma > \text{NO}_3^- > \text{CH}_3\text{COO}^- \quad \text{(Collepardi et al. 1971)}.
\]

\[
\text{Cl}^-/\text{Br}^- > \text{SCN}^- > \Gamma > \text{NO}_3^- > \text{ClO}_4^- \quad \text{(Kantro 1975)}.
\]

Figure 3 Effect of different admixtures on cement hydration (from Double 1983).

However there is considerable evidence that Cl\textsuperscript- is better at accelerating the hydration of portland cement than \text{SO}_4^{2-}. The ranking of anions can also be confounded by the presence of different cations, in particular Ca\textsuperscript{2+} (Edwards and Angstadt 1966, Double 1983, Ramachandran 1994). Double (1983) has highlighted the similarity in ranking between the accelerating effects of different anions and their representation in dissolved electrolytes that cause flocculation of hydrophilic colloids in the Hofmeister series. Highly polarisable anions such as Cl\textsuperscript- readily adsorb onto and
deflocculate mineral colloids such as C-S-H gel and therefore tend to be present in the most effective cement-setting accelerators, although this is not the only explanation for their efficacy as accelerators. Solid-state diffusivity, which is higher for small monovalent anions such as Cl\(^-\), has also been shown to contribute significantly to their capacity to accelerate cement hydration (Collepardi et al. 1971, Skalny and Maycock 1975, Kondo et al. 1977, Thomas 1987). Kondo et al. (1977) suggested that the diffusion of Cl\(^-\) through outer layers of early formed hydrates into the zone of active reaction on a hydrating C3S particle could increase the outwards diffusion of OH\(^-\) ions, resulting in the faster precipitation of Ca(OH)\(_2\) which aids the decomposition of ettringite.

In inorganic salt admixtures, the cation type also affects the acceleration of cement hydration, although this is complicated by the effects on configuration of cations by the high pH (12-13) of cement (Kantro 1975, Double 1983). Double (1983) presents the following ranking for different cations added to cement at the same ionic concentration of 0.5 g-ion/L in the form of chlorides and nitrates:

\[
0.5\text{Ca}^{2+} > 0.5\text{Ni}^{2+} > 0.5\text{Ba}^{2+} > 0.5\text{Mg}^{2+} > 0.33\text{Fe}^{3+}/0.5\text{Co}^{2+} > 0.33\text{La}^{3+} >> \text{NH}_4^+/\text{K}^+ > \text{Li}^+ > \text{Cs}^+ > \text{Na}^+.
\]

In cement paste, cations exist mostly in a dissolved hydroxylated state (e.g. Ca(OH)\(_2\)), and the relative solubility of the hydroxide can be a critical factor determining whether the hydration of C3S is accelerated or hampered (Kantro 1975). For example, if the cation immediately forms a heavy insoluble hydroxide precipitate, as is the case when compounds containing cations such as Cu\(^{2+}\), Pb\(^{2+}\) or Zn\(^{2+}\) are added, then this can form a dense, impermeable coating around newly hydrating cement clinker grains, counteracting any accelerating effect of the associated anion. The effects of substances in wood that retard cement hydration are examined in further detail below.

2. Wood-cement chemical interactions

2.1 Early studies on wood-cement compatibility problems

The earliest suggestions of the importance of the effect of wood extractives on the manufacture of wood wool cement boards were made by Christensen (1948) and Sandermann and Dehn (1951). They suggested that both wood sugars and heartwood polyphenols were the cause of poor consolidation of cement in commercial WWCBs, and investigated the use of simple additives such as CaCl\(_2\) to counter the inhibitory effects of the extractives. Sandermann and Brendel (1956) later undertook a study of the effects of the different kinds of extractives found in wood on cement hydration. In their study model sugars (glucose, fructose, xylose, saccharose, cellobiose and raffinose) were added to cement in various concentrations. The sugars strengthened cement setting at very low concentrations (~0.125%) but retarded cement setting when added at increasingly
higher concentrations. It was found that fructose was less inhibitory than the other wood sugars, which was attributed to the observation that fructose formed a sparingly soluble precipitate in limewater. Sandermann and Brendel (1956) also suggested that there was a positive correlation between the ease of alkali degradation of sugars and the capacity of the sugars to inhibit cement hydration. They could not ascertain, however, whether the sugars themselves or their decomposition products in the alkaline cement paste were responsible for inhibiting cement hydration. Their study did, however, demonstrate that by hydrolysing sugars to their respective alcohols, their inhibitory effects on cement hydration could be greatly reduced.

The inhibition of cement setting by soluble carbohydrates in wood was subsequently studied by Biblis and Lo (1968), who showed that the concentration of reducing sugars such as glucose, xylose, mannose and fructose in wood directly influenced the setting time of wood-cement mixes. Fresh, spring-cut pine sapwood was less compatible with cement than sapwood from trees cut in winter because of its higher carbohydrate content. The increased cellobiose content of decayed wood was shown by Weatherwax and Tarkow (1964) to be responsible for the strong inhibitory effect of decayed wood on cement hydration.

Later work by Fischer et al. (1974) suggested that poor cement setting around wood wool strands resulted from the leaching of water-soluble polysaccharides from wood wool into the surrounding cement paste. It was suggested that the sugars were converted into inhibitory saccharinic acids as the concentration of Ca(OH)₂ in the hydrating cement paste increased. The inhibitory effects of sucrose and D-glucose on cement were examined using SEM by Ahn and Moslemi (1980). Their micrographs showed that the two types of sugars had very different effects on the morphology of the hydrates. In the case of D-glucose, fragile arrays of very fine needles were produced, whereas in the case of sucrose a combination of unhydrated cement grains and nodular structures of poorly hydrated cement were observed. Both of these morphologies differed from that of untainted cement, and it was suggested that they were correlated with the poor bonding between the affected cement binder and the wood surface.

2.2 Effect of wood extractive content

Soluble extractives in wood were identified early on as the principal cause of wood-cement compatibility problems, however, the question of how closely wood-cement compatibility is linked to the extractive content of wood (which can be readily determined) is yet to receive a satisfactory answer. Yasin and Qureshi (1990) suggested that the hot-water-soluble extractive content of various wood species was strongly correlated with their compatibility with cement suitability for wood-cement composites. This was based on the finding that the strength of experimental CBPs was
inversely proportional to the extractive content of the wood used to manufacture the boards. Boards made from the wood of Egyptian thorn (*Acacia nilotica* (L.) Del.) with a high extractive content of 7.8% were of only moderate strength whereas white poplar (*Populus alba* L.), which had the lowest extractive content of 2.4%, produced the strongest boards. Hachmi and Moslemi (1990) further suggested that wood-cement compatibility is strongly influenced by four extractive-related variables: hot-water extractive content; pH; base buffering capacity; and acid-to-base buffering capacity ratio (ABR). Using these variables they developed a strong predictive model ($r^2 = 0.95$) for wood-cement compatibility and suggested that woods with a hot-water extractive content above 7% and ABR below 2.5 would be incompatible with cement. The pH of wood extracts can strongly influence the suitability of wood for wood-cement composites (Gnanaharan and Dhamodaran 1985). Surprisingly, these studies have given little consideration to the likely influence of the actual chemical composition of wood extractives on the inhibition of cement hydration.

