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Disposal of high-level nuclear wastes: a geological perspective

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ABSTRACT. Most countries intend to dispose of their high-level radioactive wastes by converting them into a solidified wasteform which is to be buried within the earth. SYNROC is a titanate ceramic wasteform which has been designed for this purpose on the basis of geochemical principles. It comprises essentially rutile TiO_2 , 'hollandite' $\text{Ba}(\text{Al,Ti})\text{Ti}_6\text{O}_{16}$, zirconolite $\text{CaZrTi}_2\text{O}_7$, and perovskite CaTiO_3 . The latter three phases have the capacity to accept the great majority of radioactive elements occurring in high-level wastes into their crystal lattice sites. These minerals (or their close relatives) also occur in nature, where they have demonstrated their capacity to survive for many millions of years in a wide range of geological environments. The properties of SYNROC and the crystal chemistry of its constituent minerals are reviewed in some detail and current formulations of SYNROC are summarized. A notable property of SYNROC is its extremely high resistance to leaching by groundwaters, particularly above 100°C . In addition, it can be shown that the capacity of SYNROC minerals to immobilize high-level waste elements is not markedly impaired by high levels of radiation damage. Current investigations are focused on developing a satisfactory production technology for SYNROC and progress towards this objective is described. The high leach-resistance of SYNROC at elevated temperatures increases the range of geological environments in which the waste may be finally interred; in particular, SYNROC is well adapted for disposal in deep drill-holes, both in continental and marine environments. The fact that SYNROC is comprised of minerals which have demonstrated long-term geological stability is significant in establishing public confidence in the ability of the nuclear industry to immobilize high-level wastes for the very long periods required.

KEYWORDS: radioactive waste, SYNROC, hollandite, zirconolite, perovskite, radiation damage, leaching.

HIGH-LEVEL WASTES (HLW) arising from the operation of nuclear reactors are intensely radioactive and must be isolated from the biosphere for extremely long periods, up to one million years. Most countries intend to dispose of their wastes by converting them into a solidified form and burying

this within the earth. Subsequent leaching of the wasteform by circulating groundwaters is the most likely mechanism by which radionuclides could be returned to the biosphere. It is therefore desirable that the wasteform should be constructed from a highly stable material possessing an extremely low solubility in groundwater. Thus, the wasteform itself should function as an 'immobilization barrier' fully capable of preventing any significant release of radionuclides to the biosphere for 10^5 - 10^6 years. The wasteform would be disposed of in a repository 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 these groundwaters. This constitutes the so-called 'geologic barrier' which is essentially independent of the immobilization barrier. Ideally, each of these barriers, independently, should be fully capable of preventing any significant entry of radwaste species into the biosphere.

A basic philosophy adopted in this paper is that the disciplines most directly concerned with understanding the behaviour of HLW when buried in the earth are the geological sciences. Surprisingly enough, this obvious fact has been widely neglected in the past. Many of the key decisions regarding the basic strategies of waste management have been made by executives of various national atomic energy agencies who apparently possessed little knowledge of geology and geochemistry. As we shall see, these strategies have sometimes been far from optimum when viewed from a geologic perspective.

Immobilization of HLW in borosilicate glass

The most popular immobilization barrier that has been advocated by the nuclear power industry over the last two decades has been to incorporate HLW in borosilicate glass contained in steel

canisters. This procedure was devised originally as a means of greatly reducing the volumes of liquid HLW produced by reprocessing, and facilitating the safe transport of HLW. Glass is well suited for these purposes. Only at a later stage was it proposed that the glass-filled canisters should be buried in the earth in appropriate geological repositories. The latter strategy seems less than ideal, however, because geochemists have shown that borosilicate glasses would readily disintegrate if they were placed in the earth and came into contact with groundwaters at quite moderate pressures and temperatures. Such disintegration would be accompanied by loss of some radionuclides into the groundwater.

It is disturbing to recall that, until the late 1970s the nuclear industry was confidently proposing to incorporate up to 30 wt. % HLW in borosilicate glass and to bury the glass only a few years after reprocessing. Because of the heat generated by the HLW, the centreline temperature of buried glass cylinders would have exceeded 300 °C. As evidenced by fig. 5, the glass would have disintegrated within a few days when contacted by groundwater at such temperatures. These early policies were obviously inadequate, and were criticized by geochemists (e.g. McCarthy, 1977; Ringwood *et al.*, 1979a).

Subsequently, the nuclear industry has recognized these problems and has advocated improved new waste management procedures. Examples of these are described in the Swedish KBS reports (KBS, 1978) which propose that:

(i) The amount of HLW in the glass shall be reduced to 10% or less.

(ii) The glass will be aged in intermediate storage facilities near the surface for several decades. This will permit the most important heat-producing elements to decay substantially. The net result of this policy and also of (i) above is that when glass is finally buried underground in a geological repository, its internal temperature would not substantially exceed 100 °C. Below this temperature its leachability is quite low.

(iii) The glass will be surrounded by metallic canisters composed of Ti and Pb which are highly resistant to corrosion by groundwaters.

(iv) When finally buried, the canisters will be surrounded by 'overpacks' of compacted bentonite which will greatly impede access of groundwater to the waste and will selectively adsorb and fix any radioactive elements which might be dissolved from the glass.

There can be no doubt that these procedures represent a considerable improvement upon pre-1978 policies for radwaste disposal. The vast majority of scientists working in the HLW manage-

ment field believe there is no reasonable doubt about the capacity of the new waste package (glass + canister + overpack) to maintain its integrity with negligible leakage of radionuclides for at least 1000 years, by which time the fission products will have decayed to safe levels (fig. 1). However, it is difficult to guarantee integrity of the waste package over the much longer periods, exceeding 10 000 years, required for safe decay of some actinide elements, especially neptunium. Thus, protection of the biosphere over this longer timescale depends primarily upon the ability of the geological barrier to retard access of groundwater to the wasteform and to delay migration of contaminated groundwater from the waste package to the biosphere.

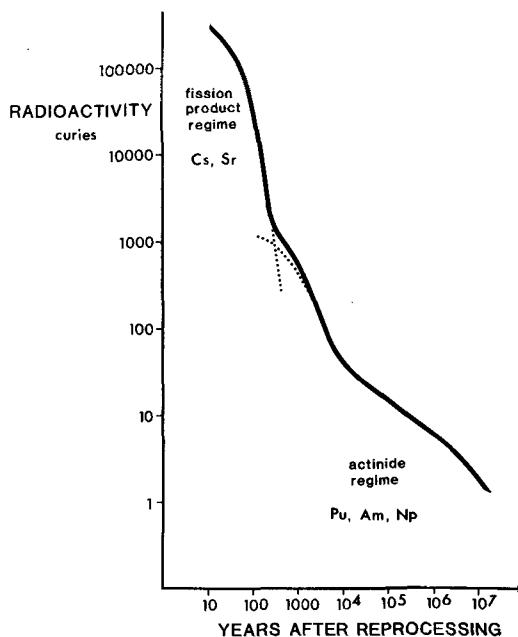


FIG. 1. The radioactivity of 1 tonne of high-level waste decreases greatly over the first 1000 years due to decay of fission products. Radioactivity over longer timescales is largely due to actinide elements and their daughter products.

The SYNROC strategy for HLW immobilization

Because of the limited capacity of borosilicate glasses to withstand leaching, particularly at elevated temperatures, there has been a strong incentive to produce an improved wasteform, possessing much greater leach-resistance, which would provide a far more secure immobilization barrier. My

colleagues and I are accordingly developing a titanate ceramic called SYNROC (an acronym for synthetic rock) for this purpose (Ringwood, 1978; Ringwood *et al.*, 1979a, b). SYNROC is a thermodynamically stable assemblage of four main minerals 'hollandite' $\text{Ba}(\text{Al},\text{Ti})_2\text{Ti}_6\text{O}_{16}$, zirconolite $\text{CaZrTi}_2\text{O}_7$, and perovskite CaTiO_3 and rutile TiO_2 . These minerals have the capacity to take nearly all the elements present in high-level wastes into their crystal structures at regular lattice sites in the form of dilute solid solutions (fig. 2). Similar minerals in nature have survived in a wide range of geochemical-geological environments for up to 2000 million years. It is this evidence of geological stability, provided by nature, 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 HLW. In fact, the SYNROC strategy for immobilization of HLW is very similar to the way in which nature immobilizes radioactive elements on a scale vastly greater than that ever contemplated by the nuclear industry. All natural rocks contain small amounts of radioactive elements (e.g. ^{238}U , ^{232}Th , ^{40}K , ^{87}Rb) that become distributed among coexisting minerals in the form of dilute solid solutions. Many of these minerals (e.g. zircon and feldspar) have demonstrated the ability to lock up small amounts of radioactive elements for billions of years. In SYNROC, the radioactive waste elements are likewise immobilized as dilute solid solutions in the crystalline lattices of their host minerals.

Composition and mineralogy of SYNROC

Several distinct SYNROC formulations have been developed for a range of radioactive wastes (see later). This paper is concerned with immobilization of HLW derived from reprocessing spent nuclear fuel from commercial power reactors. The principal formulation developed to immobilize these wastes is SYNROC-C, the composition of which is given in Table I. SYNROC-C is designed to immobilize about 20 wt. % of HLW (Table II) and comprises a mineral assemblage consisting of hollandite + zirconolite + perovskite + rutile (Table I).

