Safe disposal of high level nuclear reactor wastes: A new strategy

A. E. Ringwood

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Professor Ringwood is one of the world's outstanding geochemists. He was born in Melbourne in 1930. After a distinguished academic career at Melbourne University and a period as a research fellow at Harvard, he joined the Australian National University in 1958 and is now Director of the Research School of Earth Sciences at that University.

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Among his many honours are the Matthew Flinders Lecture and Medal, Australian Academy of Science; the Bowie Medal, American Geophysical Union; the Brittanica Australia Award for Science; the Arthur L. Day Medal, Geological Society of America; the Rosenstiel Award, Am. Assoc. Adv. Science; the William Smith Lecture, Geological Society of London; the Werner Medaille, German Mineralogical Society; the Vernadsky Lecture, U.S.S.R. Academy of Sciences; Centenary Lecturer and Medallist, Chemical Society of London; the Mueller Medal, Aust. N.Z. Assoc. for Advancement of Science; and the Mineralogical Society of America Award.

His researches have been described in 210 scientific papers dealing mainly with the composition and structure of the earth's interior, phase transformations at high pressures and temperatures, geochemistry and petrology, origin of the earth, moon and planets, and internal structure and composition of the moon. He is also the author of two books, 'Composition and Petrology of the Earth's Mantle', McGraw Hill, 630 pages, 1975, and 'Origin of Earth and Moon', Springer-Verlag, in press.

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A. E. Ringwood

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ERRATA

Table 4

Perovskite		Kalsilite	
CaO	36.2	Atomic Proportions	
		Si	1.02
		Al	1.01
		Ba	0.02
		K	0.84
		Cs	0.02
		Sum	2.91

Table 6

Col. A	
TiO_2	75.4
ZrO_2	–

p. 27 line 10 $Ba_{1/2}AlTi_3O_8$

Summary

The problems of disposing of high-level radioactive wastes from nuclear reactors are analysed from a geochemical perspective. The currently favoured technology of incorporating wastes in borosilicate glass, followed by deep burial in geological formations is shown to be suspect because the glass is very likely to devitrify, thereby greatly increasing the solubility of radioactive waste elements in groundwater. Objections based upon crystal chemistry are also levelled at an existing alternative technology of incorporating the waste in high concentrations in the so-called 'supercalcine' crystalline ceramics.

A new and improved strategy for safe disposal of radioactive wastes is provided by a study of the geochemical means by which *natural rocks and minerals* retain the elements present in high level nuclear reactor wastes. Many natural minerals are known to have the capacity to accept radioactive waste elements into their crystal lattices and to retain these elements very tightly. A number of minerals within this category are *known* to have been stable in a wide range of geological and geochemical environments for periods ranging from 20 million to 2000 million years. By comparison, the *maximum* period which is needed for decay of radioactive elements in reactor wastes is less than one million years. Thus, these natural minerals have demonstrated their capacity to retain safely dangerous radioactive waste elements for periods sufficient to ensure their decay. Moreover, the fundamental reasons underlying this capacity to immobilise these elements are well understood in terms of the basic principles of crystal chemistry, mineralogy and geochemistry.

The new strategy for immobilising radioactive wastes is based directly upon these observed properties of natural minerals. A method is described for producing synthetic igneous rock systems, 'SYNROC'. Several different SYNROC compositions have been studied. A particular example which has been investigated in detail is composed of the minerals *perovskite* ($CaTiO_3$), *barium felspar* ($BaAl_2Si_2O_8$), *hollandite* ($(K,Ba\frac{1}{2})AlTi_3O_8$), *leucite* ($KAlSi_2O_6$) and *zirconia* ($ZrO_2$). Each of these minerals belongs to a class which is *known* to have the capacity to accept radioactive waste elements into their lattices and to retain them tenaciously for many millions of years when subjected to a wide range of geochemical-geological conditions. Moreover, these crystal lattices also have the capacity to maintain their stability during the decay of radioactive elements by transmutation. Although the individual minerals are very refractory, our investigations have shown that a mixture of these minerals melts at about 1280°C and on cooling, crystallises readily to form a synthetic rock composed of well-formed crystals. The new strategy involves adding about 5 to 10 per cent of high-level radioactive waste to the SYNROC mixture of perovskite, Ba-felspar, hollandite and zirconia before melting. The resulting SYNROC mixture is then melted and allowed to crystallise. During crystallisation, the radioactive waste elements enter the lattices of the minerals of the synthetic rock to form highly stable, dilute solid solutions. Experimental data dealing with the distribution of key radioactive waste elements among the individual minerals show that crystal chemical principles are obeyed and the elements are effectively immobilised.

SYNROC thus provides a satisfactory host material in which radioactive elements from nuclear reactors can be immobilised for millions of years. The rocks are immune from devitrification and evidence is given that radiation damage to individual minerals and transmutations do not provide serious problems. The synthetic igneous rocks containing radioactive wastes may subsequently be buried deep within a suitable geological site which can then be sealed off. Confidence in the integrity of this

mode of immobilisation and disposal stems from our understanding of the principles of crystal chemistry and our prior knowledge of the stability of SYNROC minerals in appropriate geological environments for periods greatly exceeding the effective decay times of the radioactive waste elements.

Other geochemical aspects of radioactive waste disposal are also considered. These include the provision of *additional fail-safe barriers* based upon ceramic technology and known geochemical principles. In a second stage of reprocessing, SYNROC may be further diluted and incorporated in highly inert, refractory ceramic materials, e.g. Al_2O_3 and ZrO_2. It is also possible to construct waste containers from a metallic alloy (Ni_3Fe) which is far superior to stainless steel and is *known* to have withstood corrosion and to have remained intact in natural rocks for tens of millions of years. The final barrier between the radioactive waste and the biosphere is provided by the geology and geochemistry of the burial site. Certain rock types, e.g. shales and mudstones, are known to have the capacity to precipitate and strongly adsorb radioactive waste elements from aqueous solution, thereby immobilising them for extended periods. It follows that these adsorbtive properties of shales and mudstones should be utilised in constructing a repository for radioactive wastes.

In conclusion, our experimental investigations show that the general problem of radioactive waste disposal can be solved and that it is possible to confine radioactive waste elements in synthetic rocks more tightly than they are held in natural crystalline igneous and metamorphic rocks. Moreover, additional effective barriers between radioactive waste elements and the biosphere are provided by carefully chosen container materials and burial in highly retentive geological sites.

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1 Introduction

Few issues have polarised society in recent years as much as the debate on nuclear power. One of the major problems arising from the use of nuclear power is the disposal of highly radioactive wastes which must be segregated from the biosphere for periods on the order of a million years. It is an unfortunate fact that the magnitude of this problem was seriously underestimated for two decades by the US Atomic Energy Commission and by corresponding agencies in other countries. Environmentalists and others were rightly concerned by the situation and strongly criticised the official agencies and industries concerned with nuclear power. Equally unfortunate, however, much of this criticism has been based upon inadequate knowledge of the scientific and technical issues involved. As a result, the criticisms have become unnecessarily strident, emotive, and in many cases, irrational. The issue has thus become polarised to an extent which has caused an unprecedented degree of confusion throughout the community.

I believe that the problem of radioactive waste disposal is one which can be evaluated rationally, on the basis of established scientific principles and knowledge. Furthermore, I believe that when considered on this basis, the problem can be shown to be fundamentally solvable. I do *not* believe, however, that the actual waste disposal strategies which are currently favoured by the nuclear power industry are free from difficulties, or optimum for their purpose.

Most technologically advanced, industrialised countries (Australia being a notable exception) have embarked upon extensive research and development programs, aimed at the safe immobilisation and containment of high-level nuclear wastes (henceforth

to be called 'radwastes'). In a very general sense, there are two objections which can be levelled at most of the existing strategies concerned with disposal of radwaste. The first concerns the question of *cost*. The favoured strategies envisage the incorporation of radwaste within insoluble glass or ceramic materials which are subsequently to be buried deep underground in favourable geological environments. The total cost of these disposal programs is expected to amount to less than one per cent of the final cost of the electric power produced. The actual cost may well be in the vicinity of 0.5 per cent. The specific programs are not very sophisticated in a technological sense. The emphasis has been on simplicity and the adoption or modification of existing technological processes and operations.

In view of the importance of the radwaste issue to mankind in general, this approach appears unnecessarily parsimonious. It would not be unreasonable to be prepared to spend five or even ten times as much on a more sophisticated waste-disposal process, provided that worthwhile increases in the safety and reliability of the containment system were achieved. This could involve an expenditure amounting to only 5 per cent of the final cost of the power.

The second generalised criticism concerns the scientific management of existing programs. These have mostly been controlled by various national Atomic Energy Commissions, which are dominated on the scientific side by engineers, physicists, and to a lesser extent, chemical engineers. However, the sciences which are most fundamentally involved in the radwaste disposal problem are geochemistry and geology. From the author's perspective as a geochemist, the existing radwaste disposal strategies favoured by national Atomic Energy Commissions are certainly not optimal and may not even be satisfactory for their purpose. It is highly desirable that the organisations responsible for radwaste disposal include experienced geochemists and geologists in positions of responsibility. Had this been done, for example, by the US Atomic Energy Commission, earlier mistakes could have been averted.

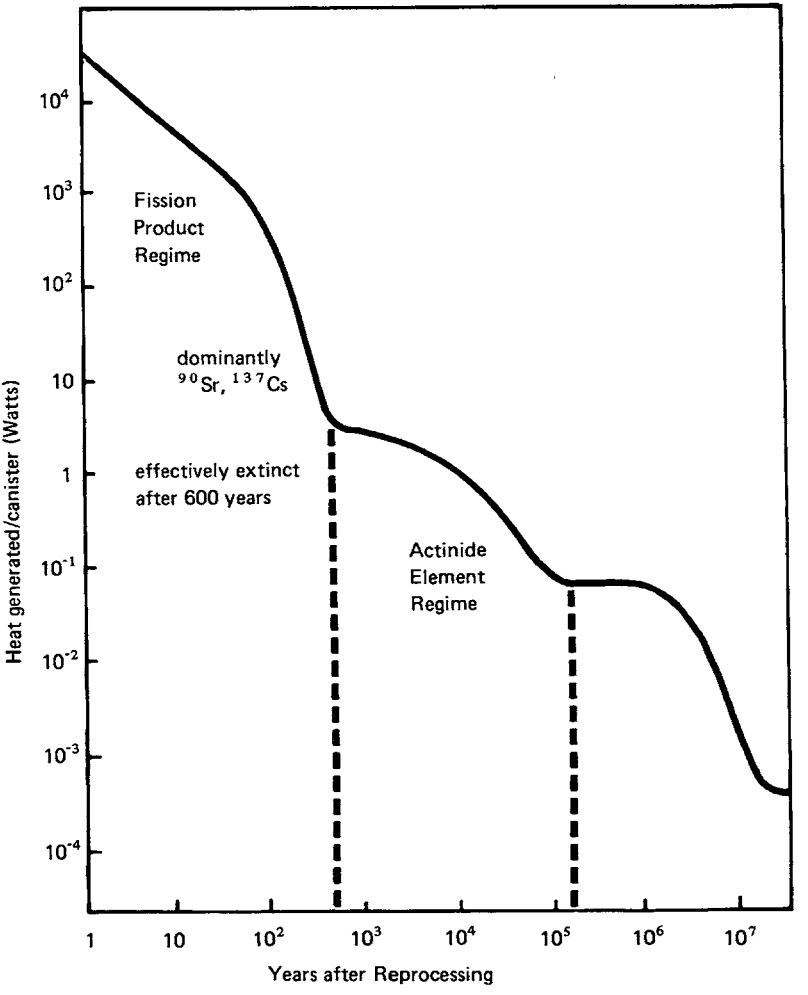
2 Radwaste disposal: multi-barrier approach

2-1 Background

Spent fuel from a nuclear power plant contains a wide range of highly radioactive isotopes. A measure of their activity is provided by a curve showing the cumulative heat generation from all radioactive species versus time (Fig. 1). One group of these radioactive species is formed by the fission of uranium (and plutonium). These elements decay mostly by the emission of beta and gamma radiation. The most important in terms of containment are caesium-137 and strontium-90. These have half-lives of about 30 years and must be contained for a period of about 600 years before they decay to safe levels. After 600 years, the dominant radioactive species are the actinide elements, principally isotopes of plutonium, americium, curium and neptunium, which decay by the emission of alpha particles. After a million years, the activity of the waste becomes comparable to that of the original uranium which was mined to produce the nuclear fuel. This is usually taken to be the ideal time limit for containment. (Actually, after a period of 10^5 years, the radiation hazard is only about twice that of the parental uranium.)

Assuming that the fuel rods are to be reprocessed to recover plutonium and unused uranium, they would be contained in cooling ponds for about a year to permit the decay of several highly radioactive, short-lived fission products. The rods would then be chopped into sections and dissolved in nitric acid. Plutonium and uranium are then recovered from this solution by a liquid-liquid extraction (Purex) process. The remaining solution constitutes the high-level wastes.

Fig. 1 Thermal power released from a typical canister filled with borosilicate glass containing 25 percent of radwaste. Such a canister contains the waste from 100 MW yr, so a typical large power plant would produce 10 canisters per year. Dimensions of glass cylinders are 300 cm (length) x 30 cm (diameter).



The intention in all countries is to transform these wastes initially into a solid, insoluble form. This is accomplished in the first instance by evaporating the radwaste solution to dryness, and calcining the material to produce a fine-grained mixture of radioactive oxides—called 'calcine' in the nuclear industry. Its composition is given in Table 1. Calcine is an unsatisfactory form for disposal because of its low density, low thermal conductivity and high solubility. Thus, further processing is necessary. This is discussed briefly in Section 2-2 and at greater length in Sections 3, 4 and 5.

Table 1 Principal components of a typical radwaste calcine

		Mol per cent
Rare earths (REE elements)	Fission products	26.4
Zr		13.2
Mo		12.2
Ru		7.6
Cs		7.0
Pd		4.1
Sr		3.5
Ba		3.5
Rb		1.3
U + Th	Actinides	1.4
Am + Cm + Pu + Np	Actinides	0.2
Fe	Processing contaminants	6.4
(PO_4)	Processing contaminants	3.2
Na	Processing contaminants	1.0
Others (mainly Tc, Rh, Te and processing contaminants)		9.0

Three primary barriers can be established with the object of preventing radwaste from entering the biosphere. The first is the *geochemical immobilisation* of radwaste in an inert, insoluble form. The second consists of placing a stable and impervious

container around the solidified radwaste. The third is the so-called *geological barrier*. Even if some component of radwaste should inadvertently escape from the other two barriers, the geochemical, hydrologic and geologic characteristics of the disposal site should be capable of preventing any significant entry of radioactive elements into the biosphere over a time interval of 10^5-10^6 years. Clearly, the efficiency of each of these barriers must be maximised. Ideally, each of the three, alone, should be capable of performing this function. In Sections 2-2, 2-3 and 2-4 we shall briefly discuss each of these barriers. Subsequently, in Sections 3, 4 and 5, we will describe an improved version of the first barrier in some detail.

