Materials Science of High-Level Nuclear Waste Immobilization

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Abstract

With the increasing demand for the development of nuclear power comes the responsibility to address the issue of waste, including the technical challenges of immobilizing high-level nuclear wastes in stable solid forms for interim storage or disposition in geologic repositories. The immobilization of high-level nuclear wastes has been an active area of research and development for over 50 years. Borosilicate glasses and complex ceramic composites have been developed to meet many technical challenges and current needs, although regulatory issues, which vary widely from country to country, have yet to be resolved. Cooperative international programs to develop advanced proliferation-resistant nuclear technologies to close the nuclear fuel cycle and increase the efficiency of nuclear energy production might create new separation waste streams that could demand new concepts and materials for nuclear waste immobilization. This article reviews the current state-of-the-art understanding regarding the materials science of glasses and ceramics for the immobilization of high-level nuclear waste and excess nuclear materials and discusses approaches to address new waste streams.

Introduction and Background

In countries such as the United States, Sweden, and Finland, commercial nuclear power generation currently employs the once-through fuel cycle, where nuclear fuel, composed mainly of enriched uranium dioxide or a uranium alloy, is irradiated to the limit of its power production usefulness during one cycle in a nuclear reactor. This spent nuclear fuel is then placed in interim storage, usually on the nuclear reactor site, but is intended for eventual disposition in a geologic repository. The worldwide use of nuclear power is expected to grow significantly to meet needs for future energy and decreased greenhouse gas emissions; however, such growth cannot sustain the once-through fuel cycle. The challenges of the growing demands for nuclear energy can be overcome by a closed nuclear fuel cycle in which the spent (i.e, irradiated) nuclear fuel is reprocessed, and the constituent radioactive elements are separated into waste streams to be either recycled back into nuclear fuel assemblies or immobilized in appropriate waste forms. The recycled nuclear fuel not only produces nuclear power, but it can also serve as a matrix for in-reactor transmutation, so-called nuclear "burning," of incorporated nuclear waste elements. This closed fuel cycle, as employed in France, can sustain the growth of nuclear power and can potentially greatly reduce the volume and activity of nuclear waste needing geologic disposal. The waste forms for such a closed nuclear fuel cycle are the subject of this article.

Although the basic principles of waste-form development for current waste streams are well understood, additional separations are planned in future advanced fuel cycles to minimize the volume and heat load of waste forms going into geologic disposal. The amount of separation and different waste streams have yet to be defined and will depend on type of nuclear fuel (oxide, nitride, or metal). Nonetheless, the baseline waste streams that might require a single global waste form or separate tailored waste forms are (1) the long-lived fission product ^{99}Tc (half-life of 2.1×10^5 years); (2) the principal heat-generating isotopes ^{137}Cs and ^{90}Sr (half-lives of 30.2 and 28.8 years, respectively); (3) lanthanides; (4) minor actinides (half-lives from 10 to 10^6 years); (5) the remaining fission products (half-lives from 1 to 10^7 years); (6) the volatile radionuclides ^{3}H, ^{129}I, ^{14}C, Xe, and Kr (half-lives from 10 to 10^7 years); and (7) the undissolved solids from fuel dissolution. The relative radioactivity from commercial nuclear reactor waste has been previously described in detail.[1] In addition, significant inventories of separated plutonium and minor actinides already exist,[2] and residual minor actinides will remain in inert matrix fuels or from other recycle processes. Fortunately, much of the research and development on new waste forms can be carried out using stable isotopes, rather than radioisotopes, except in the case of actinides, but even then, the use of surrogates, such as Ce, can often provide useful data and insights. The other exception is for self-radiation damage studies, where short-lived actinides and fission products might be utilized.

