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A. E. Ringwood, P. M. Kelly, S. H. U. Bowie and T. A. Kletz

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Immobilization of high-level waste in ceramic waste forms

By A. E. Ringwood[1], F.R.S., and P. M. Kelly[2]

[1] *Research School of Earth Sciences, Australian National University,*
G.P.O. Box 4, Canberra, A.C.T. 2600, Australia
[2] *Australian Atomic Energy Commission Research Establishment,*
Private Mail Bag, Sutherland, N.S.W. 2232, Australia

High-level wastes (HLW) can be incorporated in the crystal lattices of coexisting phases in ceramic waste forms. The properties and performances of ceramic waste forms are largely determined by their phase chemistry, phase assemblage and microstructure. Currently, the best categorized advanced ceramic waste form is SYNROC, a titanate ceramic composed of 'hollandite' $Ba_{1.1}(Al,Ti)^{3+}_{2.3}Ti^{4+}_{5.7}O_{16}$, zirconolite $CaZrTi_2O_7$, perovskite $CaTiO_3$, rutile TiO_2 and minor amounts of metal alloys microencapsulated by the titanate matrix. Two factors contribute to the capacity of SYNROC to accommodate high (e.g. 20%) loadings of HLW, together with variations in waste-stream composition. Firstly, the constituent phases can accept, as solid solutions in their crystal lattices, a broad spectrum of cationic species of diverse charge and radius, either singly or by complex substitution mechanisms. Secondly, the phase assemblage itself spontaneously adjusts its modal mineralogy in response to waste-stream fluctuations. The presence of both rutile and a source of trivalent titanium (from reaction of rutile with added Ti metal) in the SYNROC phase assemblage is largely responsible for this flexible and accommodating nature. The titanate minerals in SYNROC also occur in Nature, where they have survived for many millions of years in a wide range of geological environments. Experimental studies show that SYNROC is vastly more resistant to leaching by groundwater than borosilicate glass; moreover, its high leach resistance is maintained at elevated temperatures. Experimental and analogue studies indicate that the HLW immobilization properties of SYNROC are not significantly impaired by radiation damage. These properties show that SYNROC would provide an effective immobilization barrier for HLW when buried in suitable repositories. They also permit the use of a wider range of geological disposal options than are appropriate for borosilicate glass. In particular, SYNROC is well suited for disposal in deep drill-holes, both in continental and marine environments. The fact that SYNROC is composed of minerals that have demonstrated long-term geological stability is important in establishing public confidence in the ability of the nuclear industry to immobilize high-level wastes for the very long periods required.

1. Introduction

Early in the development of the nuclear industry, it was recognized that it would be necessary to solidify the high-level waste (HLW) liquids produced during the reprocessing of spent fuel. The primary objectives of solidification were to reduce the hazards associated with the storage of large volumes of acid waste liquids, and to facilitate transport and transient storage in above-ground engineered containment structures. Borosilicate glass was widely perceived to be a satisfactory waste form for these purposes, particularly since the technology for its large-scale production had been extensively developed for other commercial purposes. Borosilicate glass accordingly became the waste form adopted by the nuclear industry from the 1950s onwards.

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It was only at a later stage, after this policy had been widely accepted, that the problem of long-term disposal of the solidified wastes was seriously addressed. A widespread consensus emerged that the solidified wastes should be buried deep in the Earth in mined repositories constructed in suitable geological environments. This raised the question of whether glass is the most appropriate waste form for such geological disposal.

The most likely mechanism by which radionuclides could be returned to the biosphere after burial in a repository is via leaching of the waste form by circulating groundwaters. Hence it is essential that the repository be sited in a geological environment carefully selected for its capacity to minimize access of underground water to the waste, and possessing low permeability so as to inhibit circulation of groundwaters. This constitutes the so-called *geological barrier*. Safety analyses of geological barriers are necessarily site-specific and have proved to be extremely complex from the scientific point of view (USNRC 1983). Although most Earth scientists are confident that high safety standards can be achieved in certain carefully selected geological environments, it is far from certain whether ideal sites will be found in every country possessing a nuclear industry. Moreover, even when geologically suitable sites are identified, it is not uncommon for sociological pressures to impede their utilization. Because of these complex problems, and the difficulties of defining generally accepted safety standards, emphasis has shifted in recent years to so-called 'multi-barrier' strategies for the terminal disposal and isolation of high-level wastes. One of these barriers is provided by the waste form itself, which should preferably be a highly stable material with very low solubility in groundwater. Ideally, the waste form itself should function as an *immobilization barrier*, fully capable of preventing any significant release of radionuclides to surrounding groundwater for periods as long as a million years. Yet a third, *engineered barrier* can also be introduced. This may consist of a corrosion-resistant metallic canister (e.g. copper, lead or titanium) enveloping the waste form and itself surrounded by an overpack of highly impermeable and absorbent materials such as bentonite or other clay minerals. The combination of three essentially independent barriers greatly enhances the safety of the overall disposal system and provides for increased flexibility in performance standards. For example, if the geological barrier in a given site is considered to be less than ideal, greater emphasis should be placed in improving the integrity of the immobilization and engineered barriers.

The role of borosilicate glass as an immobilization barrier deserves further examination. As noted above, it was not designed originally for this purpose, and it has since been found that its capacity to withstand leaching by groundwaters is limited, particularly at elevated temperatures. Nevertheless, a majority of scientists working in management of high-level wastes believe that a 'waste package' of glass plus canister plus overpack can maintain its integrity with negligible leakage of radioactivity for at least 1000 years, by which time most fission products will have decayed to safe levels. On the other hand, confidence in the integrity of the waste package over the much longer periods, exceeding 10000 years, required for the decay of actinide elements, is not so widespread (see, for example, Castaing 1984). Thus the protection of the biosphere over these longer timescales currently relies primarily upon the ability of the geological barrier to retard access of groundwater to the waste form and to delay migration of contaminated groundwater from the waste package to the biosphere. Even the security of the geological barrier under all circumstances has been questioned in some major national enquiries (USNRC 1983; Castaing 1984).

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2. Ceramic waste forms: a historical overview

Many crystalline ceramic materials are known to be vastly more resistant to aqueous leaching than is borosilicate glass. This has provided the incentive for the development of a variety of crystalline ceramic waste forms that constitute an improved immobilization barrier. Some of the basic concepts were discussed three decades ago (for example by Hatch 1953), but the field did not begin to develop rapidly until the late 1970s. A group at Pennsylvania State University headed by G. McCarthy deserves credit for reviving systematic research in this area (McCarthy 1975). Their silicate-based ceramic waste form 'Supercalcine' was found to have rather disappointing resistance to leaching and radiation damage, and is no longer under consideration as a viable alternative to borosilicate glass. However, the scientific approach of 'molecular engineering' adopted by McCarthy and co-workers influenced the strategies of other workers, including Ringwood and colleagues, in the development of SYNROC (Ringwood 1978; Ringwood *et al.* 1979*a*, *b*).

Two principal classes of crystalline ceramic waste form can be recognized. The 'microencapsulation' technique (Forberg *et al.* 1979; Forberg & Westermark 1981) involves mixing and calcining HLW with a large excess of an insoluble and refractory material such as titanium oxide or aluminium oxide. The aggregate is sintered or hot-pressed to form a dense ceramic with low porosity. HLW particles (combined with TiO_2 or Al_2O_3) are completely microencapsulated in a continuous matrix of inert rutile or corundum, which shields the radioactive components from exposure to groundwater. A related 'macroencapsulation' technique applies one or more continuous coatings of refractory, insoluble ceramic materials (e.g. graphite, silicon carbide, corundum) over pre-formed pelletized kernels mainly composed of HLW (see, for example, Rusin *et al.* 1979).