2-2 The immobilisation barrier

By far the most popular procedure advocated by the nuclear power establishment is to incorporate the radwaste calcine into a borosilicate glass. This is accomplished by melting 20 to 30 per cent of calcine, together with other added components (mainly SiO_2, ZnO, B_2O_3 and Na_2O) to form a liquid which is poured into stainless steel cylinders and allowed to cool to form a glass. It is proposed to bury these glass cylinders in favourable geoglogical environments where leaching by water is minimised. However, it is the chemical and thermal stability of the glass itself which forms the first barrier to the entry of radioactive elements to the biosphere. We will call this the *immobilisation barrier*.

As an alternative to the use of glass as a host for radwaste, the use of crystalline ceramic materials has been proposed. The concept in this category which has been investigated most thoroughly is the so-called 'supercalcine' (McCarthy, 1977). This material is formed by adding about 50 per cent of SiO_2, Al_2O_3, CaO and SrO to ordinary calcine, pelletising, and firing in the solid state, at about 1200°C, to form a thermodynamically stable assemblage of crystalline phases, which incorporate the radioactive elements.

A third kind of *immobilisation barrier* has been developed by

the author and his colleagues. It is based upon incorporation of radwaste at much higher dilutions (5-10 per cent as compared to 50 per cent for supercalcine) within a highly specific, tailor-made assemblage of crystalline phases. This assemblage can be produced by melting and crystallisation. It employs the same principles that govern the occurrence of radioactive elements in the lattices of minerals in natural rocks which have crystallised from the molten state. An extended discussion of this latter immobilisation barrier is given in Sections 3, 4 and 5.

2-3 The container barrier

Many current discussions of radwaste disposal techniques (e.g. Cohen, 1977a) have assumed that the container material will not survive in the geological environment and does not constitute a significant barrier. This, however, may be an unnecessarily pessimistic view arising from an inadequate understanding of geochemical principles. Because of its high chromium content, stainless steel is thermodynamically unstable in natural geological environments and will surely disintegrate on a relatively short timescale. This would not happen with containers of gold or platinum, which would be ideal for the purpose. Unfortunately, they are excluded by cost.

Bird and Ringwood (1978) have pointed out, however, that the alloy Ni_3Fe is known to have been thermodynamically stable in certain natural geochemical environments for periods exceeding 100 million years. This alloy is formed during the metamorphic evolution of serpentinite rocks. There is little reason to doubt that a thick radwaste container of Ni_3Fe would be stable in the geochemical environment provided by burial within a serpentinite, or within a partially serpentinised ultramafic rock. Alternatively, an 'engineered' geochemical environment could be provided. For example, a deep cavity in granitic bedrock could be made in which Ni_3Fe containers of radwaste were placed and then surrounded with a buffer zone composed of crushed serpentinite and magnesium oxide. Any groundwater entering the cavity would cause the MgO to react to form

$Mg(OH)_2$ (brucite) thereby increasing its volume by a factor of 2 and sealing the cavity. The geochemical environment provided by the buffer (eH, pH, ionic species) would maintain Ni_3Fe in its field of thermodynamic stability, thereby providing the desired integrity of the container.

Fyfe (1977) has made an analogous proposal to use copper as a container material in view of its demonstrated long-term stability ($>10^8$ years) in geochemical environments provided by altered basaltic rocks.

The above discussion is not suggesting that a superior container material, alone, is a sufficient answer to the radwaste disposal problem. However, there is little doubt that utilisation of such a container can greatly improve our capacity to prevent radwaste from reaching the biosphere. The important point is that we are employing known geochemical principles and that it is *nature,* herself, which has provided the vital evidence that certain metallic container materials can maintain their integrity for periods exceeding 10^8 years in appropriate geochemical environments.

2-4 The geologic barrier

The principal mechanism by which radioactive elements might be removed from deeply buried radwaste and transferred to the biosphere is via leaching and transport by circulating groundwater. Consequently, it is necessary to dispose of the radwaste in a geologic environment which minimises this possibility.

Many natural rock systems have been recognised as possessing very low permeabilities to groundwater. These include thick beds of rocksalt, which are highly favoured as radwaste repositories in the USA and West Germany. Other rock systems being investigated include crystalline rocks (e.g. granites) in Sweden and Canada, shales and mudstones by various European countries, and the deep ocean floor (UK). In favourable circumstances, also, these rocks may possess very low permeabilities. This can be established by conventional measurements. Thus any leakage from a radwaste repository in such an environment would

necessarily occur at a very slow rate which can be quantified on the basis of experimental data. Providing the time constant for this leakage exceeds the characteristic times needed for decay of radioactivities to acceptable levels, the geologic barrier would be acceptable. Identification of such regions requires detailed hydrological investigations, which are now in progress in many countries. In the light of these investigations it appears almost certain that suitable geological environments for containment on a thousand-year timescale can be found. This would permit decay of fission elements. It also seems likely, but not proven, that containment for 10^6 years can be achieved, thereby permitting decay of the actinides.

Fortunately, containment of the actinides is further facilitated by another key property of selected geologic environments—the capacity of many rocks to precipitate or adsorb radioactive species from circulating groundwaters, thereby fixing them in the host rocks and preventing their entry into the biosphere. For example, Fried *et al.* (1977) investigated migration of plutonium and americium through samples of tuff, basalt and limestone. One set of experiments dealt with migration through fissures and the other with flow through pores. They demonstrated that these elements were strongly adsorbed and fixed by the minerals of these rocks. On the basis of these results, they concluded that little plutonium and americium could reach the external environment from a well-designed and isolated geological repository site. Other rock types which are known to have the capacity to precipitate and adsorb fission product elements and actinides from solution in groundwaters include certain kinds of shales and mudstones (e.g. Heremans *et al.*, 1976; Brookins, 1976). The insolubility and immobility of the long-lived actinides in appropriate geologic environments is most fortunate, and extremely important. Clearly, it is desirable to exploit these properties when selecting an appropriate repository site for radwaste.

In this section, a general discussion of the multi-barrier concept for preventing radwaste from reaching the biosphere has been

given. Each of the three separate barriers, alone, should ideally be capable of isolating the waste. We will now proceed to a detailed discussion of the first of these barriers—*immobilisation*—and investigate ways in which its security can be enhanced.

3 Current techniques of radwaste immobilisation

3-1 Immobilisation in borosilicate glass

A brief description of this process was given in Section 2-2. It is by far the most 'popular' process advocated by the nuclear power establishment. A full-scale production facility is about to begin in France, whilst extensive pilot plant studies have been carried out in the USA, UK, and other countries.

The process is appealing because of its simplicity and utilisation of conventional glass-making technology (Figs. 2, 3). The product contains about 25 per cent of radwaste and its composition is given in Table 2. It is readily transportable and resistant to radiation damage. It is also very resistant to leaching by pure water at 100°C.

Despite these important attributes, the author is unconvinced that glass is the most appropriate medium for immobilisation of radwaste. Glasses are thermodynamically unstable relative to a chemically equivalent assemblage of crystalline phases. Thus,

Table 2 Typical composition of borosilicate glass containing radwaste

	wt. %
SiO_2	27.3
B_2O_3	11.1
ZnO	21.3
$Na_2O + K_2O$	8.1
MgO + CaO + SrO + BaO	5.9
Radwaste	26.3

Fig. 2 Plant for evaporating radwaste solution to form calcine, followed by melting of calcine to glass in stainless steel canisters.

under some circumstances, they may 'devitrify' to form the stable crystalline assemblage. This may cause the leachability and surface area to be dramatically increased.

The resistance of glasses and other immobilisation media to leaching has usually been measured by solution tests in pure water at 100°C. This procedure is excessively naive and does not provide any secure grounds for predicting the stability of glass in appropriate geochemical environments, where the groundwater would be characterised by a wide range of pressure, temperature, pH, redox-potential and compositional variations. This point has been recently recognised by a working party set up to study this topic (Hench *et al.*, 1977).

In particular, borosilicate glasses readily devitrify when subjected to the action of water and steam at elevated pressures and temperatures (e.g. McCarthy *et al.*, 1978). In some postulated geologic disposal environments, the temperatures along the central axes of glass cylinders will exceed 300°C for periods of 20 years or more subsequent to burial. If the burial is at considerable depths (e.g. ~1000 metres, which is desirable for other purposes) and the repository has become sealed, the interaction of groundwater with glass in the interior of cylinders will occur at elevated temperatures and pressures (up to 200 atmospheres). Note that the glass cylinders are extensively cracked by thermal shock during fabrication (Ross, 1977) so that water would readily penetrate to the centreline once the stainless steel cladding had been breached. Under these conditions, borosilicate glasses would probably devitrify in a few weeks, as shown by the results of McCarthy *et al.* (1978) and also by unpublished work of the author. Moreover, the effects of other variables upon glasses, particularly pH and the dissolved solutes in groundwaters, remain to be investigated.

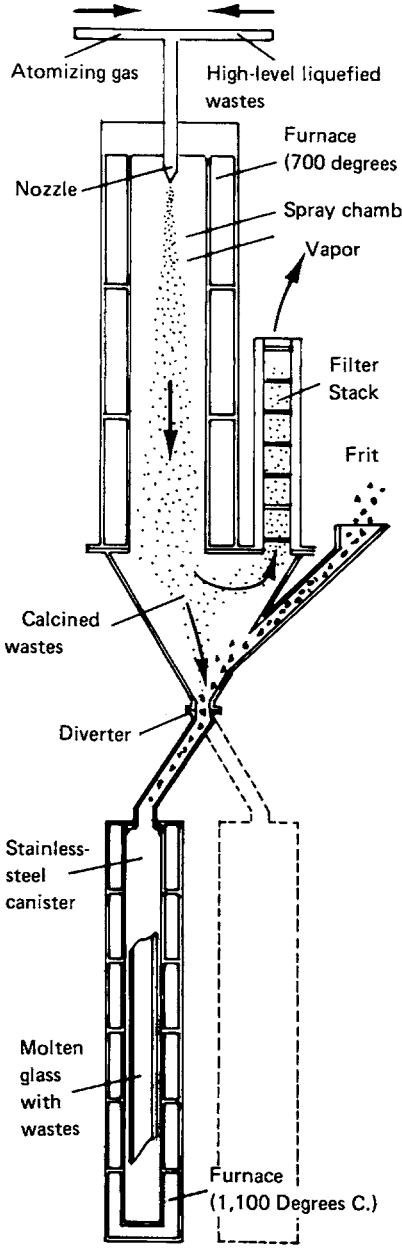

Atomizing gas
High-level liquefied wastes
Furnace (700 degrees C.)
Nozzle
Spray chamber
Vapor
Filter
Stack
Frit
Calcined wastes
Diverter
Stainless-steel canister
Molten glass with wastes
Furnace (1,100 Degrees C.)

Fig. 3 Continuous furnace for melting calcine to glass. Based upon commercial resistance-heated glass-making furnace.

There is an extensive body of opinion which maintains that burial of glass cylinders in salt formations will guarantee effective isolation from groundwater. This proposition is very doubtful. Thick salt formations commonly contain large discrete pockets of brine, the presence of which cannot be directly detected. Moreover, natural salt normally contains about 0.5 per cent of small inclusions of brine, more or less uniformly distributed (Cohen, 1977a,b). Buried radwaste establishes a thermal field and the brine migrates towards the waste cylinders by a process of solution and recrystallisation (Fig. 4). Thus, any brine within the thermal field will ultimately interact with the radwaste cylinder. Cohen (1977a,b) assumes that the brine will simply boil when it encounters the radwaste, thereby being removed from the system. However, this will depend on whether or not the repository has been sealed. If it has, the brine will interact with glass at relatively high temperatures and pressures (up to 200 atmospheres for burial at a depth of 1000 metres) and will be repeatedly recondensed and reboiled under reflux conditions. This would almost certainly cause devitrification of the glass and strong leaching of the product within a relatively short interval. Moreover, the high salt content of the brine and steam would increase its corrosiveness. Finally, the effects of radiation from the canisters may also produce highly corrosive species in the brine by radiolysis.