Considerable worldwide research has been conducted over the past 50 years on glass, ceramic, and novel waste forms for the immobilization of high-level waste (HLW) from the reprocessing of spent nuclear fuel from commercial nuclear power reactors or from government-operated plutonium production reactors,[3] as well as on immobilization of excess plutonium from weapons production.[4] This research has been largely directed at immobilizing existing HLW that consists of all of the liquid effluents from the reprocessing of commercial and defense spent nuclear fuel. With the advanced closed fuel cycle, several cycles of reprocessing and additional separations into different waste streams are envisioned. With the additional desire for high waste loadings, new waste forms tailored to specific waste streams and high loadings might be needed; in which case, past research experience on waste-form development and experience on industrial-scale vitrification should accelerate the development of new waste forms. In the United States, vitrifica-

tion of commercial HLW at West Valley (New York) has been completed; vitrification of defense HLW at Savannah River (Aiken, South Carolina) is in progress; and a vitrification plant is under construction for defense HLW at the Hanford site (Washington). In France, industrial-scale immobilization of commercial HLW into borosilicate glass is ongoing, as illustrated in Figure 1. In Russia, two full-scale vitrification plants are in operation, one for HLW, based on a Joule-heated ceramic melter, and the other for intermediate-level waste (ILW), such as the metal cladding in nuclear fuel rods, based on a cold crucible inductive melter. In Asia, Japan has probably the most mature program on HLW immobilization, with active pilot-scale borosilicate glass facilities at Tokai. India and China are carrying out some laboratory-scale research on waste forms. In Australia, the Synroc (or "synthetic rock") program has enjoyed international collaboration with the United Kingdom, the United States, Russia, Japan, and other countries since its initiation at the Australian National University in 1978.

Glass Waste Forms

Considerably more research and technology development has been conducted on glass waste forms than any other waste form over the past 50 years. This is because the amorphous and relatively disordered structures of glasses can incorporate a wide range of chemical elements.[5] Borosilicate compositions that include 30–40 different elements are used routinely for HLW glasses. Such compositions produce highly durable glasses. Most elements play one of three basic roles in glass structures: network formers, network modifiers, and intermediates. In borosilicate glass structures, the network is primarily formed of chains of borate and silicate polyhedra. Lithium, sodium, and calcium are typical network modifiers that create nonbridging oxygens or provide charge balance for some HLW elements. A commonality exists between the many different radioactive waste glass systems and the structural role components play in a glass. Compositionally, the glass-forming elements in HLW glasses constitute 60–85 wt% of the glass structure, network modifiers make up 0–25% of the glass, and the remaining 15–40 wt% consists of intermediates.[4]

Borosilicate glasses have been employed on an industrial scale to immobilize HLW from nuclear weapons programs and the reprocessing of spent fuel from commercial nuclear power plants in the United States, France, the United Kingdom,
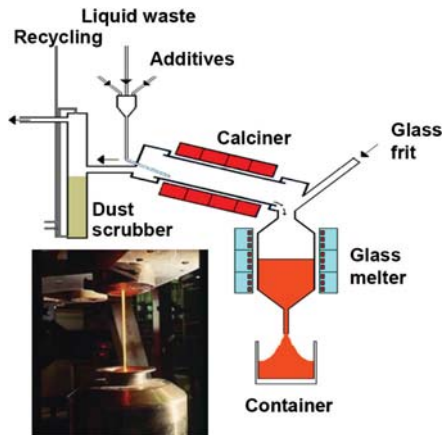

Figure 1. Schematic illustration of the French two-step calciner plus hot crucible vitrification process, with an actual pour shown in the inset (bottom left).

Belgium, Germany, and Japan.[6] In addition, considerable research has been conducted on the immobilization of existing excess plutonium and minor actinides in glasses,[4] which could address future waste streams containing both lanthanides and residual actinides. In Russia, borosilicate glasses are employed for the immobilization of ILW, whereas aluminophosphate glass is used for HLW immobilization.[7]

Ceramic Waste Forms

Borosilicate glasses have some disadvantages, notably the volatility of some HLW elements at the glass melting temperatures, which requires complex gas recovery systems, and the low solubility in glass of some important radionuclides, such as Tc and actinides. With a strong premium on repository and interim storage space worldwide, the higher waste loadings achievable by crystalline ceramic waste forms are advantageous for specific waste streams. In addition, mineral analogues for many ceramic waste forms provide evidence of long-term durability. The use of hot isostatic press (HIP) technology[8] suppresses volatile losses at the consolidation temperatures. Whereas throughput limitations were a disadvantage in the past, current designs are targeting throughputs of ~1,000 kg/day. The HIP technology can be applied to ceramics, glass ceramics, glasses, and simple consolidation of calcined powders.

