6. SOLID HIGH LEVEL WASTE

Solid high level radioactive waste consists of spent fuel or solidified products arising from its reprocessing. A wide variety of compositions and types of solid product was studied. This ranged from simple calcines, through glasses, to more advanced waste forms. The physical state of these products is particularly important in considering their long-term stability and particularly thermal effects.

Properties of high level waste

Activity

Table 36 Activity of radionuclides in high-level waste (Ci/canister)

		Time out of Reactor - y			
RN	Half-Life	10	100	1000	10000
90-Sr	29 y	1.4E+5	1.5E+4	3.5E-6	0
137-Cs	30.1 y	2.0E+5	2.4E+4	2.3E-5	0
154-Eu	8.6 y	1.0E+4	210	0	0
210-Pb	22.3 y	0	1.7E-6	1.6E-4	6.5E-3
226-Ra	1600 y	2.5E-7	2.6E-6	1.6E-4	6.5E-3
229-Th	7340 y	9.6E-8	1.7E-6	1.6E-4	1.3E-2
230-Th	7.7E+4 y	4.9E-5	7.4E-5	8.8E-4	8.1E-3
238-Pu	87.8 y	2.4E+2	120	0.28	0
239-Pu	2439 y	3.8	3.8	4.7	9.6
240-Pu	6540 y	10	20	18	7.3
241-Pu	15 y	740	11	0.72	0.34
241-Am	433 y	410	380	81	0.34
243-Am	7370 y	40	40	37	17
242-Cm	163 d	16	11	0.18	0
244-Cm	17.9 y	4.0E+3	130	0	0

Short-lived RI at 10 y : 106-Rh 369 d 1300; 125-Sb 2.73 y 1600; 134-Cs 2.06 y 1.9E+4; 144-Ce 284 d 35; 147-Pm 2.62 y 1.8E+4.
Long-lived RI at 10000 y : 93-Zr 9.5E+5 y 4.3, 93m-Nb 12 y 4.3, 99-Tc 2.1E+5 y 32, 126-Sn 1E+5 y 1.3, 129-I 1.6E+7 y 1.8E-4, 233-U 1.6E+5 y 3.6E-2, 237-Np 2.1E+6 y 0.88
Source: Data from NUREG (1979), Table A-1.

Heat generation

Table 37 Contribution to heat generation of thermally significant isotopes in PWR spent fuel (%).

time - days	30	90	365	1096	3650
Ba/La-140	13.8	0.93			
Zr/Nb-95	23.2	24.5	3.9		
Ce/Pr-144	18.0	26.9	35.3	17.3	
Cm-242	2.2	3.0	2.36		
Cs/Ba-137	1.1	2.0	5.0	14.1	35.3
Sr/Y-90	1.1	2.0	4.9	13.7	33.8
Pu-238		0.33	0.85	2.5	6.9
Cm-244			0.74	2.0	4.5

Thermal effects (IAEA 1979)

Changes in the physical state of the solidified product can occur primarily because of the effects of temperature or of radiation.

Table 38 Decrease of thermal power of HLW for different times after disposal.

Elapsed time - y	0	1E+3	1E+4	1E+5	1E+6
Fission products	85325*	1.0	0.6	0.4	0.03
Actinides	14675	194	60	4.3	2.7
Total	100000	195	60.6	4.7	2.73

*(arbitrary units)

Phase separation

One problem that has arisen in many of the solidification processes is that of the separation of a second phase on the top surface or in the top few centimetres depth of the product. It is also left on the inside walls of the ceramic melters when the melt is drained. This second phase is usually yellow and rich in sodium molybdate (the presence of sulphate in the waste also encourages its formation). It is generally soluble in water and, since it contains caesium and some strontium, it is imperative that it be dispersed uniformly in the bulk melt. At Karlsruhe, in the combined system of denitration, calcination and melting performed in a ceramic melter, the yellow phase disappeared, obviously owing to the reducing atmosphere formed by a slight excess of formic acid. It has also been demonstrated that there is a maximum amount of sodium which can be used in the glass to avoid separation of the second phase. At the HMI in Berlin it has been shown that glasses containing lithium dissolve more molybdenum trioxide than corresponding sodium glasses. In a special case, 15 wt% B_2O_3 helps

to digest molybdenum trioxide and stabilize the glass. If excessive quantities of molybdenum are present in the waste, phosphate glass compositions have been used.

Crystallization and devitrification

The effect of thermal history on the behaviour of fission product containing glasses has been studied extensively by all those groups active in the field of high level waste fixation. When a glass is cooled through the temperature range from 800 C down to less than 400 C, nucleation crystal growth can take place. The rate of crystallization will be a maximum somewhere above the transformation point, but although the rate may be low at lower temperatures, crystallization can still occur over long periods of time, depending on the glass composition. Many investigations have also shown that there can be an appreciable increase in leachability (up to three orders of magnitude) in some waste glass compositions owing to the presence of crystalline phases that appeared on crystallization. On the other hand, other compositions show very little (if any) change in leachability, and the devitrified product is often preferable as there is less tendency to cracking, particularly in massive blocks of glass. For each composition proposed, it is important to understand the effect of the crystalline phases on the properties of the product, particularly if they are likely to be held at temperatures within the above range, or even just below 400 C, for long periods of time. Most final storage containers will be at least 0.3 m in diameter, and some may be as large as 0.5 m or even 0.6 m in diameter. They will release heat from fission product decay at 50 - 100 kW/m^3 and there could be a temperature gradient of many hundreds of degrees centigrade between the centre and the wall. While the outer surface is likely to be cooled fairly rapidly after leaving the processing plant (in many cases to below 100 C since the containers will be water-cooled), the centre could well be above 400 - 500 C for appreciable periods of time. Therefore, the material near the outside may be in the vitreous state whereas that nearer the centre could be crystalline to varying amounts depending upon the exact thermal conditions. Owing to this temperature gradient, migration of single constituents could also occur.