These problems will not be solved as Cohen (1977a,b) assumes, if the entrance to the repository is kept unsealed for 20-50 years, permitting it to be ventilated. Even under these circumstances, it is proposed that the individual canisters will be deposited in holes in the salt which will be self-sealing. Water will still migrate towards the canisters and will be boiled under substantial pressure, because of the finite strength of the surrounding salt. The pressure developed in this case will be much smaller than the ultimate lithostatic pressure at the particular

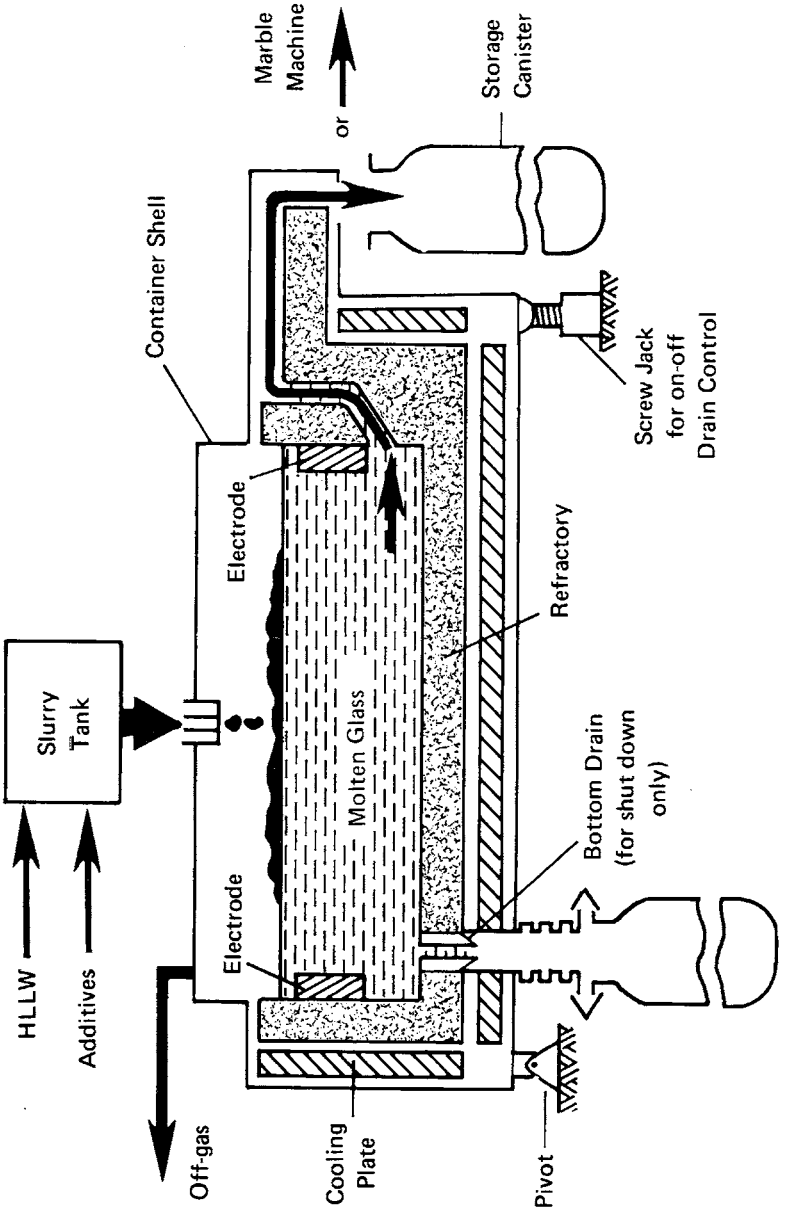
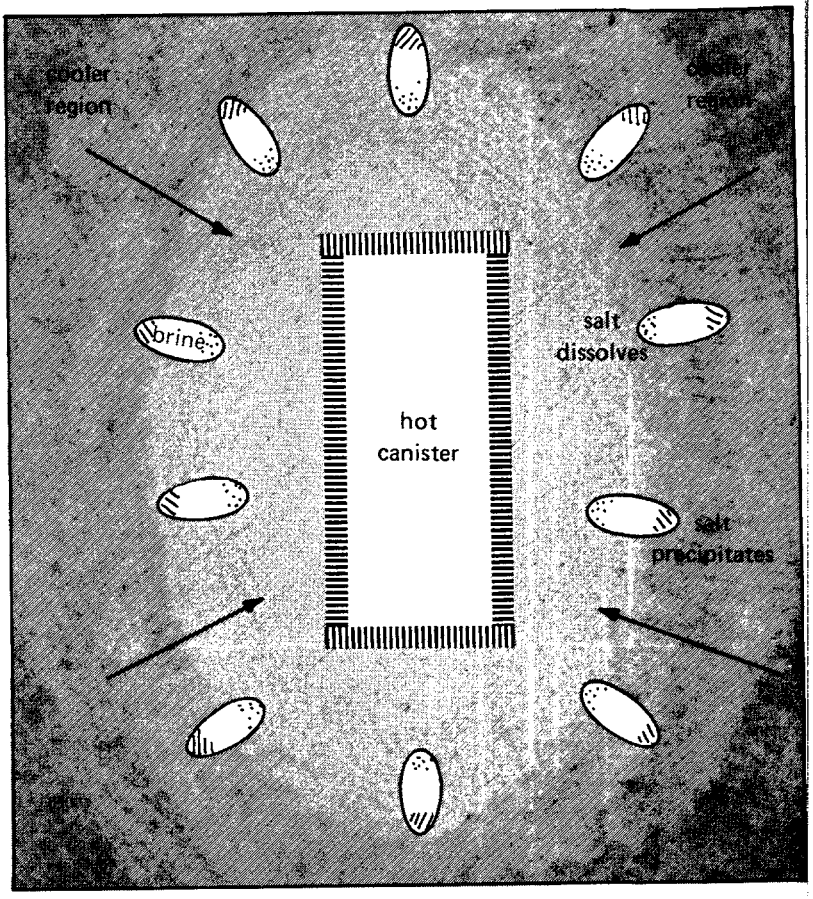

Marble Machine
or
Storage Canister
Container Shell
Screw Jack for on-off Drain Control
Electrode
Refractory
Slurry Tank
Molten Glass
Bottom Drain (for shut down only)
HLLW
Additives
Electrode
Off-gas
Cooling Plate
Pivot

Fig. 4 Heat from the waste canister buried in a salt formation causes the migration of tiny pockets of water in the direction of the higher temperature. This is caused by salt preferentially dissolving on the hotter side of the pocket (nearer the canister) and precipitating out of solution on the cooler side (away from the canister).



depth but will still be high enough to cause the saline water and steam to be strongly corrosive. Water vapour will not migrate away from the canisters as Cohen maintains. It would simply recondense in cooler regions some distance from the canister and migrate back to the canister via the effect depicted in Fig. 4. Thus, the canister will be subjected to the sustained effect of corrosive boiling brine under reflux conditions. Neither the container nor the glass are likely to survive these conditions.

Disposal of radwaste in salt beds may also raise problems of rheological stability. If cylinders are simply inserted in vertical holes sunk in salt, and later sealed, they will attract significant amounts of brine as discussed above. This will cause solution and recrystallisation within the stress field established by the waste canister. Salt will be dissolved from below and reprecipitated above, whilst the canister may migrate to the bottom of the salt horizon. This would not be a preferred outcome of this mode of disposal.

The many advocates of radwaste disposal in salt formations may well object that the preceding discussion is unduly pessimistic. This could possibly be so, but who really knows? The important point about disposal of radwaste in glass, and specifically the emplacement of glass in salt formations, is that we are dealing with a situation which is not readily predictable in the long term on the basis of existing scientific principles and practice*. It becomes imperative, therefore, to explore alternative modes of immobilisation.

3-2 Immobilisation in supercalcine

McCarthy (1977) and colleagues have previously recognised some of the uncertain aspects of glass immobilisation and have proposed that radwaste be incorporated in ceramic materials composed of crystalline phases. A phase assemblage of this

* The author's reservations about the safety of salt formations for radwaste disposal have been reinforced by a recent article in *Science*, received after this report was prepared (Carter, 1978).

nature would be much closer to thermodynamic equilibrium than glass, so that the risks arising from devitrification of glasses would be avoided. Incorporation of individual fission-product species in specific phases would be governed by the well-known principles of crystal chemistry and solid state chemistry.

The proposed ceramic host medium is termed 'supercalcine' (McCarthy, 1977). It is produced by adding about 50 per cent of the oxides of Si, Ca, Al and Sr to the solution of high-level waste before calcination. These components are added in carefully defined proportions so that during calcination they will react with the components of radwaste to form a specific as-

Table 3 Typical supercalcine formulation (McCarthy, 1977)

Millimoles in radwaste	Phase composition	Structure	Required additives
420 REE*	60 $Ca_3REE_7(SiO_4)_5(PO_4)O_2$	Apatite	180 Ca
60 (PO_4)			300 Si
80 Cs	80 $CsAlSi_2O_6$	Pollucite	80 Al
			120 Si
120 Mo	120 $SrMoO_4$	Scheelite	120 Sr
50 Sr	In Scheelite solid solution		
50 Ba			—100 Sr
120 Zr	120 ZrO_2	Fluorite	
80 Fe	6 Ni $(Fe,Cr)O_4$	Spinel	
14 Cr	41 $(Fe,Cr)_2O_3$	Corundum	
6 Ni			

1000 millimoles of waste species require these additives to form the desired supercalcine phase assemblages.	Mm	Wt %
	180 Ca	CaO 19.0
	80 Al	Al_2O_3 11.4
	420 Si	SiO_2 67.8
	20 Sr	SrO 1.8

*REE—rare earth elements

semblage of desired crystalline phases, possessing apatite, fluorite, scheelite, pollucite and spinel structures (Table 3). An important objective is to ensure crystallisation of ^{137}Cs (one of the most dangerous and mobile species) in the stable and insoluble mineral 'pollucite', $CsAlSi_2O_6$.

After preliminary heat treatment, the oxide mixture of additives and radwaste is formed into 5 mm pellets (Fig. 5) and fired at about 1200°C for 1-2 hours resulting in the formation of a finely crystalline but moderately porous phase assemblage in which radwaste atomic species are distributed according to the principles of chemical equilibrium (Fig. 6). Leaching studies in water at 100°C revealed similar solubility to borosilicate glass (however, the relevance of this test is not obvious).

McCarthy and colleagues point to some important potential advantages of supercalcine as an immobilisation medium as compared to glass.

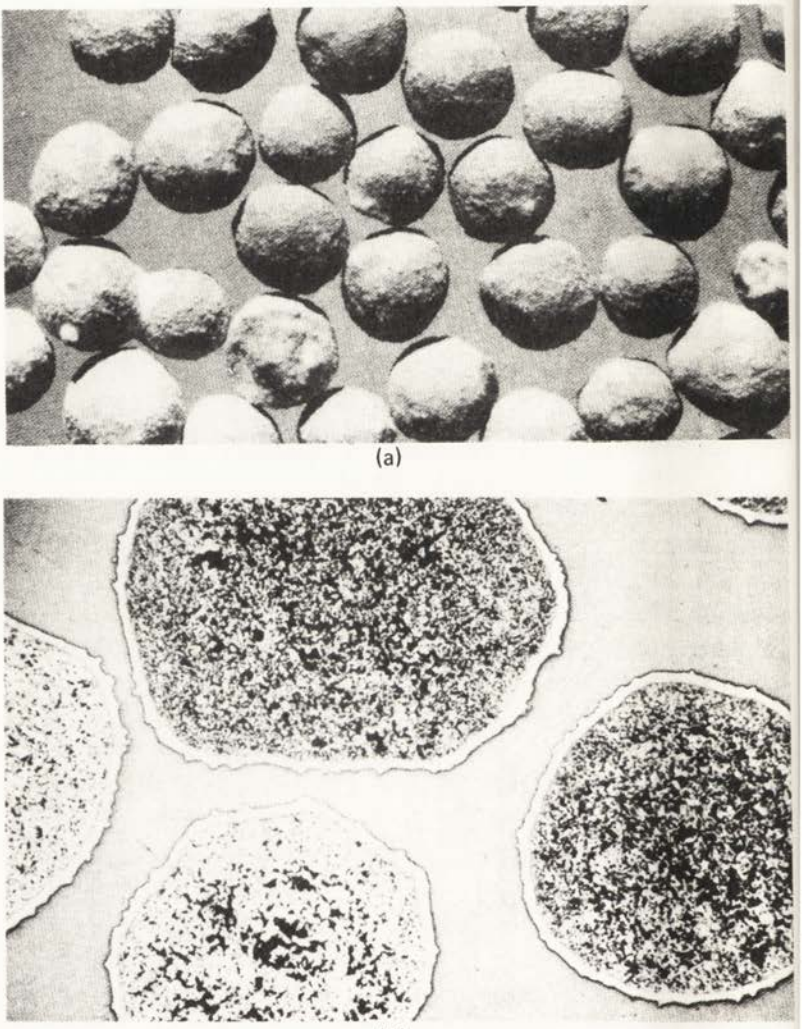
(a) Since the assemblage is already crystalline, there is no risk of devitrification, as would occur in the case of glass, accompanied by a great increase in solubility.

(b) Supercalcine has a much greater thermal stability than glass. Accordingly, additional processing can be carried out, increasing its effectiveness. For example, supercalcine pellets can be coated with a layer of impervious, refractory, inert, alumina (Fig. 5) which will greatly increase their resistance to leaching and corrosion. The armoured pellets can then be encased in a matrix of a chemically inert metal such as lead.

(c) Because of higher thermal stability, radwaste can be incorporated in supercalcine in greater concentrations (e.g. 50 per cent by weight) than in glass (20-30 per cent) and sooner after leaving the reactor.

(d) The fundamental principles governing the formation of the crystalline phases and the distribution of radwaste species among these phases are well understood. Predictions of long-term behaviour of these phases in various environments, and additional relevant experimentation can be carried out on the basis of existing knowledge of crystal chemistry and solid state

Fig. 5 Supercalcine pellets coated with alumina after firing for thermal stability, and sections of same showing core-coating interaction after 3 days at 900°C. Pellets are about 5 mm in diameter. Note that the individual crystals in supercalcine are very small, mostly less than a few microns. (From McCarthy, 1977.)



(a)

(b)

chemistry. In comparison, our understanding of the structure and behaviour of glasses at the atomic level is much less advanced, and reliable predictions cannot be made in the event of devitrification in the geological environment.

The advantages referred to above are very significant. Unfortunately, there are some accompanying disadvantages:

(a) Supercalcine contains at least 50 per cent of radwaste. (The principal motivation for this procedure seems to have been to improve its economic competitiveness with glass as a radwaste host.) Thus the crystalline phase assemblage which is formed after incorporation of the added components is dictated, to a large degree, by the composition of the radwaste (Table 1). The mineral assemblage so formed (Table 3) is not necessarily ideal for long-term containment of radwaste components.

(b) Some of the radioactive species, e.g. ^{137}Cs, which ultimately decays to strontium, and ^{90}Sr which ultimately decays to zirconium, would not be stable at high concentrations in their crystalline host phases. Thus, after a substantial proportion of the caesium in pollucite had decayed to strontium, the crystal lattice would probably be severely damaged, permitting ready leaching of much of the remaining caesium. A similar problem occurs in connection with the incorporation of ^{90}Sr in the apatite and scheelite phases (Table 1).

(c) Because of high loadings of radwaste in supercalcine, excessive radiation damage of some crystalline forms will occur. This may be particularly severe for the relatively open apatite structure, which will incorporate some of the actinide elements. Excessive radiation damage may enhance solubility in some phases. Another effect is pronounced volume expansion (1—10 per cent) caused by radiation damage to the crystalline structure leading to the so-called metamict state. This may cause cracking and increased permeability.

4 A new approach to radwaste immobilisation

4-1 Basic philosophy

An improved method of radwaste immobilisation might seek to retain the advantages of the supercalcine concept and to minimise its disadvantages. I believe that these objectives can be attained but at increased cost. This need not be a serious objection.

It seems that the principal existing programs to develop glass and supercalcine as radwaste hosts have been concerned with minimising expenditure and have accordingly preferred to incorporate very high proportions of radwaste in the chosen media. Naturally, this reduces processing,* transport and disposal costs. But these probably amount only to about half of one per cent of the cost of nuclear power. In view of the crucial social issues involved, and the immense concern with which radwaste disposal is now viewed by mankind, we can easily afford to spend 5 to 10 times as much money to obtain a widely acceptable solution.

