Nuclear waste forms

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Abstract: This review describes nuclear waste forms for high-level waste (HLW), that is, glasses, ceramics, and glass-ceramics, as well as for low- and intermediate-level waste (LILW), that is, cement, bitumen, glass, glassy slags, and ceramics. Ceramic waste forms have the highest chemical durability and radiation resistance, and are recommended for HLW and actinide (ACT) immobilization. Most radiation-resistant materials are based on phases with a fluorite-related structure (cubic zirconia-based solid solutions, pyrochlore, zirconolite, murataite). Glass is also a suitable matrix for HLW containing fission and corrosion products, and process contaminants such as Na salts. Within the framework of the HLW partitioning concept providing separation of short-lived (Cs, Sr) and long-lived (rare earth element-ACT) fractions, glass may be used for immobilization of the Cs–Sr-bearing fraction, whereas the rare earth–ACT fraction may be incorporated in ceramics. Glass-based materials or clay-based ceramics are the most promising LILW forms, but cement and bitumen may also be applied as matrices for low-level wastes (LLW).

High-level waste (HLW), intermediate-level waste (ILW), and low-level waste (LLW) are produced at all stages of the nuclear fuel cycle as well as in the non-nuclear industry, research institutions, and hospitals. The nuclear fuel cycle produces liquid, solid, and gaseous wastes. Moreover, spent nuclear fuel (SNF) is considered either as a source of U and Pu for re-use or as radioactive waste (Johnson & Shoesmith 1988), depending on whether the 'closed' ('reprocessing') or the 'open' ('once-through') nuclear fuel cycle is realized, respectively (Ewing, 2004).

Liquid HLW from reprocessing of SNF may consist of 50–60 elements, including about 90 radionuclides of 35 chemical elements of fission products (FP) and more than 120 radionuclides due to FP decay. The total activity of HLW may achieve 10^{16} Bq/m^3 (Nikiforov et al. 1985). The HLW elements can be divided into four groups: (1) fission products, such as $^{134,137}Cs$, ^{90}Sr, ^{99}Tc, ^{129}I, $^{141,144}Ce$, ^{147}Pm, ^{151}Sm, $^{152,154}Eu$; (2) corrosion products, such as Fe, Al, Si, Mo, Zr, including the activated products ^{51}Cr, ^{54}Mn, ^{59}Fe, $^{58,60}Co$, $^{122,124}Sb$; (3) minor nuclear fuel components and transmutation products comprising α-emitters ($^{235,238}U$, ^{237}Np, $^{238,239}Pu$, ^{241}Am, ^{242}Cm, ^{244}Cm); and (4) process contaminants, such as, Na, K, Ca, Mg, Fe, S, F, and Cl compounds.

In addition to HLW, reprocessing of SNF produces large amounts of low- and intermediate-level waste (LILW). The volume of LILW exceeds that of HLW by many times. The operation of nuclear power plants yields wastes such as activated coolant (water or steam), filter materials, pulps, regeneration solutions, and contour washing solutions. Non-nuclear fuel cycle institutional wastes represent solutions after regeneration of sorbents, various wastes of research laboratories, medical waste, solutions after decontamination of equipment and soils. Solid wastes from both nuclear power plants and non-nuclear fuel cycle facilities include contaminated equipment, ion-exchangers, lining and heat-insulating materials, laboratory dishes, various organic wastes, including ion-exchange resin,

cellulose, and biomaterials. Organic wastes are to be incinerated, forming incinerator ash or slag.

The inorganic wastes must be conditioned to durable waste forms. High-level wastes require long-term storage for 10^3-10^5 years depending on composition and activity. The most dangerous wastes are those containing ACT and excess weapons Pu, derived from the dismantling of nuclear weapons. These types of waste must be stored for 10^5-10^6 years. Glass and ceramic waste forms are suggested as suitable matrices for these wastes. A combined approach has also been developed on the basis of the application of glass–ceramics to the immobilization of HLW (Hayward 1988). Radionuclides partition between glass and crystals in such a way that Cs and other alkali elements enter the glass, whereas ACT and rare earth elements (REE) and possibly Sr are incorporated into crystalline phases. Recently, a HLW partitioning concept has been proposed (Actinide and Fission Products Partitioning and Transmutation 1999; Baestlé *et al.* 1999). In this scheme, HLW is to be partitioned into a short-lived Cs–Sr fraction and a long-lived REE–ACT fraction, which will be conditioned separately using borosilicate glass and crystalline ceramics, respectively.

Certain LILWs also need to be conditioned and stored for 300–500 years, and currently cement, bitumen, polymers, and composite materials are used as matrices (Sobolev & Khomtchik 1983; Dmitriev & Stefanovsky 2000). However, alternative waste forms, such as glass, glass–crystalline materials (glassy slags), and clay-based ceramics are also considered (Dmitriev & Stefanovsky 2000). Among the candidate HLW forms, glass and ceramics have been investigated in the greatest detail, and comprehensive reviews on their compositions, structure, physical properties, and geological behaviour are given, for example, by Hench *et al.* (1984), Ringwood (1985), Fielding & White (1987), Lutze & Ewing (1988), Laverov *et al.* (1994), Ewing *et al.* (1995), Merz & Walter (1996), Weber *et al.* (1997, 1998), and Ewing (1999, 2001).

Major requirements for nuclear waste forms

Nuclear waste forms have to be in compliance with the following requirements:

(1) High chemical durability;
(2) High radiation resistance (dependent on waste activity level);
(3) Long-term (thermodynamic) stability;
(4) Maximum waste volume reduction factor;
(5) Strong mechanical integrity;
(6) Appropriate thermal conductivity (for HLW forms);
(7) Appropriate viscosity and electric resistivity (for materials produced by electric melting);
(8) Homogeneous distribution of radionuclides (especially if fissile materials are present);
(9) Compatibility with geological environment;
(10) Simple, reliable, and safe production technology;
(11) Production at low temperature (T) to avoid losses of relatively volatile radionuclides (e.g., Cs, Ru);
(12) Resistance to biodegradation;
(13) Maximum difficulty to recover radioactive constituents from waste form (especially fissile materials, such as Pu).

No HLW form satisfies all the above requirements. For example, glass has high chemical durability and good radiation resistance, but the vitreous state is thermodynamically unstable and subject to devitrification. This process, taking place below the glass transformation temperature (T_g), may cause reduction of chemical durability and/or mechanical destruction. Devitrification may, however, be delayed if no aqueous phase is present, as documented by archaeological glasses. Ceramic material is an appropriate HLW form with respect to all parameters except that its production technology is not chosen yet and its compatibility with the geological environment is strongly dependent on the composition of both the ceramic and the geological medium. Nevertheless, both glass and ceramics satisfy the listed requirements to a large extent. LILW forms do not require such high chemical and physical standards. Major requirements include a maximum volume reduction factor, good chemical durability, and high mechanical integrity. Glass-based materials are the best solution in this case. Currently the most commonly used waste form for LLW is cement (Sobolev & Khomtchik 1983).

Chemical durability of waste forms

There are a number of methods for determining the chemical durability of waste forms. Different tests determine either the differential leach rate of individual constituents (in $g \cdot m^{-2} \cdot d^{-1}$) or the cumulative leaching (in $g \cdot m^{-2}$, or mol% or wt%). The differential leach rate is given by

$$L = A_i/(A_0 \times S \times t) \qquad (1)$$

in which A_i is the (thermodynamic) activity of the ith element in solution after the experiment; A_0 is the specific activity of the given element in the sample; S is the sample surface area; and t is the duration of the experiment. All tests may be divided into either static or dynamic according to the character of interaction between specimen and leachant. The most frequently applied methods for determining waste-form leachability are (Hespe 1971; US DOE 1981; IAEA 1985; ASTM 1994):

(a) *Materials Characterization Center (MCC) tests.* There are several MCC tests, performed under static (MCC-1), high-T (MCC-2), solubility-limited (MCC-3), low flow rate (MCC-4), and Soxhlet (MCC-5) conditions. The MCC-1 test is performed with monolithic samples at a specimen surface area (S) to leachant volume (V) ratio of 1:10, and under static conditions at 70 °C or 90 °C for 7 or 28 d. The other methods are normally applied for determining leach rates from glasses.

(b) *Single-Pass Flow-Through (SPFT) test.* The MCC and SPFT tests are used to determine leachability of glasses, glass−ceramics and ceramics.

(c) *Product Consistency Tests (PCT).* This test uses powdered material (149−74 µm) with $S/V = 2000$ m^{-1} at 90 °C for 7 days. The data are reported as elemental concentrations.

(d) *International Atomic Energy Agency (IAEA) test.* This test is performed under static conditions at 20 °C, with replacement of leachant every day for the first 7 d, and every week thereafter. It is used for LILW forms.

(e) *Toxicity Characteristics Leaching Procedure (TCLP).* This test uses 100 g of material with grain size <9.5 µm and requires a fluid to solid mass ratio of 20, mechanical shaking for 24 h, and filtering using a vacuum filtration apparatus. The results are reported as ppm elemental concentrations.

Owing to the use of these different methods, the results are often difficult to compare. Different procedures, however, are required to learn how waste-form materials behave under different conditions. Unless specified otherwise, all leach rates given in this chapter represent values determined with deionized water as the leachant.

Radiation resistance

The radiation stability of waste forms is determined by changes in their structure, chemical, and phase composition, and macroscopic properties such as, chemical durability, physical, and mechanical properties. These changes are due to atomic displacements, formation of point defects and ion radicals, accumulation of stored energy, formation and accumulation of He and O_2 bubbles, and radiolytic decomposition.

There are several techniques for the study of radiation resistance of actual waste forms, and they have different degrees of certainty (Ewing *et al.* 1995; Weber *et al.* 1997, 1998; Weber & Ewing 2002). One of these techniques is based on the investigation of radioactive U- and Th-containing minerals (natural analogue minerals; see Lumpkin *et al.* 2004). Maximum concentrations of $UO_2 + ThO_2$ in the minerals studied reached 58.2 wt% for brannerite, 31 wt% for pyrochlore, 23.5 wt% for zirconolite, ~10 wt% for zircon, ~6 wt% for perovskite, and 16 wt% for britholite (Alexandrova *et al.* 1966; Minerals 1967; Gieré *et al.* 1998, 2000; Lapina & Yudintsev 1999; Lumpkin *et al.* 1998a, 2000; Ewing *et al.* 1995; Ewing 1999). The cumulative α-decay dose in minerals is calculated as (Lumpkin & Ewing 1988):

$$D = 8N_1(e^{a_1 t} - 1) + 7N_2(e^{a_2 t} - 1) \\ + 6N_3(e^{a_3 t} - 1) \qquad (2)$$

In this equation, D is the dose (α-decays/g); N_1, N_2, N_3 are the amounts (atoms/g) of ^{238}U, ^{235}U, ^{232}Th, respectively; a_1, a_2, a_3 are the decay constants of ^{238}U, ^{235}U, ^{232}Th (y^{-1}), respectively; and t is the age of the mineral (y). In the absence of isotopic data, the second term can either be ignored or a concentration ratio of $^{235}U = 1/139 \times {}^{238}U$ can be assumed. Application of this method to natural glasses, however, is very limited because of their very low U and Th concentrations (typically <20 µg/g; Weber *et al.* 1997).