'Hollandite'. Natural hollandite has the formula $\text{BaMn}_8\text{O}_{16}$ with manganese occurring in 2+, 3+ and 4+ valence states. There is, however, a large number of structural isotypes, including $\text{Ba}(\text{Al},\text{Ti})_2\text{Ti}_6\text{O}_{16}$ which is employed in SYNROC and is the host for large cations such as Cs, Rb, and Ba. In the SYNROC hollandite structure the small cations (Ti^{4+} , Ti^{3+} , and Al^{3+}) are octahedrally co-

TABLE I. Composition and mineralogy of SYNROC-C.

Composition	
TiO_2	57.1 %
ZrO_2	5.4
Al_2O_3	4.4
BaO	4.4
CaO	8.9
HLW	20.
Mineralogy (approx. wt%)	
Hollandite	33
Zirconolite	28
Perovskite	19
Rutile	15
Alloy	5

HLW = calcined high-level waste

TABLE II. Composition of typical HLW calcine (PW-4b)*

Processing contaminants (wt%)		Fission Products (wt%)	
Fe_2O_3	3.7	Rb_2O	0.9
Cr_2O_3	0.8	Cs_2O	7.1
NiO	0.3	SrO	2.6
P_2O_5	1.6	BaO	3.8
Actinides (wt%)		Y_2O_3	1.5
U_3O_8	3.3	La_2O_3	3.6
NpO_2	2.1	Ce_2O_3	7.7
PuO_2	0.02	Pr_6O_{11} }	15.0
		Nd_2O_3 }	
		Pm_2O_3 }	
Am_2O_3 }	0.5	Sm_2O_3	2.3
Cm_2O_3 }			
		Eu_2O_3 }	0.8
		Gd_2O_3 }	
		ZrO_2	12.1
		MoO_2	12.7
		TeO_2	1.8
		Tc_2O_7	3.2
		RuO_2	7.3
		Rh_2O_3	1.3
		PdO	3.6
		Ag_2O	0.2
		CdO	0.2

*after Mendel *et al.* (1977)

ordinated and the octahedra linked together by edge-sharing to form double strings running parallel to the *c*-axis. The double strings of octahedra, in turn, share corners to form a three-dimensional framework which contains tunnels parallel to the *c*-axis, in which the large cations are situated. The latter are surrounded by a cage of 8 oxygen anions at the corners of a slightly distorted cube, with another 4 neighbouring

oxygen atoms positioned at a greater distance (Sinclair *et al.*, 1981). The cage-like environment prevents the free migration of large cations like Ba^{2+} and Cs^+ along the tunnels, thereby accounting for the excellent resistance of SYNROC hollandite to leaching by groundwater.

The correct formula for SYNROC hollandite is $\text{Ba}_x(\text{Al},\text{Ti})_{2x}\text{Ti}_{8-2x}\text{O}_{16}$, where x is non-integral as a consequence of superlattice ordering, and ranges from 1.08 to 1.14 (Kesson, pers. comm.). A wide range of cationic substitutions is also permitted. Ba can be replaced by a substantial proportion of Cs, Rb, and K, whilst Al can be replaced by other trivalent cations (e.g. Cr^{3+} , Fe^{3+} , Ti^{3+}) or by combination of (Ti^{4+} and M^{2+}) where $\text{M} = \text{Mg}$, Co, Ni, Fe, Mn. A caesium hollandite end-member $\text{Cs}_{2x}\text{Al}_x\text{Ti}_{8-2x}\text{O}_{16}$ also exists, with $x = 0.7-0.8$ (Bayer and Hoffman, 1966; Roth, 1981). Kesson (pers. comm.) has obtained definitive experimental evidence for continuous solid solution between Ba and Cs end-members, and, simultaneously, between Al^{3+} and Ti^{3+} in the structure. The solid solution of sodium and strontium in $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$ hollandite is limited to about 2% each of Na_2O and SrO .

The hollandite phase employed in SYNROC possesses the same structure as the mineral priderite $(\text{K}_2,\text{Ba})(\text{Fe},\text{Al})_2\text{Ti}_6\text{O}_{16}$ which occurs in c. 20-million-year-old volcanic rocks from the Kimberley region of Western Australia (Norrish, 1951) and which constitutes a resistate mineral in alluvial deposits produced by the weathering of the volcanics. This behaviour supports the expectation that the hollandite phase in SYNROC will also display a high degree of stability in appropriate geologic environments.

Zirconolite $\text{CaZrTi}_2\text{O}_7$. The confusion in the mineralogical literature between zirconolite, zirkelite and polymignite has been largely resolved by Mazzi and Munno (1983), who confirmed that although these three phases have very similar structures, zirconolite is monoclinic, zirkelite trigonal, and polymignite orthorhombic, and moreover that the crystal structures of zirconolite and zirkelite are indeed very similar, differing only in the stacking of identical pairs of polyhedra. Mazzi and Munno (1983) interpret these three minerals as polymorphs of the one compound $(\text{Ca},\text{Na},\text{REE},\text{Th}\dots)_2^{\text{VIII}}\text{Zr}_2^{\text{VIII}}(\text{Ti},\text{Nb}\dots)_3^{\text{VI}}(\text{Fe},\text{Ti})^{\text{V},\text{VI}}\text{O}_{14}$ but we prefer to recognize them as three distinct phases in a family of fluorite-related structures, because we suspect that subtle variations in chemical composition may preferentially stabilize a particular structure.

In SYNROC formulations 'zirconolite' is used as a generic term for the above family of three phases, because we recognize that small-scale intergrowths of one or more structures may occur. Nevertheless

the monoclinic zirconolite structure seems to be most common (Dr T. J. White, pers. comm.). In SYNROC formulations, zirconolite is largely responsible for the immobilization of uranium and the tetravalent actinides, and to a lesser degree, for the immobilization of rare earths and trivalent actinides. Zirconolite possesses an anion-deficient fluorite-related superstructure with a monoclinic unit cell. Detailed structural determinations and refinements have recently been conducted by Rossell (1980), Gatehouse *et al.* (1981), Sinclair and Eggleton (1982), and Mazzi and Munno (1983). Ca is co-ordinated by 8 oxygen ions positioned at the corners of a cube whilst Zr is in sevenfold co-ordination to oxygen at seven of the eight vertices of a distorted cube. Ti occupies three distinct lattice sites. In the Ti(I) and Ti(III) positions it is octahedrally co-ordinated to 6 oxygen ions and these TiO_6 octahedra are corner linked forming six- or three-membered rings respectively. The Ti(II) site is surrounded by 5 oxygen ions at the corners of a trigonal bipyramid. This is actually a pair of closely positioned sites, only one being randomly occupied by Ti^{4+} (Rossell, 1980).

Crystal chemical studies in the system $\text{CaO-ZrO}_2\text{-TiO}_2$ have shown that whilst zirconolite is intolerant to variation in its calcium content, Ti:Zr ratios may vary considerably so that the formula is better expressed as $\text{CaZr}_x\text{Ti}_{3-x}\text{O}_7$ with $0.8 > x > 1.3$ (Gatehouse *et al.*, 1981). A wide range of cation substitutions is permitted in natural and synthetic zirconolites and have recently been reviewed by Kesson *et al.* (1983). About 25% of UO_2 and ThO_2 can be incorporated in the crystal structure. In SYNROC zirconolites, the U^{4+} cation (ionic radius 0.98 and 1.00 Å in seven- and eightfold co-ordination respectively) is largely accommodated in the Zr site, and to a lesser extent in the Ca site. In contrast, the larger Th^{4+} (c. 1.03 and 1.06 Å in seven- and eightfold co-ordination) is strongly partitioned into the Ca site, and is very reluctant to enter the Zr site. When either U^{4+} or Th^{4+} replace Ca^{2+} charge balance is achieved via replacement of Ti^{4+} by divalent cations (e.g. Mg^{2+} , Fe^{2+}) or twice the equivalent number of trivalent cations (e.g. Fe^{3+} , Cr^{3+} , Ti^{3+}) in octahedral sites.

Natural zirconolites contain up to 13% rare earth oxides, whilst up to 29% REE have been incorporated under experimental conditions (Kesson *et al.*, 1983). The REE are mainly accommodated in the Ca sites with charge balance being achieved by substitution of trivalent and divalent cations for titanium (e.g. Al^{3+} , Ti^{3+} , Fe^{2+} , Mg^{2+}). A significant amount of the REE can also replace Zr in the sevenfold sites. Partition of REE between these sites is governed by ionic size. The smaller, intermediate and heavy rare earths (e.g. Yb^{3+})

preferentially enter the Zr site whilst larger light rare earths (e.g. Ce^{3+} , Nd^{3+}) enter the Ca sites. However, the zirconolite structure does not readily accept cations possessing ionic radii much larger than Ca^{2+} (1.12 Å), as shown by the limited solubility of Sr^{2+} (1.25 Å) in zirconolite. (A maximum of only 1.4% SrO has been found in zirconolites which were equilibrated with Sr-rich titanate phases (Kesson *et al.*, 1983).) Accordingly, the largest light REE (La^{3+} and Ce^{3+}) are not readily incorporated in zirconolite. In SYNROC these elements are mainly found in perovskite, in the twelvefold co-ordinated site, and in minor amounts of a phase with the *pyrochlore* structure, first identified by Dr T. J. White who has also noted that many SYNROC zirconolites may display either monoclinic or orthorhombic superstructures (pers. comm., 1983). These polytypes result from stacking and rotation of (001) planes containing rings of Ti octahedra, and may occur as intergrowths on a unit-cell scale.