In crystalline ceramic phases, radionuclides can be incorporated to occupy specific atomic positions in the periodic structures of constituent crystalline phases, which allows high loadings of

specific radionuclides. The coordination polyhedra in each phase impose specific size, charge, and bonding constraints on the radionuclides that can be incorporated into the structure. This means that ideal waste-form phases usually have relatively complex structure types, with a number of different coordination polyhedra of various sizes and shapes and with multiple substitutional schemes to allow for charge balance with radionuclide substitutions. Generally, the complexity of the HLW composition usually results in the formation of a polyphase assemblage, with unequal partitioning of radionuclides between the phases. In general, the polyphase assemblages are less sensitive to waste-stream compositions and waste loadings, which affect only the variations and abundance of the constituent phases. However, if certain elements are present that are not incorporated into existing phases, minor phases will form, including glass segregated along grain boundaries. Multiphase ceramic waste forms are compositionally tailored and processed to produce specific crystalline phases as hosts for the different radionuclides. Generally, fission products (such as Cs and Sr) are confined to one or more glass or crystalline phases, whereas the actinides (U, Np, Pu, Am, and Cm) partition into other crystalline phases. The earliest polyphase crystalline assemblage tailored specifically for the immobilization of HLW was supercalcine,[9] a silicate-based ceramic composed of highly durable mineral-like crystalline phases. Synroc and other related titanate-based ceramic waste forms have received the most attention.[10–14] Ideally, all waste-stream elements, both radioactive and nonradioactive, are important components in the phases formed. In some cases, single-phase ceramics (e.g., zirconolite, monazite, apatite, or sodium zirconium phosphate) can incorporate nearly all of the radionuclides into a single structure, especially if the radionuclides have been partitioned into chemically similar groups, such as actinides or separated Cs and Sr.

Several reviews have explored in detail the use of ceramic phases for the immobilization of actinides.[15–18] Recent work in Russia has led to new phases, namely, murataite-based[19,20] and garnet-based[21] structures, for actinide immobilization, which can be produced by melting and crystallization. Positive features of the murataite-based ceramics produced by a melting route are the zoned structure of the grains and a decrease in actinide concentration from the core to the rim, which enhances the retention of these elements in the waste form.[20] The primary crys-

talline phases identified to date for immobilizing actinides are summarized in Table I. Many of these same phases are proposed as inert matrix fuels for in-reactor burning of minor actinides and, as such, would become waste forms once out of the reactor.

A glass ceramic is a fine-grained mixture of glass and ceramic phases ideally derived from a homogeneous glass through a devitrification.[22] With careful design, glass ceramics can combine the best features of ceramics and glasses for immobilization of HLW, with durable residual glass and ceramic phases. They can be readily tailored to specific waste streams and are easily fabricated on an industrial scale using both vitrification and ceramic technology. Sphene glass ceramics, which are based on the controlled devitrification of aluminosilicate glasses, were extensively studied in Canada and demonstrated to be a highly durable waste form for Canada's waste disposal scenario because of the high durability of the aluminosilicate glass matrix and even higher durability of the sphene and other crystalline phases.[22] Celsian glass ceramics, developed at the Hahn–Meitner Institut in Berlin, Germany,[23] were based on the controlled devitrification of a borosilicate glass but exhibited chemical durability that was only comparable to that of borosilicate glasses.[22,23] A large number of other glass ceramic waste forms were also studied during this early time period, and their properties and performance are well documented.[22] More recently, an apatite/britholite glass ceramic is proposed for immobilizing actinide-contaminated waste,[7] and a highly durable zirconolite glass-ceramic waste form has been proposed based on use of a nonsilicate crystalline phase and a silica-rich residual glass.[24]

Although studied in somewhat less detail, several crystalline ceramic phases for immobilizing Cs and Sr have been identified,[16] including pollucite,[25,26] barium hollandite,[10–12] and apatite.[27] More recently, crystalline silicotitanates,[28] which have zeolite-like framework structures with high affinities for Cs and Sr, and apatitic glass ceramics[29] have been proposed for separate Cs and Sr waste streams. This is an area that requires more research.