The second technique involves incorporation of short-lived ACT isotopes such as ^{238}Pu ($t_{1/2} = 87.7$ y) or ^{244}Cm ($t_{1/2} = 18.1$ y) into the structure of the phase to be studied. Normally, 0.2 to 3 wt% ACT are incorporated to achieve 10^{18} to 3×10^{19} α-decays/g in laboratory time periods of up to several years. This technique is most suitable for simulation of radiation damage in ACT waste forms, including those for Pu immobilization.

Another, more often applied, method is the irradiation of matrices with neutrons or charged particles (electrons, α-particles, heavy ions). Advantages of this method include: short time of irradiation (min or h); direct visibility of structural damage (observed *in situ* during irradiation using a transmission electron microscope); and

the possibility of determination of radiation resistance of all phases at the temperature of the experiment. Owing to the short time of the experiments, the dose rate is higher by many orders of magnitude ($\sim 10^9$ times) compared with the dose rate of actual waste forms. Moreover, irradiation with α-particles and ions of light noble gasses (Ne, Ar, Kr) can be employed to simulate the effects of α-particles, whereas irradiation with heavy ions (Xe, Pb, Au) is an effective method to study α-recoil damage. The damage created by this technique, however, is restricted to a thin layer (typically between 0.1 and 1.0 μm) near the surface of the studied material, thus limiting the possibility of applying certain spectroscopic techniques. Similarly, electron irradiation can be used to study the effects of ionization and electron excitations from β-particles and γ-rays on glasses and ceramics; it may be applied to simulate radiation effects due to FPs. One disadvantage of the charged-particle irradiation is that all the phases in multi-phase ceramics are irradiated, including those that do not contain ACTs. Therefore, this method is most suitable for glasses and single-phase ceramics with a homogeneous ACT distribution (Weber *et al.* 1997, 1998). Irradiation with fast neutrons produces significant numbers of atomic displacements, but it does not correctly simulate damage from α-particles and α-recoils and further, it does not simulate the accumulation of He from α-particles (Weber *et al.* 1997, 1998). Boron-containing materials, usually borosilicate glasses, may be irradiated with a thermal neutron flux to generate 1.78 MeV α-particles according to the $^{10}B(n, \alpha)^7Li$ reaction (Weber *et al.* 1997). Materials doped with fissile isotopes (e.g., ^{235}U) may also be irradiated in a thermal neutron flux (Antonini *et al.* 1979; Vance & Pillay 1982) in order to provide a good simulation of spontaneous fission events in waste forms for HLW and Pu. However, spontaneous fission is a rare event, and its contribution to the total radiation damage in waste forms is insignificant.

To compare doses resulting from different types of radiation it is necessary to formulate a measure of radiation effects on the crystal structure: doses can be recalculated to the number of displacements per atom (dpa). A dose of 0.1 dpa, for example, means that one of ten atoms was displaced from its initial position. Equivalent values in dpa units may be calculated for different types of radiation from the effects of its interaction with the crystal lattice. To recalculate α-dose to dpa the following formula is used:

$$\text{Dose (dpa)} = N_d \times (D \times M)/(N_f \times N_A) \quad (3)$$

In this formula, N_d is the average number of atomic displacements per α-decay event; $D =$ accumulated α-dose; $M =$ molar mass of the compound; $N_f =$ number of atoms in the compound; and $N_A =$ Avogadro's number. The value of N_d is often assumed to be 1500, but computer codes can be used to estimate N_d and also to recalculate irradiation doses from heavy ions to dpa values (Ziegler *et al.* 1985).

Gamma-irradiation has been used to investigate effects on chemical durability of waste glasses (Lutze 1988) and to assess the effect on corrosion and defect formation in waste ceramics (Vlasov *et al.* 1987; Kulikov *et al.* 2001). Irradiation with γ-rays does not produce atomic displacements, but rather causes excitations and point defects and leads to formation of ion radicals. Therefore, this method may serve as a simulation for $\beta-\gamma$-radiation of FPs in the waste forms.

Glasses

Glass-based materials have been suggested as HLW forms due to the capability of their random network to accommodate ions with widely variable charges and radii. Other advantages of glass waste forms comprise: simple production technology (transferred from electric melting of industrial glasses); high chemical durability; and high radiation resistance due to the aperiodic structure, which minimizes the effect of ionizing radiation on the atomic arrangement (Lutze 1988; Weber *et al.* 1997).

Borosilicate glasses

HLW. Silicate glass was proposed for the first time in Canada in the 1950s for immobilization of acid HLW containing major FPs. Nepheline syenite was used as raw material, and the melting temperature of this glass was approximately 1350 °C, similar to those that are typical of silicate glasses in the system $Na_2O-(K_2O)-CaO-MgO-Al_2O_3-SiO_2$. At $T > 1200$ °C, however, Cs and Ru losses due to volatilization increase; therefore, this temperature may be regarded as an upper limit for vitrification of Cs-bearing waste.

To reduce the processing temperature it has been proposed to add boron oxide to the glass-forming system. The base system for borosilicate waste glasses is $Na_2O-B_2O_3-SiO_2$, and Li_2O may be added to further reduce the melting temperature, as well as the viscosity of the melts (Roderick *et al.* 2000). Normally, a base frit composition is chosen and then the frit is mixed with HLW calcine or slurry in either a mixer (Hamel *et al.* 1998) or directly in the

melter (Masson *et al.* 1999). A number of borosilicate frit and glass formulations were designed in various countries, mostly before 1987 (Lutze 1988), but only a few have been implemented so far. These baseline glasses are designed to achieve waste loadings of 10–30 wt%, and include (Table 1): the R7/T7 glass for French reprocessing waste; the SRL-165 and ATM-10 glasses for the Defense Waste Processing Facility at Savannah River (South Carolina) and the West Valley Demonstration Project (New York), respectively; special glasses for immobilization of various ACT wastes, that is, lanthanide-borosilicate glasses for excess weapons Pu, and Am-Cm-containing nitric acid solution (Fellinger *et al.* 1999); and U-enriched (Aloy *et al.* 2001) and Ca-Al-borosilicate ('borobasalt', Russia) glasses for Pu-containing sludges.

Actinides are the most troublesome components of silicate glasses due to their low solubility in glass and high radiation hazard. Their solubility decreases with increasing atomic number and decreasing ionic radius at the same valence (Veal *et al.* 1987). Solubility limits for UO_3 and UO_2 in the binary alkali-silicate systems were determined to be ~68 wt% and ~34 wt%, respectively (Domine & Velde 1986). Solubilities of UO_2 and PuO_2 in complex borosilicate and aluminophosphate glasses were found to be ~30 wt% and 5.6 wt%, respectively (Matyunin 2000). The PuO_2 concentration in lanthanide-borosilicate glass may reach ~11 wt% (Bates *et al.* 1996; Bibler *et al.* 1996; Mesko *et al.* 1997; Chamberlain *et al.* 1997). The solubility limit for AmO_2 in Na-Li-borosilicate glass was found to be ~2 wt% (Eller *et al.* 1985). Moreover, significant attention must be paid to ensure homogeneous distribution of ^{239}Pu and other fissile isotopes to avoid concentration in local areas, where criticality could be reached (Matyunin *et al.* 2001).

One disadvantage of borosilicate glass is the low solubility of sulphates, molybdates, chromates, and halogenides, which may cause separation of metastable phases (Fig. 1) at relatively low contents of these components (1–3 wt%, dependent on glass composition; Camara *et al.* 1980; Kawamoto *et al.* 1981; Stefanovsky 1989; Stefanovsky & Lifanov 1989). At higher concentrations, 'yellow phase' formation may occur (Morris & Chidley 1976; Stefanovsky & Lifanov 1988; Lutze 1988). The yellow phase, consisting of alkali and alkaline earth molybdates, sulphates, chromates, and halogenides, concentrates Cs and Sr radionuclides, and its presence increases leach rates of these radionuclides.

Most leach rate measurements of both matrix elements and radionuclides were performed at 90 °C using MCC-1 or PCT tests. According to these tests, leach rates range from 10^{-1} to $10 \, g \cdot m^{-2} \cdot d^{-1}$ (Lutze 1988). For example, the mass and elemental leach rates (in $g \cdot m^{-2} \cdot d^{-1}$) for the PNL 76-68 glass containing 33 wt% waste oxides were determined at: mass – 0.42, Ca – 0.068, Cs – 1.03, Mo – 1.40, Na – 1.32, Sr – 0.075, B – 1.12, and Si – 0.73. These values are typical for borosilicate waste glass as measured by the MCC-1 procedure (90 °C, 28 d). Leach rates of Fe-group elements and ACTs under the same test conditions are considerably lower (10^{-3} and $10^{-4} \, g \cdot m^{-2} \cdot d^{-1}$, respectively).

The effect of radiation on the structure of oxide glasses, including borosilicate nuclear waste glasses, depends on the type of radiation as distinguished on the basis of its linear energy transfer (LET) values. Radiation with low LET (γ-rays, β-particles, protons) causes excitation and ionization processes with formation of excitons (electron–hole pair), point defects, ion radicals, free electrons, and holes. Borosilicate glasses exhibit boron–oxygen hole centres (BOHC), silicon–oxygen hole centres (SOHC), and trapped electrons. Gamma- or electron-irradiation may disrupt Si—O or B—O bonds with displacement of O atoms to interstitial positions. This may be followed by dimerization and molecular oxygen formation (DeNatale & Howitt 1985) or formation of O_2^- and O_3^- ions (Bogomolova *et al.* 1995, 1997). Radiation with high LET values (α-particles, α-recoil, fission fragments) produces atomic displacements and displacement cascades. Damage in the high-LET regime may cause volume changes of ±1.2% of the initial volume at a dose of $1–2 \times 10^{18}$ α-decays/g (corresponding to 1×10^9 Gy) and stored energy accumulation (up to ~140 J/g at a dose of $0.1–0.3 \times 10^{18}$ α-decays/g, or 10^8 Gy). Other consequences include: He accumulation; formation of gas (probably oxygen) bubbles; increase in fracture toughness by 45%; and reduction in hardness and Young's modulus by 25 and 30%, respectively. Furthermore, there is an increase in Na diffusion by a factor of 2 to 5 below 150 °C as compared to initial values for unirradiated glasses. One of the most important radiation effects in waste glasses is the change in chemical durability. Data obtained from short-term testing of ACT-doped simulated nuclear waste glasses indicate that leach rates may increase by up to three times as a result of radiation effects from α-decay. Ion-, neutron-, and γ-irradiation to doses of up to 10^9 Gy increased the leach rate by a factor of up to four (Weber *et al.* 1997).