During the 1960s, emphasis was mainly on the development of phosphate glasses. Many workers found that, in addition to problems due to their highly corrosive nature, phosphate glasses were prone to crystallization and their leachability could increase by up to three orders of magnitude. Phosphate glasses are now only used for special wastes or when the high temperatures that can cause crystallization can be avoided (for example, by producing glass beads and embedding them in a metal matrix). A number of detailed studies have been carried out with selected glass compositions to determine the effect of various heat treatments, usually by measuring the leach rates as a guide to any deterioration in properties. In an early programme at Harwell, samples of borosilicate and phosphate glass were held at temperatures between

950 C and 400 C for periods up to four months, cooled at varying rates from 800 C/d down to 3 C/d and held in a temperature gradient from 1 000 C to 100 C for 14 weeks. No deterioration occurred to the borosilicate glass (in one case the leachability decreased by a factor of about 5 for both caesium and strontium) in any of the tests. From visual observations, some crystallization had occurred in all the glasses. However, an increase in leachability of up to two orders of magnitude occurred when the phosphate glass was held at 550 C and cerium migrated as a second heavy phase when the glass was held in a temperature gradient. Recent experiments indicate that crystallization will occur in the currently preferred glasses, but that the leachability is unlikely to change by more than a factor of 2, which is considered acceptable (probably within the limits of experimental error). Some crystallization is advantageous as the products have less tendency to crack.

A similar programme of heat treatment studies has begun at Battelle Pacific Northwest Laboratories and samples of their reference glass have been held at temperatures between 900 C and 300 C for periods from one day to one year (samples are being held for up to five years). In Soxhlet leach tests leachabilities have increased by up to a factor of 10, the maximum change occurring with samples heat-treated at 700 - 750 C. The discrete phases which form in the glasses have been identified with respect to stoichiometry, crystal structure and concentration, as functions of time and temperature. For example, in the reference glass, major devitrification products are a zinc silicate [Zn_2SiO_4] phase, a molybdate [$(CaSrBa)MoO_4$] phase and an apatite [$Ca_2(RE)_8(SiO_4)_6O_2$] phase as well as a number of minor phases. The zinc silicate phase has a different thermal expansion from that of the parent glass, and microcracking has been observed, accompanied by a 2-3% increase in porosity. As a result of these studies, it has been concluded that the zinc concentration was too high and that in a new glass, in which zinc concentration has been reduced, the maximum increase in leachability is only a factor of 2.

In Japan, crystallization has also been observed between 650 C and 800 C, with a maximum rate at about 750 C, and the leachability of the crystallized product is 10 times higher than that of the glass. In future, avoidance of crystallization will be attempted. During work with lead glasses in India, small changes have been observed (a factor of 2-4) in leachability when simulating the thermal effects that may occur in glass blocks. Some gravity settling and radial migration were also observed. In the Tarapur plant, the containers will be annealed and the maximum surface temperature will be limited to 300 C. No workers have observed devitrification in samples of glass held below about 450 C, so those groups who are worried by the possible effects are arranging the process parameters to ensure that the maximum temperatures in storage are always below 400 C. It must be kept in mind, however, that temperatures of 400 450 C are usually well below the transformation point of borosilicate glasses, and devitrification may be a very slow process, difficult to detect within the periods of time which are, in turn, long enough to investigate crystallization phenomena.

Waste forms (IAEA 1979)

Table 39 Characteristics of world's solidified high-level wastes.

Solidification process	P	WL	HTF	Density	TC	LL
Fluid bed calcination US	C	100	500	1.0-1.7	0.4-1.0	5E-1
Pot calcination ORNL/WSEP US	C	90	900	1.2-1.4	0.6-1.0	5E-1
Rising level ORNL/WSEP US	BG	30-50	900	2.9-3.1	-	1E-6
Spray solidification WSEP US	G	20-40	1200	3.0	-	1E-4
PHOSPHATE GLASS BNL/WSEP US	G	30	1200	2.7-2.9	2.0-3.5	1E-6
STOPPER US	S	-	500	-	-	1E-8
THERMALT US	AS	-	2000	2.9	-	1E-8
FINGAL AERE UK	BG	25-40	1050	2.8	2.5-4.0	1E-7
HARVEST AERE/BNFL UK	BG	25	1050	2.6	2.8-4.0	1E-7
Discontinuous process CEA F	BG	20-30	1150	-	2.8-3.6	1E-7
Continuous process CEA F	BG	20-30	1150	-	2.8-3.6	1E-7
VERA Germany	BG	20-30	1200	2.5-2.7	-	1E-7
PHOTO Germany	PG	25-35	1100	2.6-2.9	2.4	1E-7
THERMITE Germany	ceramic	25	2000	-	-	-
LOTES Eurochemic	PG	30	300	2.1	3.0-4.0	1E-5
PAMELA Eurochernic	PG	25-35	-	-	-	-
Pot solidification India	BG	22-28	1050	2.5-3.0	2.5-3.5	1E-6
ESTER Italy	BG	20-25	1000	2.7-3.0	-	1E-7
ESTER Italy	PG	20-25	900	2.3-3.5	-	1E-5

F = France, P = Product (A = alumino, G = glass, B = borosilicate, P = phosphate, S = silicate), WL = waste loading %, HTF = Highest Temperature of Formation, TC = Thermal Conductivity in mcal/cm/s/C, LL = Lowest Leachability in g/cm^2/d.