Nevertheless other studies indicate that the quantity of extractives may not be closely correlated with wood-cement compatibility. For example, Hachmi and Moslemi (1989), Hachmi *et al.* (1990) and Hachmi and Sesbou (1991) found that *Acacia mearnsii* was highly incompatible with cement even though its wood had a relatively low hot-water-soluble extractive content (7.8%) compared with other equally incompatible materials, cork oak (*Quercus suber* L.) and esparto grass (*Stipa tenacissima* L.), both of which had extractive contents in excess of 12% (Hachmi and Moslemi 1989). These findings suggest that the chemical composition of extractives may play a major role in influencing the compatibility of wood with cement. Accordingly, Hachmi and Moslemi (1989) found that the extractive content of wood could explain only 50% of the variation observed in wood-cement compatibility. Similarly, Tachi *et al.* (1988) found that *Acacia mangium* had approximately the same hot-water extractive content as three other species, *Paraserianthes falcataria, Eucalyptus deglupta* and *Gmelina arborea* (≈7%), but its inhibitory index for cement hydration was significantly higher. Another explanation for the poor correlation between watersoluble extractive content and wood-cement compatibility is that some inhibitory constituents (such as wood polyoses) are soluble in alkali but not in water (Schuerrch 1963), and their presence is therefore not reflected in water-soluble extractive content.

2.3 Effects of different wood constituents

The various components of wood react differently in the alkaline environment of portland cement paste. The retardation of cement hydration by organic admixtures has mainly been attributed to their effects on the C3S phase, but interactions with the aluminate phases may also be important (Double 1983). Inhibitory constituents in wood often cause enhanced early hydration of C3A,
resulting in greater enthalpy from wood-cement hydration samples within the first hour of mixing compared with cement controls (Wei et al. 2000a).

Lignin and cellulose have been shown to have low reactivity and therefore low inhibition of portland cement hydration (Clare and Sherwood 1954, Miller and Moslemi 1991a). Cellulose is not sensitive to alkali at ambient temperatures (Wangaard 1966, Thompson 1969) because of its crystalline nature, and therefore does not interact with portland cement to a great extent (Hachmi and Campbell 1989, Miller and Moslemi 1991a). This was demonstrated experimentally by Miller and Moslemi (1991a) by adding cellulose powder (Cellulose CP 11) and a model lignin compound (Indulin AT kraft pine lignin) at increasing amounts of up to 1% to cement and examining the effects of these on cement hydration. There was no significant decrease in enthalpy of cement hydration as a result of adding cellulose. Lignin slowly loses between 2 and 10% of its weight when exposed to alkali at ambient temperature, resulting in the formation of soluble alkali-lignin complexes (Wise and Jahn 1952, Wangaard 1966). This process is accelerated once the surrounding hemicelluloses and lignin that 'encrust' the cellulose have been degraded (Ott et al. 1954, Singh 1979). Despite this, Miller and Moslemi (1991a) found that the slow solubilisation of lignin did not greatly affect cement hydration. There is evidence, however, that wood and fibres that have been previously exposed to alkali can adversely affect cement setting (Blankenhorn et al. 1994).

While native lignin has no effect on cement hydration, lignin derivatives from the sulphite pulping process (a mixture of calcium-magnesium lignosulphonic acids), are powerful cement-setting retardants (Mark 1938) and are therefore used commercially as plasticisers and water reducers (Ernsberger and France 1945, Milestone 1976). Paradoxically, despite their effect on initial setting, lignosulphonates when added to portland cement enhance the strength and resistance to freezing, and thawing of concrete (Ernsberger and France 1945, Melnikova and Bulnaeva 1995), although the effects of lignosulphonates on the properties of wood-cement composites have not been investigated to any extent.

The water- and alkali-soluble sugars present in wood and/or their alkaline degradation products, including saccharinic acids, have all been shown to be capable of retarding cement hydration (Clare and Sherwood 1954, Sandermann et al. 1960, Biblis and Lo 1968, Fischer et al. 1974, Simatupang 1986, Miller and Moslemi 1991a). Wood sugars adversely affect cement setting in the vicinity of the wood surface (Weatherwax and Tarkow 1964, Biblis and Lo 1968). Upon drying, water-soluble sugars migrate to the surface of wood (Fischer et al. 1974, Long 1978) and can interfere with bonding at the wood-cement interface (Weatherwax and Tarkow 1964, Fischer et al. 1974, Ahn and Moslemi 1980, Hachmi and Campbell 1989). Other water-soluble wood extractives, including heartwood polyphenols, can also retard cement hydration (Weatherwax and Tarkow 1964, Hachmi
and Campbell 1989, Miller and Moslemi 1991a). The effects of wood sugars and non-carbohydrate polyphenols on cement hydration are examined in Sections 2.4 and 2.5 below.

2.4 Polyoses, alkaline degradation and the effect of sugars on cement hydration

The processes by which wood sugars (polyoses) and/or their degradation products interact with alkali and cement clinker minerals in cement paste to affect hydration reactions are complicated and, as the foregoing discussion suggests, are still not clearly understood.

Polyoses, which are defined by Fengel and Wegener (1984) as the non-cellulosic polysaccharide components of the hemicelluloses, occur as short chains (degree of polymerisation < 200) in close association with cellulose in the wood cell wall. The principal constituents of wood polyoses are the hexoses glucose, mannose and galactose and the pentoses xylose and arabinose (Fengel and Wegener 1984). Polyose chains surround the cellulose microfibrils in a loose mantle, with amorphous native lignin bonded between the microfibrils and in places penetrating the polyose mantle (Fengel 1971, Hoffmann and Parameswaran 1976). Most wood polyoses are insoluble in water but are alkali-soluble, and hence are more readily hydrolysed by acids or alkalis than cellulose (Schuerch 1963). The destabilisation of lignin in alkaline solution exposes polyose chains, making them vulnerable to alkali attack (Hoffmann and Parameswaran 1976). Polyose chains are then subject to several types of alkali-induced chemical reactions, including hydrolytic, oxidative and peeling reactions (Rowell et al. 1969, Goldstein 1984).