Accordingly, we will now describe a more expensive, but relatively simple process based upon immobilisation of radwaste in crystalline phases, in which the concentration of radwaste does not exceed 10 per cent. Moreover, if considered desirable, this percentage could be further reduced to about 2 per cent in a second stage of processing which would take place about 10 to 20 years after the first stage.

* This refers to the *high temperature* processing involved in calcine, glass or ceramic production. It does not include the low temperature reprocessing involved in extraction of plutonium and uranium from high level waste solutions.

There are some major technical advantages to be obtained by reducing the concentration of radwaste:

(a) In supercalcine, it is the proportions of elements in radwaste which most strongly control the nature of the crystalline phase assemblage. However, if the added components exceed 90 per cent, *they* will control the nature of the crystalline phases produced. The radwaste atomic species will then simply substitute in low concentrations within the crystal lattices determined by the major added components. This provides a great deal of flexibility in selecting a crystalline phase assemblage with the most desirable immobilisation characteristics. This flexibility does not exist in the case of supercalcine, in which the phase assemblage is not optimal for its purpose.

(b) It is possible to design host systems which can be totally melted at temperatures less than 1300°C and which, on cooling, crystallise completely to produce well-formed, comparatively large crystals which are capable of providing specific lattice sites in which radwaste atoms can be incorporated. This amounts to producing a synthetic analogue of a natural igneous rock, and for this reason, the acronym 'SYNROC' (synthetic rock) is used for the system described herein.

(c) Because the radwaste atoms are not major components but are distributed as dilute solid solutions, the problems connected with transmutation and radiation damage are greatly reduced. The flexibility conferred by the large proportion of added host material means that mineral phases can be produced which are known to, or likely to possess the ability to retain transmutation products in stable lattice sites and to retain radwaste species even after suffering extensive radiation damage.

(d) Another advantage of the compositional flexibility and melting behaviour of the SYNROC process is that relatively well-formed large host crystals can be produced of types which are *known* to be extremely resistant to leaching in appropriate geologic environments.

(e) Much of the technology already employed in connection with the fabrication of glass cylinders can be utilised. The

ceramic melter in Fig. 3 would be ideal for the production of SYNROC materials.

4-2 Relation of SYNROC process to natural petrological systems

All natural igneous rocks contain small amounts of radioactive elements (e.g. U, Th, ^{40}K) as well as many other minor elements which are also present in radwaste. When an igneous rock crystallises, these minor elements become distributed among the various mineral phases. Many of these mineral phases are known to be highly resistant to leaching and alteration in geochemical environments far more varied and severe than would be encountered in any radwaste repository. Thus, minerals such as zircon are known in some cases to have retained their uranium quantitatively for periods exceeding 2000 million years, in spite of radiation damage. Likewise, strontium and rubidium are known from isotopic studies to have been immobilised in minerals such as felspar for corresponding periods. Caesium can be firmly locked up in micas for hundreds of millions of years, and, in the form of the mineral pollucite, is known to have been stable for similar periods. This situation applies to all of the radwaste species except the most volatile, ^{3}H, ^{85}Kr, ^{129}I.

Thus, there already exists a vast reservoir of knowledge in the fields of geochemistry, mineralogy, petrology, crystal chemistry and solid state chemistry which can be directly applied to the problem of radwaste immobilisation. It is because of the existence of this knowledge and its applicability over timescales thousands of times longer than are necessary for the isolation of radwaste that we are in a position to *predict* with a large degree of confidence, the capacity of synthetic systems, closely related to natural rocks, to retain radwastes. This background of knowledge does not exist in the case of glasses and it is because of this that we cannot be certain of their long-term safety.

The SYNROC concept is based first of all upon the recognition of a number of types of minerals which are known either

directly, or indirectly, based upon their crystal chemical properties, to form stable hosts for radwaste elements. Phase equilibria between these minerals are then explored for thermodynamic compatibility and melting relationships. When a favourable mineral assemblage has been identified, it is synthesised from component oxides, intimately mixed with, e.g., 10 per cent of radwaste. The synthesis may be effected either under subsolidus conditions, below the melting point, or by melting and crystallisation.

5 The SYNROC process for radwaste immobilisation

5-1 Mineralogical basis

The first objective was to identify a series of natural minerals which were refractory, of proven resistance to processes of leaching and alteration in a wide range of geological environments for periods exceeding 20 million years, and which had crystal-chemical properties which would permit them to accept radwaste elements into solid solution in their lattice sites, where they would be securely bound. There are many possible candidate minerals possessing these properties and the field to be explored is vast. Most of our experimental work to date has been based upon the following mineral types, which are known to possess these desired properties.

Perovskite, $CaTiO_3$
This mineral is capable of taking an extremely wide range of other elements into stable solid solution. The elements which are capable of replacing calcium in its lattice site include Sr^{2+}, Ba^{2+}, Na^{1+}, all rare earths $(REE)^{3+}$, Y^{3+}, Cd^{2+}, Cm^{3+}, Am^{3+}, Pu^{3+} whilst the elements capable of entering the titanium lattice site include Nb^{5+}, Zr^{4+}, Mo^{4+}, Ru^{4+}, Th^{4+}, U^{4+}, Sn^{4+}, Te^{4+}, Tc^{4+}, Rh^{3+}, Fe^{3+}, Cr^{3+}, Al^{3+}. Our studies (discussed subsequently) also show that Ti^{4+} can be replaced by heavy rare earths. Many more substitutions are known, but only those relevant to radwaste immobilisation have been mentioned.

Zirconia, ZrO_2
Zirconia possesses the fluorite structure at high temperatures. This is capable of an extremely wide range of atomic sub-

stitutions. On cooling, pure zirconia transforms to a monoclinic form (baddeleyite) which has only limited ability to dissolve other elements. However, when crystallised in equilibrium with perovskite, sufficient Ca and Ti enter the lattice to stabilise the fluorite form to low temperatures. In this state, zirconia is a ready host for the actinides, U^{4+}, Pu^{4+}, Np^{4+}, Th^{4+}, Cm^{4+}, Am^{4+}, and Ce^{4+} and the trivalent rare earths, all of which are important elements in radwaste. The crystal structure of this mineral permits very large departures from stoichiometry.

The Hollandite Series, specifically $K(Al,Fe)Ti_3O_8$-$BaAlTi_3O_8$

The natural mineral $K(Al,Fe)Ti_3O_8$ is known as *priderite* and occurs in ~20 million year volcanic rocks in the Kimberley region of Western Australia. This mineral possesses the hollandite structure, which is closely related to that of rutile (TiO_2), one of the most refractory and insoluble of natural minerals. The hollandite structure is almost as close-packed as rutile but differs in having tunnels parallel to the vertical axis in which very large atoms such as K, Rb, Cs, Ba and Sr may be stably bound.

We have synthesised pure hollandite forms of $CsAlTi_3O_8$, $Ba_{\frac{1}{2}}AlTi_3O_8$, $Sr_{\frac{1}{2}}AlTi_3O_8$ and $KAlTi_3O_8$, and demonstrated the existence of extensive solid solutions between these end-members. The structure displays wide deviations from stoichiometry and forms extensive solid solutions with pure TiO_2. Because of its higher ionic charge, it can be predicted that the entry of Ba^{2+} replacing K^{1+} will lead to a strengthening of the structure and will further decrease its leachability. The hollandite structure is also capable of taking a wide range of elements into solid solution. As noted above, Na, K, Rb, Cs, Ba, Sr and Pb can be incorporated in the tunnels, whilst Mg, Co, Ni, Cu, Zn, Cr, Fe, Mn, Mo, Ru and Sn are capable of replacing Al and Ti in the lattice. It is likely that Tc^{4+} and Te^{4+} would also be able to replace Ti^{4+}.

Barium felspar or celsian, $BaAl_2Si_2O_8$

This is an extremely refractory and insoluble mineral, possess-

ing a framework structure. Felspars are the most common of all rock-forming minerals in the earth's crust. It is possible to replace the Ba^{2+} ions extensively by Ca^{2+}, Pb^{2+}, Sr^{2+}, K^{1+}, Na^{1+}, and Rb^{1+}. Limited replacement of barium by caesium is also possible. We have synthesised Ba-felspars containing over 4 per cent of caesium (as $CsAlSi_3O_8$). Felspars are usually fairly stoichiometric structures as compared to the other minerals previously mentioned.

Leucite, $KAlSi_2O_6$

Leucite, which melts around 1693°C, occurs in certain kinds of volcanic rocks and is known to have survived in geological environments for periods exceeding 50 million years. It has a similar structure to the caesium mineral *pollucite* ($CsAlSi_2O_6$), which has been found in pegmatites over 1000 million years old. We have found that it is possible to form an extensive solid solution series between the two minerals, with caesium replacing potassium in the large cage-like interstices in the leucite lattice. We have also found that a substantial amount of $BaAl_2SiO_6$ can enter the lattice in solid solution. This is expected to increase its stability and resistance to leaching. Leucite is an important mineral in radwaste immobilisation because it provides a ready host for ^{137}Cs.

Kalsilite, $KAlSiO_4$

Kalsilite, which melts around 1750°C, also occurs in some potassium-rich volcanic rocks. This phase has been identified as a crystallisation product in some SYNROC systems. The presence of a small amount of caesium in solid solution in $KAlSiO_4$ causes a change in structure. Thus, we have found a complete solid solution series between $(K_{0.85}Cs_{0.15})AlSiO_4$ and $CsAlSiO_4$ to exist at 1300°C. This solid solution series possesses the $RbAlSiO_4$ structure (Von Klaska and Jarchow, 1975). This $(K,Cs)AlSiO_4$ solid solution is likely to be of considerable importance in immobilising caesium in SYNROC systems. Gallagher *et al.* (1977) demonstrated that in pure $CsAlSiO_4$,

the caesium atoms are effectively trapped in cavities bounded by eleven oxygen atoms and that the openings are too small to permit the caesium atom to pass through. Therefore, the structure should display little ion-exchange behaviour when in contact with groundwater solutions. In future discussion, we shall call this the 'R' phase, after $RbAlSiO_4$.

Mica (specifically fluorphlogopite $KMg_3AlSi_3O_{10}(F)_2$)

Micas are among the most common rock-forming minerals in the earth's crust and are known to have survived in a wide range of geological environments for periods exceeding 2000 million years. Ancient micas containing small amounts of caesium are also known in nature. We have successfully synthesised a caesium mica $CsMg_3AlSi_3O_{10}(F)_2$ and have shown that caesium can extensively replace potassium in phlogopite. It seems that these micas may also provide an effective alternative means of immobilising fission product caesium.

Sphene, $CaTiSiO_5$

Sphene is a common accessory mineral in many natural igneous and metamorphic rocks and is highly resistant to weathering and alteration. Its structure also permits a wide range of atomic substitutions. Sphenes are known to contain substantial quantities of Na, REE, Mn, and Sr (replacing calcium) and Al, Fe, Mg, Nb, V and Cr replacing Ti^{4+}. It can be predicted on crystal chemical grounds that many other fission products and actinides in radwaste would be able to enter this lattice.

Fresnoite, $Ba_2TiSi_2O_8$

The structure of this mineral is related to melilite, which is known to accept many other elements possessing compatible ionic radii and charges into solid solution. We have not explored the properties of fresnoite in detail. However, it is expected to be refractory and non-leachable. It is also compatible thermodynamically with many of the minerals mentioned above.

5-2 Production of SYNROC systems

The minerals mentioned above constitute only a small proportion of the species having properties which would permit them to be employed for radwaste immobilisation.

The next step was to find combinations of these minerals which are thermodynamically compatible when heated to high temperatures, and also when melted. A further objective was to obtain *combinations* of these individually refractory phases which had relatively low melting points, and which, after being melted, could be crystallised completely into well-formed crystals in which the atomic species present in radwaste were effectively immobilised.

We have found several such appropriate combinations of host minerals. We will describe just one example which seems to possess the properties required and which has been studied, to date, more extensively than others. Other compatible systems possessing desirable properties are mentioned in the appendix.

The pure mineral end-members chosen were perovskite $CaTiO_3$(P), potassium hollandite $KAlTi_3O_8$(H), Ba-felspar $BaAl_2Si_2O_8$(F) and zirconia ZrO_2(Z). These mineral phases were found to be thermodynamically compatible with each other under subsolidus conditions and also during melting, although their individual compositions were modified owing to solid solution formation, e.g. extensive replacement of K by Ba in hollandite, limited replacement of Ba by K in felspar and extensive replacement of Zr by Ca + Ti in the zirconia phase.

To a first approximation, the mixtures P, H and F form a pseudoternary system, as shown in Fig. 6. The temperatures at which substantial degrees of melting occur are also indicated in Fig. 6. Although the melting points of the individual minerals are very high, the temperature at which a substantial degree of melting occurs in the mixed system is only 1280°C. The composition of the minimum melting mixture is approximately $P_{17}H_{37}F_{46}$ (in weight per cent). Zirconia can be added to this system but does not substantially affect the minimum melting point, or other phase relations. However, it crystallises as the

fluorite modification of ZrO_2. Thus, Fig. 6 can be regarded as a pseudoternary section through the pseudoquaternary system, P-H-F-Z, projected from the Z corner of the quaternary tetrahedron. Typically we include about 10 per cent of ZrO_2 in our mixes.

When melted, say at 1350°C, and cooled to about 1150°C over a wide range of cooling rates (20°C/min to 2°C/min), the system crystallises very readily into well-formed crystals (Figs. 7A, B, C, D). This is a most important attribute. Compare the quality and sizes of these crystals with those in supercalcine (Fig. 5).

We have mentioned above that the system is not strictly quaternary from a thermodynamic point of view. This results from solid solution between phases (Table 5) which causes deviations from ternary or quaternary behaviour (Fig. 6).

Thus, on cooling melts made from these minerals, the system actually undergoes *fractional crystallisation* and the minimum melting temperature is below 1280°C, probably being in the vicinity of 1150-1200°C. On cooling, the residual liquids become richer in silica and potassium, and eventually other minerals including kalsilite and leucite crystallise. Both may contain substantial amounts of barium in solid solution (Table 4). Our results indicate that kalsilite (or one of its polymorphs) is essentially an equilibrium phase in the assemblage. However, pure leucite does not appear to be compatible with hollandite. Its appearance therefore implies either a reaction relationship during crystallisation or stabilisation by other components such as $BaAl_2SiO_6$ and $CsAlSi_2O_6$.