The second class of ceramic waste forms applies the principles of crystal chemistry and phase equilibria to the design of a ceramic composed of mutually compatible crystalline phases. A key property of the phase assemblage is that HLW species form stable solid solutions in the crystalline lattices of the various constituent minerals. Waste forms of this kind are usually prepared by mixing and homogenizing various ceramic components in specified proportions with the HLW, followed by calcination and hot-pressing or sintering to yield the desired phase assemblage. The silicate ceramic 'Supercalcine' of McCarthy (1976) was one of the first of these materials. Ringwood (1978) extended this approach to produce a titanate-based ceramic, made up of phases identical or very similar to naturally occurring minerals that are known to have survived in a variety of geological environments for very long period of time, up to 2 Ga. These constitute the SYNROC (synthetic rock) family of ceramic waste forms. The primary formulation developed to immobilize HLW arising from the reprocessing of spent fuel from light-water power reactors is SYNROC-C, an all-titanate waste form composed of an assemblage of 'hollandite', zirconolite, perovskite and rutile (Ringwood *et al.* 1979*a*, *b*; Ringwood 1985). Another member of this family, SYNROC-E, combines microencapsulation and molecular engineering, by dispersing small crystals of 'hollandite', perovskite and zirconolite, with HLW species in solid solution, throughout a continuous matrix of fully densified rutile (Kesson & Ringwood 1984). A closely related all-titanate waste form was developed by Dosch *et al.* (1981, 1982). Alumina-based ceramics consisting of an assemblage of corundum, rare-earth perovskite and magnetoplumbite-type phases have also been proposed (see, for example, Harker *et al.* 1982).

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Important developments in ceramic waste forms occurred during the period 1979–82 as a consequence of a decision by the U.S. Department of Energy to support research into alternatives to borosilicate glass. Thus both glass and ceramic waste forms were evaluated for immobilization of the HLW from the U.S. defence programme currently held in tank storage at Savannah River, South Carolina. These sludges, containing only a small percentage of HLW species, are mainly composed of oxides and hydroxides of aluminium, iron, manganese, silicon and nickel introduced as processing contaminants and neutralizing agents. Ringwood *et al.* (1979*a*) developed a specific titanate-based ceramic, SYNROC-D, for the immobilization of these Savannah River sludges. SYNROC-D consists of an assemblage of zirconolite, perovskite, spinel and nepheline. The properties and production technology of SYNROC-D were developed and tested by Lawrence Livermore Laboratory during 1979–82 (see summary by Campbell *et al.* (1982); see also Hench *et al.* (1984)). SYNROC-D was designed to immobilize about 60% of calcined defence HLW, as against 25% in glass, and displayed greatly superior leach resistance for multivalent elements such as uranium and rare earths.

On behalf of the Department of Energy, a Peer Review Panel made a comparative evaluation of 16 alternative waste forms, including glasses, cements, SYNROC-D and other ceramics. As a result, SYNROC-D was chosen to be the official alternative waste form to borosilicate glass and was scheduled for further engineering development (Bernadzikowski (ed.) 1982). Political pressures intervened to curtail this programme and so glass was selected for immobilization of the Savannah River sludges on the grounds that it was cheaper and that its production technology could be developed more rapidly. The latter argument was legitimate, but the former was soon challenged. Costing of SYNROC-D had been done on the basis of an unnecessarily complex flowsheet (Stone *et al.* 1979). This was criticized by Lawrence Livermore Laboratory scientists, who used a more realistic flowsheet to estimate similar costs for both waste forms, and pointed out that future technological advances could further reduce these costs (Rozsa & Hoenig 1981). These revised estimates were not disputed by the Department of Energy. Subsequent developments in production technology for SYNROC-C (Ringwood *et al.* 1983; Ringwood 1985) have confirmed these expectations and have shown that the overall costs of immobilizing and disposing of Savannah River sludges in SYNROC-D would probably have been substantially lower than for glass.

On the other hand, the research effort on SYNROC-C has expanded considerably since 1978. The Australian government is currently funding the construction of a SYNROC Demonstration Plant, to fabricate SYNROC containing simulated HLW at a commercial scale, thereby demonstrating the engineering feasibility of the technology. The plant is scheduled to begin operation in 1986. So far, the amount of research, development, testing and production engineering on SYNROC has greatly exceeded that carried out on all high-level waste forms other than borosilicate glass. Thus SYNROC-C is at present the only ceramic waste form that can be thoroughly evaluated as a second-generation immobilization barrier in comparison with borosilicate glass. Consequently the following section will be restricted to a discussion of SYNROC-C, the reference formulation specifically developed for immobilization of HLW derived from reprocessing of spent fuel from civilian power reactors.

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3. Immobilization of HLW in synroc-c

(a) *Strategy*

synroc-c is a titanate ceramic comprising a thermodynamically stable assemblage: zirconolite $CaZrTi_2O_7$, 'hollandite' $Ba_{1.1}(Al,Ti)^{3+}_{2.3}Ti^{4+}_{5.7}O_{16}$, perovskite $CaTiO_3$ and rutile TiO_2. The first three minerals have the capacity to accept nearly all the elements present in HLW into their crystal structures at regular lattice sites. Similar minerals occur in Nature, where they have survived in a wide range of geochemical–geological environments for periods up to 2 Ga. It is this evidence of geological stability, combined with experimental observations showing that these minerals are extremely resistant to the attack of hydrothermal solutions, which suggests that synroc would provide a superior method of immobilizing high-level wastes (Ringwood 1978; Ringwood *et al.* 1979*a*, *b*). In fact, the synroc strategy for HLW immobilization is very similar to the way in which Nature successfully achieves the immobilization of radioactive elements on a vastly greater scale than is ever contemplated by the nuclear industry. All natural rocks contain small amounts of radioactive elements (e.g. ^{238}U, ^{232}Th, ^{87}Rb), which are largely contained as dilute solid solutions in the constituent minerals of the host rock. Many of these minerals (e.g. zircon, feldspar) have demonstrated the ability to lock up these radioisotopes for thousands of millions of years, as evidenced by geochronological studies. In synroc, the radioactive waste elements are likewise immobilized as solid solutions in crystalline hosts.

(b) *Composition and mineralogy*

The composition and mineralogy of synroc-c is given in table 1. An excess of TiO_2 is included in the formulation as a chemical buffer against waste-stream compositional variations, and to provide a source of trivalent titanium by reaction with titanium metal added for redox control during hot-pressing. The trivalent titanium promotes the immobilization of caesium in hollandite (Kesson 1983). The partition behaviour of the various HLW species is summarized in table 2. Most of these data were obtained by using non-radioactive preparations and deducing the partition behaviour of the tetravalent actinides from data for U^{4+} and Th^{4+} and that of the trivalent actinides from the behaviour of the rare earths (REE) according to well-established crystal–chemical principles. Limited direct experiments on actinide partitions among synroc minerals (Angelini *et al.* 1980) have confirmed this extrapolation, and more detailed studies are currently underway at UKAEA, Harwell.

Table 1. Composition and mineralogy of synroc-c

composition (%)		mineralogy (approx. % by mass)	
TiO_2	57.1	hollandite	33
ZrO_2	5.4	zirconolite	27
Al_2O_3	4.4	perovskite	20
BaO	4.4	rutile, Ca, Al titanates	15
CaO	8.9	alloys	5
HLW	20		

The hollandite phase in synroc is structurally identical with the naturally occurring titanate hollandite, priderite (Norrish 1951). In synroc hollandite, paired chains of edge-sharing $(Al,Ti)O_6$ octahedra are linked by their corners to form a framework with tunnels running parallel to the *c* crystallographic axis. Large cations such as Ba^{2+}, Cs^+ and Rb^+ are located in these tunnels, but cannot migrate freely along them (Sinclair *et al.* 1980).

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TABLE 2. PARTITION BEHAVIOUR OF HLW INTO SYNROC HOST PHASES

hollandite:	Cs, Ba, Rb
zirconolite:	U, Zr, tetravalent actinides
perovskite:	Na, Sr, rare earths and trivalent actinides
alloy:	Mo, Ru, Rh, Pd, Te ...

Lesser amounts of rare earths (intermediate and heavy) are also contained in zirconolite, whereas perovskite incorporates significant amounts of uranium.

SYNROC hollandite is more accurately described as a member of the $Ba_xCs_y(Ti,Al)^{3+}{}_{2x+y}$ $Ti^{4+}{}_{8-2x-y}O_{16}$ hollandite series. Kesson & White (1986) have demonstrated that complete solid solution is permitted between barium and caesium end-members, and, simultaneously, between Ti^{3+} and Al^{3+} in this series, subject to constraints on end-member stoichoimetries. For example, the aluminous barium end-member is $Ba_{1.14}Al_{2.27}Ti_{5.71}O_{16}$, whereas the aluminous caesium end-member, coexisting with rutile, is $Cs_{1.41}Al_{1.41}Ti_{5.59}O_{16}$. The non-stoichiometric replacement of Ba^{2+} by Cs^{+} is accommodated simply by different kinds of superlattice ordering of the large cations (White & Kesson 1986).