In alkaline solution sugars undergo a complex series of reactions resulting in isomerisation and fragmentation (Boelhouwer et al. 1956, Sowden 1957, Graham-Solomons 1984). Alkali-induced depolymerisation of wood polyoses is a stepwise process involving chain end groups, and is referred to as a 'peeling' reaction (Sjostrom 1981). Strong alkali converts monosaccharides and certain end groups of polysaccharides to various carboxylic (saccharinic) acids, successively lowering the degree of polymerisation of polyose chains (Whistler and BeMiller 1958, Sjostrom 1981). Alkaline degradation of simple monosaccharides such as D-glucose results in the formation of lactic acid plus a complex mixture of 5- or 6-carbon saccharinic acids that are isomeric to the starting sugars (Sowden 1957, Corbett 1963).

An important process in the deterioration of wood polyoses is oxidative degradation, which involves the action of molecular oxygen in the presence of alkali (Rowell et al. 1969, Goldstein 1984). Linkages between sugar units are undermined by free radicals generated by the decomposition of hydroperoxides, a process that is catalysed by the presence of transition metals such as chromium, manganese, iron, cobalt and nickel. These metals are only present in trace amounts in portland cement, except for iron which is present in larger quantities (Lea 1971). Ferric ions may also be present in common cement-setting accelerators.
Other reactions include hydrolytic cleaving of ester and acetal links of the polyose monomers, resulting in the creation of free hydroxyl groups along the chain and dissolution of acetate ions. It has been suggested that hydroxyl groups as well as carboxyl and acetyl functional groups are involved in the formation of insoluble complexes with calcium, aluminium and iron cations in cement paste which retard or disrupt cement hydration reactions (Clare and Sherwood 1954, Young 1970, Mariampolskii et al. 1974, Thomas and Birchall 1983).

The alkaline degradation of simple short-chain polysaccharides by cement paste has long been thought to be the key initial step in the inhibition of cement hydration by wood (Bruere 1966, Young 1968, Hachmi and Campbell 1989, Miller and Moslemi 1991a). Early experiments by Taplin (1960) and Bruere (1966) correctly suggested that a wide range of mono-, di-, tri- and polysaccharide chains present in plant materials would hydrolyse extensively in cement paste to produce reducing sugars which would in turn be converted into saccharinic acids containing the HO-C-C=O group. It was suggested that this functional group could be adsorbed onto hydrating cement grains, blocking access to water and preventing hydration from proceeding normally (Taplin 1960, Bruere 1966). Sugar oxidation products easily form insoluble precipitates with Ca$^{2+}$ ions, to produce insoluble products such as calcium α-D-isosaccharinate (Whistler and BeMiller 1963a and b). Cement-setting retarders containing 6-carbon aldaric (dicarboxylic) and aldonic acids (compounds resulting from oxidation of aldohexoses such as D-glucose) have also been found to form insoluble cyclic chelate compounds with Ca$^{2+}$ ions at four or more active hydroxyl sites (Mariampolskii et al. 1974). Bruere (1966) found that the non-reducing sugars, raffinose and sucrose, were more powerful retardants than reducing sugars including arabinose, xylose, mannose, galactose, glucose and fructose. In accordance with the theory of Sanderman and Brendel (1956), however, Bruere (1966) also suggested that the more stable a sugar is in alkali (using αα-trehalose as an example) the less likely it is to retard cement hydration.

Subsequent studies contradict this early theory (Previte 1971, Milestone 1977, Thomas and Birchall 1983). These later studies suggest that the more resistant a sugar or its oxidation product is to alkaline degradation in cement paste the more likely it is to retard the normal development of hydrates. Previte (1971), for example, demonstrated that mono- or polysaccharides which are stable or very slow to break down in alkaline cement paste (such as sucrose and glucose) are much more efficient at inhibiting cement hydration than sugars that are readily degraded by alkali, such as fructose, in accord with the experimental findings of Bruere (1966).

Milestone (1977) studied the effects of glucose and its alkaline oxidation to saccharinic acids on the hydration of C3A (the most important phase in the early hydration and setting of portland cement) pastes. The saccharinic acids and their derivatives, which are very stable in alkali, were ten times more inhibitory than glucose (which oxidises readily in alkali to saccharinic acids). These
studies suggested that good stability of either the sugar or its oxidation products (such as the saccharinic acids) in alkali increased the ability of the sugar to retard cement hydration. These studies also accord with the finding of Sandermann et al. (1960) that hydrolysis of alkali-resistant sugars to their respective alcohols reduces the inhibitory effects of the sugars.

Despite the lack of agreement as to how sugars affect cement hydration, it has certainly been established that different sugars vary in the degree to which they inhibit the hydration of portland cement (Double 1983, Thomas and Birchall 1983, Miller 1987). A ranking of common sugars for their retarding effect was made by Thomas and Birchall (1983) and is reproduced in Figure 4. D-glucose and D-mannose are much slower to degrade than D-fructose (Whistler and BeMiller 1958). Note, however, that glucose monomers have been ranked as neutral in terms of the ability to retard cement hydration (Double (1983).

![Figure 4](sugar_retardation.png)

**Figure 4** Sugars (reducing and non-reducing) listed in order of their capacity for retarding the hydration of portland cement (from Thomas and Birchall 1983).

### 2.5 Possible mechanisms of inhibition of cement hydration by wood constituents

Early work by Stein (1961a and b) examined the effects of non-ionic organic compounds (all polyalcohols) and ionic cations and anions on the hydration of portland cement using isothermal calorimetry. Non-ionic organic polymers were thought to be integrated into the protective ettringite sheath of hydrating C3S grains, resulting in a less permeable, longer lasting protective coating which prolonged the induction/dormant period. Organic electrolytes, on the other hand, were suggested to interfere with the normally positive surface charge on newly hydrating grains of
the silicate and aluminate phases. Organic anions would likely be removed from solution and attracted to the positively-charged surface of newly hydrating cement grains, resulting in neutralisation or conversion to a negative charge, and the suspension of further hydration while there is still a quantity of organic anions in solution. Organic anions in the form of monomers have relatively little influence on C3S, but strongly inhibit the hydration of C3A. The phenomena of adsorption and changes in surface charge of hydrates is discussed further below.

The retarding actions of polyhydroxy carboxylic and aliphatic acids such as citrates, tartrates and lignosulphonates and the naturally occurring polyoses found in wood may be different depending on whether they remain in solution in the cement suspension or are adsorbed onto newly hydrating clinker grains. In the case of the polyhydroxy carboxylic acids, cement inhibition is dependent on the presence of hydrocarboxylic groups that are capable of rapidly complexing Ca\(^{2+}\) ions in cement paste (Double 1983). EDTA is another agent which rapidly removes Ca\(^{2+}\) ions from cement suspension solutions Thomas and Double (1983). These authors showed that, in cement pastes containing an effective aliphatic compound, abnormally high levels of soluble silicate are generated in the suspension immediately, as shown in Figure 5.