Calcines (IAEA 1979)

Early workers were satisfied to immobilize the liquid waste by calcination to either a massive cake of material (the ORNL pot calcination process) or to a free-flowing granular product (the Idaho fluidized-bed waste calcination process). The latter is still an acceptable product at Idaho for the types of waste processed at that site and for the environmental conditions there. Calcines are an amorphous mixture of oxides of the fission products and other elements and they are partially, if not completely, soluble in water. They are not considered satisfactory product forms for the waste arising from reprocessing power reactor fuels.

Glasses (IAEA 1979, Grover 1962)

Most of the product forms developed so far fall into this category. Glasses were chosen because they are relatively easy to prepare, and many examples exist in nature of highly stable glasses that have been in existence for very long periods of time. Man-made glasses have also survived for thousands of years. Most glasses are supercooled liquids (i.e. thermodynamically metastable), but there is no discontinuity in the change in properties between the metastable and stable states; the distinction between glass and liquid is solely on the basis of viscosity. Glass can be regarded as a three-dimensional network of oxygen polyhedra, with a network former at the centre of each polyhedron and network modifiers contained in interstices between the polyhedra. The oxygen polyhedra, which are either triangles or tetrahedra, share corners with each other to form the three dimensional network. The strength of the glass structure will depend upon the nature of the oxygen polyhedra, the way they are linked together and the nature of the network modifiers present. These two factors can have opposite effects. The modifiers can cause a break in the continuous linkages of the oxygen polyhedra and thus weaken the structure. However, the modifier cation can go into the gap in the network caused by the break in the linkage, it will then exert an attractive force on the O- ions terminating the break and thus strengthen the structure. The net result depends upon which of the two effects is the greater. The attraction exerted by the cation will depend not only on the charge of the cation but also on the size of the cation. A small ion will be surrounded by a small number of oxygen atoms but a large ion will not fit into the interstice formed by a small number of oxygen atoms touching each other, and will therefore tend to surround itself with a large number of atoms. Only a limited number of oxides will form a glass network. The exact geometrical conditions for tetrahedral arrangement require the central ion to be of a size between 0.31 A and 0.58 A. Boron, silicon, aluminium and phosphorus fall into this size range and are the main constituents of most glasses.

For the storage of the fission product wastes the following conditions must be met the wastes must be stored in the form of a non dusty solid, during storage, the activity must not be readily leached out of the solid and the solid must not 'deteriorate' over the storage period. This could be 100-1000 years. The waste solutions to be incorporated into glasses depend upon the type of fuel being processed and the burn-up of the fuel. The percentage of waste constituents incorporated into a glass will have an important bearing on the final storage method. From an economic viewpoint the higher the percentage of waste, the smaller the volume of glass to be stored. However, the decay of the fission products gives rise to heat and the higher the %age of fission products in the glass, the higher the heat release per unit volume of glass.

Structure of glass

A simple rule have been proposed for assessing whether a mixture of oxides will form a glass or not. This is the oxygen ratio (OR) which for a simple silicate glass is the ratio of number of oxygen atoms to the number of silicon atoms. Normal, commercial glasses have an OR between 2 and 2.5, and value of 3.0 represents the borderline of practically obtainable glasses. No glass formation is possible if OR = 4. The strongest glasses have an OR of 2. Boron can be present in a glass in either the three co-ordinated state or the four-co-ordinated state. Aluminium can be present in a glass as either a net-borderline of practically obtainable glasses.

Table 40 Ionic field strengths (FS : Z/r^2), charge (C) and ionic radius (IR in 1E-12 m) of cations present in glasses.

	network formers				intermediate ions				network modifiers			
	B	P	Si	As	Be	Al	Ti	Zr	Mg	Li	Ca	Na
C	3+	5+	4+	5+	2+	3+	4+	4+	2+	1+	2+	1+
IR	20	34	41	47	31	50	68	80	65	60	99	95
FS	75	43	24	23	21	12	9	6.3	4.7	2.8	2.0	1.

Glass leaching (Paul 1977)

When a piece of ordinary glass is brought in contact with aqueous solution, alkali ions are extracted into the solution in preference to silica and an alkali-deficient leached layer is formed on the surface of the virgin glass. The formation of this layer usually reduces the rate of alkali extraction by forming a barrier through which further alkali ions must diffuse before they can be brought into solution. X-ray diffraction analysis has shown that the silica-rich films formed during the corrosion process are more closely equivalent to vitreous silica produced from the molten state, than to a hydrated silica structure. The thickness of the silica rich films and probably their compactness also vary with the composition of the glass, and for the same glass depends on the test conditions; time, temperature and pH of the solution. Under identical conditions of corrosion, a low durability glass usually produces a thicker film than a high durability glass. Corrosion of alkali-lime-silicate glasses by aqueous solutions can be described in terms of three chemical reactions: the penetration of a "proton" from water into the glassy network, replacing an alkali ion into solution, the hydroxyl ion in solution disrupts siloxane bond in glass and the non-bridging oxygen formed interacts with a further molecule of water producing a hydroxyl ion, which is free to repeat the reaction over again. The extraction of alkali from a commercial silicate glass (SiO_2 69.9%, Al_2O_3 2.6%, CaO 5.4%, MgO 3.6%, Na_2O 16.8%) was studied and it was found that the amount of sodium removed from the glass surface by the action of distilled water varied as the square root of time. From the observation they concluded that the rate-controlling process involved is one of diffusion, and that the rate of extraction of the sodium should be related to the electrical conductivity of the glass. They assumed that below the softening temperature of the glass, the atoms of the network are in fixed positions, whereas the Na+ ions can move from one site to a neighbouring site if they acquire a definite energy and that the passage of electric current through the glass takes place exclusively by migration of Na+ ions. During the diffusion of Na ions to the glass surface, the electrical neutrality of the glass must be maintained by the contra-diffusion of other ions; otherwise an electric double layer would be set up at the glass surface which would prevent further removal of sodium ions. The amount of sodium that could be removed before the double layer stopped the process was estimated to be of the order of 100 times less than the amount of sodium actually extracted. Other workers have also studied the extraction of alkali from different types of glasses as a function of time, and nearly all the available data can be summarized into two main forms of rate equation: the rate of alkali extraction varies linearly with the square root of time at short times and low temperatures, then linearly with time after sufficiently long times and/or at high temperatures. In the case of leaching of silicate glasses by aqueous solutions, sodium and silicon (in the form of soluble silicate groups) are extracted simultaneously. Factors effecting chemical durability measurements of glass are weight of glass grains used and the surface area exposed, ratio of the weight of the glass to the volume of the leaching solution, nature of the leaching solution and the frequency of replenishing it, and temperature of leaching.