SYNROC zirconolite, nominally $CaZrTi_2O_7$, is largely responsible for the immobilization of zirconium, uranium and tetravalent actinides, and, to a lesser extent, rare earths and trivalent actinides. Zirconolite possesses an anion-deficient fluorite-related superstructure, and detailed structure refinements have recently been made by Rossell (1980), Gatehouse *et al.* (1981), Sinclair & Eggleton (1982) and Mazzi & Munno (1983). The term zirconolite is used generically to embrace the closely related 'polymorphs' zirkelite (trigonal), zirconolite proper (monoclinic), pyrochlore (cubic) and polymignite (orthorhombic), all of which may occur as small-scale intergrowths in SYNROC zirconolite (White 1985). The five distinct cation-sites in the zirconolite lattice permit the structure to accommodate a diverse spectrum of cations of differing charge and ionic radii, via simple, coupled and multiple substitution mechanisms (Kesson *et al.* 1983). In this manner, zirconolite contributes to the capacity of SYNROC to accommodate waste-stream compositional variations.

In SYNROC perovskite, nominally $CaTiO_3$, the large cations (e.g. Ca^{2+}) are centrally located in 12-fold coordination between four TiO_6 octahedra. Minor distortions of this close-packed array result in orthorhombic rather than cubic symmetry for the phase. The principal HLW species preferentially incorporated in SYNROC perovskite include strontium, the larger light rare earths, trivalent actinides, and sodium, a common processing contaminant. Strontium is readily incorporated via a simple substitution for Ca^{2+}. The trivalent actinides also replace Ca^{2+} with a coupled substitution of Al^{3+} or Ti^{3+} for Ti^{4+}, so that charge-balance constraints are satisfied. In the presence of sodium a different substitution mechanism is possible; rare earths may be incorporated as an $NaREETi_2O_6$ component, which itself possesses the perovskite structure (Kesson & Ringwood 1981).

SYNROC fabrication conditions are sufficiently reducing for many 'noble metal' species in HLW, e.g. Mo, Ru, Rh, Pd, Ag and Te, to be reduced to metallic alloys. Mo-rich, Ru-rich and PdTe-rich phases have been identified. These alloys, about 5% by mass of the phase assemblage in SYNROC with a 20% waste-loading, occur as dispersed sub-micrometre-sized inclusions that are microencapsulated by the primary titanate phases. Trace amounts of a calcium-rich phosphate are also present. Its uranium and REE content is negligible, demonstrating that actinides are likewise prohibited from entering the structure.

The forgiving nature of SYNROC arises from two factors. Firstly, by means of simple or complex substitution mechanisms, the individual phases can accommodate into their crystal structures

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a remarkably broad spectrum of cations of diverse charge and radius. Secondly, spontaneous adjustments occur in the proportions of phases in the SYNROC assemblage, in response to waste-stream compositional variations. For example, excess uranium would react with perovskite and rutile to form a $CaUTi_2O_7$ component in solid solution in zirconolite:

$$\text{‘}UO_2\text{’} + CaTiO_3 + TiO_2 \rightarrow CaUTi_2O_7 \text{ s.s.}$$

Phosphorus would react with perovskite, liberating rutile:

$$\text{‘}P_2O_5\text{’} + 3CaTiO_3 \rightarrow Ca_3(PO_4)_2 + 3TiO_2.$$

Caesium would react with trivalent titanium, itself produced by reaction between rutile and added titanium metal, plus additional rutile to form a caesium hollandite component $Cs_xTi^{3+}{}_xTi^{4+}{}_{8-x}O_{16}$ in solid solution in the major hollandite phase.

The primary requirements for incorporating HLW species other than the ‘noble metals’ into SYNROC minerals are the presence of excess TiO_2, i.e. rutile saturation, and a supply of trivalent titanium. Provided that these criteria are satisfied by the initial formulation, and by redox control during processing, then the compositions and loadings of HLW can vary substantially without compromising the immobilization capacity of the waste form or leading to the formation of new and unwanted phases. For example, the one formulation can immobilize a 10, 15 or 20% loading of HLW without any diminution in performance (Ringwood *et al.* 1981).

(*c*) *Production of* SYNROC

Immobilization of HLW in SYNROC is optimized when a high degree of chemical equilibration is achieved during heat treatment. Since this is dependent upon diffusion and recrystallization in the solid state it is essential to use reactive chemical constituents and achieve a high degree of homogeneity among the various chemical components before heat treatment. Specialized techniques have been developed to produce homogeneous SYNROC precursor powders and slurries possessing very high specific surface areas (see, for example, Ringwood 1985); new methods are currently under investigation. The precursor, an intimate mixture of hydrous oxides of Ti, Zr, Al, Ca and Ba in the proportions shown in table 1, is slurried with HLW liquid and then dried and calcined in a reducing atmosphere at about 700 °C. Currently this is carried out in a rotary kiln. The powder is then converted into fully dense monoliths by hot-pressing. A novel and simple method of uniaxial hot-pressing of SYNROC powder has been described by Ringwood *et al.* (1983). SYNROC powder from the kiln is blended with 2% (by mass) metallic titanium (to control redox state) and fed into stainless steel containers having the configuration of bellows. Each bellows would contain 40–60 kg of SYNROC powder. The bellows (40 cm diameter by 60 cm long) are placed in a hydraulic press and heated to 1150–1200 °C. A steady uniaxial pressure of 10–40 MPa is then applied. The bellows collapse axially and symmetrically to form ‘pancakes’ (figure 1). During the collapse the contained powder recrystallizes to form a fully densified monolith consisting of the desired SYNROC mineralogy. The pancakes would then be stacked in stainless steel canisters for final disposal.

4. COMPARATIVE LEACHING BEHAVIOUR OF SYNROC AND BOROSILICATE GLASS

The basic evidence that demonstrates that SYNROC has the capacity to maintain its integrity as an immobilization barrier for millions of years when buried in an appropriately designed

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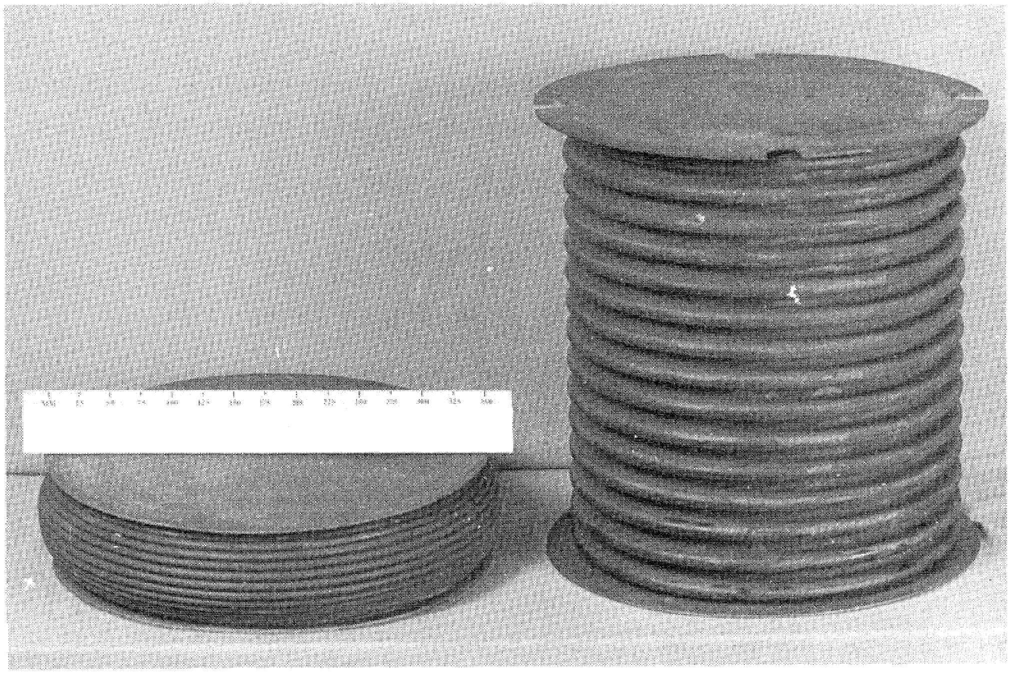

FIGURE 1. Demonstration of SYNROC fabrication by uniaxial hot-pressing at 25 Mpa. The uncompacted stainless steel bellows (right) are filled with calcined SYNROC precursor powder and heated to a uniform temperature of 1150 °C. The unsupported bellows collapse under the uniaxial load to encase a fully densified 30 kg SYNROC monolith (left). The ruler graduations are 25 mm each.

geological repository is provided by observation of the geological stability of naturally occurring SYNROC minerals. These have survived for hundreds, even thousands of millions of years, despite having been subjected to a far more intense range of geochemical leaching conditions than they would ever receive in a geological repository (see, for example, Ringwood 1985). This kind of evidence does not exist for borosilicate glasses. Accordingly, comparative assessments of the leaching behaviour of different waste forms must be based upon the results of relatively short-term laboratory tests. To make predictions about the long-term behaviour of waste forms the data must be extrapolated far into the future. These interpretations are accordingly both complex and model-dependent.