Solubilised SiO\(_2\) strongly retards the nucleation and growth of Ca(OH)\(_2\) according to the delayed nucleation theory for cement hydration. The silicate phase is solubilised by the preferential sequestration of calcium, which in turn is believed to affect the precipitation of C-S-H gel. The level of soluble silica induced by the addition of aliphatic acids such as citric acid or EDTA is initially very high but diminishes within about 10 minutes of mixing. This phenomenon is explained by Thomas and Double (1983) as the initial scavenging of Ca\(^{2+}\) by aliphatic acids which occurs in solution with a stoichiometric quantity of 1 organic anion to 1 Ca\(^{2+}\) cation. Once the organic anions are used up, further solubilisation of silica ceases, allowing growth of Ca(OH)\(_2\) and the normal hydration of the silicate phases to proceed. This delay can be lengthened in a controlled manner by the addition of greater quantities of aliphatic acid retarder or shortened by the addition less, or by the addition of extra Ca\(^{2+}\) in the form of CaCl\(_2\).

In contrast to the behaviour of aliphatic acid retarders, alkali-stable saccharinic admixtures (such as those generated by the degradation of plant carbohydrates) are believed to be adsorbed almost immediately onto the surface of newly hydrating C-S-H or Ca(OH)\(_2\) grains, creating an impermeable barrier which effectively inhibits further growth (Birchall and Thomas 1984, Taylor 1997). Figure 5 from Thomas and Double (1983) shows that the concentration of soluble SiO\(_2\) in cement paste does not begin to increase until about 10 min after mixing, after which highly inhibitory levels of SiO\(_2\) in solution accumulate over the first hours after mixing.
The accompanying precipitation of an impermeable barrier around newly hydrating cement grains was an early theory to explain cement inhibition by organic molecules that has been proposed by various researchers, including Forsen (1938), Sandermann and Brendel (1956), Suzuki and Nishi (1959), Bruere (1966), Milestone (1977), Young (1968). A complex of saccharide anion-O-Ca-OH was believed to form a densely packed sheath on the surface of growing C-S-H or Ca(OH)$_2$ nuclei.

The above ‘adsorption’ theory was first used to explain the ‘poisoning’ of cement by wood carbohydrates by Sandermann et al. (1960). Electron microscopy of hydrating cement paste containing wood flour after 1 hour indicated that the development of the microcrystalline structure in the toberomite gel matrix was severely retarded. When wood flour was present in the cement the initial hydrates, which form the nuclei for further crystallisation, started to develop normally but ceased shortly afterwards. The authors used glucose with a radioactive marker as a simple model inhibitory compound to monitor the formation of insoluble compounds between calcium and glucose. The results of Sandermann et al. (1960) supported the suggestion that the formation of an impermeable layer of calcium gluconate around developing hydrate nuclei in cement containing glucose prevented the further hydration of cement. These authors also produced the first X-ray diffraction spectra of wood and cement, illustrating the effects of adding two different kinds of inhibitory extractives from wood (tannin or starch) on the formation of calcium-silicate hydrates, which are shown in Figure 6.
The inhibition of cement hydration by organic admixtures such as saccharinic acids and lignosulphonates has been attributed primarily to their effects on the C3S phase, but interactions with the aluminate phases (such as C3A and C4AF) may also be important (Milestone 1977, Double 1983). The idea of an impermeable barrier being formed around developing hydrate nuclei by insoluble calcium gluconate has been further investigated using phase analysis. X-ray diffraction spectra (Singh 1975 and 1976) and differential thermal analysis (Milestone 1977) have been used to demonstrate that calcium gluconate (the insoluble compound identified by Sandermann et al. 1960) strongly retards the hydration of all phases of portland cement. Singh (1975) suggested that calcium gluconate retards cement hydration by preventing the development of hydrate nuclei, possibly by physically blocking the passage of water molecules to the developing nuclei. During unimpeded cement hydration, the high initial concentration of ettringite (resulting from the reaction of gypsum and C3A) in the mix rapidly tails off as hydration proceeds further. The rest of the gypsum, C3A and C3S in the hydrating cement is consumed over the next 24 hours of hydration, and there is an increase in Ca(OH)$_2$. In a cement mix containing 0.5% calcium gluconate, the formation of appreciable amounts of ettringite may be delayed until after 24 hours, with a corresponding retention of non-utilised gypsum, C3A and C3S, and very little formation of portlandite (Ca(OH)$_2$).
Glucose accelerates the early formation of ettringite, since C3A undergoes a very short period of enhanced hydration in the presence of many such inhibitory organic substances (Rossington and Runk 1968, Ramachandran and Feldman 1972, Monosi et al. 1986). Research by Blank et al. (1963) and Rossington and Runk (1968) demonstrated that larger organic molecules such as lignosulphonate are strongly adsorbed onto the newly hydrating C3A and C4AF grains in the first 15 min of hydration, effectively blocking their subsequent hydration before the silicate phases begin to hydrate. The formation of complex interlayered structures of insoluble products around hydrating C3A nuclei occurs later, retarding further hydration (Milestone 1977). The interlayered sheath initially is highly impermeable due to the presence of a compact structure of closely packed hexagonal ‘hydrates’ (Stein 1963, Young 1968). These hexagonal hydrates crystallise as thin, irregularly shaped plates in the presence of retarders (Young 1968, Gupta et al. 1973). The durability and longevity of the impermeable sheath is directly tied to the concentration of sugars or sugar acids in the cement mix (Milestone 1977), thus explaining the importance of the soluble carbohydrate content of wood in determining its compatibility with cement. Eventually the gradual alkaline degradation of the insoluble calcium gluconates disrupts the structure of the sheath, allowing water molecules access to the C3A hydrate nuclei and enabling hydration to proceed, usually at a reduced rate.