5-3 Incorporation of Radwaste in SYNROC

The next step was to mix the principal components of radwaste calcine (Table 1) into a SYNROC composition approximating that of the minimum melting composition of Fig. 6. The mixtures were then melted at 1330°C, mostly in sealed platinum tubes, and cooled at varying rates to about 1100°C, at which stage they had (usually) crystallised completely. The mineralogy of the

Fig. 6 Phase diagram for the pseudoternary system Ba-felspar-perovskite-hollandite. Approximate melting temperatures (°C) for the ternary minimum ($F_{46}P_{17}H_{37}$), binary eutectics and individual end members are shown. This system actually corresponds to a plane at 10% ZrO_2 in the pseudoquaternary system ZrO_2-F-P-H (upper right).

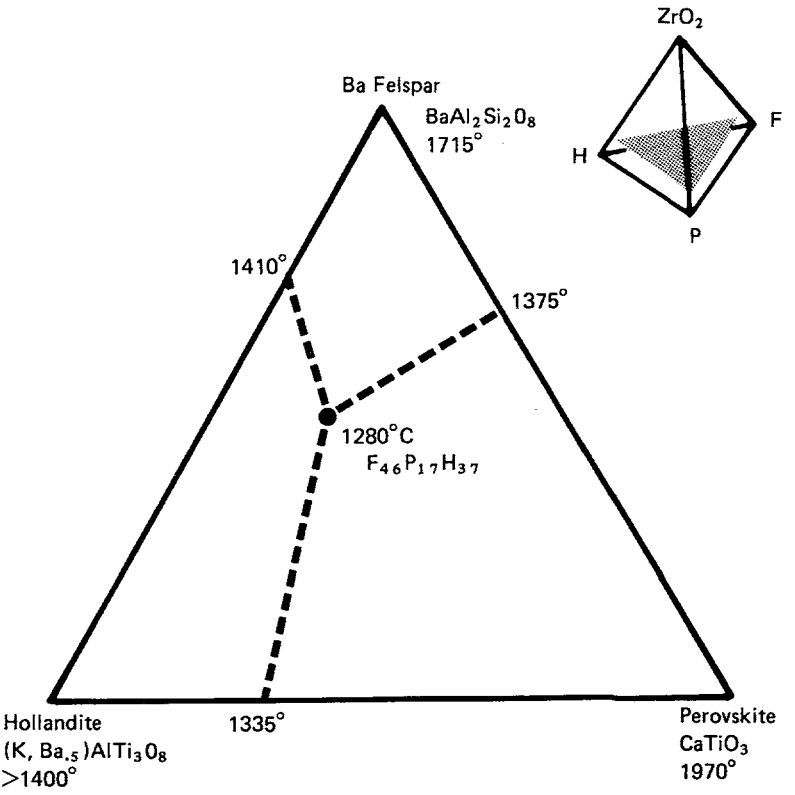


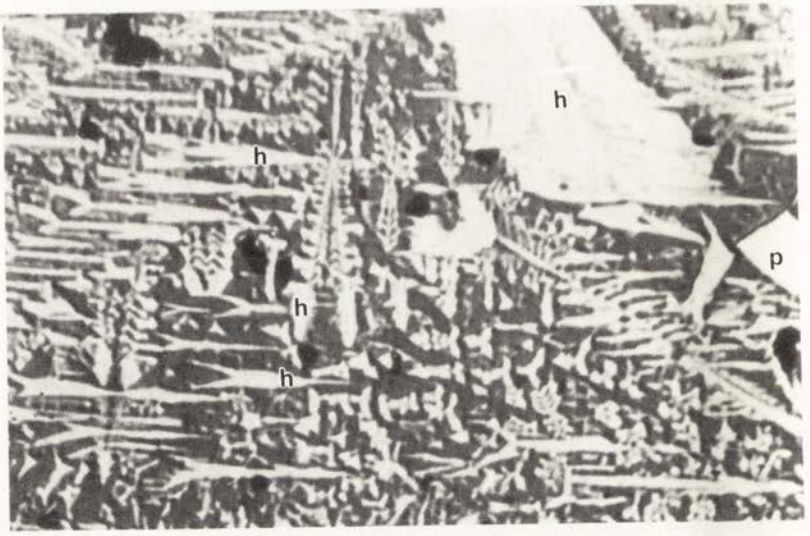
Fig. 7 A-D Reflected light photomicrographs show SYNROC produced over a range of cooling rates in the pseudoternary system Ba-felspar-perovskite-hollandite, using the composition $F_{40}P_{24}H_{36}$. Black areas are pits on the sample surface.

(A) Cooling rate 46°C/min. Perovskite (p) forms white euhedral crystals. Hollandite (h) forms light grey ragged prisms and dendritic intergrowths in the groundmass. Glassy groundmass is dark grey.

(B) Cooling rate 23°C/min. Perovskite (p) occurs as white euhedra. Light grey hollandite (h) forms elongate blades with dendritic overgrowths. Relatively clear dark grey patches consist of Ba-felspar (f). Dark grey groundmass consists of Ba-felspar plus glass.

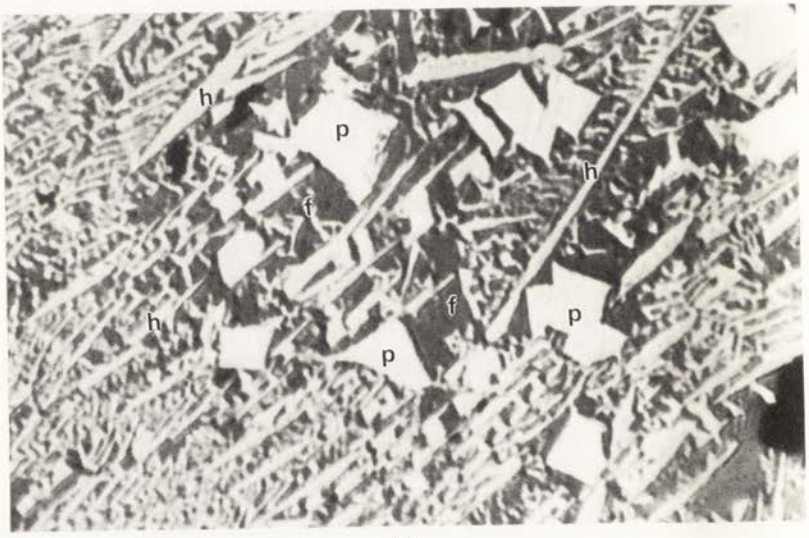
(C) Cooling rate 8°C/min. Light grey perovskite euhedra (p) are scattered throughout a network of skeletal hollandite crystals (h). Groundmass (dark grey) consists of Ba-felspar, Cs-bearing leucite and minor glass.

(D) Cooling rate 2°C/min. Large pale grey crystals of perovskite (p), hollandite (h) and dark grey Ba-felspar (f) are contained in an interlocking eutectic-type intergrowth of hollandite (light grey), Ba-felspar and Cs-bearing leucite (both dark grey).

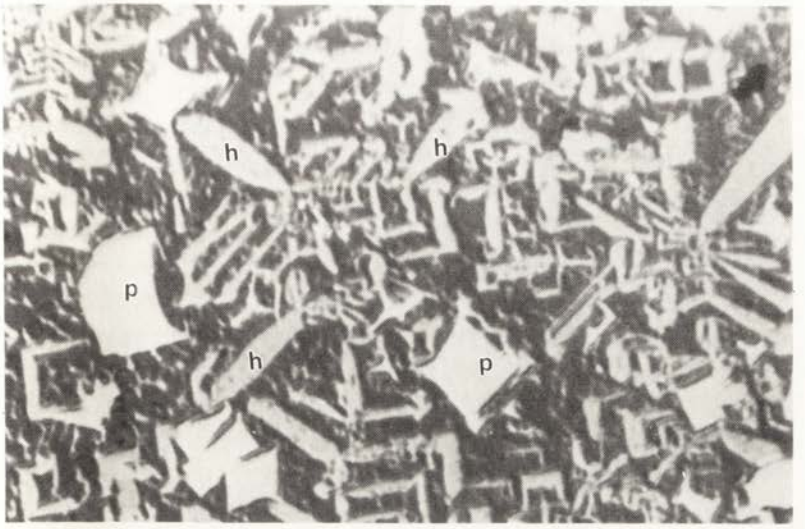


(a)

100μm

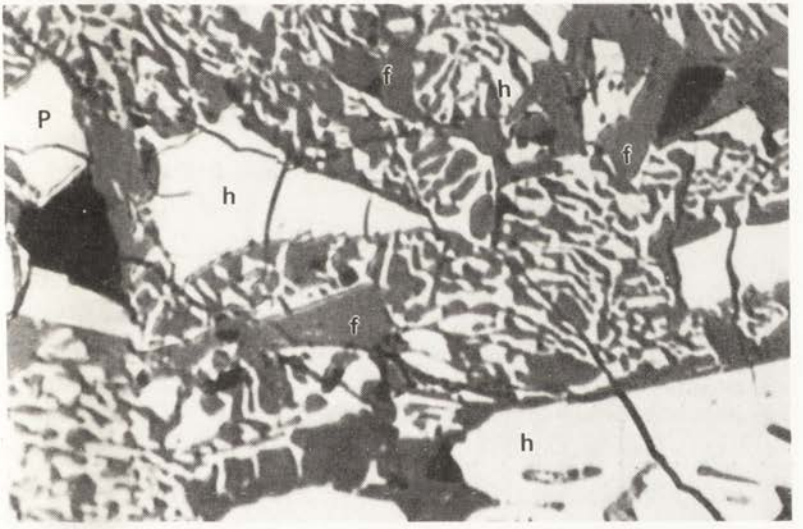


(b)



(c)

100μm



(d)

products was then studied by microscopy and X-ray diffraction, after which the distribution of radwaste elements among co-existing phases was investigated using an electronprobe micro-analyser. In some experiments, where the distributions of given elements between P, H and F phases were of primary importance, the ZrO_2 component was not introduced, in order to simplify the textural interpretation. In most experiments, SYNROC compositions were doped with one to three radwaste elements in amounts varying from one to two weight per cent of the given element.

Two important components of radwaste calcine are *zirconium* and *barium* (Table 1). Since these elements are also major components of the SYNROC phases, it is obvious that these radwaste elements will simply follow the non-radioactive common elements into the major phases. For all practical purposes, *rubidium* may be considered to be in the same category since its crystal chemical properties are almost identical to those of potassium, which is a major added element.

Although not among the most abundant species, *caesium* and *strontium* are the most dangerous fission products because of the ~30 year half-lives of ^{137}Cs and ^{90}Sr. The data in Table 4 show that *strontium* is almost totally partitioned into the perovskite phase. In other experiments, we have found up to 0.3 per cent SrO in the hollandite and 0.2 per cent SrO in the felspar.

The large ionic radius and unit charge of the *caesium* ion inhibit its entry into early crystallising Ba-K hollandite and Ba felspar phases. Accordingly, *caesium* becomes strongly concentrated in the residual liquid. Because of the large degree of substitution of potassium by barium in the hollandite structure (Table 4), the residual liquid formed during fractional crystallisation also becomes enriched in potassium and silica. In the absence of *caesium,* the last phase to crystallise seems to be kalsilite, $KAlSiO_4$ (or one of its polymorphs such as kaliophilite). However, in the presence of caesium, a related phase $(K,Cs)AlSiO_4$ possessing the $RbAlSiO_4$ structure is formed (We call this the 'R' phase). In a SYNROC system containing

radwaste, this phase is expected to be an important host for caesium. As noted earlier, it possesses the crystal chemical properties required to immobilise the caesium.

Table 4 Compositions of coexisting phases in mixture of $H_{30}F_{40}P_{20}$ doped with 6 per cent $CsAlTi_3O_8$ and 4 per cent $SrTiO_3$. Mixture was melted at 1330°C and cooled to 1100°C at 4° per minute in a sealed platinum capsule. Texture of this assemblage is similar to those of Fig. 7.

Coexisting phases	Hollandite	Perovskite	Ba-felspar	Leucite	Kalsilite*
SiO_2	—	—	34.1	40.4	38.3
TiO_2	73.8	56.2	—	—	—
Al_2O_3	15.6	0.3	26.0	24.1	32.3
CaO	—	—	0.2	0.2	—
BaO	8.4	n.d.	37.2	16.1	2.1
SrO	<.2	7.5	<0.2	<0.2	—
K_2O	1.4	—	2.1	10.6	24.8
Cs_2O	<.2	n.d.	0.2	7.9	1.9
Sum	99.2	100.2	99.6	99.3	99.4
Atomic proportions					
Si	—	—	2.09	1.75	0.637
Ti	3.05	.989	—	—	—
Al	1.01	.008	1.88	1.26	0.634
Ca	—	.907	0.01	0.01	—
Ba	.18	—	0.89	0.27	0.014
Sr	.0	.102	.0	.0	—
K	.10	—	0.16	0.59	0.527
Cs	.0	—	.01	0.14	0.007
Sum	4.34	2.006	5.04	3.99	1.82
Based on x,oxygen atoms	8	3	8	6	4

*Analyses of kalsilite was from a different, but related, run.

In other experiments where 2 per cent of Cs_2O was added to the SYNROC composition, it became strongly concentrated in the residual liquid and finally crystallised to form a leucite-type solid solution containing 8 per cent of Cs_2O. This phase also contained substantial amounts of barium as a $BaAl_2SiO_6$ component (Table 4). The conditions under which the R-type $(K,Cs)AlSiO_4$ solid solutions and leucite-type solid solutions appear during crystallisation depend upon the bulk composition of the system and have not yet been finally elucidated. The important point is that both phases are able to incorporate large amounts of caesium, thereby immobilising this dangerous radwaste element.

Because of their long half-lives, the behaviour of the actinide elements *plutonium, curium, neptunium, americium, uranium* and *thorium* are of key importance in radwaste disposal. Under typical redox conditions present during the formation of

Table 5 Compositions of coexisting phases in mixture of $H_{29}F_{39}P_{20}Z_{10}$ doped with 2 per cent UO_2. Mixture was melted at 1330°C and cooled to 1100°C at 2°C/minute in a sealed platinum capsule*.