In safety analyses one should always consider the possibility, however remote, that large volumes of groundwater may breach the repository owing to unsuspected hydrogeological factors, e.g. fractures in containment rocks caused by tectonic activity, thermal stress or human intrusion. Thus comprehensive leach testing should include an evaluation of waste-form performance under conditions in which the volume of the leach solution is large compared with the volume of the waste form. The leach solution may thus remain undersaturated with respect to the waste form. Tests of this nature provide the most relevant and direct evidence on the *intrinsic* immobilization capacity of the waste form, independent of interactions with its local geological–geochemical environment.

The single-pass leaching system of Coles (1981) reproduces these conditions, and the IAEA method (Hespe 1971), which involves periodic replacement of leachant, also provides a good approximation. Other test methods have been advanced by the Materials Characterization Center (MCC 1981) to simulate static (MCC-1), high temperature (MCC-2), solubility limits

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(MCC-3), low flow rate (MCC-4) and Soxhlet (MCC-5) conditions. In all these tests the leach rate of each element from the waste form is calculated from the formula

$$\text{leach rate}/(\text{g m}^{-2}\,\text{d}^{-1}) = \text{fraction of element leached} \times W/At,$$

where W is the initial mass of the test specimen in grams, A the geometric surface area of test specimen in square metres, and t the time in days.

Figure 2 shows the leach rates of the more soluble elements in SYNROC at 90 °C. The rapid decrease in leach rate with time is characteristic of SYNROC. These tests were carried out on monolithic specimens under static (MCC-1) test conditions. Differential leach rate data beyond seven days were obtained by replacing the leachant and repeating the test. Previous work (Reeve *et al.* 1984) has established that the frequency of leachant replacement does not affect the cumulative loss of these elements.

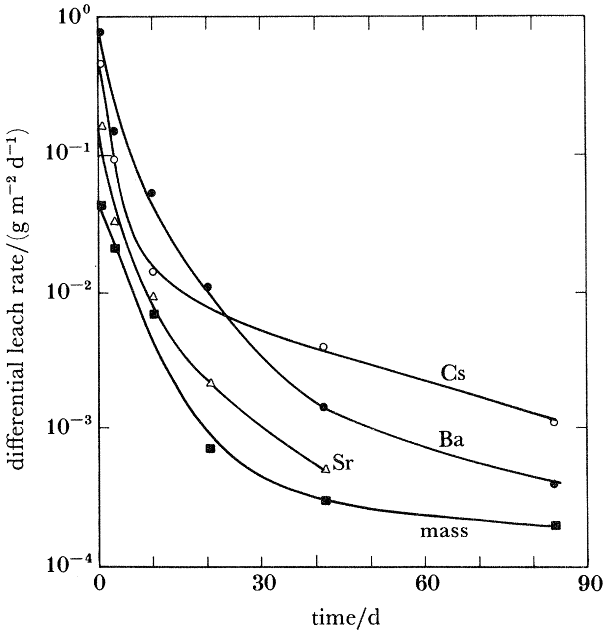

FIGURE 2. Leach rates of SYNROC containing 10% (by mass) simulated HLW in deionized water at 90 °C (MCC-1 Test Procedures).

In figure 3, leach rate data for several elements from SYNROC (Ringwood *et al.* 1981; Oversby & Ringwood 1981*a*, 1982; Kesson & Ringwood, unpublished 1985) are compared with corresponding data for a typical borosilicate glass (PNL 76-68) proposed for immobilization of radioactive waste (Mendel *et al.* 1977). The leach rates for most elements from borosilicate glass are seen to fall within a limited range and do not change strongly with time, showing that, when the leachant is regularly replenished, glass dissolves congruently. In sharp contrast, wide variations occur in leach rates for different elements from SYNROC. It is evident that the response of SYNROC to leaching under these conditions is highly incongruent.

The leach rates of monovalent and divalent cations (Cs^+,Sr^{2+},Ba^{2+},Ca^{2+}) from SYNROC are independent of solid surface area/leachant volume (Woolfrey & Levins 1984) so that tests with monolithic specimens (figure 2) and powders (figure 3) give similar results. After 30 days the leach rates of these elements are one hundredth to one thousandth of those from borosilicate

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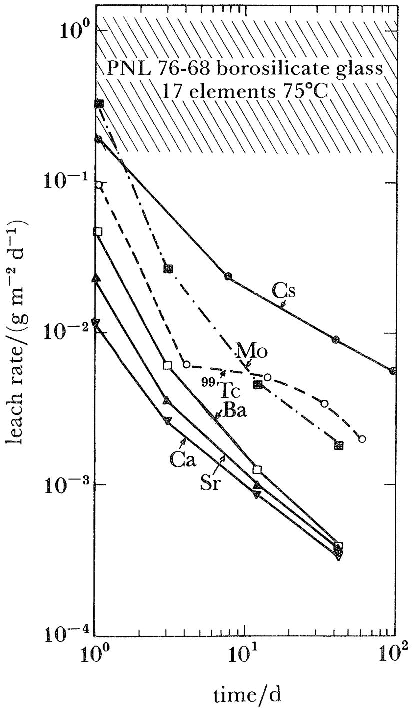

FIGURE 3. Crushed (100–150 μm) SYNROC-C + 20 % simulated HLW was leached in deionized water at 95 °C. Leach rates for Mo, ^{99}Tc, Cs, Ba, Sr and Ca fell by more than an order of magnitude in the first month. Cs, Ca were determined by atomic absorption, ^{99}Tc radiometrically (courtesy Dr Levins, AAEC) and all others by argon ICP analysis. Leach rates for a typical borosilicate glass are by contrast, fairly constant with time (shaded region). (Data from Coles (1981) and Ringwood *et al.* (1981).)

glass. Figure 4 shows that the differences are even greater for most of the trivalent and tetravalent elements. Under conditions where the leachant is regularly replaced (i.e. at high groundwater flow rates), the leachabilities of Nd^{3+}, U^{4+}, Zr^{4+} and Ti^{4+} from SYNROC are about one ten-thousandth of those for glass. Transuranic elements generally possess chemical properties similar to the rare earths and uranium. It is therefore expected that their leach rates will be in the vicinity of those displayed by Nd^{3+} and U^{4+}.

The Australian Atomic Energy Commission has recently fabricated SYNROC containing actinides. Preliminary leaching tests on samples spiked with ^{241}Am and ^{239}Pu indicate low leach rates for these elements. Preparations are well advanced to extend the active waste programme to include fission product wastes resulting from the irradiation of UO_2 to produce ^{99m}Tc for medical purposes (Reeve 1985). A parallel programme will be executed during 1985–86 in the UKAEA, where SYNROC samples containing high-level waste from the reprocessing of advanced gas-cooled reactor fuel will be prepared and subjected to various leaching tests.

The sharp reduction of leach rate with time displayed by SYNROC (see figures 2–4) is believed to be due to two factors (Ringwood *et al.* 1981). Firstly, imperfect equilibrium may be achieved during hot-pressing and small amounts of metastable phases may occur, particularly at grain boundaries. These are likely to be more leachable than the stable major phases. Leach rates accordingly fall with time as these phases are selectively removed from the surface. Secondly, studies of leaching mechanisms show that monovalent and divalent elements are selectively removed from the surfaces of phases, leaving skins enriched in TiO_2 and ZrO_2 (see, for example,

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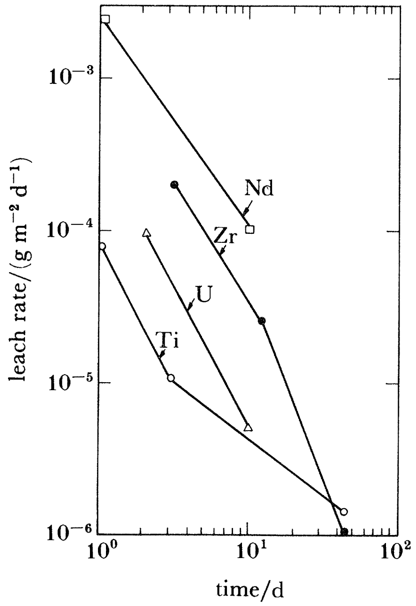

FIGURE 4. Leach rates for the matrix elements Ti and Zr, and multivalent species, e.g. Nd and U, are much lower than those in figure 2*a*. Ti and Zr were determined by argon ICP, and Nd and U by isotope dilution.