Thomas and Burchall (1983) provide a good discussion of the complex chemical processes involved in the inhibition of cement hydration by sugars and sugar acids. Like the chemical processes involved in cement hydration itself, its inhibition by sugars of various types is not very clearly understood and has been the subject of different explanations and contradictory theories. The earlier models discussed above rely on the formation of insoluble precipitates or complexes between Ca\(^{2+}\), oxygen, Ca(OH)\(_2\) and sugars which encrust initiated Ca(OH)\(_2\) and/or C-S-H and aluminate hydrate nuclei thus preventing their further growth by physically blocking access to water (Forsen 1938, Suzuki and Nishi 1959, Milestone 1977, Young 1968). Later theories developed by Milestone (1977), Singh and Ojha (1980) and Thomas and Birchall (1983) suggest that sugar and/or saccharinic acid molecules are directly adsorbed onto the Ca\(^{2+}\) ions that surround the hydrating C3S particles, changing the surface charge or ‘zeta potential’ from positive to negative. This inhibits further hydration by keeping Ca\(^{2+}\), OH\(^-\) and silicates in a ‘solubilised’ form through chelation. No mention is made of an impermeable sheath surrounding hydrate nuclei or the physical blocking of water to newly hydrating cement grains. Furthermore, Thomas and Birchall (1983) showed experimentally that sugars were incapable of forming insoluble complexes with silicates in the cement paste, previously thought to be a primary cause of disruption of hydration of the silicate phases in portland cement.
The calcium binding capacity of an inhibitory sugar or sugar acid has been directly linked to its ability to retard cement hydration (Skalny and Young 1980). The importance of hydroxyl groups in affecting the ability of a compound to inhibit cement hydration was first identified and discussed by Clare and Sherwood (1954, 1956). These authors, using tartaric acid (which contains hydroxyl groups on the terminal carboxyl groups and on the two secondary alcohol groups) and calcium or ferric tartrate (which contains free hydroxyl groups only on the alcohol groups), demonstrated that adjacent hydroxyl groups actively participate in chelation and the retarding hydration reactions. They suggested that, in the high pH (11-12) of cement suspension, hydrogen ions are dissociated from the hydroxyl groups, as demonstrated for polysaccharides in alkaline media above pH 10 by Saric and Schofield (1946), and two closely adjacent O' sites then readily link up to a Ca\(^{2+}\) ion (in a bi-dentate chelate configuration). This scavenging and immobilisation of Ca\(^{2+}\) ions was thought to prevent the normal process of Ca(OH)\(_2\) formation and crystallisation during hydration and hardening of the matrix. CaCl\(_2\) was shown by Clare and Sherwood (1956) to be a very effective agent for neutralising the inhibitory effects of tartrate, and was suggested as providing a quantity of additional Ca\(^{2+}\) ions for immediate occupation of the active hydroxyl sites. Mariampolskii et al. (1974) further suggested that the configuration of the molecule and the distance (3.2-3.6 Å) between the reactive hydroxyl sites was critical to its efficacy as a retarder.

However, the simple bi-dentate chelation model may not be the most accurate way of representing the processes involved in the inhibition of cement hydration, and clearly more complex chelation processes are involved. Work by Thomas and Burchall (1983) found that the most effective retarding sugars, i.e. the non-reducing sugars such as sucrose and raffinose, are less effective calcium scavengers than the reducing sugars, including glucose, lactose, maltose and cellobiose, which are less inhibitory of cement hydration. According to the theories of Thomas and Birchall (1983) and Birchall and Thomas (1984), it is the configuration in which Ca\(^{2+}\) is chelated that determines the inhibitory potential of an inhibitory admixture. Reducing sugars (those in which ring opening occurs in alkaline solution) bind very effectively with Ca\(^{2+}\) ions but in a simple bidentate configuration in the cement suspension, resulting in the formation of smaller, more discrete complexes that are less readily adsorbed onto hydrate nuclei.

A different mode of chelation of Ca\(^{2+}\) ions occurs with non-reducing sugars that retain their structure, which has a more deleterious effect on cement hydration (Thomas and Birchall 1983). In these cases, lime is solubilised by the non-reducing sugars, resulting in a half-salt which attaches to pentose (5-carbon) units of the intact, alkali resistant di- or polysaccharides. This then results in the adsorption of large organic molecules, via a pendant Ca\(^+\)-OH group, onto the surface of initiated Ca(OH)\(_2\) nuclei. This altered surface chemistry and charge (zeta potential) causes the build-up of Ca\(^{2+}\) and OH\(^-\) ions in solution, since they are unable to precipitate into portlandite (Ca(OH)\(_2\))
crystals. The Ca\(^{2+}\) ions are then kept in a solubilised form and unavailable for precipitation into portlandite by a particularly effective mode of chelation that ‘encages’ them in an octahedral coordination complex. Adsorption of the sucrose half-salt onto silicate hydrate nuclei was also suggested as being responsible for inhibiting the hydration of the silicate (C-S-H) phase toberomite gel. This was accompanied by the observed accumulation of high levels of solubilised SiO\(_2\) in cement paste containing inhibitory sugars.

2.6 Effects of non-carbohydrate wood extractives

There are fewer studies that have investigated the inhibition of cement hydration by non-sugar extractives. Miller and Moslemi (1991a) examined the effects of a range of different wood extractives, i.e. a terpene (\(\alpha\) pinene), a fatty acid (oleic acid), a resin acid (abietic acid), a sterol (\(\beta\)-sitosterol) and a tannin (dihydroquercetin) on the hydration of portland cement. At additions of up to 1% w/w, all compounds except for dihydroquercetin had negligible effects on hydration. At a level of 1% the addition of abietic acid caused a small decrease in hydration maximum temperature, whereas dihydroquercetin strongly inhibited cement setting.

Although non-polar terpenes, fats and resins do not actively inhibit cement-setting reactions, particularly if they are present in small quantities, they do migrate to wood surfaces during drying (Zavarin 1984). It has been suggested by Miller and Moslemi (1991a) that this phenomenon may produce a hydrophobic wood surface which could reduce hydrogen bonding between the wood and cement, thus weakening the interfacial bonds in cement-bonded wood composites. However, no studies have been undertaken to confirm this.

Bark and dark-coloured heartwoods are generally incompatible with cement owing to the presence of high quantities of hydrolysable tannins (Weatherwax and Tarkow 1964, Biblis and Lo 1968). Far less is known about how heartwood polyphenols chemically interfere with cement hydration reactions. The deleterious effects of wood tannins (a complex range of polar, water- and alkali-soluble polyphenols) on cement setting were first demonstrated experimentally by Sandermann and Brendel (1956) and Sandermann et al. (1960) using the commonly occurring flavonol dihydroquercetin (Hillis 1962).

Later studies have isolated and tested the effects of specific heartwood polyphenols on cement hydration. The ethylacetate fraction of western red cedar (\(Thuja plicata\)), which consisted of polar polyhydric (hydroxylated aromatic) compounds, was found by Tachi et al. (1987) to be a strong inhibitor of cement hydration. Within this fraction (A-70) an acidic compound, plicatic acid, was isolated and shown to be largely responsible for the inhibitory effect of western red cedar heartwood on cement hydration (Yasuda et al. 1989). Hydroxylated aromatics were also found to be responsible for the inhibition of cement setting by the heartwood of sugi (\(Cryptomeria japonica\))
(Yasuda 1992). Yasuda et al. (1986) isolated a water-soluble phenol glycoside and hopeaphenol compounds (in the form of aglycones) from mangassinoro (Shorea spp.) which strongly inhibited cement hydration. Polyphenols in woods occur in the form of aglycones in the heartwood, commonly with a corresponding glycosidic form of the polyphenol occurring in the sapwood (Hillis 1962). The glycosidic forms of polyphenols are part of the carbohydrate content of sapwood and they contain glycosidic links to sugars (often glucose) at 4' on the B-ring.