Thermochemistry

Thermodynamics is crucial to waste-form development and qualification in several ways. First, a waste form must incorporate the loading of HLW elements in a manner that is sufficiently stable with little or no thermodynamic driving force for the radionuclides to separate from the

Table I: Potential Phases for Immobilizing Actinides.

Structure Type	
Oxides	**Composition**
Fluorite	ThO_2, UO_2, PuO_2, ZrO_2, CeO_2
Pyrochlore	$A_2B_2O_7$, $RE_2Ti_2O_7$, $Gd_2Ti_2O_7$
Zirconolite	$CaZrTi_2O_7$
Perovskite	$CaTiO_3$
Murataite and related phases	$A_3B_6C_2O_{20-x}$ (3C), $A_8B_{14}C_4O_{47-x}$ (8C), $A_5B_8C_2O_{27-x}$ (5C), $A_7B_{10}C_2O_{34-x}$ (7C)
Garnet-structure ferrites	$Ca_{1.5}GdTh_{0.5}ZrFeFe_3O_{12}$, $Ca_{2.5}Ce_{0.5}Zr_2Fe_3O_{12}$
Silicates	
Zircon	$ZrSiO_4$
Apatite	$Ca_{4-x}RE_{6+x}(SiO_4)_6O_{1+0.5x}$
Titanite (sphene)	$CaTi(SiO_4)O$
Phosphates	
Monazite	$CePO_4$, $LaPO_4$
Apatite	$Ca_{10-y}RE_y(SiO_4)_y(PO_4)_{6-y}F_2$
Sodium zirconium phosphate (NZP)	$NaZr_2(PO_4)_3$
Thorium phosphate diphosphate	$Th_4(PO_4)_4P_2O_7$
Xenotime	YPO_4

Note: A, B, and C refer to different cation sites in these complex crystal structures, and RE represents a rare earth element.

matrix and accumulate locally in high and potentially dangerous concentrations. Second, the waste form must be thermodynamically resistant to leaching of radionuclides into the aqueous environment. Finally, crystal chemistry, phase stability, chemical durability, and radiation damage are interrelated, so one might use thermodynamic principles to design more radiation-resistant and chemically durable waste forms. Over the past three decades, considerable work has been done in each of these areas, and brief examples here provide a flavor of the scientific issues and approaches.

The immobilization of minor actinides is of interest for the closed fuel cycle, and the importance of thermodynamics is illustrated in recent work on the immobilization of plutonium in a ceramic waste form consisting mainly of a pyrochlore phase in the $CaHfTi_2O_7$–$CaPuTi_2O_7$–$CaUTi_2O_7$–$Gd_2Ti_2O_7$ system. Using cerium as an analogue for plutonium, the enthalpies of formation of the end-member pyrochlore phases have been measured, and a thermodynamic model for the quaternary system has been developed.[30] The enthalpies of formation from the binary oxides vary in a systematic way with the ratio of the atomic number, Z, to the ionic radius, r, of the tetravalent ion, as shown in Figure 2. However, the limit-
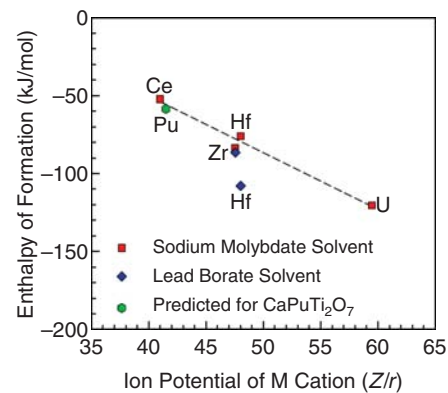
Figure 2. Enthalpy of formation from the oxides as a function of ionic potential (ratio of atomic number, Z, to ionic radius, r) for the CaMTi₂O₇ pyrochlore and zirconolite samples. Adapted from Reference 30.

ing stability is not with respect to decomposition to binary oxides, which is unfavorable in all cases, but with respect to decomposition to $CaTiO_3$ perovskite, residual rutile, and actinide oxide (i.e., $CaATi_2O_7 = CaTiO_3 + TiO_2 + AO_2$, where A represents an actinide). The formation of UO_2 or PuO_2 (or any actinide oxide solid solution) as a separate phase would be deleterious in terms of actinide leaching and might also lead to criticality concerns

if segregation in large regions occurred. Thus, it is desirable for waste-form compositions to lie in a region of composition space where such phase separation is thermodynamically unfavorable. Although such thermodynamic constraints were not explicitly included in the waste-form design, Figure 3 shows that the suggested composition does indeed lie within the region where pyrochlore is stable. Recent measurements of the enthalpy of formation for $CaPuTi_2O_7$ pyrochlore at Los Alamos National Laboratory have validated the use of the cerium analogue and crystal chemical systematics.