Myhra *et al.* 1985). These oxides are extremely insoluble in groundwater and tend to protect the surface from further leaching.

The leaching of SYNROC containing simulated HLW has also been investigated at 100–300 °C by Reeve *et al.* (1980) and at 200 °C by Ringwood *et al.* (1981). Its behaviour is generally similar to that shown in figure 3, except that the differences between glass and SYNROC are substantially greater. SYNROC also displays high stability in water at temperatures exceeding 600 °C (Ringwood *et al.* 1979*b*), whereas glass rapidly disintegrates at temperatures above 300 °C.

The above data demonstrate the intrinsic superiority of SYNROC over borosilicate glass in terms of its resistance to groundwater leaching (figures 3 and 5). Extensive data have also been obtained on the effects of waste-loading on SYNROC leachability (Ringwood *et al.* 1981; Oversby & Ringwood 1982; Reeve *et al.* 1983; Kesson & Ringwood, unpublished 1985). These data show that at 95 and 200 °C the leachability of SYNROC is essentially independent of increases in waste loading from 9 to 20 % HLW simulate. Moreover, SYNROC leach rates have been shown to be relatively insensitive to pH over a very wide range, from 2 to 10 (Levins & Smart 1984).

The basic reasons for the very different leaching behaviours of SYNROC and glass lie in the nature of the principal components of their respective matrices. Table 3 shows that, even under static leaching conditions, the sodium borosilicate matrix of glass is four or more orders of magnitude more soluble in pure water than the titanium and zirconium oxides that dominate the SYNROC matrix. When glass is leached, incorporated HLW species are released at the same rate at which the matrix is dissolved. These species may either remain dissolved (if the water is unsaturated) or re-precipitate as ill-defined, porous and amorphous mixtures of hydrated oxides (if the leachate becomes saturated). The relatively low leach rates of Sr and Ca from glass in table 3 are caused by precipitation of these elements, probably as carbonates (Strachan 1983). Under flow conditions, the leach rates of Sr and Ca approach the high values of monovalent (Cs,Na) and anion-forming elements (Mo,B). In SYNROC, the release of HLW

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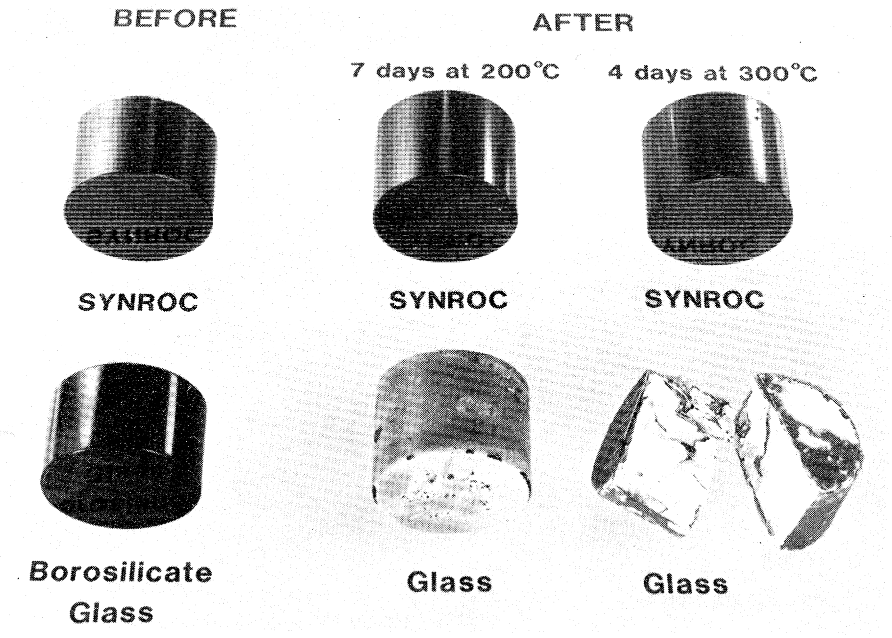

FIGURE 5. Comparative leaching behaviour of 5 cm diameter cylinders of SYNROC and borosilicate glass, both containing simulated HLW, in water at 200 and 300 °C.

TABLE 3. LEACH RATES (GRAMS PER SQUARE METRE PER DAY) OF ELEMENTS FROM SYNROC AND BOROSILICATE GLASS IN DEIONIZED WATER

(MCC-1 test conditions at 90 °C for 28 days.)

	SYNROC-C batch 325	waste glass PNL 76-68
mass	0.005	0.42
Al	< 0.01	n.a.
Ba	0.036	n.a.
Ca	0.0065	0.068
Cs	0.033	1.03
Mo	0.12	1.40
Na	< 0.2	1.32
Sr	0.010	0.075
Ti/Si*	< 0.00005	0.73
Zr/B*	< 0.0006	1.12

Notes: n.a., not available; *, SYNROC data refer to Ti and Zr, glass to Si and B.

species in the long term is largely governed by the rate at which the TiO_2 and ZrO_2 matrix can be removed from the surface.

Extensive studies of the leaching behaviour of individual SYNROC phases have also been made (Ringwood *et al.* 1981; Kesson 1983), and are consistent with results obtained on bulk SYNROC samples. Zirconolite and hollandite are found to be appreciably more resistant to leaching than is perovskite. This behaviour is probably a consequence of the larger proportion of relatively leachable calcium (*ca.* 40% CaO) present in perovskite. When this is selectively removed by leaching, the surrounding titania-rich skin is accordingly quite porous and permits further leaching to occur by diffusion through the water-saturated pores. Recent studies by Myhra

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et al. (1984, 1985) have confirmed that perovskite is nevertheless sufficiently resistant to leaching in a variety of aqueous media to be a perfectly acceptable host for radioactive waste. In comparison, zirconolite and hollandite contain much smaller proportions of divalent elements (about 16% CaO and BaO respectively). Selective removal of these components leaves protective TiO_2-rich skins, which probably possess a much lower porosity than the corresponding skin that surrounds perovskite.

5. Radiation damage

It is well known that crystalline materials are susceptible to radiation damage, predominantly arising from α-emission recoils. The possibility that these effects may seriously impede the capacity of crystalline host phases to immobilize HLW must be carefully examined. Some very relevant evidence on this topic is provided by nature. The α-emitting actinides in SYNROC are incorporated in zirconolite and perovskite. Sinclair & Ringwood (1981) studied the crystal structures of a collection of naturally occurring zirconolites and perovskites of differing ages, containing varying amounts of radioactive U and Th. These minerals have accordingly received different cumulative α-radiation doses ranging from 5×10^{17} to 10^{20} g^{-1}. These doses can be equated with the doses that the same phases would receive as a function of time, in SYNROC containing, for example, 10% of HLW (their 'SYNROC age'). These data are presented in figure 6.