Table 1. *HLW glass compositions for industrial applications*

| Type	R7/T7 (SON 68)	SRL-165 (Defence Waste Processing Facility)	ATM-10 (West Valley Demonstration Project)		Borobasalt	Na–aluminophosphate glass
Country	France	USA	USA	USA	Russia	Russia
Waste	Raffinates from reprocessing of commercial LWR fuel at La Hague	Defence waste from the Savannah River Site	HLW from reprocessing of commercial SNF	Excess weapons plutonium	Excess weapons plutonium	HLW from reprocessing of SNF from water–water energetic reactors
Composition (in wt%)						
B_2O_3	16.9	8–9	11.2–14.8	10.4	22.2–28.0	20–24 (Al_2O_3 + Fe-group element oxides)
SiO_2	55.0	48–52	39.5–48.4	25.8	29.0–33.7	—
Al_2O_3	5.9	4–5	5.6–7.1	19.0	8.1–9.6	
Fe_2O_3	—	11–13	10.7–13.5	—	5–6	—
CaO	4.9	—	0.2–0.6	—	14.4–16.6	—
Na_2O	11.9	12–13	7.1–8.6	—	1.9–5.7	24–27 (alkali oxides)
K_2O	—	—	4.1–5.3	—	0.5–0.9	—
Li_2O	2.4	3–4	3.3–4.2	—	—	—
MgO	—	~2	0.7–1.3	—	2.9–4.7	—
MnO	—	—	0.7–0.9	—	—	—
ZnO	3.0	—	—	—	—	—
SrO	—	—	—	2.2	—	—
TiO_2	—	—	0.7–0.9	—	0.5–0.9	—
P_2O_5	—	—	1.0–1.4	—	—	50–52
La_2O_3	—	—	—	11.0	—	—
Nd_2O_3	—	—	—	11.4	—	—
Gd_2O_3	—	—	—	7.6	—	—
ZrO_2	—	—	1.2–1.4	1.2	—	—
ThO_2	—	—	0.1–3.6	—	—	—
U_3O_8	—	~1	0.1–0.8	—	—	—
Waste loading	28 wt%, including 18.5 wt% of total fission products, ACTs, noble metals and Zr	Up to 33 wt%, including ^{137}Cs (~0.02 Ci/kg), ^{90}Sr (~0.2 Ci/kg), and ^{238}Pu (0.02–0.03 Ci/kg)	^{137}Cs and ^{90}Sr in concentrations of about 10 Ci/kg	11.4 wt% PuO_2	Up to 5 wt% PuO_2	Up to 10 wt% HLW oxides
References	Petitjean et al. 2002	Bibler et al. 1999; Marra et al. 1999	Barnes & Jain 1996; Jain & Barnes 1997; Palmer & Misercola 2003	Ramsey et al. 1995; Bibler et al. 1996; Mesko et al. 1997; Chamberlain et al. 1997; Meaker et al. 1997; Riley et al. 2000	Matyunin et al. 2001; Minaev et al. 2001	Vashman & Polyakov 1997
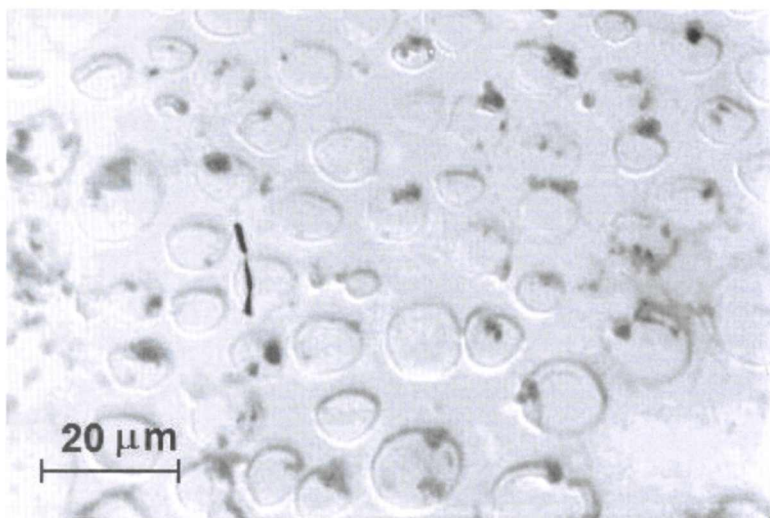
Fig. 1. Secondary electron micrograph of Na–borosilicate glass loaded with 30 wt% waste oxides and containing 0.9 wt% SO_3 (etching with 0.1 M HCl). Droplets with chemical durability lower than matrix are a sulphate-enriched phase (Stefanovsky 1989).

LILW. Vitrification of LILW was proposed in the late 1970s as an alternative to the bituminization process (Sobolev & Khomtchik 1983). Institutional and nuclear power plant wastes contain major amounts of Na-nitrate and minor amounts of Ca-, Mg-, Fe-nitrates and -carbonates. Some waste streams may additionally contain SO_4^{2-} and Cl^-, which can lead to yellow phase formation (Stefanovsky & Lifanov 1988). Operational wastes from nuclear power plants with a Russian water–water energetic reactor or pressurized water reactor (PWR) contain B, and thus, vitrification of these wastes may be performed with B-free fluxes (Lifanov *et al.* 1998, 2003). To vitrify Russian B-free institutional or channel fast-neutron reactor wastes, however, B-containing fluxes are required. Naturally occurring datolite, $CaBSiO_4(OH)$, is commercially available in Russia and has been proposed as a B source, whereas sandstone, loam clay, and bentonite have been chosen as glass-forming additives. The resulting materials are Na-Ca-borosilicate or B-free Na-aluminosilicate glasses (Sobolev *et al.* 1995a; Lifanov *et al.* 2003). The properties of these glasses are largely determined by the base oxides forming the matrix glass, because the radionuclide contents in LILW are at the level of 10^{-2}–10^{-5} wt% and they cannot affect the structure and properties of the glass. The major radioactivity in the LILW is due to β–γ-emitting $^{134,137}Cs$ and ^{90}Sr. Their leach rates (28-d IAEA test at 20 °C) from the glasses are 10^{-1}–10^{-2} g·m^{-2}·d^{-1}. Gamma-irradiation to a dose of 10^5 Gy (such a dose will be accumulated by solidified LILW during storage for ∼300 y) caused only formation of point defects and ion radicals and did not affect the leach rate of radionuclides. Because these glasses are produced by electric melting, viscosity and electric resistivity are important parameters. They were found to be 4–7 Pa·s and 0.03–0.05 Ω·m, respectively (Dmitriev & Stefanovsky 2000).

Phosphate glasses

Development of phosphate-based glasses for HLW processing started in the early 1960s (Clark & Godbee 1963; Hatch *et al.* 1963). The main advantages of these glasses include low melting temperature (<1000 °C) and high solubilities of sulphates, chromates, molybdates, F, Cl, I, and oxides of multivalent elements, including ACT (Clark & Godbee 1963; Hatch *et al.* 1963; Brezhneva *et al.* 1976; Nikiforov *et al.* 1985; Stefanovsky *et al.* 1995; Vashman & Polyakov 1997; Badyal *et al.* 1999; Fujihara *et al.* 1999; Matyunin 1995, 2000). Phosphate melts, however, are extremely corrosive, requiring platinum pot lining to be produced, and the resulting phosphate-based glasses are more easily devitrified and have a lower chemical durability under hydrothermal conditions than borosilicate glasses (Brezhneva *et al.* 1976; Mukhamet-Galeyev *et al.* 1995).

The Russian *Na–aluminophosphate glass* contains mainly alkali oxides, Al_2O_3 and other oxides of the Fe group, P_2O_5, and up to 10 wt% other waste oxides including FPs and ACTs (Table 1). Leach rates determined by the IAEA procedure at room temperature for 7 d are $\sim 10^{-2}\,g \cdot m^{-2} \cdot d^{-1}$ for Na, Cs, and Sr, and $\sim 10^{-3}\,g \cdot m^{-2} \cdot d^{-1}$ for Pu. Glass annealing at 450 °C increases the Na leach rate by approximately two orders of magnitude due to crystallization of Na-phosphates and aluminophosphates with low chemical resistance. Gamma-irradiation of the glass to a dose of 10^8 Gy increases its surface damage depth from ~ 5 nm to ~ 100 nm after 10 min of water contact. The Na leach rate changes insignificantly with dose. ACT-doped glass demonstrated no crystallization or liquid–liquid phase separation at a dose of 2×10^{24} α-decays/m^3 ($\sim 8 \times 10^{17}$ α-decays/g). Physical properties of this glass are given in Table 2 (Vashman & Polyakov 1997).

Lead–iron phosphate (LIP) glass was proposed for immobilization of HLW with high Fe contents. The composition of the base glass corresponds to $Pb(PO_3)_2$ doped with 9 wt% Fe_2O_3. This glass may be prepared and poured at ~ 800 °C, and is very resistant to devitrification. The structure of this glass consists of polyphosphate chains cross-linked by octahedrally coordinated Fe^{3+} ions with a Fe–O distance of 0.19 nm. The coordination number of Pb^{2+} is 8 or 9, and the polyhedra are considerably disordered with an average Pb–O distance of 0.24 nm. Such a structure strengthens the polyphosphate network, thereby blocking the percolation of Pb and hydronium ions so that the chemical resistance of the overall structure in aqueous solutions is increased, leading to very high chemical durability. The net release of all elements from LIP glass loaded with commercial HLW is between 100 and 1000 times less than the corresponding release from the borosilicate glass PNL 76-68. For example, Cs, Sr, and U leach rates at 90 °C (MCC-1 test, 30 d) from the LIP glass loaded with defence HLW are <0.02, <0.02, and $<0.001\,g \cdot m^{-2} \cdot d^{-1}$, respectively, whereas the corresponding values for the PNL 76-68 glass are ~ 1.0, 0.04, and $0.1\,g \cdot m^{-2} \cdot d^{-1}$. The LIP glass has a higher density ($4.9 \pm 0.2\,g/cm^3$) due to the high PbO content than both Na–aluminophosphate and borosilicate glasses, thus increasing the waste volume reduction factor. The LIP glass seems to be preferable for immobilization of defence HLW, because the HLW loading of 16 wt% is much higher than the 6.5 wt% in commercial HLW (Sales & Boatner 1988).