	Fluorite-type Phase (zirconia)	Perovskite	Ba-felspar	Hollandite
SiO_2	—	—	34.6	—
TiO_2	40.1	56.1	—	68.5
ZrO_2	39.5	0.8	<0.1	1.0
UO_2	3.8	1.6	<0.2	0.3
Al_2O_3	2.1	—	26.4	14.2
BaO	—	—	37.5	13.5
CaO	14.6	41.4	0.2	0.4
K_2O	—	—	1.0	2.1
Total	100.1	99.9	99.7	100.0

*A very small amount (< 1 per cent) of residual glass (?) containing 0.5 per cent UO_2 was also present.

SYNROC, the stable cations are Pu^{4+}, Am^{4+}, Np^{4+}, U^{4+}, and Th^{4+}. These elements have very similar crystal chemical properties in the tetravalent state and their behaviour may be effectively modelled by a study of the distribution of U^{4+}. Curium may occur either as Cm^{4+} or as Cm^{3+}. In the former state it is similar to U^{4+}, whilst in the latter, it closely follows the rare earths, which are discussed subsequently.

We have studied the crystallisation of a P-H-F-Z SYNROC composition (Table 5) doped with a small amount of *uranium*. It is seen that the *uranium* is strongly partitioned into the zirconia solid solution (3.8 per cent UO_2) with about half that amount entering into the perovskite. The only other phase to contain uranium was hollandite (0.3 per cent UO_2). We can confidently expect that the other tetravalent actinides will display similar behaviour and will become effectively immobilised in the perovskite and zirconia phases.

The most abundant components of radwaste fission products are the *rare earth elements* (Table 1). We have studied the behaviour of three elements which possess crystal chemical properties representative of this family; lanthanum, a light rare earth, gadolinium, an intermediate rare earth and yttrium, which although not a rare earth, nevertheless has crystal chemical properties which are essentially identical to those of the heavy rare earth, ytterbium. Results are given in Table 6, columns A and B. The system studied did not include the fluorite-type ZrO_2 solid solution. It is seen that the *rare earths* were almost totally partitioned into the perovskite structure. A small amount of gadolinium entered the hollandite. It is not possible to determine La in hollandite because of analytical interference with Ba. However, the analysis does not sum to 100 per cent and we suspect that the hollandite incorporated about one per cent of La_2O_3.

A second experiment was carried out in which 10 per cent of ZrO_2 was added to the SYNROC system. Results are given in Table 6, columns C, D and E. It is seen that the rare earths and yttrium are in fact more strongly partitioned by a factor of

about 4 into the zirconia phase than into the perovskite. It is clear that both phases would provide excellent hosts for immobilising the rare earths and also other elements possessing similar crystal chemical properties, such as Cm^{3+}. If SYNROC is synthesised under highly reducing conditions, it is possible that some Pu^{3+} and Am^{3+} would be produced. These species would also be expected to enter the zirconia and perovskite phases.

Two of the most abundant individual elements among fission products are *molybdenum* and *ruthenium* (Table 1). Their behaviour during the crystallisation of SYNROC compositions is strongly dependent upon redox conditions. Under reducing conditions (e.g. oxygen fugacity smaller than at the Fe-FeO

Table 6 Distribution of La, Gd and Y between perovskite, hollandite and zirconia solid solutions in typical SYNROC compositions cooled from 1330 to 1100°C at 2°C per minute. Samples were doped with 2 per cent each of La_2O_3, Gd_2O_3 and Y_2O_3.
Columns A and B refer to a SYNROC composition not containing zirconia. Columns C, D and E refer to a separate SYNROC composition in which 10 per cent of ZrO_2 was present.

	A	B	C	D	E
	Hollandite	Perovskite	Hollandite	Perovskite	Zirconia
TiO_2	—	53.4	69	57.8	38.6
ZrO_2	75.4	—	2.8	1.6	38.3
Al_2O_3	13.9	1.4	11.2	0.6	4.6
La_2O_3	—	5.0	<0.4	0.8	3.0
Gd_2O_3	0.2	7.0	0.1	0.8	3.4
Y_2O_3	<0.1	7.0	0.1	0.9	3.8
BaO	6.8	—	13.0	—	—
CaO	—	26.2	1.2	36.8	10.5
K_2O	2.4	—	2.3	—	—
	98.7	100	99.7	99.3	102.2

No rare earth elements were detected in Ba-felspar.

buffer), Mo, Ru (and also Pd) are reduced to form a metallic alloy which occurs as small inclusions within the major SYNROC crystals. This alloy is expected to be extremely inert in the geochemical environment of a radwaste repository and these elements would be effectively immobilised. Under oxidising conditions, as for example, when SYNROC plus radwaste is melted in the presence of air, ruthenium occurs dominantly in the Ru^{4+} state which displays a remarkable preference to enter the hollandite lattice, replacing Ti^{4+}. In a SYNROC sample doped with 2 per cent RuO_2, the hollandite phase contained up to 12 per cent RuO_2 as compared to a maximum of 0.2 per cent RuO_2 in the perovskite. However, under these conditions, *molybdenum* was dominantly oxidised to the hexavalent state and apparently formed K_2MoO_4. This is soluble in water. It is clear, therefore, that if this SYNROC composition were to be melted under oxidising conditions, it would be necessary to conduct a second stage of reprocessing as is discussed in Section 6-2. In this second stage, after some 10-20 years of ageing, the SYNROC would be crushed and leached, thereby removing all soluble species. The remaining material would then be hot-pressed with excess alumina, to form a highly inert, dilute form of SYNROC. The molybdenum in solution would then be pre-

Table 7 Compositions of hollandite and perovskite phases present in SYNROC compositions doped with 3 per cent MoO_2 and cooled at 2°C per minute from 1330°C to 1100°C in a sealed molybdenum capsule.

	Hollandite	Perovskite
TiO_2	71	55.9
MoO_2	7.5	1.3
Al_2O_3	9.1	0.4
CaO	0.2	42.0
BaO	11.0	—
K_2O	1.6	—
	100.4	99.6

cipitated and solidified in an inert form according to conventional technology.

In a further experiment, SYNROC containing 3 per cent MoO_2 was cooled in a sealed molybdenum capsule from 1330°C to 1100°C at 2°C per minute. Compositions of coexisting hollandite and perovskite phases are given in Table 7. The hollandite contained 7.5 per cent MoO_2 as compared to 1.3 per cent MoO_2 in the perovskite. It is clear that if SYNROC containing radwaste is melted under controlled redox conditions so that molybdenum is present in the Mo^{4+} state, it will readily enter the hollandite, and to a lesser extent, the perovskite phase, thereby becoming effectively immobilised.

Technetium possesses chemical and crystal-chemical properties which are very similar to molybdenum and similar behaviour may be expected. Among the remaining fission products mentioned in Table 1, *tellurium* is likely to substitute as Te^{4+} for Ti^{4+} in hollandite and perovskite, whilst *rhodium* and *palladium* would probably be reduced to the metallic state which would be extremely inert geochemically. These predictions will be checked in the near future.

The experiments described above demonstrate the capacity of the minerals of our chosen SYNROC composition to accept into solid solutions and thereby immobilise most, if not all, of the principal fission products and actinide elements generated in nuclear reactors.

5-4 Radiation damage and transmutations

One of the most serious problems encountered by *supercalcine* was the decay by transmutation of ^{137}Cs and ^{90}Sr into barium and zirconium respectively, which would not necessarily be stable in their lattice sites. In the present system, the severity of this problem is much reduced because the radioactive species are greatly diluted as compared to supercalcine. Thus, the crystal lattices are determined by and dominantly formed from the added components. In the present case, we see that the barium produced by decay of caesium is already stable in the leucite

lattice (Table 4) and is therefore not expected to migrate out readily, although there will be a small degree of internal solid-state exsolution of other phases in order to maintain electroneutrality. Similarly, most of the strontium enters the perovskite lattice and in this structure zirconium produced by decay is already known to be highly stable. Moreover, this accommodation is favoured by the non-stoichiometric nature of perovskite.

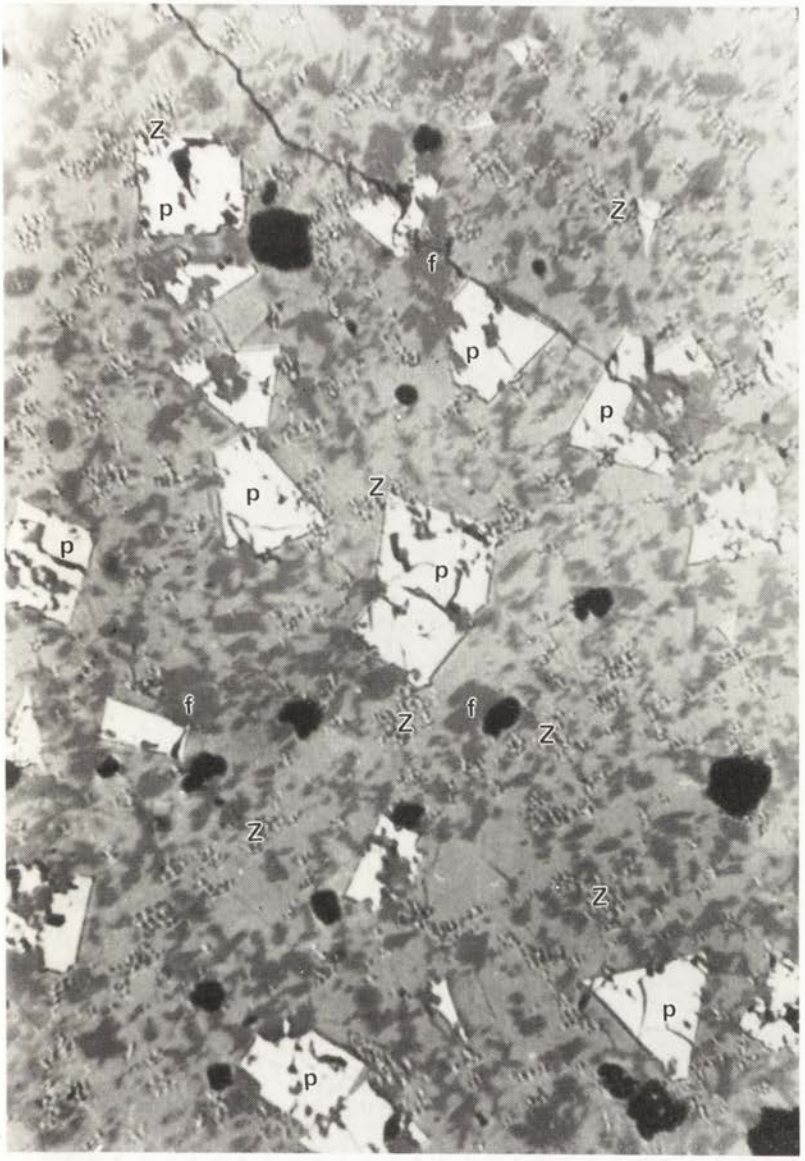
The occurrence of radiation damage to crystals has also been of concern to many who have discussed incorporation of radwaste in ceramic materials. Radiation damage, principally from actinide elements which emit alpha particles, causes disorder of the host lattice and sometimes extensive (e.g. 0.5 to 10 per cent) of volume expansion. This is known as the metamict state, and it has been feared that radwaste elements would be more readily leached from such metamict crystals. (Note that although metamict minerals do not diffract X-rays, they are not nearly as disordered as glasses.)

One of the minerals most susceptible to radiation damage is zircon, $ZrSiO_4$, a major host for uranium and thorium in natural rocks. Radiation damage from these elements may cause a volume expansion in zircon exceeding 10 per cent. However, experiments by Pidgeon *et al.* (1966, 1973) demonstrated that the uranium remained tightly bound in the metamict state. Pidgeon *et al.* heated 500 million year old fully metamict zircon containing 0.6 per cent of uranium in 2 m NaCl solution at 1000 bars fluid pressure over a wide range of temperatures ranging from 350°C to 800°C and for periods up to 2 months. No significant loss of uranium was observed. Whilst the uranium was shown to be highly immobile under these extreme conditions, much of the lead produced by decay of uranium was removed. These experiments indicate that, providing a radioactive element is situated in a stable crystallographic site, it can be tightly bound in the metamict state. On the other hand, the decay product, lead, cannot be incorporated in the zircon lattice because of its incompatible ionic radius and charge. It is therefore much more mobile.

Fig. 8 Reflected light photomicrograph shows typical crystallisation behaviour of ZrO_2 in SYNROC. ZrO_2 (z) forms clusters of fine granular crystals a few microns across, distributed fairly homogeneously throughout the sample. White euhedra are perovskite (p) dark grey areas are Ba-felspar (f) and medium grey regions are glass plus very fine crystalline material. Black areas correspond to pits in the sample surface.

Crystals of essentially pure uraninite (UO_2) are known to have survived intact for over 2000 million years in the conglomerates of the Witwatersrand whilst 500 million year old thorianite (ThO_2), derived from the weathering of pegmatites, occurs in alluvial gravels in Ceylon. Although subjected to intense radiation damage and a wide range of geological environments, loss of U and Th from many of these crystals has been minor. Similar behaviour has been observed in many other uranium- and thorium-bearing minerals. An analogous capacity of uraninite to retain many fission products and actinides for periods up to 2 billion years has been demonstrated by the Oklo natural uranium reactor in Gabon (Frejacques and Hagemann, 1976).

In the present SYNROC system, most of the actinides would be incorporated in zirconia, which has the same structure as uraninite and thorianite. This mineral is much more close-packed than zircon and is expected to retain its actinides at least as tenaciously. A study of severe radiation damage in ZrO_2 showed that expansion of the lattice was only about 2 per cent, much smaller than displayed by zircon (Clinard, 1977). Because of the small size of individual ZrO_2 crystals (Fig. 8), it is believed that the synthetic rock host for radwaste will be able to accommodate this small expansion of radiation-damaged zirconia without a significant deterioration of its strength and impermeability. It should be noted, however, that further experimental studies of the effects of radiation damage on the crystalline phases under consideration will be necessary.


Z
p
f
100 μm

6 Further development of SYNROC process

6-1 Incorporation of radwaste in synthetic metamorphic rocks

Most metamorphic rocks in the earth's crust are produced by recrystallisation of former sedimentary rocks at elevated temperatures and pressures, but essentially in the solid state. Minor elements such as U, Th, REE, Sr and Cs become distributed among mineral phases according to well-established chemical partition equilibria. The SYNROC approach can also be employed in such a way as to provide a close analogy with natural metamorphic rocks.