Glass ceramics (IAEA 1979)

The glass ceramics are prepared from glasses by a special process of heat treatment. First the glass is annealed at the temperature of maximum nucleation rate. Once the nuclei have formed, a second annealing step is carried out at a temperature high enough to yield the optimum crystal growth rate. The product consists of a continuous glassy phase with crystals homogeneously dispersed in it. To obtain a fine-grained bulk crystallization, nucleus-forming oxides such as TiO_2 and/or ZrO_2 are frequently added. By proper choice of the original glass composition, crystalline species may be formed that are resistant host phases for long-lived radionuclides. It is important, however, that the glassy phase should be as resistant as the crystalline phases. The main crystalline phases that have been identified are celsian, diopside, eucryptite and perovskite. Glass ceramics are characterized by their stability to mechanical impact and they should be thermally more stable than glasses, which tend to crystallize with time at temperatures above the transformation point and to devitrify below this point, possibly producing an undesirable change in properties. Glass ceramics are only produced from borosilicate glasses. Phosphate glasses may not be transformed into useful glass ceramics, although phosphate-bonded ceramics have been produced by controlled heating and melting of crystalline sodium aluminium phosphate compounds.

SYNROC (Ringwood 1982)

Most countries intend to dispose of the high-level radioactive wastes arising from the operation of nuclear reactors by converting them into a solidified form and then burying the solids within the earth. It is necessary to ensure that radionuclides from the waste form are not returned to the biosphere. Subsequent leaching of the waste form by circulating groundwater is the most likely mechanism by which this might happen. It is therefore desirable that the waste form be constructed from a highly stable material possessing an extremely low solubility in groundwater. Ideally, the waste form itself should function as an immobilization barrier, fully capable of preventing any significant release of radionuclides into the biosphere for 1E+5 - 1E+6 years. The waste form would be buried in a repository located in a geological environment that had been carefully selected for its capacity to minimize access of groundwater to the waste and for its low permeability, which would thus inhibit the circulation of groundwater. This kind of environment constitutes a geologic barrier, which is essentially independent of the immobilization barrier. Yet a third, independent, engineered barrier can be constructed, by utilizing canisters made of highly corrosion-resistant alloys and surrounded by absorbent materials capable of greatly delaying the migration of any ions in the waste that may have been dissolved inadvertently in the groundwater. Each of these barriers, independently, should be able to prevent significant entry of radionuclides into the biosphere. The immobilization strategy favoured by the nuclear industry has been to incorporate the wastes into a borosilicate glass. Such a glass is already being manufactured in France. In the US, borosilicate glass is under serious consideration at the Savannah River Plant for immobilization of defense wastes. However, the capacity of borosilicate glasses to withstand leaching by groundwater is limited, particularly at high temperatures. Because of this limitation, many scientists concerned with immobilization of HLWs have turned to the development of alternative waste forms possessing vastly greater resistance to leaching. My colleagues and I are investigating a titanate ceramic called SYNROC an acronym for synthetic rock-consisting of a thermodynamically stable assemblage of three main minerals: hollandite, $BaAl_2Ti_6O_{16}$; zirconolite, $CaZrTi_2O_8$; and perovskite, $CaTiO_3$. These minerals have the capacity to take nearly all of the elements present in high-level waste into their crystal structures at regular lattice sites in the form of dilute solid solutions. Similar minerals in nature have survived in a wide range of geochemical-geological environments for up to 2 000 million years. 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. In fact, the SYNROC strategy for immobilization of such wastes is very similar to the way in which nature successfully 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 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 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

The SYNROC composition currently under study is given in Table bellow. SYNROC with this composition readily incorporates 20% by weight of fission products and actinide elements found in high-level waste. When subjected to hot pressing under subsolidus conditions at about 1 150 C, it forms a synthetic rock composed of hollandite (~40%), zirconolite (~35%), and perovskite (~25%).

Table 41 Typical composition of SYNROC and its constituent minerals (weight %, H= Hollandite, Z = Zirconolite, P = Perovskite, BS = Bulk SYNROC).

	H	Z	P	BS
TiO_2	71.0	50.3	57.8	60.3
ZrO_2	0.2	30.5	0.2	10.8
Al_2O_3	12.9	2.5	1.2	6.3
CaO	0.4	16.8	40.6	16.2
BaO	16.0	-	-	6.4

The mineral constituents of SYNROC are capable of, taking into solid solution a large variety of ions possessing diverse radii and charges. Moreover, the chemical equilibria between the minerals are highly flexible, with a wide range of compensating ionic substitutions being possible in order to achieve charge balance, without altering the fundamental oxygen stoichiometry of the crystals. These characteristics yield a waste form in which large variations in both the composition of the waste input and the amount of waste that is incorporated do not lead to formation of new and unwanted phases, SYNROC can readily accept 20% by weight of fission products and actinide elements found in high-level waste, without formation of new phases other than small amounts of metal and phosphate. The distribution of radwaste species among coexisting SYNROC phases, determined from electron-probe analyses, is:

Table 42 Distribution of principal high-level waste elements among constituent minerals of SYNROC.