The compositional variety amongst natural and synthetic zirconolites demonstrates that the structure can accommodate a wide range of cation substitutions. This capacity arises because of the five distinct cation-acceptor sites in the lattice; the Ca-, Zr-, Ti(I), Ti(II), and Ti(III) sites, are suitable for a wide variety of species possessing diverse charges and radii. There is accordingly a great deal of flexibility in the zirconolite lattice to accommodate simple, coupled and multiple substitutions of various kinds so that charge balance is preserved. In this manner zirconolite contributes to the capacity of SYNROC formulations to accommodate considerable variation in the composition of the high-level waste-stream.

Zirconolite is found in terrestrial alkaline rocks, mafic rocks and carbonatites up to 2 billion years old. It also occurs as a resistate mineral in the gem gravels of Sri Lanka. It is often metamict owing to radiation damage caused by naturally radioactive U and Th contained in its lattice. Nevertheless, despite their great ages and complex geological histories, natural zirconolites usually appear to have been successful in quantitatively retaining their U and Th and lead daughter products (Section 7), and have displayed a high degree of stability in a wide range of geological environments.

Perovskite CaTiO_3 . In the perovskite structure the small cations (e.g. Ti^{4+}) are surrounded by regular octahedra of oxygen ions which are linked by sharing corners to form a three-dimensional framework. The large cations (e.g. Ca^{2+}) are centrally located in twelvefold co-ordinated positions between groups of four TiO_6 octahedra. The ideal ABO_3 perovskite structure can be formed only for a rather restricted size-range for A and B cations. The A cations have to be sufficiently large to form a

close packed array with oxygen anions whilst the B ions must fit within the octahedral holes of the A-O close-packed array. When these requirements are not met the simple perovskite lattice may become distorted, giving rise to several closely related structures with lower symmetry. The co-ordination numbers of the A cations in these distorted perovskites (which represent the most common members of this family) may be smaller than twelve.

The perovskite family of structures possesses the capacity to accept a remarkably wide range of elements into solid solution. In SYNROC the principal radioactive waste elements which are preferentially incorporated in perovskite are strontium, rare earths and trivalent actinides (e.g. Pu^{3+}). Sr is readily incorporated via a simple substitution for calcium. Rare earths and trivalent actinides also preferentially replace calcium, with charge neutralization being achieved by replacement of Ti^{4+} by Al^{3+} or Ti^{3+} . In the presence of sodium, a different substitution mechanism is possible; rare earths may be incorporated as an $\text{NaREETi}_2\text{O}_6$ component which itself possesses the perovskite structure (Kesson and Ringwood, 1981). Perovskite occurs in alkaline mafic and ultramafic rocks and in carbonatites, where it is known to have survived in a wide range of geological environments for periods exceeding 1000 million years.

Incorporation of radwaste elements in SYNROC

The objective of the SYNROC process is to incorporate high-level nuclear waste species as minor components in solid solution in the crystal lattices of the constituent minerals—hollandite, zirconolite, and perovskite. Since there are upwards of 30 elements in radwaste, possessing different radii and charges, (Table II) doubt is sometimes expressed about the capacity of such a relatively simple wasteform to perform this function without the formation of new phases possessing undesirable properties (e.g. Tempest, 1981).

Current formulations of SYNROC are based on the equilibrium four-phase assemblage hollandite + zirconolite + perovskite + rutile. In addition, at the redox state under which SYNROC is prepared, a small amount of dispersed metal alloys plus trace amounts of a Ca-rich phosphate are present. The 'forgiving' nature of SYNROC as a wasteform arises from the capacity of the individual minerals to incorporate a remarkably wide range of cations possessing different radii and charges into their crystal structures. Twenty wt. % of (calcined) high level waste (Table II) can readily be accommodated in solid solution in SYNROC minerals. Even at these concentrations, the three principal host minerals, hollandite, zirconolite, and perovskite,

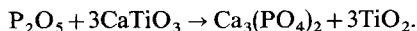
are undersaturated with respect to any specific HLW element; hence wide variations in waste composition are permitted without stabilizing new and unwanted phases. The distribution of HLW elements in SYNROC phases is summarized in fig. 2.

HOLLANDITE	Cs, Ba, Rb, K, Cr
ZIRCONOLITE	Th, U, Pu and tetravalent Actinides, Zr
PEROVSKITE	Sr, Na, trivalent Actinides, Rare Earths
ALLOY	Tc, Mo, Ru, Pd, S, Te

FIG. 2. Each SYNROC phase is the primary host for a number of HLW elements, as shown.

SYNROC is fabricated under reducing conditions at oxygen fugacities near those of the Fe-FeO buffer. In practice these conditions are achieved by calcining the precursor at 800 °C in an Ar-4% H₂ atmosphere and introducing *c.* 2% of finely dispersed Ti metal powder prior to hot-pressing. The Ti metal reduces some Ti⁴⁺ to trivalent Ti³⁺ which enters into solid solution in hollandite, and to a lesser degree, into zirconolite and perovskite. The rationale behind the introduction of rutile into the phase assemblages of all current SYNROC formulations is to provide a reservoir of excess Ti⁴⁺ for this purpose. In phase assemblages which were not rutile-saturated, the oxidation of Ti metal to Ti³⁺ would proceed via consumption of the Ti⁴⁺ in the other SYNROC phases, thereby permitting the stabilization of Ti-poor phases, e.g. CsAlTiO₄, which in turn can be responsible for the inferior leaching performance of some SYNROC preparations (Kesson, 1983). The recommended redox conditions prevent Cs from combining with Mo in HLW to form a soluble molybdate phase and also contribute to optimizing the immobilization of Cs in hollandite (Kesson, 1983). At the iron-wüstite oxygen fugacity buffer, Mo, Ru, Rh, Pd, Te, Ag, Ni, and some Fe are reduced to metallic alloys. These form dispersed micron-sized inclusions which are micro-encapsulated by the primary titanate phases. The remaining iron (introduced into the waste-stream as a processing contaminant) enters hollandite as a Ba(Fe²⁺, Ti⁴⁺)Ti₆⁴⁺O₁₆ component.

The compositional flexibility of SYNROC is best illustrated by some specific examples. If the Cs content of the waste-stream were higher than normal, the excess Cs would combine with appropriate molar proportions of 'Ti₂O₃' (i.e. Ti³⁺) and TiO₂ to form a Cs_{2x}Ti_{2x}Ti_{8-2x}⁴⁺O₁₆ component which would enter into solid solution in hollandite. Excess U (and tetravalent actinides) would react with an equimolar amount of rutile plus perovskite, to form a CaUTi₂O₇ component in solid solution in zirconolite. Phosphorous (introduced as a processing contaminant) reacts with perovskite to liberate rutile



Sr reacts with excess rutile to form SrTiO₃ which enters perovskite.

REE are preferentially incorporated in perovskite, relative to zirconolite. This partition behaviour is most pronounced for the light rare earths (Ryerson, 1983). Entry of REE and trivalent actinides into perovskite occurs mainly via formation of REEAlO₃ and REETi³⁺O₃ which form solid solutions with CaTiO₃. Entry of these elements into zirconolite occurs via related coupled substitutions as discussed earlier. Na can also be present in the waste-stream as a processing contaminant. When present in small amounts, it is incorporated in the major titanate phases which accept 1-2% of Na₂O. In higher concentrations, sodium can be specifically incorporated in perovskite as an NaREETi₂O₆ component (Kesson and Ringwood, 1981).

The primary requirements for incorporating HLW elements (other than those forming metallic alloys) into the SYNROC minerals are the presence of excess TiO₂ (i.e. rutile saturation) and some trivalent ions (e.g. Ti³⁺) in the wasteform. Providing these conditions are satisfied (by the initial wasteform formulation and redox control during processing), the composition and loadings of HLW can be varied widely (within reasonable limits), without compromising the immobilization capacity of the wasteform, or causing the formation of new or unwanted phases. Earlier formulations of SYNROC (Ringwood *et al.*, 1979a, b) were designed to accept 10% HLW. The waste-loading has since been increased to 20% without any diminution in performance (Ringwood *et al.*, 1981) and without unduly compromising flexibility.

The proponents of borosilicate glass frequently claim that this wasteform is more tolerant to waste-stream variations than ceramics (e.g. Tempest, 1981). This claim is open to question. Current processes for manufacturing borosilicate glasses are unable to achieve satisfactory control of redox conditions (a feature of the SYNROC process). If

conditions become too oxidizing, an immiscible 'yellow phase' containing alkali molybdates, sulphates, and chromates, may separate. Since this contains much of the Cs and Mo and is highly soluble in water, the consequences are undesirable. On the other hand, if excessively reducing conditions prevail in the melter, metallic alloys of Mo, Ni, Fe, Tc will precipitate in addition to Ru, Pd, Rh, and Ag which do not readily dissolve in the glass under normal manufacturing conditions. The metallic sludges interfere with the operation of the melter; moreover any dispersed alloys incorporated in the glass could initiate stress corrosion cracking and greatly shorten the effective lifetime of the glass after final underground burial (Ringwood and Willis, 1984).