Instead of melting the mixture of radwaste (~10%) and added components (~90%), the oxide mixture can be recrystallised essentially in the solid state by calcining for 1 to 2 hours at 1150-1200°C. The texture of the resultant mineral assemblage is much finer grained than is the igneous version of the SYNROC process, and is similar in this respect to supercalcine (Fig. 5b). We have carried out a limited amount of work on this version of the process. For the starting composition discussed in Section 5-2, the subsolidus mineral assemblage would consist of Ba-felspar, hollandite, perovskite, zirconia and minor kalsilite. A leucite-type mineral would probably not form since this phase results from fractional crystallisation from the molten state. The distribution of radwaste elements between these minerals will be similar to that described in the igneous case (Section 5-3) except that most of the caesium seems to be partitioned into solid solution in the highly stable and insoluble Ba-felspar phase (as $CsAlSi_3O_8$) and also into the $(K,Cs)AlSiO_4$ solid solution (R-phase).

If sintered at 1000-1200°C without the application of pressure, the resulting sample has substantial strength but appreciable

porosity. The porosity can be removed, and a coarser grainsize achieved by the technique of hot-pressing, in which the sample is subjected to a high pressure whilst being heated and recrystallised. The resultant metamorphic rock assemblage would have essentially zero porosity and also high strength. The introduction of remote-controlled hot-pressing of such radioactive materials is well within the capabilities of existing technology, but would increase the overall costs. It can be predicted that synthetic 'metamorphic rock' formed in this way would provide an effective means of immobilising radwaste.

6-2 Further applications of ceramic technology

There are a number of additional steps which can be taken to further improve the capacity of SYNROC to immobilise radwaste.

(a) After melting, the radwaste mixture can be disintegrated into ~5 mm drops which cool and crystallise separately, instead of being poured into large cylinders. Alternatively, the mixture can be pelletised and sintered in the solid state to form strong coherent spheroids of about 5 mm diameter as in supercalcine (Fig. 5a). These drops and spheroids can then be coated with a layer of impervious, chemically inert alumina as is proposed for supercalcine. The armoured pellets can then be incorporated in a suitable chemically resistant matrix.

(b) An alternative approach could be applied either to large cylinders of SYNROC crystallised from the liquid state (Section 5-3) or to hot-pressed smaller cylinders, recrystallised in the solid state (Section 6-1).

Because of their high strength, thermal stability and thermal conductivity, these cylinders could be fabricated within a year of removal of fuel rods from the reactor. They could then be stored at the surface in simple concrete air-cooled structures for a period of 10-20 years. During this period, many of the radwaste elements with short half-lives would decay and heat production would fall by more than a factor of ten (Fig. 1).

The cylinders would then be finely crushed and leached in

dilute nitric acid to remove any radwaste elements that were loosely bound at surface sites, particularly those formed by transmutations of short half-life elements. The leachant solution would then be recycled to the mainstream formed during the primary dissolution of fuel elements.

After drying, the ground radwaste host rock material would be mixed with an excess of highly inert ceramic such as alumina or zirconia and hot-pressed under subsolidus conditions to form cylinders which would possess high strength, high thermal conductivity, essentially zero porosity and extremely high resistance to any form of leaching or corrosion. The proportions of alumina to radwaste rock might be in the vicinity of 4 to 1, so that the final cylinders would contain only about 2 per cent of actual radwaste. These cylinders should retain radwaste elements for indefinitely long periods in almost any conceivable geologic storage site.

This additional processing step would of course increase the cost of radwaste disposal. Moreover, it would involve the transport and disposal of volumes of cylinders which are about twelve times greater than those of the equivalent number of glass cylinders (25% radwaste) according to currently favoured technology. This would also add to the costs of the operation, but not proportionally. Because the radwaste would have been aged and greatly diluted before disposal, the problems of radiation shielding during transport and ultimate disposal would be greatly reduced. The ceramic cylinders would have far higher thermal stability and strength than glass, so that transport hazards would be greatly reduced, even allowing for the increase in volume. Although the total volume to be disposed of would be twelve times greater than for disposal of glass cylinders, the absolute volumes would still be quite small. I doubt whether the costs associated with this double processing would amount to more than three or four times the costs of the conventional glass disposal methods. This would still constitute a small proportion of the final cost of power produced.

The point to be made is that technology exists to provide

almost any desired degree of safety and integrity of media for immobilising radwaste. There is a trade-off between the costs of this technology and the degree of absolute insurance required by society. We should accept the possibility that society might prefer to have a very high degree of over-insurance and redundancy built in to the final disposal system, providing that the costs are acceptably small (e.g. less than 5 per cent) in relation to the final cost of the power produced. There can be little doubt that this objective can be achieved.

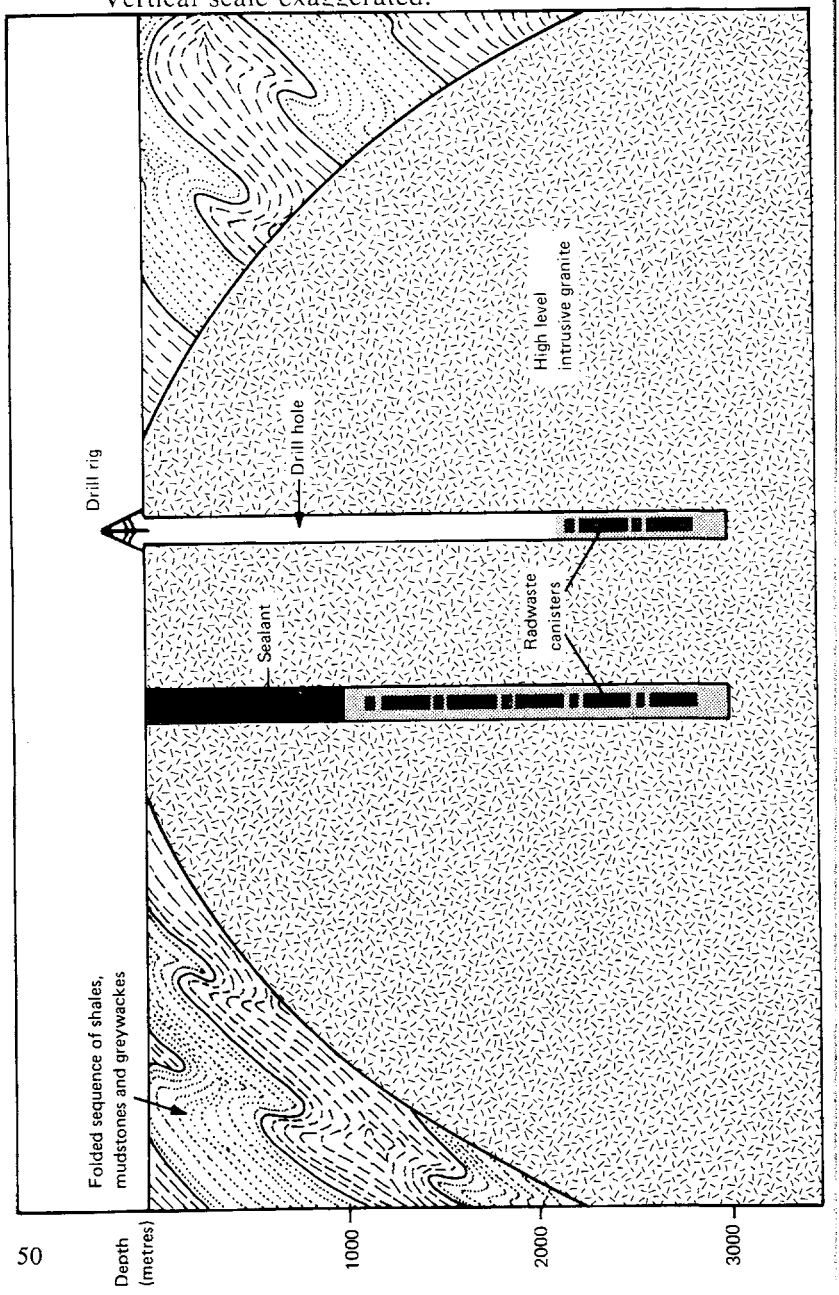
6-3 A notional example of a multi-barrier radwaste repository

We have described the immobilisation of radwaste in SYNROC composed of minerals which are *known* to have the crystal-chemical capacity to incorporate specific radwaste elements into stable solid solutions and which are *known* to have remained stable in a wide range of geological environments for periods varying from at least 20 million to 2000 million years. We have also described a second stage of processing whereby these rocks are crushed, their surfaces leached, and the highly diluted crushed rock re-incorporated in ceramic material of high strength and extreme chemical inertness.

Materials so fabricated must then be buried underground in a suitable geological environment. Characteristics to be sought are tectonic stability, low permeability to circulating groundwater and the capacity to chemically buffer circulating groundwater so that this would be neither highly acidic nor alkaline. Many different classes of geological environments are being explored as potential repositories. A notional sketch of one such conceivable repository is given in Fig. 9.

This shows a small, exposed, high-level granitic pluton which has been intruded into an older folded series of sediments—principally carbonaceous shales (to provide reducing conditions), mudstones, limestones and greywackes—a common sedimentary succession. The granite would be demonstrated by geophysical methods, prior drilling and hydrological studies to be relatively impermeable and not strongly jointed or fractured. Except for the

Fig. 9 Example of a notional radwaste repository in granite. Vertical scale exaggerated.



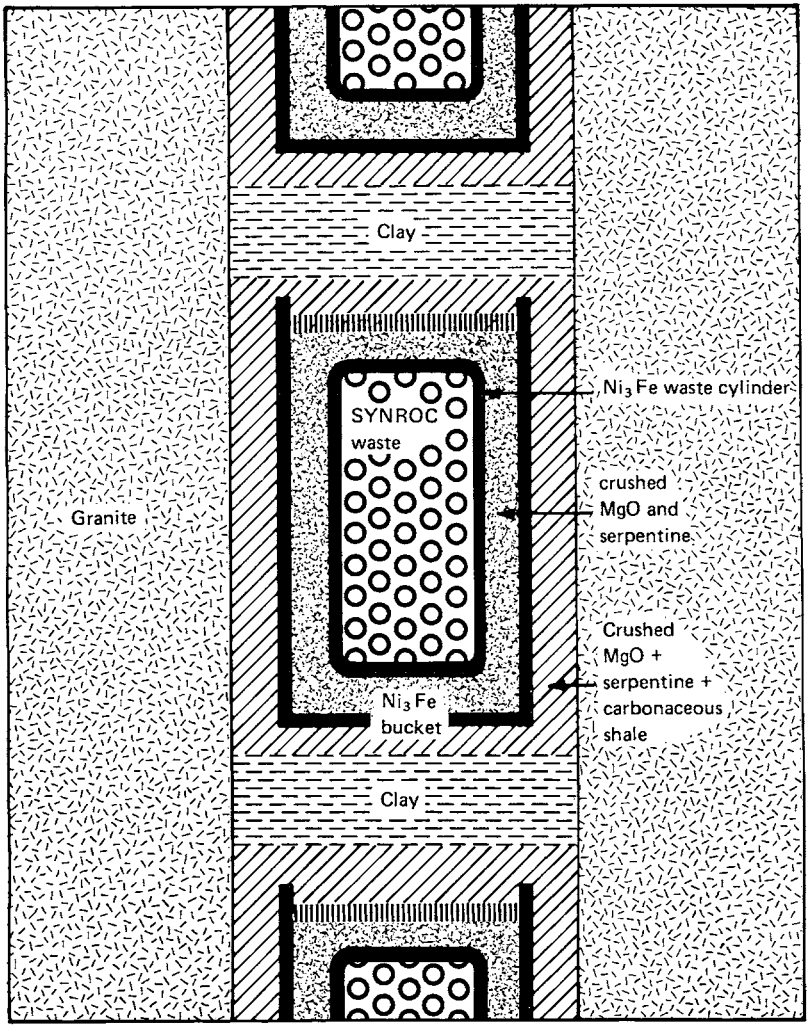
granite area exposed at the surface, the sediments are draped over the granitic pluton to form a confined domal structure.

A series of vertical holes is then drilled from the surface to a depth of 3000 metres. (Mining operations in crystalline rocks on the Canadian shield have shown that in extensive regions, joints are closed at depths below 1000 metres and groundwater is essentially absent.) Radwaste cylinders are buried in these holes. The synthetic rocks containing radwaste are encapsulated in cylinders of $Ni_{.5}Fe$ alloy, which in turn are surrounded by mantles of compacted magnesia and serpentine, and held in $Ni_{.5}Fe$ buckets (see Section 2-3). A bucket would be lowered to the bottom of a hole and surrounded by a mixture of crushed magnesia, serpentine, and some carbonaceous shale (to maintain mildly reducing conditions), as in Fig. 10. A layer of clay would then be introduced, providing an impermeable barrier between the lower cylinder and the next cylinder to be introduced. The hole would then be filled in this way with more radwaste cylinders to within 1000 metres of the surface, after which it would be filled and sealed, making extensive use of impermeable clays and mudstones.

Twenty such holes would be able to incorporate 8000 cylinders of standard size (300 cm x 30 cm). Based on the projections of Cohen (1977 a, b), but assuming SYNROC to contain only 10 per cent of radwaste, the twenty holes would be able to hold the waste produced from nuclear power stations generating a total of 8000 megawatts and operating over a period of 40 years. This is comparable to the current time-averaged consumption of electrical power in Australia. In the case where SYNROC had been further reprocessed to form hot-pressed ceramic cylinders containing only 2 per cent of radwaste, one hundred drill holes would be needed to provide the same capacity.

It is extremely improbable that any significant amount of radwastes confined as described above could reach the biosphere within timescales less than many millions of years. Even if a small amount of radwaste elements somehow escaped from the

Fig. 10 SYNROC waste disposal within a hole drilled in granite. SYNROC waste is encapsulated and transported in Ni_3Fe containers. Crushed MgO (magnesia) and serpentine surround the containers, and an impermeable clay seal separates each unit. (Not to scale.)



SYNROC-ceramic cylinders and diffused outwards and upwards along joints in the granite, most would be trapped by the overlying dome of folded sediments. Here they would be precipitated and adsorbed, causing a drastic reduction in their rate of upward migration (Fried *et al.*, 1977).