Production technology

Silicate glasses. Borosilicate glass has been used in France for conditioning of actual HLW since 1969. The currently implemented process at La Hague, the so-called two-step AVM process, uses a horizontal rotary calciner and an induction-heated metallic melter. The process has been in active operation since June 1978, and 8250 canisters of fully active glass have been produced so far (Masson *et al.* 1999; Petitjean *et al.* 2002). Currently, replacement of the induction-heated metallic melter by a cold-crucible melter is being considered (Petitjean *et al.* 2002). In the USA, the Department of Energy (DOE) recommended borosilicate glass as waste form for HLW in 1979 (Hench *et al.* 1984; Hamel *et al.* 1998). In March 1996, the Defence Waste Processing Facility began radioactive operations using a single-step vitrification process with slurry feeding into a Joule-heated ceramic melter (Marra *et al.* 1999). The West Valley Demonstration Project began production of borosilicate glass in June 1996 using the same process (Palmer & Misercola 2003). Borosilicate glasses are also considered as a primary HLW form in the United Kingdom, Germany, Belgium, Italy, Japan, and Korea (Lutze 1988). In Russia, immobilization of HLW in borosilicate glass has been suggested for implementation at the RT-2 plant of Krasnoyarsk Mining and Chemical Combine, Siberia (Aloy *et al.* 1998; Borisov *et al.* 2001), but the glass composition has not yet been chosen.

Vitrification of LILW is currently considered as a prospective process for waste dispositioning in various countries, including the USA (Whitehouse *et al.* 1995), whereby both borosilicate and B-free aluminosilicate glasses have been suggested. The Russian method of LILW vitrification is based on the inductive cold-crucible melting (ICCM) technology, developed at SIA Radon since the mid-1980s (Sobolev *et al.* 1995a,b). The full-scale vitrification plant with three cold crucibles and a total glass productivity of ~ 75 kg/h was put into active operation in 1998, producing borosilicate glass with a waste loading of 30–35 wt% LILW. Liquid waste is concentrated in a rotary film evaporator to a salt concentration of 1000–1100 g/L. This concentrate is mixed with datolite, bentonite, and sandstone to form a paste with a moisture content of 20–25 wt%, which is then fed into the cold crucibles. The molten glass is poured into 10 L containers, annealed in a tunnel furnace, and sent to a near-surface repository (Sobolev *et al.* 1995a, b). The stored glass is periodically sampled and

Table 2. *Comparison of properties of various HLW forms*

Properties	Borosilicate glass PNL 76–68	Russian Na-aluminophosphate glass	Synroc-C
Density, g/cm^3	2.6	2.5	4.35
Thermal conductivity, $W/(m\ K)$	1.1	0.7–1.5	2.1
Linear expansion coefficient, $1/K$	8.1×10^{-6}	$(8-10) \times 10^{-6}$	10.5×10^{-6}
Specific heat capacity, $J/(g\ K)$	0.9	0.9–1.0	0.55
Glass transition temperature, K	725–775	700	–
Viscosity, Pa s (T, K)	5–20 (1375–1425)	3–7 (1125–1175)	0.5–1 (1550–1600)
Electric resistivity, Ω cm (T, K)	0.8–0.9 (1375–1425)	0.3–0.4 (1125–1175)	0.1–0.2 (1550–1600)
Flexural strength, MPa	68–74	40–46	110
Compressive strength, MPa	200–400	90–130	793
Young's modulus, GPa	82	54	134–203
Fracture toughness, MPa m$^{-0.5}$	0.77	–	1.83
Poisson's ratio	0.22	–	0.30
Microhardness	7.2	–	8.4
Leach rates, $g/(m^2\ day)$,*			
mass	0.42	–	0.005
Al	~0.01	–	<0.01
B	1.12	–	–
Ba	–	–	0.036
Ca	0.068	–	0.0065
Cs	1.03	0.35	0.033
Mo	1.40	–	0.12
Na	1.32	0.59	<0.2
Si	0.73	–	–
Sr	0.075	0.05	0.010
Ti	–	–	$<5 \times 10^{-5}$
Zr	–	–	$<6 \times 10^{-4}$
REE	0.01–0.05	$<10^{-3}$	$10^{-4}-10^{-3}$
ACT	0.01–0.05	–	$2 \times 10^{-5}-5 \times 10^{-4}$
References	Ringwood *et al.* 1988	Vashman & Polyakov 1997	Ringwood *et al.* 1988

*determined by MCC-1 test (90 °C. 7 d. deionized water)

examined with respect to occurrence of crystalline phases and surface alteration. Long-term studies (up to 15 y) revealed a high chemical durability of the stored glasses (Sobolev *et al.* 1996).

The transportable vitrification system (TVS), operated in the USA, uses a Joule-heated ceramic melter (Whitehouse *et al.* 1995), which has been proposed for installation in other countries as well. However, a cold-crucible melter has also been considered for waste treatment in the USA, Italy, and Korea (Jouan *et al.* 1998).

Phosphate glasses. Currently, Na–aluminophosphate glass is produced in a Joule-heated ceramic melter at the RT-1 plant of Production Association 'Mayak', Ural region, Russia. This plant has a waste capacity of up to 500 L/h, and by the end of 1995, the plant has treated 1974 t of HLW, or 2.4676×10^8 Ci (Glagolenko *et al.* 1996; Vashman & Polyakov 1997). The production of LIP glass is not yet implemented.

Ceramics

Single-phase ceramics

The hosts for ACT and REE immobilization are phases with a fluorite-derived structure (cubic zirconia-based solid solutions, pyrochlore, zirconolite, murataite), and zircon. The REEs and minor ACTs may be incorporated in perovskite, monazite, apatite–britholite, and titanite. Perovskite and titanite are also hosts for Sr, whereas hollandite is a host phase for Cs and corrosion products. None of these ceramics is truly a single-phase material, and other phases such as silicates (pyroxene, nepheline, plagioclase), oxides (spinel, hibonite/loveringite, crichtonite), or phosphates may be present and incorporate some radionuclides and process contaminants. A brief description of the most important phases suitable for immobilization of ACTs and REEs is given below.

Pyrochlore, $^{VIII}A_2{}^{VI}B_2{}^{IV}X_6{}^{IV}Y$ ($Fd3m$, $Z = 8$) has a fluorite-derived structure, in which the A sites are occupied with large cations (Na, Ca, REE, ACT), and the B sites with lower-radius and higher-valence cations (Nb, Ta, Ti, Zr). Oxygen ions enter the X sites, and the Y sites are filled with additional ions or remain vacant.

The effect of α-decay on the pyrochlore structure $Gd_2Ti_2O_7$ doped with ^{244}Cm has been investigated in detail (Weber *et al.* 1998). The material was completely amorphized at a dose of 3.1×10^{18} α-decays/g. Amorphization is accompanied by volume expansion and increase of dissolution rate (by approximately a factor of

2.5), but leach rates of Gd and Cm may increase by factors of 20–50 due to incongruent dissolution. Samples of pyrochlore ceramic doped with 8.7 wt% ^{238}Pu and composed of mainly pyrochlore and minor brannerite (UTi_2O_6), rutile, and a fluorite-structure phase ($(Pu,U)O_2$) were kept for 6 months, and the volume expansion was found to be 1.2–1.6%. Most of the X-ray diffraction peaks have disappeared at a dose of 8.8×10^{17} α-decays/g. Another pyrochlore-based sample doped with ^{238}Pu has been amorphized at a similar dose of about 1×10^{18} α-decays/g, and the dissolution rate in water remains low (~ 0.04 g/m²; Strachan *et al.* 2002).

Natural pyrochlores have been systematically studied as analogues of ACT host phases (Lumpkin *et al.* 1994, 1999, 2001). They were rendered amorphous at doses of 0.7–17 dpa, whereas synthetic samples became metamict at a significantly lower dose (0.3 dpa). Such a difference in irradiation doses causing complete structure disordering of natural and synthetic samples is due to radiation annealing of the lattice defects in minerals over geological time periods. This process is facilitated at elevated T, for example, due to metamorphism or natural geothermal gradients (Lumpkin *et al.* 1999).

The radiation resistance of the pyrochlore-structure phases has also been studied by ion irradiation (Smith *et al.* 1998; Weber & Ewing 2002; Chen *et al.* 2002; Lian 2002*b*). In all cases, the critical amorphization dose increases with T and with increasing Zr substitution for Ti in the series $Gd_2Ti_{2-x}Zr_xO_7$. Pyrochlores with $x \geq 1.8$ were not amorphized, even at 25 K. For example, $Gd_2Zr_2O_7$ is radiation resistant to a 1 MeV Kr^+ ion irradiation at 25 K at doses of up to 5 dpa. The radiation resistance of $A_2Zr_2O_7$ (A = La, Nd, Sm, Gd) increases with decreasing A-site cation radius, that is, from La^{3+} to Gd^{3+}. $La_2Zr_2O_7$ is the only zirconate pyrochlore that can be amorphized by ion-beam irradiation, and the critical amorphization temperature for $La_2Zr_2O_7$ irradiated by 1.5 MeV Xe^+ is ~ 310 K (Chen *et al.* 2002). For a recent review on pyrochlore as a nuclear waste form for the immobilization of Pu, the reader is referred to Ewing *et al.* (2004).

Zirconolite, ideally $CaZrTi_2O_7$, incorporates ACTs and REEs by the isomorphic substitutions: $Ca^{2+} + Ti^{4+} = (ACT,REE)^{3+} + Me^{3+}$ (Me = Al, Fe, Cr); $Ca^{2+} + Zr^{4+} = 2$ $(ACT,REE)^{3+}$; $Ca^{2+} + Ti^{4+} = ACT^{4+} + Me^{2+}$ (Me = Mg, Fe, Co, Mn); $Zr^{4+} + Ti^{4+} = (ACT,REE)^{3+} + Me^{5+}$ (Me = V, Nb, Ta); and $Zr^{4+} = ACT^{4+}$ (Gieré *et al.* 1998). There are several zirconolite poly-

types with monoclinic (2M, 4M), trigonal (3T, 6T), and orthorhombic (3O) symmetry (Mazzi & Munno 1983; White 1984; Bayliss *et al.* 1989; Smith & Lumpkin 1993; Coelho *et al.* 1997; Begg *et al.* 2001). Both natural and synthetic zirconolites are leach-resistant, and even meta-mict samples with accumulated doses up to $\sim 10^{19}$ α-decays/g (~ 2 dpa) retain U and Th and their daughter products in the structure (Ringwood *et al.* 1988). Elemental release rates from zirconolite-based ceramics (7-d MCC-1 test, 90 °C) were found to be (in $g \cdot m^{-2} \cdot d^{-1}$): 10^{-1}–10^{-2} for Ca, 10^{-3}–10^{-4} for Nd, 10^{-4}–10^{-5} for U and Pu, 10^{-2} for Al, 10^{-6} for Ti, and 10^{-7} for Zr (Vance *et al.* 1995, 1996*a*; Hart *et al.* 2000). Zirconolite also exhibits exceptional corrosion resistance below 250 °C in various acidic and basic fluids over a wide range of pH. Between 250 and 500 °C, zirconolite is subject to partial corrosion in acidic and basic media, and significant corrosion occurs only above 500 °C (Gieré *et al.* 2001).