Hollandite : Cs^+, Rb^+, K^+, Ba^{2+}, Fe^{3+}, Cr^{3+}, Ni^{2+}, Mo^{4+}
Zirconolite : U^{4+}, Th^{4+}, Pu^{4+}, Cm^{4+}, Np^{4+}, Actinides^{3+}, Rare earths, Sr^{2+}
Perovskite : Na^+, Sr^{2+}, Pu^{3+}, Cm^{3+}, Np^{3+}, Rare earths, Actinides^{4+}
Metal : Ru, Tc, Mo, Ni,Pd, Rh, Te, S, Fe

The most desirable radwaste immobilization characteristics are produced when a high degree of chemical equilibration is achieved during heat treatment. This depends upon diffusion and recrystallization in the solid state, and so it is essential, prior to heat treatment, to mix the components with a high degree of homogeneity. It is important to maintain non oxidizing conditions during the heat treatment of SYNROC, so as to prevent the formation of soluble cesium molybdate. This is accomplished either by heating to about 800 C in an atmosphere of Ar-4%H_2 or by adding 2-3% of metallic titanium powder to the feedstock prior to hot-pressing. Under these conditions, hexavalent molybdenum is reduced to the metallic or quadrivalent state, and cesium becomes incorporated in the "hollandite" lattice.

Leaching behaviour

The leach rates of most elements from a borosilicate glass at 75-95 C fall within a limited range and do not change much with time. In sharp contrast, at a similar temperature, there are wide variations in the leach rates for different elements from SYNROC. Moreover, the leach rates decrease strongly with time over the first 10 - 30 days, often by as much as two orders of magnitude, and only later do they level off. The sharp reduction in the leach rate with time displayed by SYNROC is believed to be due to two factors. First, the equilibrium achieved during hot-pressing may be imperfect, and small amounts of metastable phases may be present, particular at grain boundaries. These metastable phases are likely to be more leachable than the stable, major phases, and as they are selectively removed from the surface, leach rates will decrease. Second, studies of leaching mechanisms show that univalent and divalent elements are selectively removed from the surfaces of the phases, leaving skins enriched in titanium and zirconium oxides. These oxides are extremely insoluble in groundwater, and initially they tend to protect the surface from further leaching. Later on, as a result of steady-state dissolution of titanium-oxide rims, as well as diffusion of cations through these rims, leach rates level off. At these steady-state, lower levels, the leachabilities of univalent and divalent elements (Cs^+, Sr^{2+}, Ba^{2+} and Ca^{2+}) from SYNROC at 95 C are 500 to 2,000 times smaller than those from borosilicate glass. The differences are even in the case of trivalent and tetravalent elements, the leachabilities being about 10,000 times smaller than those from glass. Elements in the actinide series generally possess chemical properties similar to those of the rare earths and uranium. It is expected, therefore, that their leachabilities will be in the vicinity of those of Nd^{3+} and U^{4+}. Changes in waste-loading do not cause the appearance of new phases, and substantial changes in the composition of the waste can likewise be tolerated. These properties derive from the wide range of acceptor sites in the host crystals and the complex charge balances, which ensure that the limits of solid solubility of high-level waste elements in the host crystals are not exceeded. In this sense, SYNROC, like glass, may be said to be a "forgiving waste form." It should be noted that the leachability of glass, also, is affected only slightly-by a factor of about two-by waste-loadings over the range of 0-30%. The insensitivity of glass leachability to a wide range of waste-loadings and compositions is one of the most important attributes of glass.

Radiation damage

The question has sometimes been raised as to whether radiation damage, caused predominantly by the emission of alpha particles during radioactive decay of actinide elements, may cause serious deterioration in the ability of crystalline host phases to immobilize radwaste elements. Key evidence on this topic is provided by nature. The alpha emitting actinides in SYNROC are incorporated in zirconolite and perovskite. We studied the crystalline structures of a collection of naturally occurring zirconolites and perovskites of differing ages that contain varying amounts of uranium and thorium. The cumulative radiation doses received by these minerals were found to range from 5E+17 to 1E+20 alpha particles/g (a/g). We found that natural zirconolite receiving an alpha dose equivalent to a SYNROC age of 1 000 years (1.3E+18 a/g) remained fully crystalline but expanded in volume by 2%. With more intense irradiation (8E+18 a/g, equivalent to a SYNROC age of 4E+5 years), natural zirconolite transformed from its normal monoclinic structure to a cubic-defect fluorite-type structure, with a volume increase of less than 3%. The zirconolite and fluorite structures are, in fact, very closely related, and it thus appears that the main effect of alpha irradiation was to cause a certain degree of disorder of the cations, leaving the fluorite-type anion sublattice essentially intact. This behaviour persisted up to SYNROC ages exceeding 1E+6 years. With even heavier irradiation (8E+19 alpha/g, equivalent to a SYNROC age of 4E+8 years), zirconolites ceased to diffract x-rays-i.e., they became metamict, according to conventional terminology. Electron diffraction studies, however, showed that our samples possessed a considerable degree of short-range order and contained areas of crystalline domains. Moreover, the expansion in volume from the original state was less than 3%. Thus, even with this enormous degree of radiation damage, the zirconolites, although metamict to x-rays, remained essentially in the crystalline state and did not revert to the highly disordered structure of a true glass.