Comparative leaching behaviour of SYNROC and borosilicate glass

In safety analyses, one must always consider the possibility, however remote, that large volumes of groundwater may breach the repository, owing to unsuspected hydrogeologic factors, e.g. fractures in containment rocks caused by tectonic activity, thermal stress or human intrusion. For example, the role of ice ages in causing fracturing of repository wall rocks is often overlooked in analyses of long-term repository behaviour. One or more extensive periods of glaciation are likely to occur during the next 100 000 years. A large ice sheet can depress the Earth's surface by 100 to 1000 metres. It is now recognized that isostatic recovery after melting may be accompanied by extensive formation of new fractures and joints in the upper kilometre or so of the crust (Morner, 1978). The presence of a large mined repository at a depth of 300-1000 metres would act as a focus for the regional stress and intensified jointing and fracturing may occur in the neighbourhood of the repository. Accordingly, it cannot be assumed that the current hydrogeological regime around repository sites in the regions subject to glaciation will necessarily prevail for periods of the order of 10^5 years.

Realistic leach testing of wasteforms should be designed conservatively to allow for such possibilities. The leachability of the wasteform should therefore be measured under conditions in which the volume of the leachate solution is large compared to the volume of the waste. The leachate thus remains undersaturated with respect to the wasteform.

The single-pass leaching system of Coles *et al.* (1978) reproduces these conditions, whilst the IAEA method (Hespe, 1971) also provides a good approximation. According to this method, the wasteform is leached with a fixed volume of deion-

ized water in a closed container for a finite time, after which the solution is decanted, chemically analysed, and then replaced by a fresh batch of water. Leach rates are calculated using the relationship:

$$\text{leach rate} = \frac{l \cdot w}{c \cdot t \cdot s}$$

where l = quantity of ion in leach solution

c = quantity of ion in solid sample

w = initial weight of solid test specimen

t = time of leach

s = geometrical surface area of test specimen.

The data are presented graphically as logarithmic plots of leach rates *vs.* time and compared with similar leaching data for a typical borosilicate glass (PNL 76-88) proposed for radwaste immobilization (Mendel *et al.*, 1977), in figs. 3 and 4.

It is seen in figs. 3 and 4 that the leach rates of most elements from borosilicate glasses fall within a limited range and do not change strongly with time. In sharp contrast, wide variations occur in leach rates for different elements from SYNROC. Moreover, the leach rates decrease strongly with time over the first 10-30 days, often by two orders of magnitude. The sharp reduction of leach rate with time displayed by SYNROC is believed to be due to two factors (Ringwood *et al.*, 1981). First, imperfect equilibrium may be achieved during hot-pressing and small amounts of metastable phases may occur, particularly at grain boundaries. These are likely to

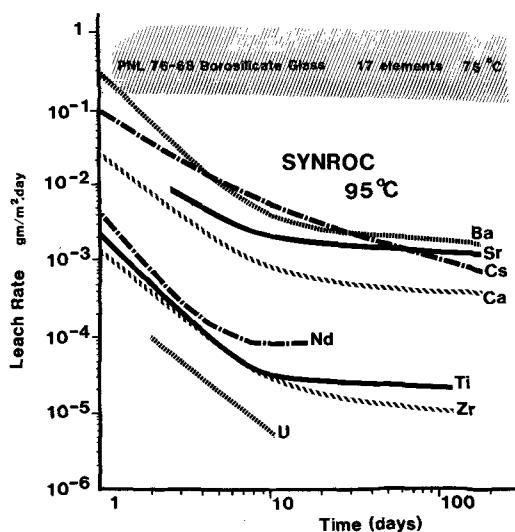


FIG. 3. Comparative leaching behaviour of SYNROC-C + 20% simulated HLW in water at 95°C, and PNL 76-68 borosilicate glass at 75-95°C.

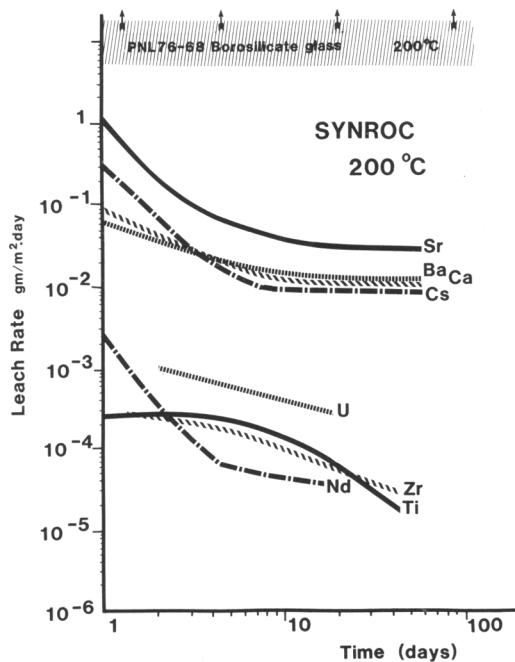


Fig. 4. Comparative leaching behaviour of SYNROC-C+9% simulated HLW and PNL 76-68 borosilicate glass in water at 200°C.

be more leachable than the stable major phases. Leach rates therefore fall with time as these phases are selectively removed from the surface. Secondly, studies of leaching mechanisms (Ringwood *et al.*, 1981) show that univalent and divalent elements are selectively removed from surfaces of phases, leaving skins enriched in TiO_2 and ZrO_2 . These oxides are extremely insoluble in groundwater and tend to protect the surface from further leaching.

Data shown in fig. 3 (see also Ringwood *et al.*, 1981; Oversby and Ringwood, 1982), show that after about 30 days the leachabilities of univalent and divalent elements (Cs^+ , Sr^{2+} , Ba^{2+} , Ca^{2+}) from SYNROC at 95°C are about 500 to 1000 times smaller than from borosilicate glass. The differences are even greater in the cases of trivalent and tetravalent elements. The leachabilities of Nd^{3+} , U^{4+} , Zr^{4+} , and Ti^{4+} from SYNROC are about 10000 times smaller than for glass. Actinide elements generally possess chemical properties similar to the rare earths and uranium. It is therefore expected that their leachabilities will be in the vicinity of those displayed by Nd^{3+} and U^{4+} .

Fig. 4 demonstrates similar comparative leaching behaviour at 200°C. Leach rates for the glass are based on extraction of soluble species such as Cs, Na, Si, and B. Other components in the glass,

e.g. Ca, are found to precipitate from the leachate solution to form indeterminate new phases, so that lower bounds only can be placed on their intrinsic leachabilities. More limited experimental data (Ringwood *et al.*, 1979a) show that SYNROC continues to display excellent resistance to leaching at much higher temperatures, in the range 300–800°C, whereas glass rapidly disintegrates under these conditions (fig. 5).

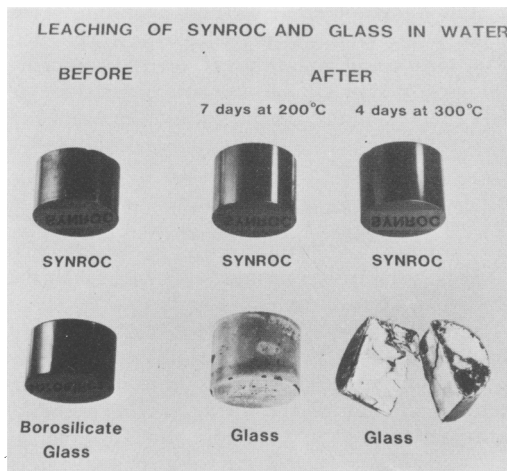


Fig. 5. Comparative leaching tests on 5 cm diam. cylinders of SYNROC and borosilicate glass, both containing simulated HLW, at 200 and 300°C. The glass cylinder leached at 300°C shattered during the test.

Figs. 3, 4, and 5 clearly demonstrate the vast superiority of SYNROC over borosilicate glass in its capacity to resist leaching by groundwater. This superiority is maintained at high temperatures and is particularly manifest in the case of multivalent elements, which include the long-lived alpha-emitting actinide elements. The implications of these data for disposal of HLW are self-evident. The effects of varying pH on the leaching of SYNROC have been investigated by Levins and Smart (1984). He did not find any appreciable change in leach performance as pH was varied from 4 to 9.

Extensive studies of the leaching behaviour of individual SYNROC minerals have also been carried out (Ringwood *et al.*, 1981; Kesson, 1983). They are closely consistent with results obtained on bulk SYNROC samples. Zirconolite and hollandite are found to be appreciably more resistant to leaching than perovskite. This behaviour is probably a consequence of the large proportion of relatively leachable Ca (c. 40% CaO) in perovskite. When this is selectively removed by leaching, the

surrounding titania-rich skin is accordingly quite porous and permits further leaching to occur via diffusion through the water-saturated pores. On the other hand, zirconolite and hollandite contain much smaller proportions of divalent elements (about 16% CaO and BaO respectively). Selective removal of these elements leaves a resistate TiO_2 -rich skin possessing a much lower porosity than the corresponding skin which surrounds perovskite.

