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Characterisation of metakaolin-based geopolymers using beam-based and conventional PALS

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Abstract. The nano-porosity of metakaolin-based geopolymers and the effect of heat-treatment on porosity have been studied with conventional and beam-based positron annihilation lifetime spectroscopy (PALS). Conventional PALS found significant nano-porosity in the geopolymers, as indicated by the presence in the PALS spectrum of two long lifetime components, $\tau_3 = 1.58$ ns and $\tau_4 = 47$ ns, associated with pore diameters of approximately 0.5 and 3 nm respectively. The lifetime of the shorter component was found to decrease monotonically with successive heat treatments of 300°C and 600°C. Beam-based PALS, conducted at 5 keV, also indicated two long lifetime components, $\tau_3 = 4.84$ ns and $\tau_4 = 54.6$ ns. These are significantly longer than those observed by conventional PALS and the monotonic decrease of τ_3 with successive heat treatments was not observed. As the beam-based PALS probed only the near-surface region, with an average implantation depth of about 350 nm, these results suggest that the near-surface structure may vary significantly from that of the bulk. This could be an inherent property of the samples or an artefact caused by surface effects or sample outgassing.

1. Introduction

Geopolymers are a class of inorganic polymers that are based on aluminosilicates. They are a potential replacement for traditional building materials such as Portland cement because of their superior fire and acid resistance and their manufacture requires a much lower calcining temperature and produces only 10-20% of the CO₂ per unit mass compared to ordinary cement. Other potential applications include, for example, immobilisers for radioactive and toxic waste, as refractory and fire resistant products, and composite materials for aircraft and automobile interiors [1].

Geopolymers are usually produced by adding a reactive aluminosilicate precursor, such as fly ash or metakaolin, to a highly alkaline silicate solution in order to facilitate the break-up of the primary aluminosilicate framework, leading to polymerisation and solidification. Then curing at 25-90°C in a humid atmosphere for hours or days completes the process. If the Si/Al molar ratio is ≥ 1.5 the resulting structure does not display long-range atomic order; it is amorphous with respect to X-ray

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powder diffraction. The amorphous regions are comprised of SiO_4 and AlO_4 tetrahedra distributed randomly along cross-linked polymeric chains creating a complicated network of pores [1-3].

The mechanical properties of cementitious materials are heavily influenced by porosity, since the volume and size distribution of pores control both their strength and durability [4, 5]. A detailed characterisation of the pore structure and the factors that affect it are thus crucial to advancing the design of these materials; however, classical porosimetry methods such as mercury intrusion and gas adsorption cannot always be relied upon to extract information on pores smaller than a few nanometres [3-5]. Positron annihilation lifetime spectroscopy (PALS) possesses several advantages over these conventional techniques. It is sensitive to both open and closed porosity, and pores in the size range of 0.1-10 nm typically can be resolved. In this paper the porosity of metakaolin-based geopolymers and the effect of heat treatment on porosity has been investigated by both beam-based and conventional PALS.

2. Experimental procedure

The geopolymers studied have Si/Al and Na/Al molar ratios of 2.0 and 1.0 respectively. Metakaolin is produced by heating kaolinite at 750°C for 15 hours in air, which renders the kaolinite X-ray amorphous. The batch compositions consisted of 33.7% metakaolin, 63.0% sodium silicate D solution and 3.3% deionized water. The sodium silicate solution was added to a mixture containing the various additives, and after agitating for 5 minutes, the composite solution was poured into a polycarbonate cylindrical jar and covered with a screw cap. The samples were shaken for 5 minutes on a vibrating table to de-air. They were cured at ambient for 24 hours and then at 40°C for a further 24 hours. To ascertain the effect of heat treatment on porosity, two of the samples were heated in air at either 300°C or 600°C for 3 hours.