Irradiation caused an increasing degree of lattice disorder accompanied by a swelling of up to 3 vol. % as the 'SYNROC age' reaches 1 Ma. With heavier irradiation zirconolite became

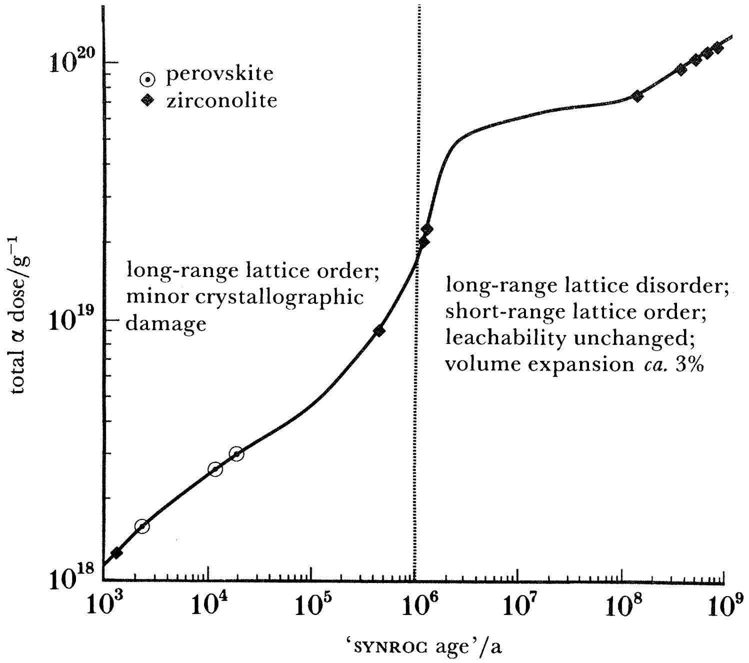

FIGURE 6. The curve shows the cumulative α-radiation dose that SYNROC with 10% HLW would receive over a period between 10^3 and 10^9 years. A suite of naturally occurring zirconolites (solid symbols) and perovskites (open circles) with known cumulative radiation doses are plotted on this curve to obtain their equivalent 'SYNROC age'.

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metamict to X-rays, but its volume expansion did not greatly exceed 3%. Electron diffraction studies of metamict zirconolites nevertheless show a considerable degree of short-range crystallographic order in small domains at 'SYNROC ages' equivalent to 400 Ma. Analogous studies of natural perovskites possessing 'SYNROC ages' up to 20000 years showed that the degree of irradiation caused a volume increase of up to 2%, but with little broadening of X-ray peaks.

Oversby & Ringwood (1981) analysed a collection of natural zirconolites and perovskites for uranium and lead by isotope dilution, and for Pb isotopic composition. These studies demonstrated that zirconolites possess a remarkable capacity to immobilize U, Th and their decay products although they have suffered extremely high radiation doses. For example, Sri Lanka zirconolites that have experienced α doses exceeding 8×10^{19} g^{-1} have nevertheless remained as closed systems to U, Th and Pb decay for 550 Ma. More limited data on perovskites indicate that this mineral is likewise highly retentive.

Measurements of the leachability of zirconolites and perovskites that have experienced varying degrees of radiation damage have also been reported (Ringwood *et al.* 1981). For example, the bulk leach rates at 200 °C (based on U loss) of natural zirconolites increased from 3.5×10^{-4} g m^{-2} d^{-1} for a crystalline zirconolite that had received 1.3×10^{18} α g^{-1} to 1.8×10^{-3} g m^{-2} d^{-1} for a metamict zirconolite that had received 8×10^{19} α g^{-1}. These leach rates differ by only a factor of 5 and are very low in comparison with borosilicate glass at this temperature. These results demonstrate that high radiation doses do not necessarily lead to unacceptably high leach rates.

SYNROC containing 10% by mass of non-radioactive waste has been irradiated in a fast neutron (greater than 1 MeV) flux to simulate the radiation damage that would result from long-term α-irradiation (Reeve & Woolfrey 1980; Woolfrey *et al.* 1982; Reeve 1985). The integrated doses to the specimens were equivalent, in terms of displacements per atom, to a 'SYNROC age' of 2200 to 450000 years. Increasing the irradiation dose resulted in significant increases in volume and corresponding decreases in density (up to 7.5%). However, all specimens remained intact after irradiation and showed no obvious signs of physical deterioration. Metallographic examination revealed some microcracking for volume expansions above 4%. Such microcracking is expected in SYNROC because of the anisotropic crystal structure of the component phases, which expand differentially upon irradiation, and because some preferred orientation develops during hot-pressing. Microcracking was accompanied by a slight increase in open porosity; however, the maximum increase was only 0.03% of specimen volume for a volume expansion of 7.5%. After fast neutron irradiation to complete loss of X-ray structure, simulating up to 450000 years of storage, SYNROC showed only a small increase (by less than a factor of 3) in the caesium leach rate. Of far greater practical importance is the rapid decrease in leach rate with time (by a factor of 100 or more in the first 50 days) that occurs irrespective of the extent of radiation damage.

During the period 1985–86 UKAEA at Harwell will prepare SYNROC samples containing various levels of curium-244. This will permit the effect of α-radiation damage on the properties and leachability of SYNROC to be determined.

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6. PHYSICAL PROPERTIES

Several physical properties of SYNROC are compared with those of glass in table 4. Some of these are relevant to waste form performance, particularly those that determine the effective surface area of the waste form when exposed to groundwater. Because of its higher thermal conductivity and strength, SYNROC is less susceptible to thermal shock than glass. Gamma radiography has not revealed any cracks in 30 kg blocks of SYNROC fabricated by hot-pressing at the Lucas Heights Demonstration Plant.

TABLE 4. PHYSICAL PROPERTIES OF SYNROC AND BOROSILICATE GLASS

(After Ringwood *et al.* (1981).)

property	SYNROC	glass
thermal conductivity/(W M^{-1} K^{-1})	3.0 ± 0.1	1.0 ± 0.2
density/(g cm^{-3})	4.35	2.9
tensile strength/MPa	75.6	37.0
crushing strength/MPa	810	260
bulk modulus/GPa	161	33
shear modulus/GPa	79	24
melting temperature/°C	*ca.* 1350	*ca.* 1100
thermal expansion coefficient, 0–1000 °C	*ca.* 9×10^{-6}	*ca.* 9×10^{-6}

On the other hand, because of relatively low thermal conductivity and tensile strength, glasses possess poor resistance to thermal shock. The surface area of a commercial-scale borosilicate glass monolith typically increases about tenfold owing to thermal stress-induced cracking during cooling (Ross *et al.* 1977).

The susceptibility of waste forms to stress-corrosion cracking requires more attention than it has previously received because this process has the capacity to produce a considerable increase in the surface area exposed to leaching (Weiderhorn 1977). Studies by Ringwood & Willis (1984) and Bates *et al.* (1984) showed that borosilicate glasses of the type used for waste forms are particularly susceptible to stress-corrosion cracking in the presence of water and water vapour, and that this can introduce large uncertainties in predicting the long-term survival of glass. Fracture parameter investigations by Cook *et al.* (1982) have shown that SYNROC is much more resistant to stress-corrosion cracking than glass. Plots of lifetime parameters against applied stress for SYNROC, Pyrex glass and soda-lime glass are shown in figure 7 (after Cook & Lawn 1984). In the low-to-moderate stress régime, the lifetime parameter for SYNROC is about 10^6 times that of Pyrex, which is a premium quality, annealed, high-silica, borosilicate glass. This, in turn, is vastly superior to the soda-lime glass over most of the stress range. Because of their chemical composition (high soda, low silica), pre-stressed state and presence of crystalline inclusions that act as stress centres (Ringwood & Willis 1984), the performances of borosilicate glasses of the types used for waste immobilization may be inferior to the soda-lime glass studied by Cook & Lawn. The implications of these experiments for the long-term survival of borosilicate glass waste forms are obviously serious. There is an urgent need for investigations of fracture properties to be carried out on these glasses.

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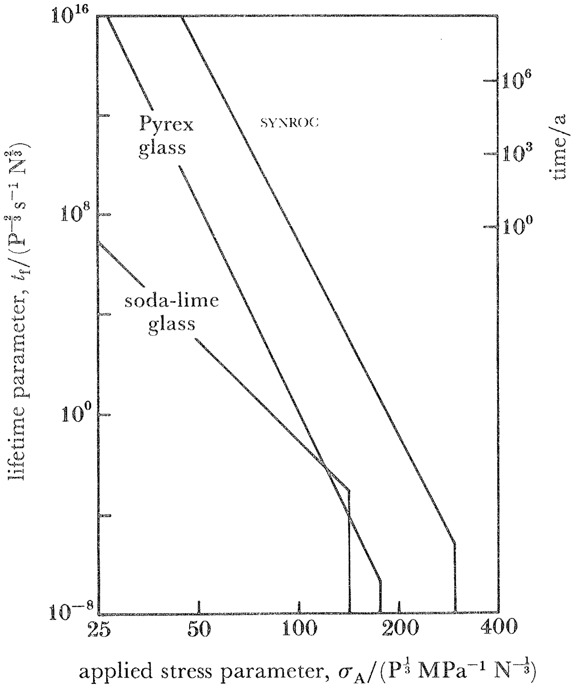

FIGURE 7. Plots of lifetime against applied stress parameters for SYNROC, Pyrex glass and lime-soda glass. (From Cook & Lawn (1984), figure 6.) Calculated lifetimes on the right of the diagram were provided by Cook (personal communication).