Thermodynamic vs. kinetic stability of wasteforms. Nesbitt *et al.* (1981) have shown that titanate minerals such as perovskite are thermodynamically unstable in the presence of groundwater. They imply that this is a serious inadequacy of SYNROC as a wasteform. However, their point is of limited relevance. The silicate minerals of crystalline rocks which comprise the vast bulk of the continental crust are likewise thermodynamically unstable in groundwaters, characteristically altering to form clay minerals and other hydrated silicates. The resistance of the wasteforms (and crystalline rocks) to degradation by groundwater is based primarily on kinetic factors rather than considerations of thermodynamic equilibrium. As discussed above, many titanates have important advantages over silicates, and especially over silicate glasses, in their resistance to weathering. After leaching of monovalent and divalent near-surface cations, they tend to be protected from further attack by skins of rutile (or anatase) which are extremely insoluble in groundwater. Secondly, titanate minerals do not form stable hydrated low-temperature phases analogous to the clays produced by the weathering of silicates.

It is sometimes suggested (e.g. Nesbitt *et al.*, 1981) that the wasteform should be buried in a repository excavated from rocks which are in thermodynamic equilibrium with the minerals of the wasteform. On closer examination this approach is not found to be advantageous. Chemical reactions between wasteforms and surrounding rock occur via the medium of groundwater diffusion and transport. As noted above, the vast majority of crystalline rocks are themselves thermodynamically unstable in the presence of groundwaters at low temperatures. There is little point in attempting to obtain a wasteform in equilibrium with surrounding silicate rocks when *both* systems are thermodynamically unstable in the presence of groundwater.

Although the above discussion emphasizes the importance of kinetic stability in determining the behaviour of wasteforms, it should be noted that the thermodynamic factors nevertheless have a significant role. SYNROC consists of a thermodynamically stable assemblage of mineral phases in contrast to glass which is intrinsically metastable. This factor contributes to the relative kinetic

stability of SYNROC. Moreover, the protective titania-rich rims developed during leaching of titanate minerals are in equilibrium with most groundwaters which are normally saturated with TiO_2 .

Current formulations of SYNROC

The prototype SYNROC formulation (SYNROC-A; Ringwood, 1978) comprised a phase assemblage of silicates plus titanates prepared by melting and crystallization. When leaching tests revealed that its capability to immobilize Cs was no better than borosilicate glass, SYNROC-A was superseded by formulations exclusively composed of titanates which were prepared by hot-pressing in the solid state. These titanate ceramics were designated SYNROC-B and SYNROC-C (Ringwood *et al.*, 1979a, b), with SYNROC-B being the precursor material to which HLW were added to make SYNROC-C.

SYNROC-C is designed to immobilize the HLW arising from the reprocessing of spent fuel from nuclear power reactors. Initially it comprised only three major phases, hollandite, zirconolite, and perovskite, but it has since been modified to include rutile in the phase assemblage (Table I), thereby improving the potential flexibility of the wasteform (Section 5). SYNROC-C is commonly prepared with 20 wt. % of high-level waste simulate.

Recent studies on SYNROC hollandite phases (Kesson, 1983) have led to the development of additional formulations. Although ^{137}Cs is a major contributor to the radiation from HLW during the first few hundred years, it is effectively extinct after about 600 years. Studies of long-term releases of radionuclides from HLW into the biosphere (NAS, 1983) showed that because of its relatively short half-life, Cs actually presents a far smaller hazard than some of the long-lived transuranic elements. The amount of hollandite (33%) dedicated to the immobilization of Cs might therefore appear unnecessarily high. Recent studies by Kesson and Ringwood (1984) have shown that, providing a substantial excess of rutile is present, there is no need to add Ba and Al to the SYNROC precursor so as to form $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$ as a host for Cs. The HLW already contains substantial amounts of Cs, Ba, and Rb isotopes, about one-third of which consists of ^{137}Cs . If hot pressing is carried out under reducing conditions, thereby producing substantial amounts of Ti^{3+} , it is found that the Cs, Ba, and Rb in the simulated HLW combine with excess Ti^{4+} and Ti^{3+} to form a Cs-rich hollandite solid solution $(\text{Cs,Rb,Ba})_x\text{Ti}_y^{3+}\text{Ti}_{8-y}^{4+}\text{O}_{16}$ which is highly resistant to leaching. Further studies (see next section) show that the long term stability of this

phase is unlikely to be deleteriously affected by the transmutation of ^{137}Cs ultimately to barium.

If this approach is used to immobilize Cs, Ba, and Rb in the HLW, a proportionately smaller amount of hollandite can be used in the wasteform. This provides the opportunity to increase the waste-loading. Currently, a SYNROC formulation designed to immobilize 40% of HLW is showing promising results. This wasteform may yield very substantial cost savings.

SYNROC-E is another specialized wasteform for immobilizing HLW which utilizes a Cs-rich hollandite phase. It comprises the same phase assemblage as SYNROC-C but in markedly different proportions, and contains only 5–7% HLW (Table III). Because neither BaO nor Al_2O_3 are included in the formulation, the hollandite phase is Cs-rich, made up solely from Cs and Ba in the HLW, plus trivalent and tetravalent titanium, i.e. $(\text{Cs}_{\frac{1}{2}}\text{Ba})_{2x}(\text{Ti}^{3+})_{2x}\text{Ti}_8^{4+}\text{O}_{16}$. In SYNROC-E, c. 20% of the three primary SYNROC phases are embedded and microencapsulated in a continuous rutile matrix (Kesson and Ringwood, 1984). SYNROC-E follows the SYNROC-C strategy of HLW immobilization in phases with naturally occurring ancient mineral counterparts and also shares the merits of a wasteform in which rutile microencapsulation contributes to a very high resistance to groundwater leaching as a conse-

quence of the very low solubility of the rutile matrix (Forberg *et al.*, 1979; Bauer and Ondracek, 1983). Because of its reduced thermal output and improved long-term leaching performance relative to SYNROC-C, SYNROC-E is especially suitable for geological disposal in salt or in deep-sea sediments. It would also be an appropriate wasteform for immobilization of partitioned transuranic elements as proposed in the Castaing Report (Castaing, 1982).

SYNROC-D is specifically designed to immobilize the HLW produced by the US Defense program. These wastes contain large amounts of processing contaminants (Fe, Al, Mn, Ni, Si, and Na). SYNROC-D is accordingly prepared with high waste-loadings (60–70%). Its phase assemblage thus comprises zirconolite, perovskite, spinel ss., and nepheline (approximately 16, 11, 55, and 18 wt. % respectively) with the processing contaminants being largely converted to the two latter phases. Hollandite is not included in the phase assemblage because Cs is partitioned into nepheline (Ringwood *et al.*, 1979b; 1980).

SYNROC-F differs from all the above formulations in that it is designed for 'once-through' fuel cycles, in which reprocessing and plutonium recycling are not undertaken. The spent nuclear fuel can be converted into a ceramic wasteform, SYNROC-F which consists of a pyrochlore-type phase CaUTi_2O_7 , a Ba-rich hollandite ($\text{Ba}(\text{Al}, \text{Ti}^{3+})_2\text{Ti}_6\text{O}_{16}$) and rutile (Table IV) and has a spent fuel loading of c. 50%. The structure and properties of CaUTi_2O_7 are closely related to those of zirconolite phase $\text{CaZrTi}_2\text{O}_7$ used in SYNROC-C. The similarity is enhanced by the effects of radiation damage from alpha recoils which cause disordering of the $\text{CaZrTi}_2\text{O}_7$ lattice into a defect-fluorite structure (Sinclair and Ringwood, 1981). CaUTi_2O_7 can be expected to behave similarly, based upon observations of the effects of radiation on $\text{CaPuTi}_2\text{O}_7$ (Clinard *et al.*, 1982). Partition experiments have shown that the large cations (Cs^+ , Ba^{2+}) are immobilized in hollandite whilst the pyrochlore phase is host to Sr, REE and U (Kesson and Ringwood, 1983).

SYNROC-F is fabricated using the same technology currently utilized for SYNROC-C (see later). It is much more resistant to leaching and groundwater attack than untreated spent fuel (Kesson and Ringwood, 1983) and displays resistance to leaching which is very similar to that of SYNROC-C (fig. 6). Moreover the constituent phases of SYNROC-F are analogous to natural minerals which have survived a variety of geochemical environments for millions of years.

Because of its continued integrity at high temperatures, SYNROC-F can be buried without the

TABLE III. Bulk composition and mineralogy of SYNROC-E

TiO_2	87.6%	Rutile	~80 wt%
ZrO_2	3.0	Hollandite	~ 5
CaO	2.2	Zirconolite	~ 7
HLW	7	Perovskite	~ 7
SUM	~100	(?)Pyrochlore	~ 2

Microprobe analysis of typical phase assemblage in SYNROC-E (7% HLW)

Hot-pressed in graphite at 10 Mpa, 1300°C, 1 hour with 2% Ti added.