Similar studies of natural uranium-bearing perovskites with SYNROC ages of up to 20 000 years showed that irradiation had caused volume increases of up to 1.8%. The x-ray powder patterns of the perovskites were sharply resolved and showed no evidence of lattice damage. Comparative studies showed that the perovskite lattice is more resistant to alpha-irradiation than is zirconolite. Overall, the studies 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 a mass-spectrometric study, in which a collection of natural zirconolites and perovskites was analyzed for uranium and lead, by isotope dilution, and for lead isotopic composition. This study demonstrated that zirconolites possess a remarkable capacity to immobilize uranium, thorium, and their decay products, even when they have suffered extreme degrees of radiation damage. For example, Sri Lanka zirconolites, which have experienced doses exceeding 8E+19 a/g, have nevertheless remained as closed systems to uranium, thorium, and lead for 550 million years. More limited data on perovskites indicate that this mineral will also be stable enough under radiation to be a satisfactory host for high-level waste elements. Measurements of the leachabilities of zirconolites and perovskites that have been subjected to varying amounts of radiation damage have also been reported. At 200 C, for example, bulk leach rates, based on uranium loss, were 3E-4 $g/m^2/day$ for zirconolite that had been subjected to a cumulative dose of 1E+18 a/g and 2E-3 $g/m^2/day$ for Sri Lanka zirconolite subjected to 8E+18 a/g. These leach rates are much lower than those for borosilicate glass at this temperature and demonstrate that extreme radiation damage does not lead to unacceptably high leachability. The natural zirconolites and perovskites that were studied had experienced complex geological histories, including elevated temperatures and pressures, contact with groundwater, and weathering and erosion over periods hundreds or even thousands of times longer than those required for decay of high level waste to safe levels. They had been subjected to a range of geochemical stresses that were far more intense than those likely to be found in any radwaste repository. Despite this, they were found to have retained their entire complements of alpha emitting waste elements and their daughter products. These observations provide strong grounds for confidence that the integrity and safety of SYNROC as a waste form will not be adversely affected by radiation damage before the high-level wastes have decayed to safe levels.

Process technology

Except for the final hot-pressing step, the production of SYNROC uses only process technology that had already been developed and applied in the fabrication of borosilicate glasses under fully radioactive conditions. In a program operated jointly by the Australian Atomic Energy Commission (AAEC) and the Australian National University (ANU), several alternative production flow sheets are being tested and evaluated. Tetraisopropyl titanate and tetrabutyl zirconate are used as sources of titanium and zirconium oxides and are mixed with nitrate solutions of the other components. The product is coprecipitated in basic solution and then washed. It possesses a very large surface area and functions as an effective ion-exchange medium. It is mixed with a nitrate solution of high-level waste, to form a thick, homogeneous slurry. The slurry is dried at 130 C, using a steam-heated rotary drum drier. It is then in the form of a free-flowing powder, which is introduced into a fixed vertical kiln, where it is calcined at 750 C in the presence of a reducing atmosphere ($Ar-4\%H_2$). This calcination step drives off highly volatile components, such as water and oxides of nitrogen, but there is negligible loss of radioactive species such as 137-Cs and 106-Ru. The devolatilized powder is then deposited in a steel container fabricated in the form of a bellows. After vibrating the container to achieve maximum powder density (20-25% of the theoretical value), the container is evacuated and sealed. The powder is consolidated into fully dense monoliths by heating it to 1 150 -1 200 C and simultaneously subjecting it to a pressure of 100 - 150 MPa. The reference process used for this step is hot isostatic pressing (HIP), which is widely utilized on a commercial scale for the manufacture of specialized ceramics and alloy steels. After hot-pressing, the fully dense SYNROC cylinders, encased in collapsed bellows, are stacked in a large canister, which is sealed when full. The canister is then ready for final disposal.Isostatic hot-pressing using argon as the pressure medium is applied because it is currently in commercial use. However, an alternative consolidation stage employing uniaxial hot-pressing is under development by the AAEC and ANU. It is simpler and promises greater ease of operation by remote control. In this uniaxial consolidation stage, the bellows containers are placed within the thick-walled disposal canister, which is directly heated to 1150 - 1200 C by induction coils. A uniaxial load is then applied vertically by a piston, causing the SYNROC to be hot-pressed to the fully dense state within the final disposal canister. According to a second variant of this process, the bellows are heated independently and are then uniaxially hot-pressed to form "pancakes," which are stacked in the final disposal canister.

The hot-pressing strategy proposed for SYNROC should possess significant advantages over glassmaking technology in the area of radiological cleanliness. The calcine from the kiln is enclosed in sealed metal containers prior to the final hot-pressing step, so that there is no loss of any volatile components or particulate material at this stage. By contrast, melting of glass at 1100 - 1150 C yields large amounts of dust-laden off-gases which also carry significant amounts of volatilized, highly radioactive elements, such as cesium and ruthenium. These elements must be removed from the off gases and recycled by complex filtering equipment. These stages add significantly to the cumulative radiological exposure of plant personnel. The basic processing costs of immobilizing high-level wastes in glass and SYNROC are expected to be in the same neighbourhood. However, there are additional factors bearing upon waste-disposal technology that are likely to lead to major savings if SYNROC is used. Another factor that makes SYNROC cheaper than glass involves the waste-loading. SYNROC can readily incorporate 20% by weight of high-level waste. Since the density of SYNROC is 4.5 g/cm^3, compared with about 2.9 g/cm^3 for the density of glass, which will be limited to about 10% by weight of high-level waste, this means that SYNROC would contain about three times as much high-level waste per unit volume as glass. The number of standard-size canisters required to immobilize a given quantity of radwaste will thus be reduced threefold, which yields major savings in the costs of canisters, transportation, storage, and geologic disposal.