The radiation resistance of zirconolite has been tested with ^{238}Pu- and ^{244}Cm-doped and ion-irradiated samples (Weber *et al.* 1998; Weber & Ewing 2002). Amorphization of zirconolite occurred at doses corresponding to ~ 0.3–0.5 dpa at room temperature. Dose–age relationships have been determined by analytical transmission electron microscopy for the onset dose and critical amorphization dose of a suite of natural zirconolites (Lumpkin *et al.* 1994, 1998*b*).

Cubic fluorite-structure (Fm3m) zirconia-based solid solution, $(Zr,ACT,REE)O_{2-x}$, exhibits significant compositional flexibility to incorporate high concentrations of Pu, neutron absorbers, and impurities contained in Pu-bearing wastes (Gong *et al.* 1999). The phase has excellent radiation stability. No amorphization was observed under ion irradiation at room temperature to a dose corresponding to 200 dpa, and at 20 K to a dose of 25 dpa. Irradiation with I^+ and Sr^+ up to 300 dpa produced defect clusters in Y-stabilized zirconia, but did not cause amorphization. Amorphization

was achieved only after irradiation with Cs^+ at room temperature to a dose of 1×10^{21} ions/m^2, or 330 dpa (Wang *et al.* 2001).

Murataite, a cubic phase with a fluorite-related structure (*F43m* or *F432* or *F3m*), exhibits wide compositional variation, and thus its exact formula is not established yet; the recently suggested formula is $^{VIII}A_3\,^{VI}B_6\,^{V}C_2O_{22-x}$ (Urusov *et al.* 2002). The natural variety has a structure characterized by a three-fold elementary fluorite unit cell with $a = 1.4863$ nm (Adams *et al.* 1974) or 1.4886 nm (Ercit & Hawthorne 1995), whereas the synthetic analogue has a unit-cell parameter of $a = 1.4576$ nm. Murataite has been found in Synroc-type ceramic containing simulated Russian HLW and produced by ICCM (Sobolev *et al.* 1997*c*); here, the murataite content was only ~ 5 vol%, but the phase accumulated about 40 wt% of the total U introduced. Several murataite polytypes with three- (3C), five- (5C), seven- (7C), and eightfold (8C) elementary fluorite unit cells (Fig. 2) were observed (Stefanovsky *et al.* 1999; Yudintsev *et al.* 2001; Kirjanova *et al.* 2002). Murataite exhibits very high chemical durability, with U and Pu leach rates of 10^{-6}–10^{-7} $g \cdot m^{-2} \cdot d^{-1}$ (Yudintsev *et al.* 2001). A special feature of the murataite-5C variety is a zoned distribution of waste elements, whereby the highest ACT concentration occurs in the core of the grains (Fig. 3, Table 3). In addition to the high leach resistance, a major advantage of murataite is its capability to simultaneously incorporate ACTs, REEs, corrosion products and some process contaminants (Na) in its structure. Therefore, it is a very promising host for immobilization of the ACT-REE fraction of partitioned HLW and ACT-bearing wastes with complex composition. The radiation resistance of murataite is comparable with that of pyrochlore: the critical amorphization dose under 1 MeV Kr^+ ion irradiation was found to be 1.82–1.85×10^{18} ions/m^2 (0.14–0.15 dpa), corresponding to $\sim 3 \times 10^{18}$ α-decays/g (Lian *et al.* 2002*a*).
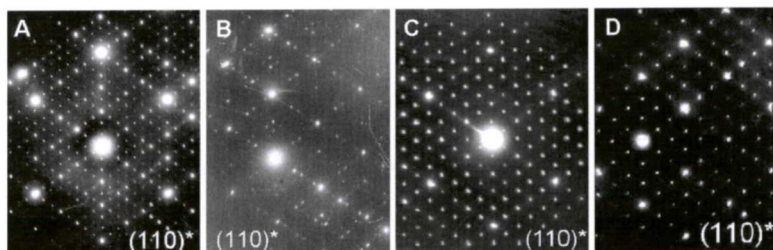

Fig. 2. Selected area electron diffraction patterns of the murataite varieties with (A) eight-, (B) seven-, (C) five-, and (D) threefold elementary fluorite unit cells.
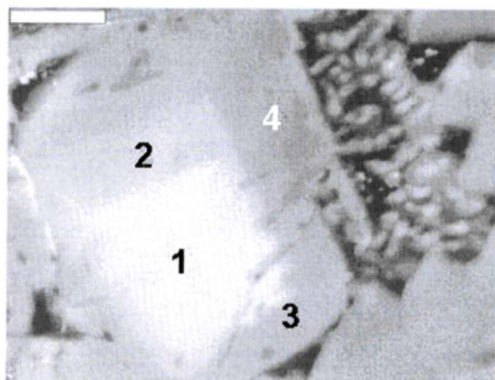
Fig. 3. Backscattered electron image of a zoned murataite-5C crystal in a Synroc-type ceramic containing 20 wt% HLW surrogate produced by ICCM at SIA Radon (Sobolev *et al.* 1997c). Scale bar: 5 μm. Numbers mark locations of analyses listed in Table 3. ACT concentrations in the core are approximately 10–20 times higher than at the edge.

Perovskite, $CaTiO_3$ (*Pnma*), may incorporate Sr instead of Ca, and trivalent ACT and REE and Fe-group elements via the substitution $Ca^{2+} + Ti^{4+} = REE^{3+} + Me^{3+}$ (Me = Al, Fe). Limited incorporation of tetravalent ACTs in the Ca site is also possible, whereby the solid solubility limit for tetravalent U and Pu is 0.01–0.1 atoms per formula unit (Vance *et al.* 2000). On the other hand, the trivalent REEs are capable of replacing Ca completely, thus forming a continuous solid solution, for example $CaTiO_3$–$GdAlO_3$ (Vance *et al.* 1996c). Trivalent Pu and Cm can also substitute for Ca. Perovskite is more leachable than zirconolite and pyrochlore (Ringwood *et al.* 1988).

Table 3. *Chemical composition of zoned murataite crystal (analysis spots shown in Fig. 3)*

wt%	1	2	3	4
Al_2O_3	0.8	1.6	3.7	2.8
SiO_2	0.2	0.5	0.2	0.3
K_2O	0.1	0.3	0.7	0.1
CaO	15.6	16.5	13.0	15.9
TiO_2	54.8	56.5	62.9	65.9
Cr_2O_3	0.3	–	0.2	–
MnO	3.6	4.1	5.7	5.6
FeO	0.2	–	0.1	–
NiO	0.2	–	–	0.2
ZrO_2	5.7	6.0	3.8	4.3
BaO	–	3.4	3.7	–
Ce_2O_3	6.0	2.9	2.7	3.7
UO_2	11.9	7.0	2.0	0.8
Total	99.4	98.8	98.7	99.6

Leach rates of ^{90}Sr, ^{147}Pm, ^{238}Pu, and ^{241}Am from perovskite ceramics are approximately $10^{-4}\ g \cdot m^{-2} \cdot d^{-1}$, whereas the leach rate of ^{238}U is higher by about two orders of magnitude.

Natural perovskites are normally crystalline; no traces of amorphization were found in samples with accumulated doses of up to 2.6×10^{18} α-decays/g. Significant damage was observed in perovskite containing ~6 wt% ThO_2 and with an accumulated dose of ~1×10^{19} α-decays/g (Lumpkin *et al.* 1998a). Perovskite was amorphized after irradiation with 1.5 MeV Kr^+ ions to a dose of ~1.8×10^{19} ions/m^2. The critical amorphization dose for perovskite is higher than for zirconolite by a factor of 2–4 (Smith *et al.* 1998).

Hollandite is one of the major Synroc phases incorporating Cs and corrosion products (Fe-group elements). Its generalized formula is $A_xB_yC_{8-y}O_{16}$, where $x \leq 2$. The A sites are occupied by large mono- or divalent cations (Na^+, K^+, Rb^+, Cs^+, Sr^{2+}, Ba^{2+}, Pb^{2+}), and various cations with a charge of +2 to +5 enter the B and C sites. Incorporation of Cs and Ba in hollandite is achieved under reducing conditions, thus suppressing formation of Cs and Ba molybdates and pertechnates, because Mo and Tc are reduced to their metallic state and form a separate phase, that is, a metal alloy (Ringwood *et al.* 1988).

Hollandite does not contain long-lived ACTs and, therefore, it is undergoing β–γ-irradiation from fission and corrosion products, but in multiphase ceramics it can also be α-irradiated from neighbouring ACT-bearing phases. Irradiation by α-particles from external $^{238}PuO_2$ sources and heavy ions results in a volume expansion of 2–2.5% and transformation of tetragonal to monoclinic symmetry.

Zircon, $ZrSiO_4$ ($I4_1amd$, $Z = 4$), has been suggested as a promising host for ACTs (Ewing *et al.* 1995). Specific interest in zircon was enhanced by its occurrence in the Chernobyl lavas as an important ACT host phase (Ewing *et al.* 1995). However, later studies showed that the isomorphic capacity of zircon with respect to REEs and ACTs is very limited. The solubilities of $USiO_4$ and $ThSiO_4$ in zircon do not exceed 6 and 3 mol%, respectively (Ushakov 1998). Nevertheless, the radiation effects in zircon have been studied in detail using ^{238}Pu doping, heavy ion irradiation, and natural analogue studies (Ewing *et al.* 1995; Ewing 1999; Weber *et al.* 1998). The critical amorphization dose has been found to be >8×10^{18} α-decays/g.