	Rutile	Hollandite	Zirconolite	Perovskite
TiO_2	97.1%		42.7%	47.7%
ZrO_2	2.1		30.3	0.4
UO_2	-		4.7	3.1
REE_2O_3	-	Cs-rich too fine grained for satisfactory analysis	8.5	17.
FeO	-		0.4	0.2
CaO	0.1		11.9	29.6
SrO	-		-	1.3
BaO	-		-	-
Cs_2O	-		-	-
SUM	99.5		98.5	99.3

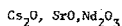
TABLE IV. SYNROC-F Bulk Composition and Mineralogy

TiO ₂	40.6%	Pyrochlore	95 wt.%
UO ₂	47.6	Hollandite	5
Al ₂ O ₃	0.9	Rutile	5
CaO	9.5		
BaO	1.07		
SUM	~100		

Typical coexisting phases in SYNROC-F

	Pyrochlore	Hollandite	Rutile
TiO ₂	38.0%	68%	97.0%
UO ₂	49.3	<.1	1.4
Al ₂ O ₃	0.4	11.1	1.3
Nd ₂ O ₃	0.5	<.1	<.1
CaO	10.8	0.2	0.2
SrO	1.3	<.1	<.1
BaO	<.6	18.	<.9
Cs ₂ O	<.2	1.4	<.2
SUM	100.3	98.7	99.9

Starting composition: SYNROC-F + 2% Ti metal, doped with



Experimental conditions: 5 kbar, 1250°C, 1 hour, Ni capsules.

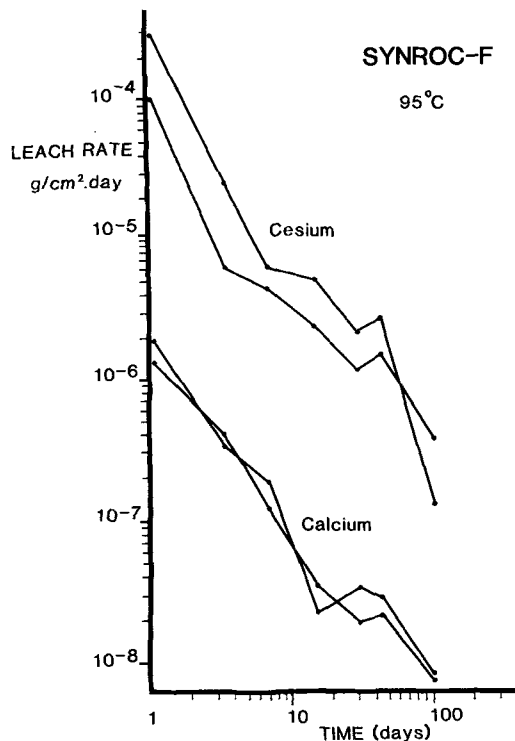


FIG. 6. Leaching of Cs and Ca from SYNROC-F at 95°C.

costly and complex canisters and overpacking necessary for the direct disposal of spent fuel, and does not require intermediate surface storage. Furthermore, it can be buried irretrievably in widely scattered deep drill-holes, a disposal strategy which offers reduced environmental hazards and negligible risks of proliferation.

Radiation damage

Concern has sometimes been expressed as to whether radiation damage, predominantly caused by alpha radiation recoils, may cause serious deterioration in the ability of crystalline host phases to immobilize HLW elements. Key evidence on this topic is provided by nature. The alpha-emitting actinides in SYNROC are incorporated in zirconolite and perovskite. Sinclair and Ringwood (1981) studied the crystal structures of a collection of naturally occurring zirconolites and perovskites of differing ages which contain varying amounts of radioactive U and Th. These minerals have accordingly received varying cumulative radiation doses, ranging from 5×10^{17} to 10^{20} α /gm. These doses can be directly related to the doses which would be received by the same minerals occurring in SYNROC containing, for example, 10% of HLW,

over given intervals (the 'SYNROC age'), as shown in fig. 7.

They found that natural zirconolite receiving an alpha-dose equivalent to a SYNROC age of 1000 years remained fully crystalline but expanded in volume by 2% (1.3×10^{18} α /gm). With more intense irradiation (8×10^{18} α /gm, equivalent to a SYNROC age of 4×10^5 years), natural zirconolite transformed to a cubic defect fluorite-type structure with a volume increase less than 3%. The zirconolite structure is, in fact, very closely related to the fluorite structure. Thus, it appears that the main effect of the radiation dose was to cause a degree of disorder of the cations, leaving the fluorite-type anion lattice essentially intact. This behaviour persisted up to SYNROC ages exceeding 10^6 years. With even heavier irradiation (8×10^{19} α /gm, equivalent to SYNROC ages of 4×10^8 years), zirconolites ceased to diffract X-rays, i.e. they became metamict according to conventional terminology. However, electron diffraction studies of these samples showed that they possess a considerable degree of short-range order and contain areas of crystalline domains. Moreover, the expansion in volume from the original state was less

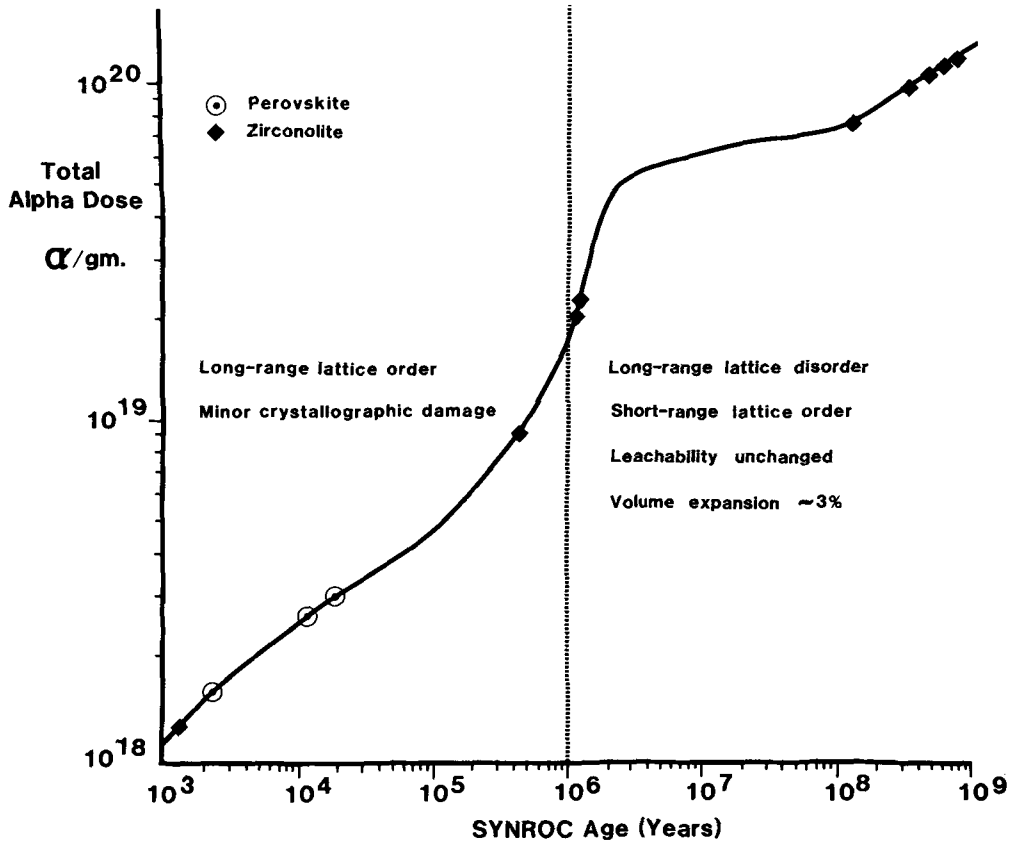


FIG. 7. The curve shows the total alpha-dose that SYNROC with 10% HLW would be expected to receive over a period between 10³ and 10⁹ years. Also shown are the cumulative radiation doses received by naturally occurring perovskites (open circles) and zirconolites (solid circles) containing uranium and thorium.

than 3%. The results showed that even with this enormous degree of radiation damage, the zirconolites, although metamict to X-rays, were still essentially in the crystalline state and did not resemble the highly disordered structure of a true glass.

Similar studies (Sinclair and Ringwood, 1981) of natural perovskites possessing SYNROC ages up to 20 000 years showed that this degree of irradiation caused volume increases up to 1.8%. The X-ray powder patterns of the perovskites were essentially unchanged. The results demonstrated that zirconolite and perovskite, which are the hosts for alpha-emitting actinide elements in SYNROC, are highly resistant to the effects of nuclear radiation and should provide stable crystal structures for the containment of radioactive waste elements during the time required for the radioactivity to decay to safe levels.

This conclusion was further supported by

the work of Oversby and Ringwood (1981) who analysed a collection of natural zirconolites and perovskites for U and Pb 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, even though they have suffered extremely high radiation doses. For example, Sri Lanka zirconolites which have experienced alpha doses exceeding 8×10^{19} α/gm have nevertheless remained as closed systems to U, Th, and Pb for 550 m.y. More limited data on perovskites also indicate that this mineral will be sufficiently stable under radiation to be a satisfactory host for HLW elements.