Disposal strategy

We propose to dispose of the waste in a widely dispersed array of deep (4 km) drill holes about 1 m in diameter, carefully sited within impermeable crystalline-rock formations. Canisters would be emplaced in the lower 2.5 km of the hole, and the top 1.5 km would be sealed. One such hole would have the capacity to accept the waste generated by 80 large (1 000 MW) nuclear power stations in a single year. There are several advantages to this strategy. In general, the greater the depth at which the waste is emplaced, the more secure the geologic barrier becomes. Moreover, the permeability of most rock systems decreases with depth, and mining activities have shown that some crystalline-rock formations are essentially dry below 1 km. With adequate exploration, it should be possible to delineate large areas of igneous and metamorphic rocks that have very low permeability and are essentially dry below 1.5 km. Disposal of high level waste in such rocks would thus minimize the access of groundwater to the waste, thereby curtailing the principal means by which radioactive-waste species could be transported to the biosphere. Recent experience in several countries demonstrates that it is difficult to locate acceptable sites for large, centralized, mined repositories. Disposal of high-level waste in deep drill holes would increase considerably the number of sites that are acceptable on technical grounds.

Drilling causes minimal damage, to rock systems, and drill holes are readily sealed. Construction of large mined repositories, however, may be accompanied by formation of fractures in surrounding rock, which could serve as conduits for circulating groundwater. Mined repositories are also likely to be more difficult to seal than isolated drill holes. The distribution of high-level waste in a densely packed horizontal array of the kind envisaged in a mined repository causes thermal stresses, which may lead to fracturing of the host rock, thereby enhancing groundwater circulation. This problem can be reduced to negligible proportions by disposing of waste in a three-dimensional configuration in an array of widely spaced, deep drill holes. The use of glass as an immobilization medium, on the other hand, restricts the depth of disposal because of the increase of temperature with depth in the earth, generally 20 - 30 C/km. The combined effect of the increase in temperature with depth and the 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 groundwater to waste, the possibility of water entering must always be considered as a factor in risk assessment analyses. Entry of water into a borosilicate glass waste form at 200 C would cause rapid disintegration. By contrast, SYNROC displays a high degree of stability under these conditions. The combination Of SYNROC and deep drill hole disposal thus maximizes the integrity of both the geologic and immobilization barriers.

Interim storage

The storage of spent nuclear fuel rods, after they were removed from the reactor, was not considered a problem in the early days of commercial nuclear power since it was assumed that all spent fuel would be reprocessed in the processing plants then being developed. The government's decision in the 1970s not to permit spent fuel to be reprocessed in this country because of concerns that the recovered plutonium and uranium were subject to pilferage or loss of accountability put the burden of spent fuel storage on the nuclear utilities, which were not prepared for it. The Nuclear Waste Policy Act of 1982 confirmed that utilities owning and generating spent fuel were responsible for storing it until January 31, 1988 when the federal government was scheduled to begin accepting it for disposal.

Spent fuel storage (Berlin 1989)

On site water storage in pools originally constructed for short-term storage of irradiated fuel has been utilized for 40 y at nuclear power plants. However, since the utilities must now store the spent fuel for an extended period, some nuclear utilities are running out of storage space. As one measure of this problem, the DOE estimates that 67 U.S. plants will lose "full core reserve" storage capacity by 2000. To alleviate this situation, the utilities have both undertaken to enhance at-reactor storage capacity and are looking into new storage methods. The utilities began pool reracking in the 1970s to accommodate additional fuel rods in existing pools, and have been transshipping spent fuel from one plant to another (usually newer) in the 1980s to make use of unused storage capacity. Among the methods now being considered to enhance at-reactor storage capability are the expansion of existing water storage capacity, more efficient use of available capacity though fuel rod consolidation, the construction of additional at-reactor storage facilities using either wet storage or, alternatively, dry storage of spent fuel in dry storage casks, and the development of away-from reactor (AFR) storage facilities. These approaches can be grouped, from the standpoint of technologies employed into on site wet pool storage, dry storage, and AFR storage.

Wet pool storage (Berlin 1989)

More than 95% of the existing spent fuel inventory in the United States is stored in water pools (F-3) at reactor sites, and this storage method will be used for all the LWRs that are currently under construction. A major advantage of wet storage is that it is well suited for removing the radioactive decay heat generated by the spent fuel in the period of several months immediately after its discharge from the reactor, when the decay heat rate is at its highest and dropping off rapidly. A typical spent fuel storage pool is rectangular in shape, constructed of reinforced concrete, and frequently lined with metal plates to which the storage racks are attached. The spent fuel assemblies are placed in the storage racks at the bottom of the pool which are designed both to hold the assemblies securely and maintain the required spacing to prevent criticality. While the pools at reactor facilities vary in length and width, they are generally 12-13 m deep permitting a minimum 3-m layer of water over the fuel assemblies to provide radiation shielding of operating personnel. The original wet storage pools at many reactor facilities are filling up, and approaches are being sought to enhance existing fuel storage capability. One attractive approach to provide this enhanced storage is to expand the existing wet storage capacity if space permits. By using the existing storage facility, costs of expansion are minimized. Two ways are available to expand the water volume capacity: reracking of the pool to increase storage density and consolidation of spent fuel rods by dismantling the fuel assembly and rearranging the spent fuel rods into close-packed geometry in a storage canister. Reracking can be accomplished by the replacement of non poisoned racks with racks incorporating boron in stainless-steel or aluminum matrices to absorb neutrons and thus permit closer spacing of the fuel assemblies, the replacement of existing non-fuel-storage racks with racks suitable for fuel storage, or the replacement of the original spent fuel storage racks with stainless-steel racks that permit closer spacing of the stored assemblies. Reracking has been used for a number of years and the technology continues to improve. However, storage capacity increases from reracking are limited by the storage pool volume, and constrained by structural considerations for the additional weight. Rod consolidation, which has the potential to substantially increase spent fuel storage capacity at some reactors, is also constrained by structural strength requirements to support the additional weight. Another way some utilities have gained short-term additional storage capacity is to temporarily encroach on the full core reserve (FCR) (space reserved in the spent fuel pool for unplanned discharge of the entire reactor core loading). This occurs when the utility chooses to gamble that the FCR will not have to be used for a period of time and uses this space for spent fuel assemblies. In certain cases it may be cost effective for a utility to construct an additional separate storage pool, particularly if the new pool can be used to serve a number of nuclear power plants.