Investigation of nuclide release from zircon with various U and Th contents as a function of α-dose showed that within a dose range of 10^{19}

to 10^{21} α-decays/g, the leach rate increased from 2.9×10^{-4} to 2.3×10^{-3} g·m^{-2}·d^{-1}. For fully metamict zircon, the leach rate was $<1.8 \times 10^{-2}$ g·m^{-2}·d^{-1}. Alpha-decay damage in zircon causes an increase in the unit-cell volume and in the total macroscopic swelling. The value of total macroscopic swelling at saturation was measured to be 16.6% and 18.4% for Pu-doped and natural zircons, respectively (Ewing et al. 1995).

Titanite, CaTiSiO$_5$ (C2/c), may incorporate Na$^+$, REE^{3+} and minor ACT in the Ca site, and Fe^{3+}, Al^{3+}, Nb^{5+} in the Ti site. The ThO$_2$ content of natural titanite may reach 0.28 wt% (Hayward 1988). Measured isomorphic capacities of titanite with respect to U^{4+}, Pu^{4+}, Pu^{3+}, Hf^{4+}, and Gd^{3+} are (in atoms per formula unit): 0.02–0.05 (Vance et al. 2000) or 0.07 (Stefanovsky et al. 2000b); 0.02; 0.05; 0.5; 0.3 (Vance et al. 2000) or 0.25 (Stefanovsky et al. 2000b), respectively. Due to limited solubility of ACTs and REEs in the structure, titanite is preferably considered as a host phase for these elements when their content is low, such as in titanite-based glass–ceramics developed for Canadian waste (Hayward 1988).

The radiation resistance of titanite was estimated both by the study of natural samples and by ion irradiation (Hayward 1988; Weber et al. 1998). Synthetic titanite irradiated with Ar$^+$ to a dose equivalent to 7×10^{18} α-decays/g was rendered completely amorphous, consistent with data for natural analogues (5×10^{18} alpha-decays/g).

Garnet-structure phases (Ia3d, Z = 8) with the general formula ^{VIII}A$_3$^{VI}B$_2$[XO$_4$]$_3$, where X = Si, Al, Fe, Ge, V, have also been proposed as host matrices. Natural silicate garnets contain small amounts of ACTs and REEs (typically <0.1 and <4 wt%, respectively; Minerals 1967). However, it is possible to produce garnet-structure aluminates and ferrates with high ACT and REE contents: the highest ThO$_2$, UO$_2$, and PuO$_2$ contents (16–20 wt%) were achieved in Gd–Zr–Fe garnet. An increase of the Gd content reduces the U content to 3–6 wt%, because both elements occupy the B sites in the garnet structure, although unlike Gd, U may also enter the A sites (Yudintsev 2001). Both silicate- and ferrite-aluminate garnets are susceptible to amorphization induced by ion irradiation below 1000 K: at room temperature, they have similar critical amorphization doses of about 0.2 dpa. The Si-free Ca–U–Zr–Fe–Al garnet (20.5 wt% UO$_2$) demonstrated the high-est radiation resistance, and its critical amorph-ization temperature was 890 K (Utsunomiya et al. 2002).

Phosphates and silicophosphates, such as apatite, Ca$_5$(PO$_4$,SO$_4$)$_3$(F,Cl,OH), and britholite, Ca$_{4-x}$(REE,ACT)$_{6+x}$(SiO$_4$)$_{6-y}$(PO$_4$)$_y$O$_2$, as well as monazite, REEPO$_4$, and kosnarite, NaZr$_2$(PO$_4$)$_3$, may be also considered as matrices for immobilization of various waste elements (Roy et al. 1982; Boatner & Sales 1988; Kryukova et al. 1991; Sheetz et al. 1994; Ewing et al. 1995; Wronkiewicz et al. 1996; Hawkins et al. 1997; Carpena et al. 1998; Aloy et al. 2002; Boatner 2002). Naturally occurring apatites contain limited amounts of ACTs (0.02 wt% U, 0.9 wt% Th; Heinrich 1958), but synthetic britholites may incorporate trivalent REEs and ACTs in significant concentrations. Synthetic britholite has been amorphized after 1.5 MeV Kr$^+$ irradiation at room temperature to a dose of 0.4 dpa. This phase may also be amorphized as a result of α-irradiation of incorporated ^{244}Cm (Weber et al. 1998).

Monazite is a mixed lanthanide orthophosphate proposed as a host phase for ACTs and REEs. Natural monazite contains <27 wt% UO$_2$ + ThO$_2$ and remains crystalline in spite of high accumulated α-doses (Boatner & Sales 1988; Weber et al. 1998). However, 1.5 MeV Kr$^+$ irradiation amorphizes monazite at a dose of 2.56×10^{18} ions/m^2 (Meldrum et al. 1996). Even fully amorphized monazite demonstrated low leachability, and the leach rate remained at the same level as that of unirradiated samples (Sales & Boatner 1988; Weber et al. 1998).

Multiphase ceramics

Synroc. Synroc is a titanate ceramic consisting of primarily zirconolite, hollandite, and perovskite, and of minor amounts of rutile, Magneli phases, hibonite/loveringite, metallic alloys, and phosphates. One variety of Synroc, Synroc-C, contains 20 wt% waste oxides from commercial power reactors, 57.0 wt% TiO$_2$, 5.4 wt% ZrO$_2$, 4.3 wt% Al$_2$O$_3$, 4.4 wt% BaO, and 8.9 wt% CaO. It consists of ~30 wt% zirconolite, 30 wt% hollandite, 20 wt% perovskite, 15 wt% Ti oxides and Ca–Al titanates, and 5 wt% alloys and phosphates. Zirconolite is the major host for ACTs and a minor host for REEs, Sr and corrosion products (Fe-group elements), hollandite is the main host for Cs and Fe-group elements, and perovskite accommodates most of the Sr and REEs and some Fe-group elements and ACTs (Ringwood et al. 1988).

In addition to the conventional Synroc-C, other Synroc formulations were designed. The first Synroc variety, Synroc-A, contained the silicates kalsilite, leucite and celsian, and was

produced via melting/crystallization. Synroc-D was specifically designed to immobilize the defence HLW at the Savanna River Site; because these wastes contain large amounts of process contaminants (Fe, Al, Mn, Ni, Si, Na), a special phase assemblage comprising zircono-lite ($\sim$16 wt%), perovskite ($\sim$11 wt%), spinel ($\sim$55 wt%), and nepheline ($\sim$18 wt%) was designed (Hench *et al.* 1984). Another variety, Synroc-E, consisted of Synroc-C incorporated in a rutile matrix. Synroc-F (for SNF) was distinctly different from the other Synroc varieties and was composed of major pyrochlore, perovskite, and uraninite, and minor hollandite (Ringwood *et al.* 1988).

All Synroc varieties, except for Synroc-A, were produced via the hot-pressing route. Production of these waste forms via melting, especially cold-crucible melting, resulted in formation of additional alkali and alkali earth molybdate phases, namely Cs and Ca molybdates (powellite) due to the oxidizing conditions during preparation (Knyazev *et al.* 1996). Other features of ICCM-produced Synroc ceramics are larger crystals and higher porosity and, as a result, lower density as compared to the hot-pressed samples (Fig. 4). In the late 1990s, Synroc–glass forms were suggested to accommodate complex radioactive waste (e.g., alkali-bearing waste from Hanford, USA), and conventional glass melting technology was utilized for their production (Vance *et al.* 1996*b*, *d*). Within the framework of the HLW partitioning concept, special Synroc formulations were developed in Australia (Hart *et al.* 1996) and Russia (Lashtchenova 1999); these varieties consist of major perovskite and hollandite, and minor Cs titanates, and were designed for immobilization of the Cs–Sr fraction of HLW.

Most of the detailed examinations were performed for the Synroc-C variety (Ringwood *et al.* 1988). Table 2 compares typical elemental leach rates (7-d MCC-1 test, 90 °C) from Synroc-C containing 10 wt% HLW calcine with those from borosilicate and aluminophosphate glasses, documenting that Synroc-C exhibits the lowest leach rates.

The high resistance of Synroc phases to α-decay damage was first recognized on the basis of estimates for natural zirconolites and perovskites, both containing substantial amounts of U and Th. The first quantitative evaluations of radiation stability were obtained from irradiation experiments of Synroc and its constituents with fast neutrons in a nuclear reactor. The specimens, produced by cold pressing and sintering and hot pressing, were irradiated to a dose corresponding to 0.7 dpa, or 8×10^{18} α-decays/g (recalculated), resulting in larger volume expansion for the cold-pressed and sintered specimen than for the hot-pressed one. Accelerated tests were also performed using a ^{238}Pu-doped material (2 wt% and 5 wt%). X-ray diffraction revealed that the Pu-doped zirconolite and perovskite phases were rendered amorphous after accumulation of a dose of 2.8×10^{18} α-decays/g ($\sim$0.37 dpa). Volume expansion was found to be 6–8% (Ringwood *et al.* 1988).

Other multiphase ceramics. Numerous multiphase ceramic formulations for conditioning of various wastes have been designed (Harker 1988). These so-called 'tailored ceramics' were developed for immobilization of complex defence wastes at the Savannah River Plant and Rockwell Hanford Operation (Harker 1988). Tailored ceramics include ACT and REE hosts (fluorite-structure solid solutions, zirconolite,
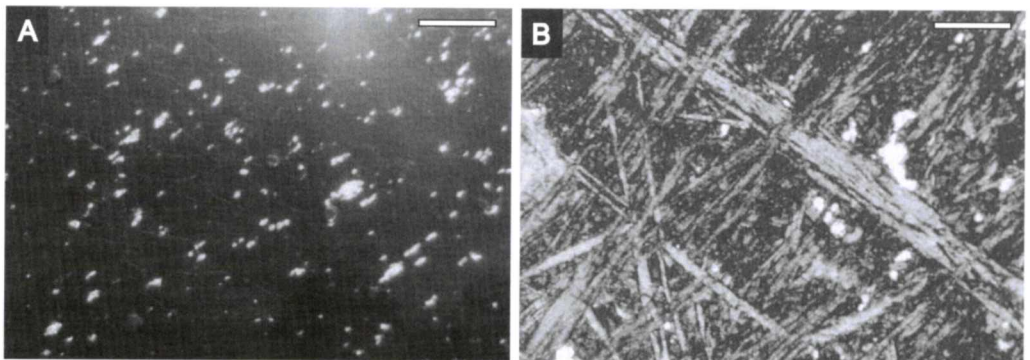

Fig. 4. Optical micrographs of (A) hot-pressed (at ANSTO) and (B) ICCM-produced (at SIA Radon) Synroc-C, loaded with 20 wt% HLW oxides. Scale bars: 500 μm (Sobolev *et al.* 1997*d*).

pyrochlore, perovskite, monazite, zircon), Sr and other alkaline earth hosts (magnetoplumbite, perovskite, hollandite), alkali hosts (nepheline, perovskite, interstitial glass), metal host phases (alloy), and non-FP host phases (spinel, corundum, rutile, pseudobrookite). Moreover, minor cubic murataite-type $(Zr(Ca,Mn)_2(Fe,Al)_4Ti_3O_{16})$ and loveringite-type $((Ca,Ce)(Ti,Fe,Cr,Mg)_{21}O_{38})$ phases were also found. The 'Supercalcine' composed of pollucite $(CsAlSi_2O_6)$, scheelite-structured Sr molybdate $(SrMoO_4)$, fluorite-structure solid solutions of REE $(REEO_2)$, and REE-rich apatite solid solution as well as zirconia (ZrO_2), corundum (Al_2O_3), spinel $(NiFe_2O_4)$, and various perovskites were designed to immobilize HLW from the PUREX (Pu–U-recovery–extraction) process.