There is only one published paper (Tachi et al. 1989) that has investigated how specific acacia heartwood polyphenols might affect cement hydration. The effects of acacia polyphenols on the hydration of portland cement were discussed comprehensively in Chapter 9.

2.7 Hardwood and softwood differences in compatibility with cement

Previous studies of wood-cement compatibility indicate that, as a general rule, hardwoods are less compatible with cement than softwoods (Weatherwax and Tarkow 1964, Sandermann 1971, Simatupang et al. 1977, Lee et al. 1987, Moslemi 1988, Frick 1989, Miller and Moslemi 1991a), although there are exceptions. For example, the heartwoods of larches (Larix spp.) strongly inhibit the hydration of cement (Sandermann and Kohler 1964, Zhengtian and Moslemi 1986). Lower wood-cement compatibility among hardwoods has been attributed to their higher content of hemicelluloses compared to most softwood species (Simatupang et al. 1977, Hachmi and Campbell 1989). As discussed earlier, wood hemicelluloses inhibit cement hydration as they readily hydrolyse in dilute acids and bases to monomers and sugar acids (Sandermann and Brendel 1956). Differences in wood-cement compatibility between hardwoods and softwoods may be attributed to differences in the quantity of hemicelluloses, their composition and their location within the wood-cell wall.

Softwoods and hardwoods differ in the percentage total of polyoses, the composition of the polyoses and the percentage of individual polyose units, as outlined by Fengel and Wegener (1984) and Sjostrom and Westermark (1999). The principal polyose types in softwoods are galactoglucomannans (15-20%), with arabinoglucuronoxylan present in smaller amounts (5-10%). The principal polyose type in hardwoods is glucuronoxylan, which can be present in large quantities (15-30%). Glucomannan is a minor constituent in hardwoods (2-5%).

Hardwoods are generally more susceptible than softwoods to chemical degradation by both acids and alkalis, primarily because they contain a higher ratio of pentoses to hexoses (Thompson 1969). Pentoses tend to be concentrated in the amorphous regions of the wood cell wall making them more accessible to acids or alkalis (Wangaard 1966). Hardwoods also tend to contain a much higher proportion of xylose (pentose) units and acetyl groups than softwoods (Timell 1967, Fengel and Wegener 1984). Hardwoods such as birches (Betula spp.) and beeches (Fagus spp.) can contain very high quantities (up to 25%) of acetylated xylans (Timell 1969). These woods have been shown
to have low compatibility with cement (Sandermann and Kohler 1964). The amounts of xylose and mannose present in lignocellulosic materials were found to significantly affect the inhibitory indices of a range of hardwoods, softwoods and agricultural residues when they were tested for their compatibility with cement by Choi et al. (1984). No correlation was found, however, between inhibitory index and glucose content of the different materials. In low-compatibility beech (Fagus crenata) wood sucrose forms the major carbohydrate fraction (70%) responsible for retarding cement hydration (Imai et al. 1995). Sucrose is an effective retarder due to its pentose content and stability in alkali as discussed earlier. Small amounts (<6%) of glucose, fructose and inositol were also found in beech, and although these are effective cement-setting retardants, their small quantities contributed very little to the capacity of beech wood to inhibit cement hydration.

The mechanism by which hardwood xylans inhibit cement hydration reactions may be different to that attributed simply to the degradation of the polyose chains via peeling reactions. The highly inhibitory nature of xylans accords well with the theory of Thomas and Birchall (1983) that the pentose unit provides the linkage via a Ca"--OH intermediary to the surface of hydrate nuclei. Hardwood xylans are also quite stable in alkali at ambient temperature (Timell 1967). They have at their ends a sequence of xylose, rhamnose and galacturonic acid units which, following the removal of the xylose reducing end unit, become stable and resistant to further peeling in alkali due to the presence of the galacturonic acid unit (Ericsson et al. 1977, Johansson and Samuelson 1977). This resistance to further de-polymerisation may be related to the ability of xylan chains to inhibit cement hydration reactions in accordance with the theory that alkali-resistant polysaccharides are potent hydration inhibitors. The same alkali-resistant end sequence has also been found on spruce (Picea abies) xylan (Andersson et al. 1983), a wood species that has a high compatibility with portland cement (Sandermann and Kohler 1964). This is likely because the wood of spruce contains only a very small quantity of xylan compared with most hardwood species.

A further difference between softwood and hardwood xylans is that softwood xylans are more tightly bound in the higher-lignin-containing secondary wall, making them less accessible to alkali-induced leaching (Timell 1967). They also do not contain acetyl groups (Fengel and Wegener 1984). This difference can be seen in the structures of chains from hardwood and softwood xylans shown in Figure 7. Hachmi and Campbell (1989) (without detailed chemical analysis) suggested that the components of the hardwood xylan chain responsible for retarding cement hydration were the acetyl groups, which undergo hydrolysis or cleavage in alkaline solution (Browning 1967, Goldstein 1984). These cleaved groups have been implicated in the formation of insoluble calcium-acetate, and possibly other metal-acetate complexes, which can retard cement hydration (Hachmi and Campbell 1989, Miller and Moslemi 1991a). This is an alternative (but unproven) mechanism to help explain the lower compatibility of many hardwood species with portland cement.
Figure 7 Partial chemical structures for (a) O-acetyl-4-methylglucuronoxylan from hardwood and (b) arabino-4-O-methylglucuronoxylan from softwood (from Fengel and Wegener 1994).

The most comprehensively studied case of a softwood species with low wood-cement compatibility is the heartwood of western larch (*Larix occidentalis*) (Sandermann and Kohler 1964, Zhengtian and Moslemi 1986, Molsemi 1988), and that of other *Larix* species (Xu 1984). The heartwood of larch contains large quantities (up to 25%) of a water-soluble polyose, arabinogalactan, which is comprised of galactose and arabinose units (Cote *et al.* 1966, Wenzl 1970, Sjostrom 1981), and is shown in Figure 8.