7. THE CASE FOR ADVANCED WASTE FORMS

Evidence reviewed in previous sections shows that it is possible to produce waste forms that are far more leach-resistant than borosilicate glasses. SYNROC has been discussed in detail because its properties have received the most extensive study. It should also be recognized that other ceramic materials with comparable or even better performances may be developed in the future. However, a large and influential section of the nuclear industry believes that there is no need for such advanced waste forms. According to this view, existing waste management strategies involving glass as the immobilization barrier, surrounded by an engineered overpack and interred in a geological repository, constitute an entirely satisfactory and safe isolation system. The following discussion suggests that this view may need to be reconsidered.

(*a*) *An independent immobilization barrier*

The multi-barrier approach to HLW management aims to provide a series of barriers, each of which complements the other, and in the last resort provides a high degree of redundancy in the event of unexpected failure of any one barrier. There is a substantial degree of flexibility in the emphasis that can be placed upon each of these barriers. The quality of the geological barrier varies considerably from site to site and some countries may not have access to 'geologically ideal' sites within their borders. It would be prudent to compensate for this variance in quality by additional emphasis upon the integrity of the immobilization and engineered barriers.

In many HLW disposal scenarios, the integrity of glass as an immobilization barrier cannot be guaranteed after a few thousand years. Beyond that period, it is likely to have transformed into a poorly defined mixture of hydrated oxides and secondary minerals, which become a

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component of the geological barrier. Primary responsibility for protecting the biosphere during the long periods required for decay of transuranic elements to safe levels is accordingly transferred to the geological barrier. In contrast, an advanced ceramic waste form such as SYNROC should be able to maintain its integrity as an independent immobilization barrier over periods exceeding a million years.

(*b*) *Repository design*

The strategy adopted in most countries is to dispose of radioactive waste canisters in large centralized mined repositories at depths typically in the range of 500–1000 m. However, a strong case can be made, on the grounds of safety, costs and socio-political considerations, that it would be preferable to dispose of HLW in a widely dispersed array of deep (4 km) drill holes carefully sited within impermeable crystalline rock formations (Ringwood 1980; Woodward-Clyde 1983).

The use of glass as an immobilization medium under these conditions is not advisable because the temperature of the waste form at the bottom of these deep holes may exceed 200 °C (even after 50 years of near-surface intermediate storage of the waste form). If water were to obtain access to a borosilicate glass waste form at 200 °C it would cause rapid disintegration (figure 5). In contrast, SYNROC displays a high degree of stability under these conditions. Thus the combination of an advanced waste form with deep drill-hole disposal has the capacity to maximize the integrity both of the geological and immobilization barriers.

(*c*) *Technological advances and geological disposal*

Some countries (e.g. the U.K., France and Japan) are planning to hold glass waste forms in intermediate storage for 50 years or more before final geological disposal in comparatively shallow mined repositories. The latter procedure employs engineering technology that has been available for many decades and is unlikely to change strategically during the next 50 years. On the other hand, the technology of drilling very deep, large-diameter holes in crystalline rocks is comparatively new and is rapidly being improved. It is reasonable to expect major advances in this technology over the next 50 years. As noted above, the disposal of HLW in deep drill holes is an attractive strategy even today. In 50 years' time, its advantages are likely to be far more compelling, because entirely new and advanced geological disposal strategies, not foreseen today, may become available. These may include new technologies for drilling into marine sediments and the oceanic crust. (Political and social pressures are likely to require any waste form destined for marine disposal to possess exceptionally effective retention properties.)

These considerations strongly suggest that current policies should place a high priority on the use of a waste form with properties that permit a multiplicity of disposal systems both now and in the future. A waste form possessing extremely high leach resistance over a wide range of temperatures has advantages in this context. It would be short-sighted to employ a waste form that is not capable of taking full advantage of the superior disposal options likely to be available 50 years hence. In the light of these circumstances glass may not be the optimum choice.

(*d*) *The fast breeder* (*FBR*) *fuel cycle*

Although the use of this fuel cycle has been deferred, it is likely to provide an important energy option for the world during the twenty-first century. Britain is currently planning to establish

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a pilot facility for the reprocessing of fast breeder fuel and solidification of FBR HLW at Dounreay, in Scotland.

Because of its stability at high temperatures, SYNROC would appear to possess some specific safety advantages over glass as a solidification medium for FBR wastes. A fully integrated FBR energy economy would require prompt reprocessing of fuel after removal from the reactors. The liquid wastes will be very 'hot' and will require interim storage in stainless steel tanks. There are important gains both in terms of costs and safety in solidifying these wastes as soon as possible. Because of the higher thermal conductivity of SYNROC (table 3) and its stability at high temperatures it would be possible to solidify FBR liquid wastes substantially earlier in SYNROC than in glass. There is no reason why the centre-line temperature of SYNROC monoliths in storage should not be as high as 800 °C. (Actually, storage at elevated temperatures is advantageous for SYNROC because the rate of annealing of radiation damage increases rapidly above 200 °C (Clinard *et al.* 1983).)

(*e*) *Public acceptability*

Although qualified scientists are generally confident that current systems of waste management can provide a very high level of safety, this belief has not dispelled the widespread public apprehension about nuclear waste disposal. It is important to appreciate that perceptions of safety by waste-management experts may differ considerably from the perception of safety by laymen who lack familiarity with the relevant scientific data. Because of this situation, the public is likely to require a waste-management strategy with an *extremely* high degree of demonstrable safety and fail-safe redundancy. Waste-management experts may well consider such systems to be unnecessarily 'over-safe', but this is beside the point. If public acceptability is to be achieved, the experts may well be obliged to design systems that conform to the safeguards required by the public. An advanced waste form that constitutes a demonstrably secure long-term immobilization barrier should be an important component of such a system.

It is also desirable that the scientific basis and rationale of a waste-management system should be understandable to the layman. This objective is not achieved by most of the current strategies, which are complex and difficult to evaluate. To a large degree this is caused by the excessive emphasis placed on the geological barrier, the analysis of which is hard to explain adequately to a non-scientist.

On the other hand, a strategy employing an advanced waste form such as SYNROC possesses some distinct advantages in this respect because of the geological evidence for long-term survival of its constituent minerals. It is this kind of evidence, provided directly by nature, that provides assurance that the successful immobilization of nuclear wastes can indeed be achieved over the very long periods required.

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Discussion

S. H. U. Bowie, F.R.S. (*Tanyard Farm, Clapton, Crewkerne, Somerset, U.K.*). Titanates containing appreciable amounts of α-emitting nuclides will become metamict with time – in other words analogous to glass – with an increase in volume of up to 10%. This will cause the capsule to fracture and the waste will present a much increased surface area to any circulating groundwater. Leach characteristics of SYNROC are likely to be very much different in 10000 years' time from what they are now. Naturally occurring accessory minerals contain actinides but only at a level such as to give the host rock a content of U or Th in the parts per million range. Such minerals were crystalline when formed and only became metamict after a long period of time. Tests are necessary with a full loading of radionuclides to ascertain what proportion will actually be accommodated in the titanate phases and how much is relegated to interstitial material which is more readily leached.

P. M. Kelly. We would agree with Professor Bowie's statement that tests of SYNROC with a full loading of radionuclides are necessary. Such tests will be performed at UKAEA, Harwell, and JAERI in Japan under collaborative R&D agreements. The point about SYNROC becoming metamict – i.e. glass-like – after long periods of self-irradiation has been recognized for some time. Experiments using neutrons to simulate damage indicate that microcracking does not occur until an equivalent SYNROC age of some hundreds of thousands of years has been reached; there is no large-scale cracking or loss of structural integrity and leach rates show only minor increases (by less than a factor of 3) even when the samples are essentially metamict. Much less cracking would be expected in practice where the damage is spread over a long period of time and the resulting strain rate is many orders of magnitude lower. This is confirmed by observations on naturally occurring perovskite and zirconolite subjected to damage equivalent to 100 Ma of SYNROC age. These samples (some 5 cm in size) were not cracked, and although metamict did not show enhanced leach rates. Finally it is worth remembering that at least 1 Ma is required for SYNROC with normal waste loadings to become completely metamict.

T. A. Kletz (*Department of Chemical Engineering, University of Technology, Loughborough, U.K.*). The greater public acceptability of SYNROC may be due to the fact that 'rock' suggests strength and permanence ('rock of ages') while 'glass' suggests fragility. Perhaps we should find another name for glass.