Measurements of the leachability of zirconolites and perovskites which have suffered varying amounts of radiation damage have also been reported. For example, at 200 °C, bulk leach rates

(based on U loss) were 3.5×10^{-4} g/m²·day for Kaiserstuhl zirconolite (1.3×10^{18} α/g) and 1.8×10^{-3} g/m²·day for Sri Lanka zirconolite (8×10^{19} α/g). These leach rates are very low in comparison to borosilicate glass at this temperature and demonstrate that high radiation doses do not lead to unacceptably high leachability. Reeve and Woolfrey (1980) described the effects of fast neutron irradiation on SYNROC and its constituent minerals. After receiving irradiation in one month equivalent to a SYNROC age of 10 000 years, perovskite expanded in volume by 2.6%. Bulk samples of SYNROC expanded by 1.7%.

The natural zirconolites and perovskites studied in these investigations had experienced complex geological histories, including elevated temperatures and pressures, contact with groundwaters, weathering and erosion over periods hundreds or even thousands of times longer than are needed for decay of high-level waste to safe levels. They have been subjected to a range of geochemical stresses far more intense than are likely to be found in any radwaste repository. Despite this, they have retained their waste elements (alpha-emitters) quantitatively. These observations provide strong grounds for confidence that the integrity and safety of SYNROC as a wasteform will not be adversely affected by radiation damage before the high-level wastes have decayed to safe levels.

Transmutations. The effects of radioactive transmutations on the stabilities of crystalline phases should also be considered. Two of the principal transmutations occurring in HLW are of radioactive ¹³⁷Cs ultimately to Ba and of ⁹⁰Sr ultimately to Zr. Cs and Ba occupy the same types of lattice site in hollandite. Decay of Cs⁺ to Ba²⁺ is accompanied by loss of an electron which is accepted by neighbouring Ti⁴⁺, converting it to Ti³⁺, which remains stable in octahedral co-ordination in the same lattice site. The ability of Ti to change oxidation states in the same lattice site thus provides an 'electron buffer' for the transmutation of ¹³⁷Cs. It seems likely that hollandite containing initially large concentrations of ¹³⁷Cs would remain stable during decay of this radionuclide. This is an important factor in the current development of new forms of SYNROC containing much smaller proportions of hollandite than were originally proposed for SYNROC-C, or alternatively, much higher waste loadings (see previous section).

In perovskite, ⁹⁰Sr occupies the Ca site, and ultimately decays to Zr⁴⁺. Because CaZrO₃ has a perovskite structure, it might be expected that Zr⁴⁺ would prefer to substitute for Ti⁴⁺ in CaTiO₃. This is demonstrated by the extensive solid solutions which occur between these compounds. However,

in a study of site occupancies in SYNROC perovskite, Tafto *et al.* (1983) demonstrated that Zr⁴⁺ was actually located in the Ca²⁺ site, with charge balance being maintained by substitution of divalent and trivalent elements for Ti⁴⁺. Thus, the Zr⁴⁺ produced by the transmutation of ⁹⁰Sr would occupy a stable lattice position. If the perovskite contains exceptionally high loadings of ⁹⁰Sr, it may also be necessary for some Zr⁴⁺ to diffuse to a neighbouring Ti⁴⁺ site, leaving a hole at the Ca²⁺ site. Perovskite structures are known to tolerate substantial deviations from stoichiometry. In both cases, electron balance would be achieved via reduction of two Ti⁴⁺ to Ti³⁺ ions for every ⁹⁰Sr → Zr decay. Providing the concentration of ⁹⁰Sr in the perovskite phase does not exceed a few per cent the stability of perovskite is unlikely to be impaired by transmutation.

The transuranic elements Pu, Np, Cm, and Am are either quadrivalent or trivalent in SYNROC. The differences in ionic radii for these species in the two oxidation states are quite small. Transmutations affecting the transuranic elements would not affect their stability in existing lattice sites in zirconolite and perovskite. Charge balance would be maintained by the Ti³⁺ ⇌ Ti⁴⁺ buffer.

Production technology

The Australian Government is providing support for the construction of a demonstration plant to produce SYNROC containing simulated non-radioactive waste at output levels comparable to commercial glass solidification systems. The demonstration is a joint project involving the Australian Atomic Energy Commission and the Australian National University and the plant is being constructed at the AAEC site at Lucas Heights, Sydney. In addition, the AAEC will produce and characterize small quantities of fully radioactive SYNROC in their hot cells.

A projected flowsheet is shown in fig. 8. The SYNROC precursor is prepared in advance. A homogeneous and highly reactive feedstock is prepared from hydrolysed Ti, Zr, and Al alkoxides boiled with Ca and Ba hydroxides (Ringwood and Kesson, in prep.). The SYNROC precursor is then slurried with the high-level waste solution in proportions such that after calcination, the resultant powder contains 20 wt. % of HLW. The slurry is then gravity fed into a rotary alloy-steel calciner and heated to a maximum of 800 °C in a gaseous reducing atmosphere. The rotary calciner itself is heated by high frequency induction coils or by a surrounding stationary kiln. The slurry is thereby flash-dried and then calcined to a homogeneous, devolatilized powder comprising an intimate

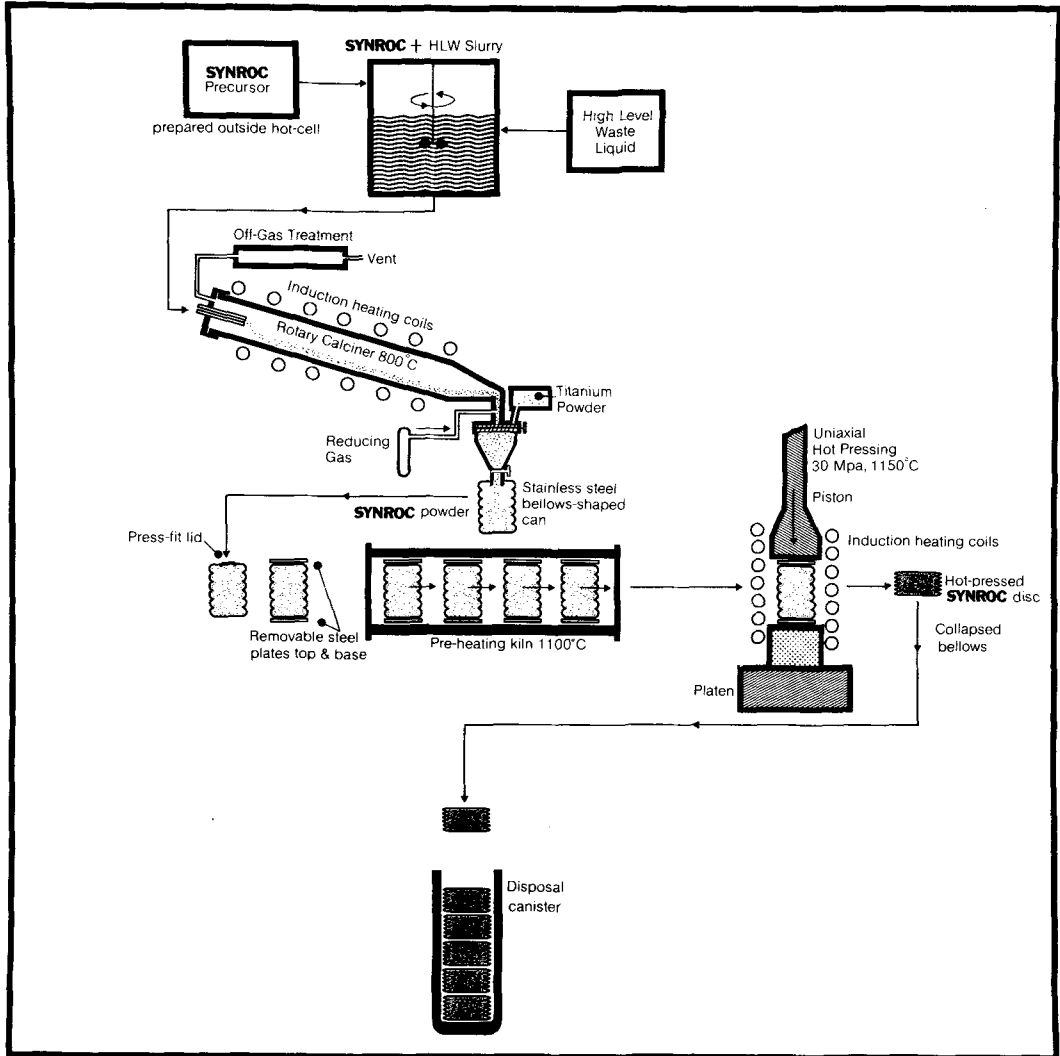


FIG. 8. Conceptual flowsheet for SYNROC production.

mixture of the oxides of HLW elements with SYNROC additive oxides. To this stage, the technology is generally similar to systems that have already been developed for the production of borosilicate glass. Other techniques for drying and calcining have also been developed and applied to alternative methods of glass manufacture. These include spray drying and calcining, fluidized-bed calcining and fixed vertical bed calcining. These techniques could likewise be readily adapted to the preparative stages of SYNROC manufacture.

The essential difference between glass manufacture as in the French AVM process (Bonniaud *et al.*, 1980) and SYNROC production occurs in the fabrication operation, after the powder has left the kiln. In the AVM process, the calcine is mixed with glass frit and transferred to an inconel container in which it is melted to a glass at about 1150 °C. In the SYNROC process, the powder is consolidated into a fully dense ceramic by subjecting it simultaneously to high temperatures (typically 1150 °C) and modest pressures (e.g. 30 MPa). This hot-pressing operation is carried out entirely in the solid state

and causes the powder to recrystallize to form the thermodynamically stable assemblage of SYNROC minerals containing HLW elements immobilized in their crystalline lattices.