Figure 8 Partial chemical structure of arabinogalactan from larch wood (from Fengel and Wegener 1984).
The solubility in water of this polyose is a result of its highly branched structure (Sjostrom 1981). It also differs from most other softwood polyoses in that it is extra-cellular, i.e. it is not deposited within the cell wall matrix (Sjostrom and Westermark 1999). These characteristics make this polyose readily accessible and soluble in water and/or weak alkali, in accord with the suggestions of Wanggaard 1966 and Hoffmann and Parameswaran (1976), which accounts for why larch heartwood severely inhibits cement hydration.

3. Cement supplements and alternative mineral binders to portland cement type I

3.1 Alternative portland cement compositions used in wood-cement composites

Although ordinary portland cement (ASTM Type I) is mainly used in the manufacture of wood-cement composites today, various different kinds of portland cement have been tested and used in the past. This has been driven by the relatively slow curing rate of portland cement Type I and its vulnerability to 'poisoning' by wood extractives. There are five main compositions of portland cement available to suit different concreting applications and these are listed below in Table 2 (from Ramachandran 1994).

Table 2 Phase composition, fineness and compressive strength characteristics of five common types of portland cement.

<table>
<thead>
<tr>
<th>ASTM Type</th>
<th>C3S</th>
<th>C2S</th>
<th>C3A</th>
<th>C4AF</th>
<th>Fineness (cm²/g)</th>
<th>Compressive strength (% of Type 1 cement)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>50</td>
<td>24</td>
<td>11</td>
<td>8</td>
<td>1800</td>
<td>100 100 100</td>
</tr>
<tr>
<td>II</td>
<td>42</td>
<td>33</td>
<td>5</td>
<td>13</td>
<td>1800</td>
<td>75  85  90</td>
</tr>
<tr>
<td>III</td>
<td>60</td>
<td>13</td>
<td>9</td>
<td>8</td>
<td>2600</td>
<td>190 120 110</td>
</tr>
<tr>
<td>IV</td>
<td>26</td>
<td>50</td>
<td>5</td>
<td>12</td>
<td>1900</td>
<td>55  55  75</td>
</tr>
<tr>
<td>V</td>
<td>40</td>
<td>40</td>
<td>4</td>
<td>9</td>
<td>1900</td>
<td>65  75  85</td>
</tr>
</tbody>
</table>

Schwarz and Simatupang (1983) examined the effects of various kinds of portland cements on the compressive strength of composites made from compatible spruce particles and less compatible beech particles. They found a good negative correlation between the C3S contents of the cements and the compressive strength of the spruce composites, whereas the relationship for beech particles was less clear. Another study (Lange and Simatupang 1985) found that the mechanical properties of poplar CBPs were improved through the use of a high early strength cement (PZ55) with a very high surface area of ≈5200 cm²/g. The positive effect was less pronounced in boards made from spruce. When cements with a high C3S content are used for the manufacture of CBP, a quicker setting, high early strength cement (ASTM Type III), is recommended. The reactivity of Type III portland cement is enhanced by its greater fineness, as indicated in Table 2. Schubert et al. (1990a) tested the effects of 18 different types of cement on the hydration and properties of WWCBs made from aspen (Populus tremuloides) or scots pine (Pinus sylvestris). As a result of their findings the
authors recommended the use of low alkali cements, preferably in combination with the more compatible Scots pine for best results.

Moslemi and Pfister (1987) compared the effects of portland cement ASTM Types I and III at different cement ratios on the properties of CBPs made from lodgepole pine (Pinus contorta). They reported strong interactive effects between cement type and wood-cement ratio on the bending strength of boards. The highest MOR (around 25 MPa) was achieved using the Type III cement at a cement/wood ratio of 2. Although the Type III cement is a little more expensive than Type I, high C3S cements have been widely used for the commercial manufacture of wood-cement composites. Examples include the manufacture of WWCBs in the USA (Lee and Hse 1993) and by the German CBP manufacturer Bison-Werke Bahre and Greten GmbH & Co. KG (Moslemi and Pfister 1987). High C3S- and C4AF-containing cements (ASTM Type II) have also been recommended for the manufacture of WWCB by Kamil (1970) and Kollmann (1963a).

3.2 Supplements for portland cement

The supplementation of portland cement by siliceous reactive pozzolans such as rice-hull ash (RHA), fly ash or blast furnace slag has the potential to reduce its inhibition by wood constituents, lower the cost of the binder and even improve the strength properties of the composite (Aho 1989, Lange et al. 1989, Feldman et al. 1991). Other potential benefits include improvements to the water resistance and durability of the binder and composite. Binders based on partially or fully substituted portland cement are examined here because of their considerable potential for use in wood-cement composites as factors such as cost, energy, board production time, and the need to reduce wood specificity and pre-treatment drive technological change in the mineral-bonded wood composite industries.

Studies have shown that fly ash or silica fume (a highly siliceous pozzolan) can be successfully used to supplement portland cement to facilitate the manufacture of wood-cement composites from incompatible woods and improve their moisture resistance (Simatupang et al. 1987, Lange et al. 1989, Miller et al. 1989). The addition of fly ash to cement enabled CBPs to be manufactured from wood species (birch, oak and larch) that have low compatibility with cement (Lange et al. 1989). MOR increased from <5-6 MPa for boards containing no fly ash compared to 15 MPa for boards containing 40% fly ash. Sun et al. (1997) manufactured CBPs containing a fly ash:cement mix of ratio of 0.4:1, binder:wood ratio of 2.5:1 andpressed boards at 120°C for 1.5 min/mm. The resulting boards had good strength properties. According to Lange et al. (1989), finely ground silica in fly ash intercepts soluble CaOH⁺ as it is generated during cement hydration, forming calcium silicates, thereby reducing the alkalinity of the paste. This reduces the leaching of alkali-soluble extractives from wood, thus lowering its inhibitory effect on the hydration of cement.
The addition of fly ash to cement may also improve the water resistance and longer term durability of wood-cement composites (Kawai et al. 1999a and b). In response to the problem of cracking and deformation of wood aggregate-cement sidings made from pure portland cement, 30 to 40% fly ash was added to the composite. Boards containing fly ash were stronger than those containing pure portland cement, but, more importantly, their thickness swelling after prolonged exposure to water was very low (<0.2%) and their resistance to freeze/thaw cycling was increased four-fold.

Major drawbacks to the utilisation of fly ash are its higher cost and lower availability compared to portland cement (Lange et al. 1989). For these reasons, rice hull ash (RHA) has also been tested as a possible siliceous supplement for the manufacture of wood-cement composites. RHA can impart improved strength properties to wood-cement composites made from wood species with low compatibility with cement, but the optimum level of addition is much lower than for fly ash (Lange et al. 1989).