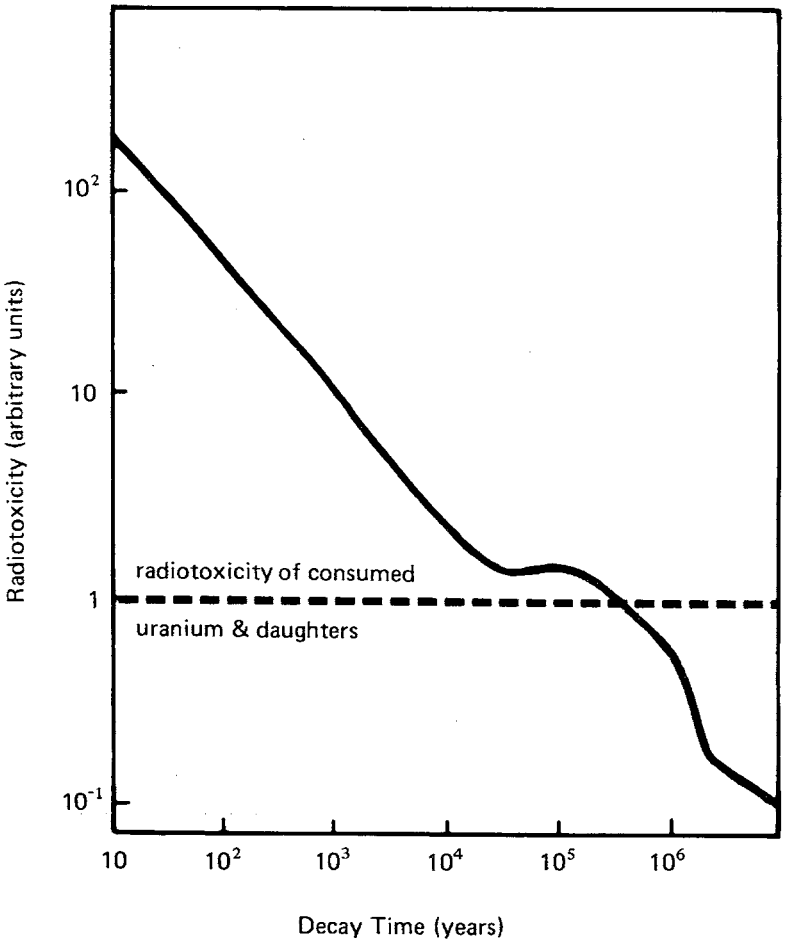
7 Geochemical perspective

To human beings, the objective that radwaste be immobilised for periods as long as one million years sometimes seems difficult to comprehend. However, geological and geochemical processes deep within the earth's crust do not operate on the timescale of human lives but on timescales which often extend over millions to hundreds of millions of years.

In Fig. 11, the hazards caused by human ingestion of long-lived actinide elements in radwaste are compared with the ingestion hazard of the uranium which was originally mined to fuel the nuclear reactor which produced that amount of radwaste. It is seen that after 10^6 years, the radwaste actinides have decayed to a level where they are less hazardous than the original uranium which was mined from the ground. After one hundred thousand years, the danger is only twice as great as that from the original uranium, whilst after 600 years the danger is about sixteen times greater than the parental uranium.

The rocks of the upper crust of the earth contain about 2.7 parts per million of uranium and 10.8 parts per million of thorium on the average. Although thorium is four times as abundant as uranium, its radioactivity is only about one-fourth as intense of that of uranium. Thus, we may say that crustal rocks contain an average of 5.4 parts per million of 'uranium equivalent'. Whilst most of this 'uranium equivalent' is tightly bound in refractory minerals such as zircon, sphene and monazite, about 25 per cent is situated in a soluble form along grain boundaries where it can be leached and remobilised by circulating groundwater. A cubic kilometer of average crustal rocks therefore contains 14,000 tons of equivalent uranium, one-quarter of which is present in a highly soluble form.

Fig. 11 Radiotoxicity for ingestion of long-lived actinide elements in radwaste as a function of decay time. Horizontal line shows radiotoxicity of the parental uranium from which the radwaste was ultimately derived via nuclear reactor(s). From OECD Report (1977).



In a radwaste repository, the radioactive elements would be highly concentrated in a small region, in which average levels of radioactivity would be far higher than in average crustal rocks. Thus, the radiologic hazard to the (local) biosphere would be increased because of the localised concentration. This fact should nevertheless be placed in an appropriate geochemical perspective.

The repository would presumably be situated in a remote region, far from human habitation. If we consider the surface region within a radius of 10 km from the central repository, then the uranium equivalent present in the natural rocks to a depth of 3 km is 1.3×10^7 tons. This would generate an amount of alpha-producing waste similar in ingestion toxicity to that produced by burning 800,000 tons of natural uranium in nuclear reactors and allowing it to decay for 600 years (Fig. 11). A repository storing the wastes from burning this amount of uranium would be regarded as being very large indeed.

Bearing in mind the circumstance that synthetic radwaste would be more tightly confined in synthetic rock than in average crustal rocks, this comparison suggests that the period of one million years which is sometimes recommended as being appropriate for radwaste confinement may be longer than is necessary. After a period of 600 years, the fission products will have decayed whilst the long-lived alpha activities of the actinides will be smaller and these elements more securely bound than those contained naturally in rocks within 10 km of the repository. If we adopt as a criterion of safety the requirement that hazards from deeply buried radwaste be small compared to the hazards produced by the radioactive elements occurring naturally in rocks present within 10 km of the repository, then the period over which the integrity of the repository should be guaranteed would probably be less than 10,000 years and conceivably could be as small as 1000 years in some circumstances. There can be no reasonable doubt that the containment strategy and techniques discussed in Sections 3, 4 and 5 are more than capable of meeting this requirement.

8 Conclusion

The principal conclusion of this book is that the problem of isolating high level nuclear wastes from the biosphere can be solved. Although there may be other objections to the use of nuclear power, the radwaste problem cannot reasonably be cited in justification of policies to abandon its use.

This conclusion is based directly upon studies of natural geochemical and geological processes, combined with the application of well-understood principles of crystal chemistry and solid state chemistry.

The fact that we can identify minerals which are known to have been stable for at least 20 to 2000 million years in a wide range of geological environments and which are able to incorporate radwaste elements in stable solid solutions is crucial. It is this fact which gives us confidence that the required long timescale for isolation of radwaste can be achieved. We have seen in the present paper that it is possible to synthesise these minerals and rocks using appropriate technology and to incorporate radwaste elements in the synthetic rocks in low concentrations. The indications are that the cost for this process will not be excessive. The safety of the SYNROC immobilisation barrier can be further enhanced by utilising known geochemically stable alloys as containers. Finally, deep disposal in an appropriate geological-geochemical environment is capable of providing an independent fail-safe barrier.

Although we have concluded that the radwaste disposal problem can be solved, there is a great deal of research and development to be carried out before we will be in a position to choose the most appropriate disposal system for general application. There are many variables yet to be investigated so that the

conditions for disposal can be optimised. It is not suggested that the process described in this paper is necessarily the best possible process. There may well be even more effective SYNROC systems. Certainly there are many possibilities to be explored before a final disposal system can be agreed upon. The principal objective of this book has been to define a *strategy* for radwaste disposal, and to show by comparison with known geochemical behaviour of minerals, rocks and radwaste elements, that the problem is fundamentally solvable.

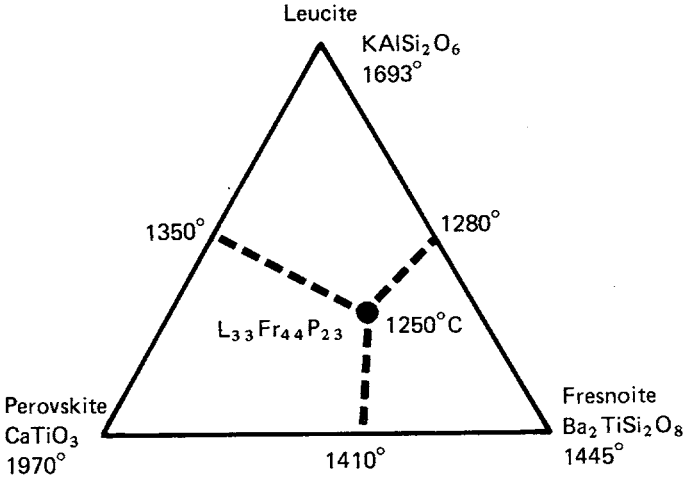
Appendix

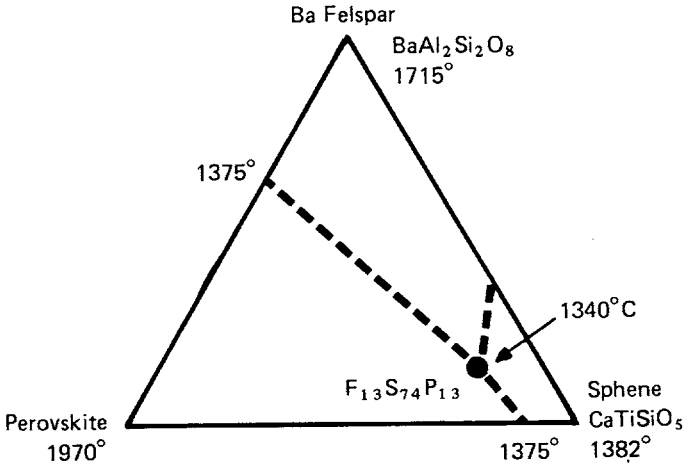
In the main body of this book, the behaviour of a particular SYNROC composition was discussed in some detail. Actually, we have studied a wide range of other SYNROC systems which may provide suitable hosts for radwastes. The criteria by which promising systems can be recognised are (a) thermodynamic compatibility of individual minerals (b) ability of minerals to incorporate radwaste elements into stable solid solutions (c) known capacity of the individual minerals to remain stable for periods exceeding 20 million years in a wide range of geological environments (d) that the SYNROC systems melt at temperatures less than 1350°C and on cooling can be crystallised into well-formed crystals.

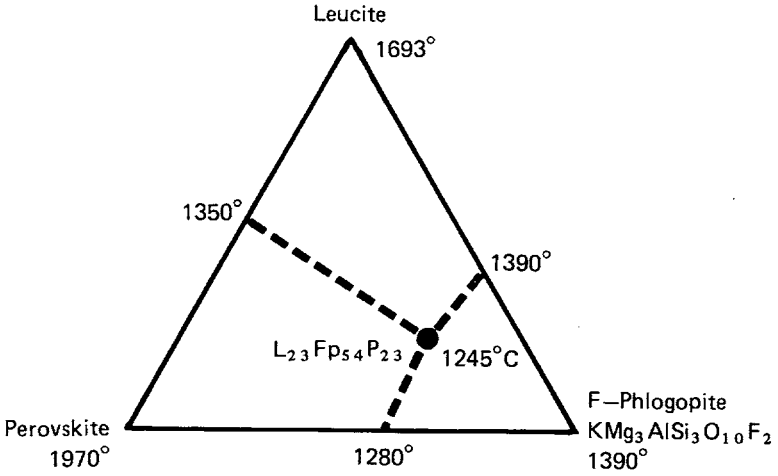
The four SYNROC types depicted in Fig. 12 appear to meet these requirements. The minimum melting temperatures shown are those at which substantial melting is observed when mixtures of end-members are batch-heated. However, it should be noted that some of these systems are essentially pseudoternary in their thermodynamic behaviour so that during fractional crystallisation from the molten state, final crystallisation may occur at temperatures below the designated minima and additional minerals may be formed. We expect kalsilite and leucite to be in this latter category. Another promising series of SYNROC systems can be constructed from hollandite(Ba-rich)-perovskite-kalsilite mixtures. It should also be possible to replace leucite by kalsilite in the systems shown in Fig. 12. Other systems with potential are perovskite-phlogopite-Ba-felspar and perovskite-phlogopite-nepheline.

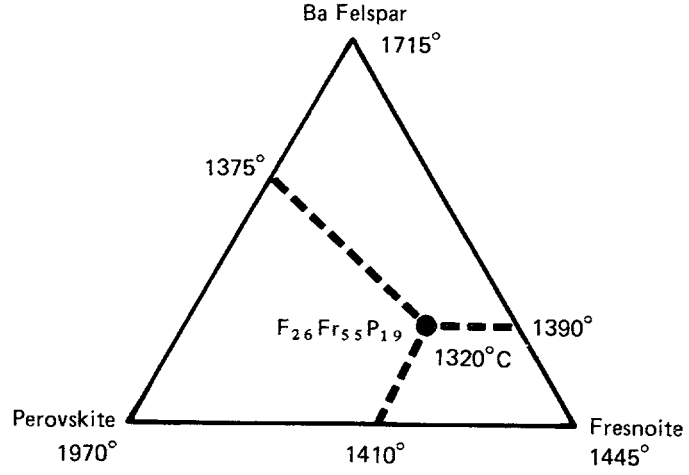
Our preliminary experiments indicate that these systems would remain in equilibrium with zirconia (ZrO_2) rather than zircon

Fig. 12 Other pseudoternary systems currently under investigation. Approximate melting temperatures (°C) and compositions of the ternary minima are shown, together with melting temperatures for binary eutectics and individual end-members.






Leucite
1693°
1350°
1390°
$L_{23}Fp_{54}P_{23}$
1245°C
Perovskite
1970°
1280°
F—Phlogopite
$KMg_3AlSi_3O_{10}F_2$
1390°


Ba Felspar
1715°
1375°
$F_{26}Fr_{55}P_{19}$
1390°
1320°C
Perovskite
1970°
1410°
Fresnoite
1445°

($ZrSiO_4$). Thus, zirconia could be added to these compositions to provide a host for actinides as is shown in Fig. 6.

So far, we have not carried out any detailed experiments upon the partition of radioactive waste elements among the minerals of these other SYNROC systems. However, from the known properties of the constituent minerals, we expect that they are likely to provide satisfactory hosts as discussed elsewhere in this book. Further work is clearly required.

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A new and improved strategy for safe disposal of wastes from nuclear reactors is provided by a study of the geochemical means by which natural rocks and minerals retain the same elements that are present in these wastes. Certain natural minerals have demonstrated the capacity to immobilise radwaste elements for periods up to 2000 million years, and the fundamental reasons underlying this capacity are well understood in terms of the basic principles of geochemistry.

Professor Ringwood outlines his SYNROC process, which utilises currently available technology to produce synthetic igneous rocks in which high-level wastes are incorporated. Following nature's example, the synthetic minerals making up these rocks are specially tailored to immobilise the radwaste elements. New methods of processing and storing SYNROC materials provide additional fail-safe barriers which further prevent nuclear wastes from entering the biosphere.

Ringwood's principal conclusion is that the problem of isolating high-level nuclear wastes from the biosphere can be solved.

This slim volume will present no storage problems: it may solve many.