A novel and simple method of uniaxial hot-pressing of SYNROC powder has been developed by Ramm and Ringwood (1980, 1982) and Ringwood *et al.* (1983). SYNROC powder from the rotary kiln is blended with 2% of metallic titanium powder (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 and their contents are heated to a uniform internal temperature of about 1150 °C. They are then pressed by one of two alternative methods.

In the 'free-standing mode', the bellows (typically 40 cm diameter by 60 cm long) are placed in a hydraulic press and the wall temperature is maintained at about 1100 °C by induction heating. A steady uniaxial pressure of 10–40 MPa is then applied. The bellows collapse axially and symmetrically to form 'pancakes' (fig. 9). No external radial support is required (Ringwood *et al.*, 1983). During the collapse, the contained powder recrystallizes to form a fully densified monolith consisting of the desired SYNROC mineralogy. The pancakes would be stacked in cylindrical steel containers or canisters, typically 3 m long. This outer canister would be sealed, thereby providing a double encapsulated package (cf. fig. 8). In a second variant called 'in-can hot pressing' (Ramm and Ringwood, 1980), hot-pressing is carried out within the final disposal canister, which itself is heated to 1150 °C by

induction coils. The preheated bellows are thrust upwards by a hydraulic ram into the heated canister and are axially compressed to full density. The canister is progressively filled by repeating this operation.

An attractive aspect of either variant of this technology is that it can readily be applied to consolidate several different kinds of radioactive waste materials. Zircaloy fuel hulls remaining after dissolution of spent fuel in nitric acid are contaminated with fuel residues. These constitute a voluminous source of intermediate level waste. Ringwood *et al.* (1983) demonstrated that zircaloy cladding fragments contained in bellows at packing densities of about 20% could be consolidated into fully dense monoliths at pressures of 10–40 MPa and temperatures of 1000–1100 °C. Other classes of inorganic high and intermediate-level wastes, such as dissolver tank sludges and incineration residues, could be treated similarly.

Geological disposal strategy

The strategy adopted in most countries is to dispose of radwaste canisters in large, centralized mined repositories at depths typically in the range 500–700 metres. It has been demonstrated elsewhere (Ringwood, 1980*a, b*) that a preferable strategy from safety and sociopolitical considerations would be to dispose of the waste in a widely dispersed array of deep (4 km) drill holes carefully sited within impermeable crystalline rock formations.

This concept is shown in fig. 10. Canisters would be emplaced in the lower 2.5 km of the hole (1 metre diameter) and the top 1.5 km sealed. One such hole has the capacity to accept the waste generated by 80 large (1000 MW) nuclear power stations in a single year. This strategy possesses several advantages:

(i) Generally speaking, the deeper the waste is emplaced, the more secure the geological barrier becomes.

(ii) The permeability of most rock systems decreases with depth. Mining activities have shown that some crystalline rock formations are essentially dry at depths below 1 km. With adequate exploration it should be possible to delineate large areas of igneous and metamorphic rocks which possess very low permeability and are essentially dry at depths below 1.5 km. Disposal of HLW in such rocks would minimize access of groundwater to the waste thereby curtailing the principal means by which radioactive waste species could be transported to the biosphere.

(iii) Recent experience in several countries demonstrates that it is difficult to locate acceptable

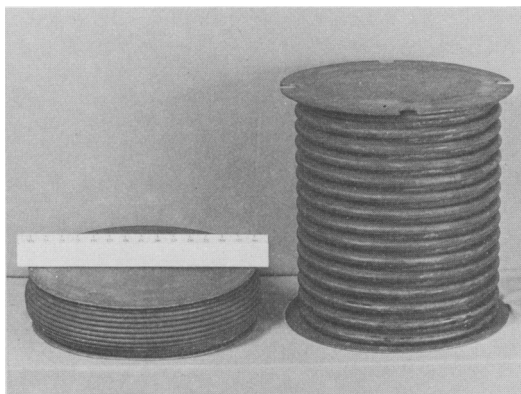


FIG. 9. Demonstration of SYNROC manufacture by uniaxial hot-pressing of unsupported stainless steel bellows at *c.* 1150 °C. The uncompact bellows on the right collapse to encase a pancake of fully densified SYNROC (left).

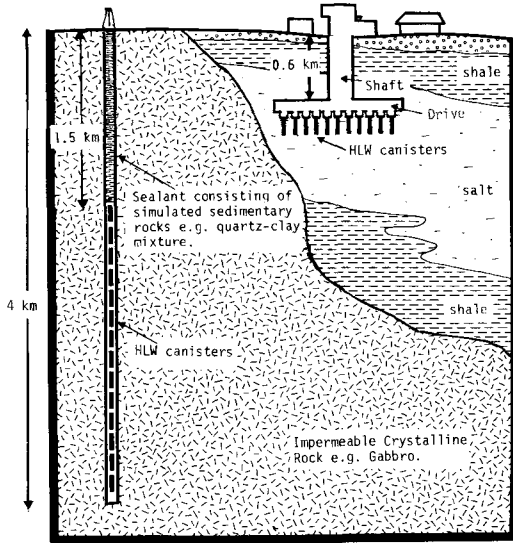


FIG. 10. Notional comparison of a centralized mined repository with deep drill hole disposal.

sites for large, centralized mined repositories. Disposal of HLW in deep drill-holes would considerably increase the number of sites which are acceptable on technical grounds.

(iv) Drilling causes minimal damage to the rock systems and drill holes are readily sealed. However, the construction of large mined repositories may be accompanied by formation of fractures in surrounding rock which could serve as conduits for circulating groundwater. Mined repositories are likely to be more difficult to seal than isolated drill holes.

(v) The distribution of HLW in a densely packed horizontal array as envisaged in a mined repository causes thermal stresses which may lead to fracturing in the host rock, thereby enhancing groundwater circulation. This problem can be reduced considerably when waste is disposed of in a three-dimensional configuration within an array of widely spaced deep drill holes.

The use of glass as an immobilization medium restricts the depth of disposal because of the increase of temperature with depth in the earth, generally 20–30 °C per km. The combined effects of increase of temperature with depth and radioactive heat generation even after 40 years of surface storage, would cause the temperature of glass in a deep hole to exceed 200 °C. Although the strategy of deep drill-hole disposal is aimed at minimizing access of water to waste, the possibility of water entry must always be considered as a factor in risk assessment analyses. If water obtained access to a

borosilicate glass wastefrom at 200 °C, it would cause rapid disintegration. In contrast, however, SYNROC displays a high degree of stability under these conditions. Thus, the combination of SYNROC with deep drill-hole disposal maximizes the integrity both of the geologic barrier and the immobilization barrier.

Technological advances and geological disposal. Some countries (e.g. UK, France, Japan) are planning to hold glass wasteforms in intermediate storage for 50 years or more before final geological disposal. This policy raises issues which deserve more consideration than has been accorded to date. Generally speaking, geological disposal in relatively shallow mined repositories employs mining engineering technology which 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 being rapidly improved. It is reasonable to expect major advances in this technology during the next 50 years. As noted above, the disposal of high-level nuclear wastes in deep drill-holes in the continental crust even today, is an attractive strategy possessing major potential advantages in safety, public acceptability and probably in costs, over conventional disposal in shallow mined repositories. In 50 years' time, these advantages are likely to be far more compelling. It should also be borne in mind that during the next 50 years, entirely new and advanced geological disposal technologies, not foreseen today, may become available. These may include new technologies for drilling deep holes into marine sediments and the oceanic crust.

These considerations strongly suggest that current policies should place a high priority on the use of a wastefrom with properties which permit a multiplicity of disposal systems both now and in the future. The potential of the various forms of SYNROC in this respect was outlined earlier. It would appear short-sighted to employ a wastefrom which is not capable of taking full advantage of the superior disposal options which are likely to be available 50 years hence. Glass seems to represent a questionable choice in the light of these circumstances.

Public acceptability

Although qualified scientists are generally confident that current systems of waste management can provide a very high degree of safety, this belief has not sufficed to dispel 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 should design systems which conform to the safeguards required by the public.

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 technological complexity can be traced to the early choice of borosilicate glass as the preferred wasteform. Because of its instability above 100°C, additional precautions are needed to achieve the desired degree of safety, thereby complicating the overall system. As already noted, the use of glass unnecessarily constrains the strategy for geological disposal. Moreover, it places the entire responsibility for preventing re-entry of long-lived transuranic elements into the biosphere, on the geological barrier provided by a mined repository.

On the other hand, the combination of an advanced wasteform such as SYNROC, with deep drill-hole disposal provides a simple, yet extremely safe strategy, which, can readily be explained to, and understood by laymen. The SYNROC strategy of nuclear waste disposal is readily capable of meeting the 'public acceptability' criteria described above. The wasteform itself is composed of minerals which are known to have survived in nature for many millions, even billions of years, despite receiving very high radiation doses and experiencing far more extreme geochemical conditions than would ever be encountered in a man-made repository for radioactive waste. It is this kind of evidence provided directly by nature, which provides assurance that the successful immobilization of nuclear wastes can indeed be achieved over the very long periods required.

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