In Russia, various polyphase ceramic compositions were developed in the late 1990s to immobilize the REE-ACT fraction of partitioned HLW. These ceramics are based on assemblages of perovskite, cubic oxide, pyrochlore, zirconolite, hibonite, loveringite, brannerite, and murataite (Stefanovsky *et al.* 1999, 2000a, 2001; Yudintsev *et al.* 1999, 2001). Moreover, it has been found that various garnet-containing assemblages (Burakov *et al.* 1999; Yudintsev 2001; Yudintsev *et al.* 2002) are promising matrices for ACTs, REEs, and Fe-group elements. The MCC-1 procedure revealed that leach rates were on the order of 10^{-5}–10^{-4} g·m^{-2}·d^{-1} for ACTs and REEs, and 10^{-4}–10^{-2} g·m^{-2}·d^{-1} for Fe-group elements. The lowest ACT leach rates were observed for murataite-containing ceramics (10^{-6}–10^{-5} g·m^{-2}·d^{-1}). The murataite (5C variety) grains exhibit ACT zoning (Fig. 3), with ACT concentrations in the core approximately 10–20 times higher than at the edge (Stefanovsky *et al.* 1999; Yudintsev *et al.* 2001). This zoning creates an additional barrier against leaching, but at the same time, it may cause a considerable problem by differential swelling due to α-decay damage (Chakoumakos *et al.* 1987). High radiation resistance of these ceramics has been confirmed by ion-irradiation tests up to a dose of 5×10^{18} ions/m^2 (Lian *et al.* 2002a; Utsonomiya *et al.* 2002).

Ceramic technologies

There are several possible technologies for production of ceramics, and all have been tested for inactive materials. The best-known technologies are based on high-T sintering of fine powders either under atmospheric pressure (cold pressing and sintering) or at high pressure (hot uniaxial or isostatic pressing). For example, the Synroc ceramics were produced by all three technologies; the hot uniaxial pressing in bellows, originally developed at the Australian Nuclear Science and Technology Organisation (ANSTO), was implemented as production technology at the Synroc demonstration plant. Synroc powder is heated to 1150–1200 °C and uniaxially pressed at 14–21 MPa into 'pancakes', which can be stacked on top of one another in the disposal canister. To improve product quality, a special precursor is prepared using wet milling or sol-gel techniques (Ringwood *et al.* 1988). The cold pressing and sintering technology was developed at the US Lawrence Livermore National Laboratory for immobilization of excess weapons Pu in pyrochlore- and zirconolite-based ceramics (Brummond & Armantrout 1998). This process involves mixing of Pu oxide and a neutron absorber (Gd_2O_3 or HfO_2) with ceramic additives (TiO_2, ZrO_2, CaO, Al_2O_3) and cold pressing of the powder at 14–21 MPa in 300 g pucks (~9 cm in diameter, ~1.6 cm thick, density = 2.37 g/cm^3, corresponding to 51% of the theoretical density), followed by heat treatment and a 4 h exposure to 1300 °C, and cooling for 14 h in a turned-off furnace. The final product (259 g pucks, diameter = 6.86 cm, thickness = 1.57 cm) has a density of 4.46 g/cm^3 (~95% of theoretical density).

Another technology for production of high-quality ceramics is based on the ICCM process. The cold crucible is a vessel fabricated from water-cooled Cu or stainless steel pipes, energized from a high-frequency generator operated within the range of ~200 kHz to ~13 MHz. The melt is heated by an electromagnetic field penetrating through the gaps between the crucible pipes. A special feature of the cold crucible is formation of an intermediate layer ('skull') between the melt and the cold-crucible pipes. This protects the cold-crucible walls from corrosion due to interaction with the melt and provides the following advantages relative to other melters: longer lifetime; higher achievable process temperature; no contact between melt, refractories and electrodes; smaller overall dimensions; and higher specific productivity because of the active hydrodynamic regime. The ICCM technology is currently being developed for the production of high-fusible glassy and ceramic waste forms in Russia (Sobolev *et al.* 1997a, b, c, 1998) and France (Jouan *et al.* 1996a, b). A number of polyphase ceramics based on zirconolite, pyrochlore, and murataite, as well as glass–ceramics have been produced by this method using laboratory- and bench-scale facilities and subsequently examined in detail.

An additional ceramic production method, developed mainly in Russia, is the self-sustaining

synthesis (SSS). This process is based on redox reactions in oxide–metal mixtures, where the oxidizer is the oxide of a multivalent element in its highest oxidation state (MoO_3, WO_3, Fe_2O_3), peroxide (CaO_2) or nitrate, and the reducing agent is metallic (Ti, Zr, Al). Inert components used to produce the ceramic matrix are Ca, Ti, Zr, or calcine. An exothermic reaction is initiated in a local zone of batch mixture and then the burning process is self-sustained up to the formation of the ceramic or glass–ceramic. The SSS procedure was applied to production of zirconolite- and pyrochlore-based ceramics, including Pu-doped, and the leach resistance of these ceramics was comparable to ceramics produced by the cold pressing and sintering methods (Postnikov *et al.* 2001; Glagovsky *et al.* 2001).

Glass–ceramics

A number of glass–crystalline materials (GCM) have been proposed for immobilization of HLW. They can be classified in two groups: those produced by spontaneous crystallization, and those formed by induced (catalytic) crystallization.

Spontaneously crystallized GCM are composed of a vitreous phase and an uncontrolled amount of one or more crystalline phases. These GCM are called 'mineral-like materials' in the Russian literature, and 'glassy slags' in the English literature. They are normally produced by the ICCM method (Vlasov *et al.* 1987; Demine *et al.* 2001; Matyunin 2000; Matyunin *et al.* 2001), but may also be produced by the SSS technology (Glagovsky *et al.* 2001; Postnikov *et al.* 2001). These materials are very similar to glassy slags produced by plasma melting (Dmitriev *et al.* 1995; Feng *et al.* 1997), and contain 10–40 wt% crystalline phases distributed in a glassy matrix.

The GCM produced by *induced crystallization*, mostly via nucleating agents, are actual glass–ceramics. These GCM are composed of a target crystalline phase, which is embedded in interstitial glass and which amounts to <80 vol% of the material. The glass–ceramics may be produced using well-developed glass melting technologies in Joule-heated ceramic or cold-crucible melters (Hayward 1988; Dmitriev & Stefanovsky 2000) as well as in plasma furnaces (Dmitriev *et al.* 1995; Feng *et al.* 1997). The melts must then be either slowly cooled under controlled conditions, or quenched glasses must be annealed for a certain time to induce crystallization.

Best studied among these GCM materials is the titanite glass–ceramic (originally known as sphene-based glass–ceramic) developed in Canada (Hayward 1988). It is composed of titanite as the major crystalline phase (other minor phases may be present) and interstitial Na–aluminosilicate glass. Importantly, thermodynamic calculations indicate that titanite is stable in the Ca–Na–Cl brines typically encountered in the Canadian shield. Furthermore, analyses of natural specimens indicate that the titanite structure is able to accommodate ACTs, REEs, Na, Mn, Sr, Ba in the Ca site, and Fe and other transition metals in the Ti site. Both crystalline and metamict natural titanites are chemically durable, and the interstitial aluminosilicate glass also appears to be chemically durable. The titanite glass–ceramic is produced by melting at 1300–1400 °C, followed by cooling and thermal treatment (annealing) at 950–1050 °C for 1 h or more to induce crystallization. The resulting titanite concentrates REEs and corrosion products, whereas Cs^+ and U^{6+} remain in the vitreous phase. The Sr^{2+} ions are equally partitioned between titanite and the glass. Leach rates of major waste elements (Cs, Sr, U, La) are intermediate between those of borosilicate glass and Synroc. This glass–ceramic demonstrated good radiation stability and strong mechanical integrity.

A number of other glass–ceramics have been developed in various countries (Hayward 1988). At the Hahn–Meitner Institute, Germany, precursor borosilicate glasses melted at 1100–1400 °C were devitrified through a controlled heat treatment (typically at 530–720 °C), producing glass–ceramics with the target phases celsian ($BaAl_2Si_2O_8$), eucryptite ($LiAlSiO_4$), spodumene ($LiAlSi_2O_6$), nepheline ($NaAlSiO_4$), perovskite ($CaTiO_3$), and diopside ($CaMgSi_2O_6$). To produce celsian glass–ceramics, precursor glasses were melted at 1175–1250 °C and then heat-treated in two stages, that is, at 600–650 °C (3 h) to create centres of crystallization, and at 800–850 °C (10–20 h) to crystallize the target phases (additional minor phases may be present). Leach rates of waste elements determined by the MCC-1 procedure were ~ 1 $g \cdot m^{-2} \cdot d^{-1}$. Irradiation with α-particles emitted from incorporated ^{239}Pu or ^{244}Cm increased the dissolution rate by 1–1.5 orders of magnitude due to radiation damage. Fresnoite ($Ba_2TiSi_2O_8$) glass–ceramics can be produced by melting at about 1200 °C and heat treatment at ~ 700 °C for nucleation, followed by heat treatment at 900–960 °C for crystallization of fresnoite and minor other phases.

Glass–ceramics based on natural or synthetic basalts, various zeolites, and apatite/britholite were also developed (Saidl & Ralkova 1966; Hayward 1988; Wronkiewicz *et al.* 1996; Sinkler

et al. 2000; Nakazawa *et al.* 2001; Zhao *et al.* 2001; Tolstova *et al.* 2002).