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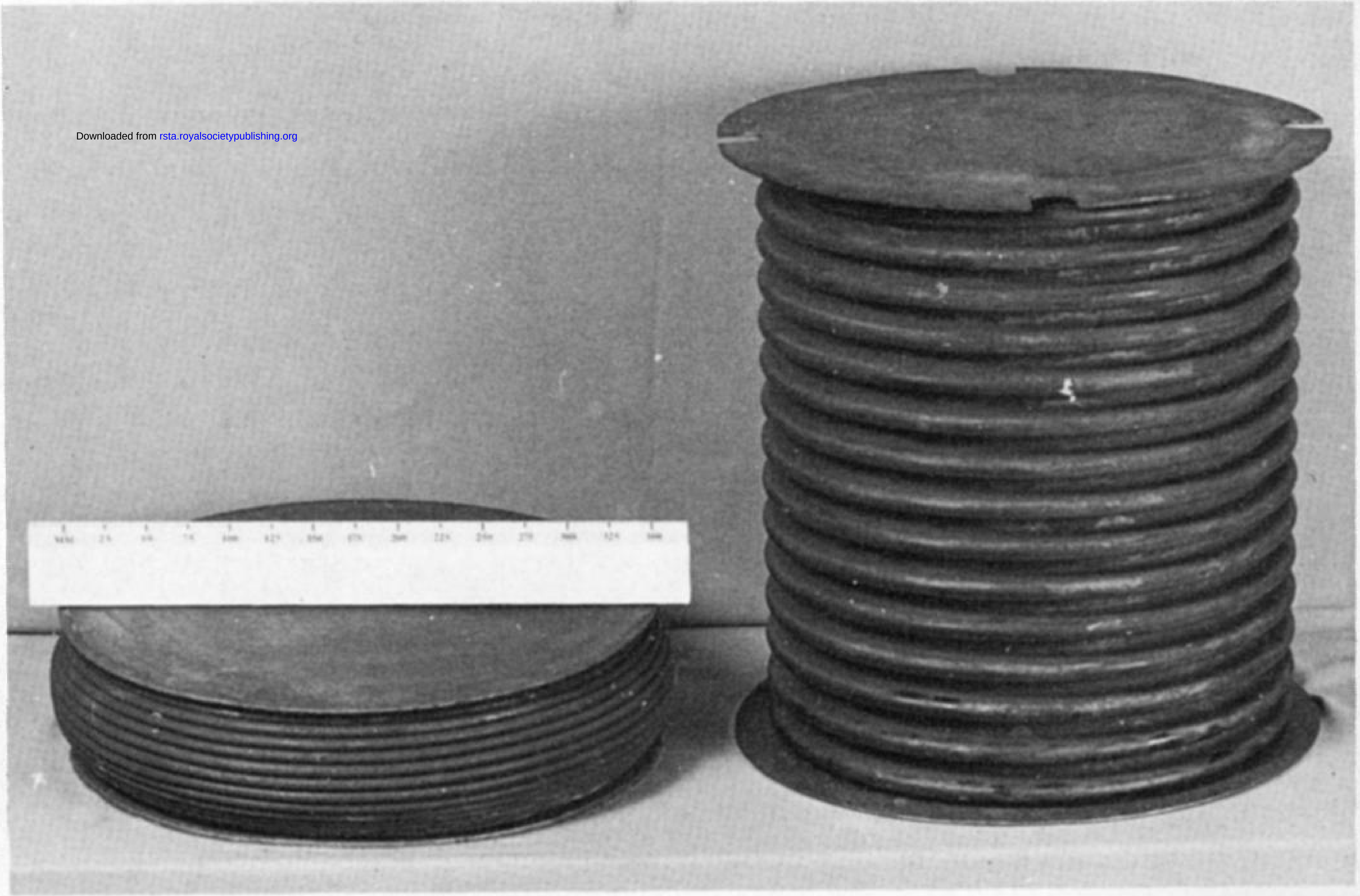

IGURE 1. Demonstration of SYNROC fabrication by uniaxial hot-pressing at 25 Mpa. The uncompacted stainless steel bellows (right) are filled with calcined SYNROC precursor powder and heated to a uniform temperature of 1150 °C. The unsupported bellows collapse under the uniaxial load to encase a fully densified 30 kg SYNROC monolith (left). The ruler graduations are 25 mm each.

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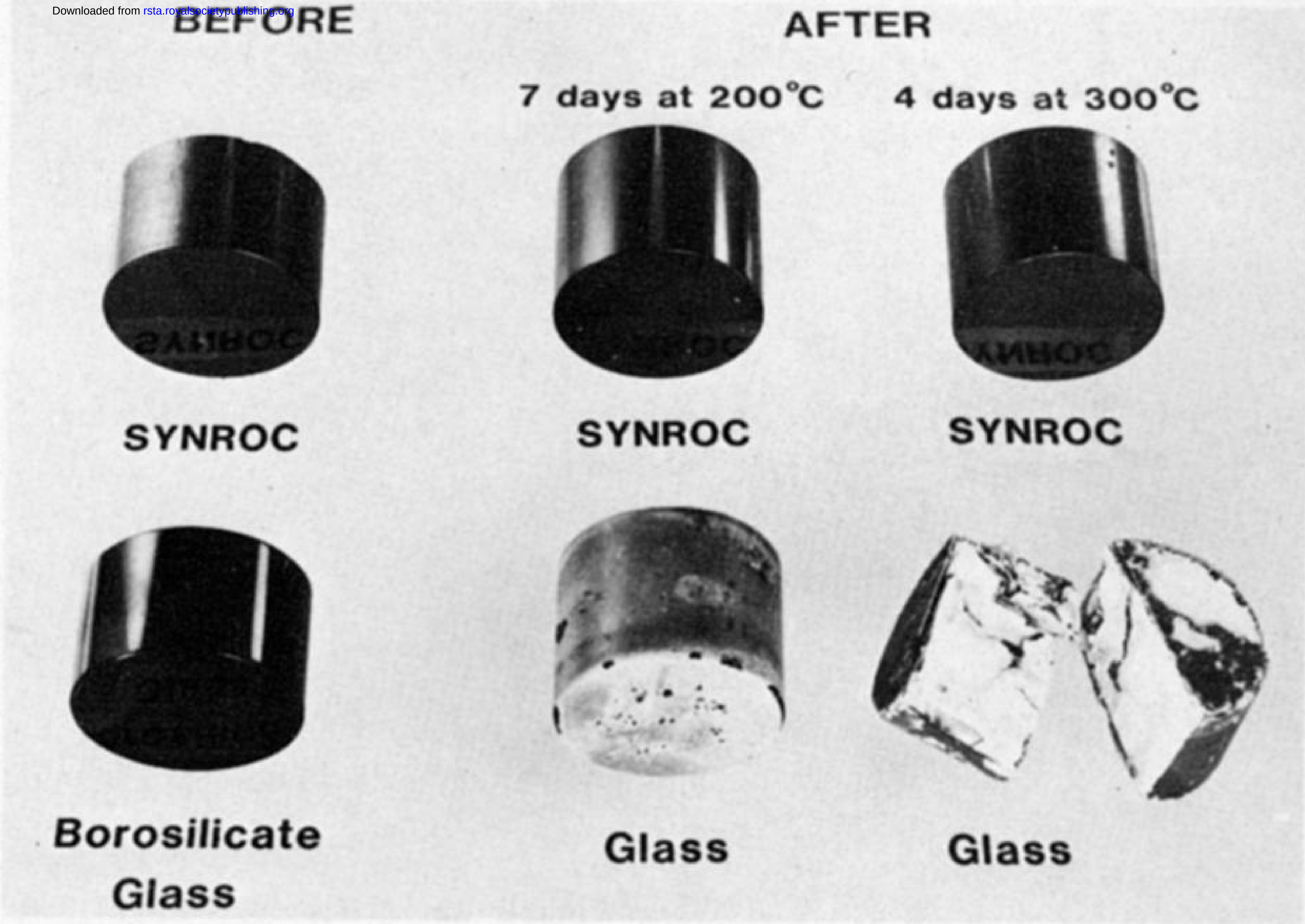

IGURE 5. Comparative leaching behaviour of 5 cm diameter cylinders of SYNROC and borosilicate glass, both containing simulated HLW, in water at 200 and 300 °C.