RHA has been tested in the manufacture of WWCBs with mixed results. Eusebio et al. (1998b) found that it was possible to manufacture WWCBs with good properties (MOR almost 7 MPa) from untreated wood wool of *Gmelina arborea* when the portland cement binder contained up to 30% w/w RHA. It was not possible to manufacture WWCBs from this species using pure portland cement Type I. In contrast to these results, the addition of RHA was shown to be ineffective in enhancing the properties of WWCBs made from *Acacia mangium* (Lynch 1997, Mills 1998). Both these studies used untreated wood wool in combination with Type I portland cement supplemented by up to 30% RHA. Lynch (1997) found that addition of RHA to portland cement resulted in boards with reduced strength properties. It was necessary to pre-soak the wood-wool in cold water for 24 hours to improve the bending strength of boards and allow the addition of up to 10% by weight of RHA without significantly reducing board strength properties. Mills (1998) found it was necessary to add 4% CaCl₂ and 2.7% lime (w/w cement) to ensure adequate consolidation of WWCBs made from untreated *A. mangium* and a 20% RHA-supplemented cement binder. Average MOR of boards attained in his study was 6 MPa. Nevertheless, both studies found that the addition of RHA significantly improved the resistance of boards to water (through reduced thickness swelling) and their ability to maintain their strength after exposure to water.

Charcoal has also been tested as a possible supplement for portland cement. The addition of activated charcoal in conjunction with CaCl₂ has been found to increase the total enthalpy generated by a wood-cement mixture by over 50% (Souvat et al. 1999) by enhancing the reactivity of the silicate phases in cement. Peng et al. (2000) added ordinary pulverised charcoal to the portland cement binder to manufacture of CBP from inhibitory Chinese fir (*Cunninghamia lanceolata*). Surprisingly, the addition of charcoal was reported to reduce the density and increase the strength
properties and moisture resistance of boards. In contrast, a study by Bao et al. (2001) found that increasing the pulverised charcoal content of CBPs containing sugi (Cryptomeria japonica) wood (to above about 0.05 parts charcoal) significantly reduced board flexural properties and greatly increased the moisture sensitivity of boards. Clay minerals such as metakaolin have also been tested as a mineral supplement for portland cement but were found to be ineffective for the purposes of wood-cement board manufacture (Simatupang 1998).

3.3 Alternative mineral binders to portland cement

Pulverised blast furnace slag is probably the most common alternative mineral binder to portland cement for the manufacture of wood-cement composites. Slag-based binders have been widely tested in the manufacture of wood-cement composites, particularly from inhibitory wood species. It is a recyclable waste product from steel production that is cheaper than portland cement and has been extensively investigated as a means of reducing the long pressing and curing times of wood-cement composites (Forss 1987, Anon. 1988, Lange et al. 1989, Aho 1989, Hsu 1992, 1993, Ledhem et al. 2000b). Blast furnace slag has a similar mineral composition to portland cement clinker, but contains a lower proportion of CaO and higher proportions of SiO₂ and Al₂O₃. Hydration is activated by heat (120-140°C) and OH⁻ or SO₄²⁻ ions generated from the addition of approx. 10% w/w NaOH, lime, portland cement or gypsum. A brief description of the commercial production and properties of slag-bonded particleboards is reproduced from Aho (1989). To manufacture 1 m³ of boards bonded with blast furnace slag 800-900 kg ground blast furnace slag, 300-400 kg wood particles, 70-90 kg chemical activator (NaOH) and sodium silicate as fortifier and 200-300 kg water are first mixed together. Mats are formed in the same manner as that used in the manufacture of conventional CBP. Mats are pressed at 120-140°C for about 10 min (for 12-mm boards), after which they are stacked to cool for 24 h. Unlike the manufacture of CBP, there is no need to feed clamped stacks of boards through a heated curing chamber or maintain inventories of boards during curing. Mechanical properties of boards include: density ≈1333 kg/m³; MOR ≈ 10.5 MPa; MOE ≈ 5300 MPa; IB ≈ 0.85 MPa; and thickness swelling after 24 h immersion in water is very low (<1.5%).

Kliwon (1999) attempted to manufacture WWCBs from slag-supplemented portland cement. Board properties and production economics were not greatly altered by supplementing with one-third slag when manufacturing WWCBs in the conventional manner from pre-soaked Sumatran pine (Pinus merkusii) in Indonesia. No other examples of the manufacture of WWCBs from slag or slag-supplemented portland cement were found in the literature.

An isolated reference (Logvinenko et al. 1976) refers to 'nepheline' cement, another waste product from minerals (in this case alumina) processing, which has been shown to be far less
susceptible than portland cement to retarded hydration by inhibitory wood extractives. However there are no references to this binder in any Western literature.

The problem posed by inhibitory wood extractives has also fostered the development and use of magnesite or 'Sorel' cement as an alternative mineral binder to portland cement for wood-cement composites (Simatupang and Schwarz 1975, Simatupang 1988, Pazner and Klemerevski 1989). Sorel cement is a thermo-setting mixture of calcined magnesium oxide and magnesium sulphate and/or magnesium chloride whose rapid setting is practically unaffected by wood sugars (Paszner and Klemerevski 1989). Its use in the mineral-bonded wood composite industries, however, is limited by the high energy required for curing and the diminished moisture resistance of the boards (Liori 1981).

Another magnesia-based binder, magnesium oxyphosphate cement, has also been investigated and adapted for use in the manufacture of wood-cement composites (Paszner 1978, 1987, Paszner and Klemerevski 1989). Dead burned mangesium oxide (MgO) can be reacted extremely rapidly with ammonium polyphosphate to produce a dense, water-resistant solid with unusually high compressive strength (Limes et al. 1966, Paszner 1978). Ammonium polyphosphates are produced by reacting concentrated superphosphoric acid with ammonia in the presence of water under carefully controlled conditions. The higher the degree of polymerisation the higher the strength and water resistance of the reacted mangesium oxyphosphate binder.

According to Pazner and Klemerevski (1989) MgO can be substituted by up to 70% with carbonates of magnesium (magnesite) or calcium (dolomite) to reduce the relatively high cost of the binder. The rapid reaction is not sensitive to wood sugars or polyphenols, allowing any type of wood or bark to be used in composite manufacture, and the rate of reaction and curing can be carefully controlled by heating or cooling during pressing. However, the reaction generates large amounts of water and ammonia, requiring an appropriate ammonia gas management strategy in the pressing line.

Despite the claims discussed above there are surprisingly few subsequent studies that have investigated the adoption of these types of binders as potential substitutes to overcome the long curing times and vulnerability to poisoning by wood constituents that hamper the use of portland cement. Although dolomite is readily available in many countries, other aspects including: the cost of manufacture or procurement of ammonium polyphosphates; the management of ammonia off-gassing; and the need to control the reaction rate may detract from the research and adoption of this technology in many developing countries.