Conventional PALS measurements were obtained using a fast-fast spectrometer with detectors comprising of a BC418 plastic scintillators coupled to a Burle 8850 photomultiplier tube. In these measurements about 30 μCi of $^{22}\text{NaCl}$ was deposited on 7 μm Kapton foil (grade HN from Goodfellow) and sandwiched between two identical geopolymer samples. The time resolution of the system is about 200 ps as determined from analysis of a spectrum of high purity, annealed nickel. The spectra comprise of at least 2 million counts and have been analysed using PASCUAL version 1.3.0 [6].

Beam-based PALS was performed at the Australian Positron Beamline [7], which is based on the Surko buffer-gas trap system. This technique has been implemented to produce sub-nanosecond positron pulses, enabling positron lifetime studies of materials to be performed. For gamma detection a BaF_2 scintillator and an XP2020Q photomultiplier are employed. Timing information is obtained using a Comtech P7889 Fast Timing Card and the timing resolution of the system was approximately 800 ps. Analysis of lifetime spectra has been carried out with custom-written Matlab software CAMSfit [7].

3. Results and discussion

Table 1 shows results obtained with conventional and beam-based PALS for the three geopolymer samples studied, one without any heat treatment, and the others after being heated to either 300°C or 600°C. With conventional PALS, four lifetime components could be extracted from the spectra for each sample. The two shortest components are associated with p-Ps and free positron annihilation in the bulk of the material, as well as annihilations in the source material and supporting foil. One of the longer lifetime components ($\tau_3 = 1.58$ ns) extracted from the spectrum of the untreated geopolymer is close to the approximate 1.7 ns o-Ps lifetime of free water [8]. Similar lifetimes have also been observed in cement and the intensity of this spectral component has been used to monitor changes in hydration over time [4, 5].

Heat treatments of 300°C and 600°C led to a monotonic decrease in τ_3 and after heating to 300°C the intensity of this component (I_3) decreased by a factor of about 1.5. The decrease in the lifetime and intensity after heat treatment may be due to the removal of free water from pores, because heating to greater than 150°C is sufficient for this purpose [9]. The decrease in the lifetime after the 600°C heat

treatment could be due to the early stages of a transition to a dense glass ceramic. However, the intensity (I_3) is approximately the same as that of the 300°C sample. Using the RTE model [10] these longer lifetimes correspond to pore diameters in the range of 0.5 nm.

The behaviour of τ_3 is in broad agreement with the results of Vance et al [11], where conventional PALS was performed on metakaolin geopolymers subjected to heat treatments over a larger temperature range. However, Vance et al did not observe the fourth lifetime component, τ_4 , of about 50 ns observed in these samples, corresponding to pore sizes in the range of 3 nm. The intensity of this component varied from 7 to 9%, however, it did not show a dependence on heat treatment, as identical results were obtained for the untreated geopolymers and the 600°C sample. The absence of strong temperature dependence could suggest that this component is associated with o-Ps annihilation in empty pores, that is, pores that do not contain water.

There are differences in the lifetimes and intensities obtained with conventional and beam-based PALS. Like conventional PALS, beam-based PALS produces two long lifetime components; however, there are significant differences in the lifetimes measured using the two techniques. τ_3 for beam-based PALS is larger by a factor of 2.8-4.4, and the monotonic decrease in lifetime with heating seen with conventional PALS is not observed. The trend in the intensity of this component is similar however to conventional PALS and I_3 decreases by a factor of about 2.3 after the 300°C heat treatment. Using the RTE model, this lifetime can be equated to pores with diameter 0.9-1.2 nm. The τ_4 values from beam-based PALS are in closer agreement to those from conventional PALS; however, they still differ by about 14%. As with the data from conventional PALS, this component does not display a strong dependence on heat treatment and would correspond to pores of diameter 2.8-3.4 nm.