Numerous studies have also been performed on glass–ceramics containing various Synroc phases, mainly zirconolite (Hayward 1988; Vance *et al.* 1996c, d; O'Holleran *et al.* 1997; Advocat *et al.* 1998; Lashtchenova & Stefanovsky 1998a, b; Loiseau *et al.* 2001; McGlinn *et al.* 2001; Martin *et al.* 2002). The precursor glasses were produced at 1300–1500 °C followed by slow cooling (~5 °C/h) or additional heat treatment at 900–1000 °C to produce the target phases. Actinides and REEs, and some Sr are incorporated into zirconolite, and Cs and the remaining Sr into the vitreous phase. As a rule, leach rates of ACTs and REEs from zirconolite glass–ceramics are between 10^{-4} and 10^{-2} g·m^{-2}·d^{-1}, and they are lower by 2–3 orders of magnitude than the Cs leach rate. The problem of Cs leaching is absent when glass-ceramics are used to immobilize separated ACTs.

A number of GCMs were developed on the basis of various natural rocks and industrial wastes for conditioning of LILW, mixed, and hazardous wastes. Such materials can be produced by smelting of various liquid and solid radioactive wastes (Kupfer *et al.* 1976; Komatsu *et al.* 1981; Palmer *et al.* 1981; Nomura *et al.* 1985; Lebeau & Girod 1987; Stefanovsky *et al.* 1992; Dmitriev *et al.* 1995; Lashtchenova *et al.* 1997) and by '*in situ*' vitrification (Ewing 1988; Timmons & Thompson 1996; McGlinn *et al.* 1998; Hartmann 2000). All these materials have chemical durabilities comparable to those of HLW glasses.

Cement

Portland cement has been extensively used since the early 1960s to immobilize LLW in many countries (Sobolev & Khomtchik 1983; McDaniel & Delzer 1988; Dmitriev & Stefanovsky 2000). Portland cement has a chemical composition of 64–67 wt% CaO, 21–25 wt% SiO$_2$, 4–8 wt% Al$_2$O$_3$, and 2–4 wt% Fe$_2$O$_3$, but minor alkali, Mg, Ti oxides, sulphates and phosphates may also be present. Major phases in the cement clinker are 3CaO·SiO$_2$ (alite, 42–60 wt%), 2CaO·SiO$_2$ (belite, 15–35 wt%), 3CaO·Al$_2$O$_3$ (tricalcium aluminate, 5–14 wt%), and 4CaO· Al$_2$O$_3$·Fe$_2$O$_3$ (brownmillerite, <5 wt%). The cement clinker is characterized by three parameters (weight concentration ratios), which must be kept within the following ranges: hydraulic modulus $m = $ CaO/(SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$) = 1.9–2.4; silica modulus $n = $ SiO$_2$/(Al$_2$O$_3$ + Fe$_2$O$_3$) = 1.7–3.5; and alumina modulus $p = $ Al$_2$O$_3$/Fe$_2$O$_3$ = 1–3. The cement clinker is

mixed with water producing a grout. Mixing of dry clinker or grout and liquid and/or solid waste yields the cement waste form.

Currently, cement waste forms are used for immobilization of LLW and mixed wastes rather than HLW because of the low chemical and radiation resistance of the cement waste forms. The only exception is FUETAP (Formed Under Elevated Temperature And Pressure) concrete (McDaniel & Delzer 1988). Actual LLW normally contains NaNO$_3$ and other alkali salts, which compromise the properties of the final product as compared to those of waste-free cement. In particular, NaNO$_3$ retards the curing and reduces the mechanical integrity. An increase of the NaNO$_3$ concentration in LLW to 150 g/L reduces the compressive strength of the cement only insignificantly as compared to cement prepared with pure water (5–7 MPa). Higher NaNO$_3$ concentrations, however, result in strong reduction of the compressive strength (to <1 MPa). The appropriate waste:cement ratio is equal to 0.67 at an NaNO$_3$ concentration in LLW lower than 150 g/L. Leach rates of Cs and Sr from the cemented LLW as determined by the IAEA procedure (28 d, 20 °C) are relatively high at ~10^2 g·m^{-2}·d^{-1} (Sobolev & Khomtchik 1983).

Major advantages of cement waste forms include very simple production and relatively low cost of both clinker and cementation technology. At the same time, however, there are numerous disadvantages of the conventional cement waste forms and cementation technology. The major disadvantage is that the waste volume increases by 10–30% relative to the initial material. Other drawbacks are low chemical, radiation, and freeze resistance, low mechanical integrity, and microbiological degradation. As a result, a number of attempts have been made to modify cement compositions in order to improve the waste-form properties. Cements have been modified by addition of clays, sand, rutile, plasticizers, milled incinerator bottom ash, fly ash, and other waste products (McDaniel & Delzer 1988; Jiang *et al.* 1993; Peri 1996; Dmitriev *et al.* 1999). Other cement waste forms have been designed on a non-Portland cement basis (Cougar *et al.* 1996; Siemer *et al.* 1997; Dmitriev *et al.* 1999). The FUETAP concrete, for example, consists of about 22 wt% cement, 11 wt% fly ash, 7.5 wt% clay, 28 wt% sand, 15 wt% simulated waste solids, 15 wt% water, and 0.75 wt% NaNO$_3$. This material has a density of 2 g/cm^3, a compressive strength of 60–100 MPa, a thermal conductivity of 1 W·m^{-1}·K^{-1}, and a porosity of 22–26%. Leach rates for Cs, Sr, and Pu were 10^{-2}, 1,

and 10^{-4} g·m^{-2}·d^{-1}, respectively, and radiation stability was acceptable (McDaniel & Delzer 1988).

In Russia, extensive studies have been performed in regard to joint cementation of liquid and solid LLW, such as, incinerator ashes, contaminated soils, silts, and various other wastes accumulating through decommissioning of nuclear facilities (Sobolev & Khomtchik 1983; Dmitriev *et al.* 1999). The cementation process of radioactive silt (institutional or nuclear power plant waste) uses a fine-grained mixture of silt and/or ground CaO and Al$_2$O$_3$ additives, and dried radioactive waste salts. After heat treatment at 700–850 °C for 0.5–1 h, this material is transformed into a clinker with cement-like properties. After curing for 28 d, the cement exhibits a compressive strength of 20–35 MPa and a leach rate of 0.1–1 g·m^{-2}·d^{-1} (IAEA test, 20 °C), that is, lower by 2 to 3 orders of magnitude than for conventional cement waste forms (Dmitriev *et al.* 1999; Sobolev *et al.* 1999).

Cement is primarily considered as a matrix for LILW, and the main efforts are directed to improve the conventional cementation technology. One of the promising improvements is the application of high-energy mixers (e.g., inductive mixer with vortex layer) and vibration handling of the container during filling with high-penetrating cement grout (Sobolev *et al.* 1999).

Other waste forms

In addition to the waste forms described above, some other matrices for HLW and LILW were proposed. These include various recently developed composite materials, such as, glass composites (Sobolev *et al.* 1995*b*, 1997*b*); glass-encapsulated Ca-phosphate-based ceramics (Donald *et al.* 2002); glass-bonded sodalite (Esh *et al.* 1999; Pereira *et al.* 1999; Sinkler *et al.* 2000; Morss *et al.* 2000; Lambregts & Frank 2002; Jeong *et al.* 2002); apatite (Raicevic *et al.* 1999); silicotitanates (Nyman *et al.* 1999; Su *et al.* 1999); and complex Th-phosphates (Dacheux *et al.* 1999). Zeolites and zeolite-type compounds as well as phosphates were selected for immobilization of halogen-containing wastes due to their capability to accommodate halogens in their structure. Glass-bonded zeolites exhibit good radiation resistance to α-decay (Frank *et al.* 2002). Spent nuclear fuel can also be considered as a waste form (Johnson & Shoesmith 1988) as several countries show interest in direct disposal of SNF (for more details, see Buck *et al.*, 2004).

Recently, a new porous crystalline matrix ('Gubka') has been prepared on the basis of fly ash from power stations to incorporate complex ACT-containing wastes by means of repeated saturation–drying–calcining cycles. This matrix can accommodate up to ∼50 wt% nitrate salts (after drying) and ∼35 wt% calcine. The waste-loaded material can be consolidated by hot pressing with a 35% volume reduction (Aloy *et al.* 2000; Tranter *et al.* 2002).

Finally, a bitumen waste form should also be mentioned, as it has been widely applied for conditioning of LILW, particularly in Russia (Sobolev & Khomtchik 1983). The bituminization process is rather simple and consists of drying of the liquid waste, followed by mixing with molten bitumen. The bitumen waste form has many drawbacks, including: no waste volume reduction; fire danger; low chemical and radiation stability; low resistance to biodegradation; soil contamination with nitrates; however, bitumen as a waste form is still used in both Russia and Belgium. A recent study (Sobolev *et al.* 2000) has demonstrated that the bitumen waste form falls between the cement and glassy waste forms in terms of its chemical durability under near-surface repository conditions.

Outlook

To date, the most developed and commercially pursued HLW conditioning process is vitrification, which is implemented on a full-scale in the USA, France, and Russia. Borosilicate glasses are recognized to be more technologically and ecologically feasible as compared to phosphate-based glasses. Nevertheless, Russian HLW is vitrified at the Production Association 'Mayak' in the Ural region, yielding a Na–aluminophosphate glass, which is melted at lower temperature than borosilicate glass. Both borosilicate and aluminophosphate glasses are used for immobilization of non-partitioned HLW containing only traces of ACTs. To immobilize waste with a relatively high ACT content (e.g., ACT or REE-ACT fraction of HLW, whose separation is provided for by the HLW partitioning concept), glass is not a suitable matrix due to its thermodynamic instability and its insufficient chemical durability and radiation resistance. From this point of view, the ceramic materials are considered as an alternative to glass. The Synroc ceramic was designed for conditioning of non-partitioned HLW. Within the framework of the HLW partitioning concept, glass or special Synroc formulations may be used for immobilization of the short-lived Cs–Sr fraction, whereas crystalline waste

forms based on zirconolite, pyrochlore, or perovskite are suggested as hosts for ACTs and REEs of the long-lived ACT-REE fraction. Extensive research was also performed on incorporation of excess weapons Pu, and phases with fluorite-derived structures (zirconolite, pyrochlore, zirconia-based solid solution) were recognized as most promising. Combined glass–ceramic forms also have a certain potential to be applied for conditioning of complex HLW and ILW.

Low- and intermediate-level waste is currently converted to cement and bitumen waste forms, but the existing trend is toward an increase in the radiation safety levels and reliability of immobilization. From this point of view, LILW should also be incorporated in vitreous and crystalline matrices. Current Russian and US experience on vitrification of such waste demonstrates the potential of the melting/vitrification process. Major advantages of vitrification over bituminization and cementation are a greater waste volume reduction, higher productivity, and higher durability of the final product.

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