Dry storage

It is apparent that none of the wet storage or intra utility transshipment approaches will entirely alleviate the problem of loss of FCR before the government is able to assume responsibility for the spent fuel. Both the DOE and industry have been working to find alternative solutions, with an emphasis on dry storage (F-2,F-10) as a viable alternative. The DOE has used dry storage methods for military reactor fuel for more than 20 y. Dry storage offers a number of advantages as an interim storage concept. It provides the flexibility to meet a range of utility spent fuel storage needs, permits completely passive cooling, thus precluding safety and performance concerns regarding interruption of coolant flow, permits less extensive cover gas control and monitoring requirements for most dry storage concepts than the comparable requirements for wet storage, permits, in certain cases, the addition of capacity in modules minimizing capital investment, and generates less secondary radioactive wastes as compared to wet storage. Dry storage modules at reactor sites can be large metal storage casks, concrete storage silos, or dry wells. The major developmental dry storage program in the United States is a cooperative effort involving the DOE, the Virginia Power Corporation, and the Electric Power Research Institute (EPRI). Under this program, Virginia Power ships spent fuel to the DOE's Idaho National Engineering Laboratory (INEL) where it is placed in large metal storage casks and monitored. This test program will provide performance data on the storage concept, and promote the development of dry rod consolidation technology and prototypical equipment. The DOE's stated program goal "is to remove conservatism from the licensing of dry storage casks and provide a storage technology that is generically applicable so that the Nuclear Regulatory Commission can license dry storage of spent fuel by rule." There are four dry storage casks tested under the program: the Castor V/21 from General Nuclear Systems, Inc., the TN-24P from Transnuclear Inc., the MC-10 (F 5-18) from Westinghouse Electric Corporation, and the NAC5100 Nuclear Assurance Corporation. The GNSI Castor V/21 is being used in the first dry storage program to be conducted at a commercial nuclear power plant in the United States. The Virginia Power Company's Surry station has established an Independent Spent Fuel Storage Installation (ISFSI). The ISFSI consists of the concrete storage pads (230 ft long x 32 ft wide x 3 ft thick), each capable of storing 28 casks. The utility had five casks loaded by 1987, and plans to load an additional thee to four a year at Surry. The utility was licensed in 1986 for 20 y of dry storage.

Concrete silos (F-2,F-10) make use of the concrete to dissipate the heat generated by the spent fuel, with the spent fuel placed within a sealed chamber in the concrete. There are a number of design concepts for such silos, one of which is planned for a cooperative program between the DOE and Carolina Power & Light (CP&L) Company at their Robinson-2 plant. This plan involves the use of the second currently licensed dry storage system in the United States: the Nutech Horizontal Modular System (NUHOMS), a concrete module and stainless steel horizontal silo storage system. A 20-y license for dry storage has been issued by the NRC at Robinson-2. CP&L is currently using thee of the modules at the site and may eventually install up to eight of the NUHOMS modules. Dry wells use cylindrical chambers that are sunk into the ground and into which the spent fuel is lowered. The decay heat from the spent fuel is dissipated in the surrounding soil. Dry wells have been used by the DOE to store spent fuel at the Nevada Test Site.

Table 43 Large metal dry storage cask characteristics

Characteristic	Castor	TN-24P	MC-10	NAC 5100
NRC license status	L	U	U	U
Capacity (PWR)	21	24	24	28
Construction materials	iron	steel	steel	SS/Pb/SS
Neutron shielding	PE	BP	BP	SS/Pb/SS
Maximum weight-tons	115	100	100	?

L = Licensed, U = Unlicensed, SS = Stainless steel, PE = Polyethylene, BP = Borated plastic.

Away from reactor storage (Berlin 1989)

Away-from-reactor (AFR) facilities, defined as all spent fuel storage facilities not integrated within a reactor plant, include those located at reprocessing plants, disposal sites, or other nuclear fuel cycle facilities. There are currently two AFR wet storage facilities operating all the United States, in storage pools at the Morris, Illinois and West Valley, New York former reprocessing facilities. As dry storage technologies are developed, they will be increasingly used for AFR storage. Although there are no dry AFR storage facilities as yet in the United States, dry AFR facilities have been constructed in Europe, with the Gorleben AFR facility in Germany being a typical example. An AFR design concept being considered in the United States for long-term storage of spent fuel (and possibly high level waste) is the Monitored Retrievable Storage (MRS) facility, which would incorporate such dry storage concepts as sealed concrete storage casks (silos) and dry wells. It is important to note that the wet and dry storage concepts for spent fuel are intended as interim measures pending the operability of a geologic repository.