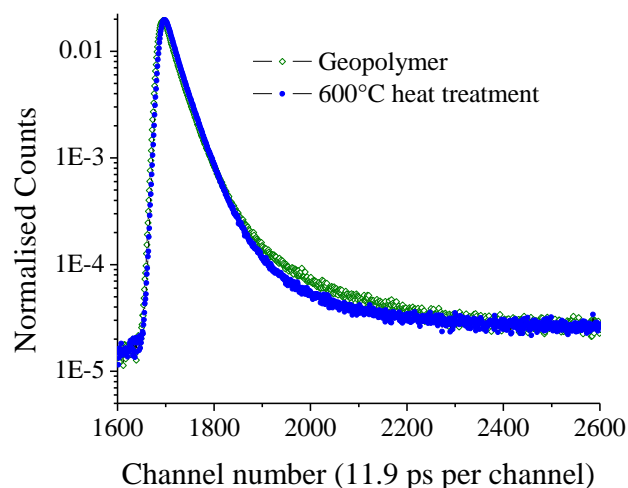
In conventional PALS the energy spectrum of ^{22}Na positrons has its peak at 0.545 MeV - hence positrons penetrate deep into the sample and the signal is averaged over a large volume (thus in this case positrons are implanted within about 1mm of the geopolymers' surface). In contrast, beam-based PALS provides the means to study near-surface layers and to obtain information as a function of depth. In this study the measurements were conducted at an incident energy of 5 keV; for which 99.9% of positrons thermalise within 1 μm of the surface and the mean implantation depth is about 350 nm [12]. The differences observed could suggest that the porosity in the near surface region differs from that of the bulk material. However, these differences may also be the result of outgassing, or surface effects associated with beam-based PALS. Outgassing of the samples could selectively modify the near surface region, giving rise to significant differences between the two methods. Beam-based PALS was performed at approximately 10^{-7} Torr and outgassing of the samples was observed; conventional PALS measurements were then carried out in air. PALS studies of zeolites and mesoporous silicates performed at different vacuum levels reveal that very long lifetime components emerge when measurements are performed under vacuum conditions [14]. This is largely attributed to the quenching of ortho-Positronium by air; such dramatic differences are not seen in the data presented here. Only a moderate increase in τ_3 is seen in the beam-based data and the τ_4 values are comparable. Surface effects associated with Positronium escaping from the surface and annihilating outside of the viewing angle of the detector may distort beam-based PALS data. To reduce the contribution from surface effects, and to facilitate a better comparison between beam-based and conventional PALS, future studies will be performed over a wider range of energies (0.5-20 keV).

4. Conclusion

Studies of metakaolin-based geopolymers with conventional and beam-based PALS reveal two long lifetime components, indicating that the geopolymers contain significant nano-porosity. τ_3 obtained with conventional PALS is close to that of free water and a monotonic decrease in the lifetime and intensity of this spectral component is observed upon heating to 300°C and then 600°C, which may signal the removal of free water. τ_3 for beam-based PALS conducted at 5 keV is larger by a factor of 2.8-4.4 and the decrease in lifetime with heating is not observed. This could suggest that the porosity in the near-surface region is greater than the average porosity in the underlying bulk. However, we cannot eliminate sample outgassing or surface effects as the underlying cause of these differences.

Table 1. Lifetimes and intensities obtained with conventional and beam-based PALS for the three geopolymers studied. Standard deviations are given in the brackets.

Geopolymer treatment	Conventional PALS				Beam based PALS at 5 keV			
	τ_3 (ns)	I_3 (%)	τ_4 (ns)	I_4 (%)	τ_3 (ns)	I_3 (%)	τ_4 (ns)	I_4 (%)
No heat	1.58 (0.02)	6.2 (0.1)	47 (2)	7.2 (0.2)	4.84	3.1	54.6	6.0
300°C	1.42 (0.03)	4.1 (0.3)	50 (2)	9.2 (0.6)	6.22	1.3	58.5	6.4
600°C	1.34 (0.03)	4.3 (0.2)	47 (2)	7.4 (0.2)	3.70	0.9	41.4	4.1

**Figure 1.** Lifetime spectra obtained with conventional PALS of an untreated geopolymer and a geopolymer heated at 600°C for 3 hours

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