Spent fuel and other uranium-containing wastes corrode in an oxidizing aqueous environment to form solutions of U^{6+}, which, in turn, precipitate a wealth of uranyl mineral phases (hydroxides, carbonates, phosphates, silicates). The extent to which uranium is transported to the far-field environment depends both on the dissolution of the waste form (releasing actinides) and on the precipitation of such solid uranyl phases (retarding actinide transport). Despite their importance, the thermodynamics of uranyl phases are not well known, but recent calorimetric studies have increased our understanding of their formation.[31–33] In some natural and some spent fuel environments, a competing phase, studtite, $(UO_2)(O_2)(H_2O)_4$, forms, in which the uranyl ion is charge-balanced with a peroxide ion. Thermodynamic calculations based on recently measured thermochemical data for studtite[31] indicate that this phase can form in low peroxide concentrations (about 10^{-14} M H_2O_2). Whereas dehydrated schoepite is an alteration product often found in the sequence of mineralogical reactions leading to the formation of uranyl oxide hydrates and uranyl silicates in nature, studtite is thermodynamically the dominant phase where peroxide occurs. After a few hundred years, the α activity of spent fuel declines only slightly by 10,000 years and by a factor of about 10 by 100,000 years. This activity remains much higher than the radioactivity of natural uranium for millions of years. Therefore, studtite or metastudtite is likely to persist at the surface of spent nuclear fuel in contact with water in a nuclear waste repository. These peroxide phases must be considered in assessing the release of radionuclides in a repository.

It is desirable that waste-form ceramics be radiation-resistant so that volume and reactivity changes resulting from radiation-induced amorphization do not compromise their properties. A systematic ion beam irradiation study on titanate
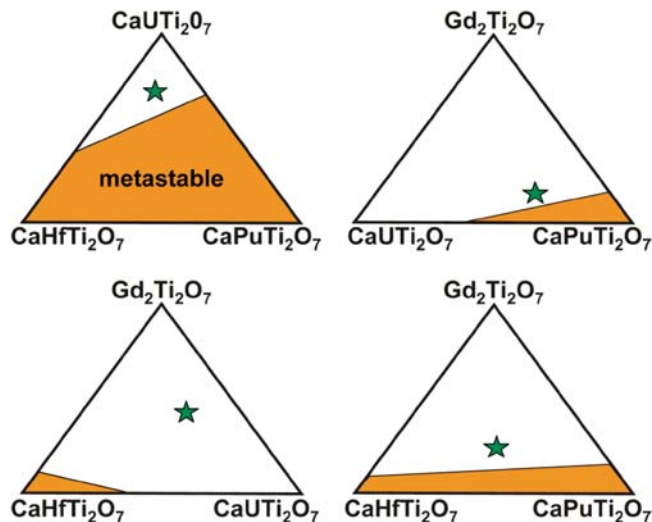

Figure 3. Calculated stability fields for pyrochlores in a waste form proposed for excess weapons plutonium. The star indicates the proposed waste-form compositions, for which pyrochlores are indeed stable. Adapted from Reference 30.

pyrochlores has been completed, and thermochemical measurements have been performed on the same (unirradiated) samples.[34,35] As shown in Figure 4, there is a remarkable consistency and linear correlation between the measured enthalpy of formation from the binary oxides and the "resistance" to radiation damage, as indicated by the critical amorphization temperature, which is the temperature above which annealing kinetics exceed damage kinetics and amorphization does not occur. As the propensity of the material to exhibit crystalline disorder increases, its radiation damage resistance increases, and the pyrochlore structure becomes less stable in enthalpy with respect to the disordered fluorite phase and the binary oxides, thus providing a basis for the correlation seen between enthalpy of formation and critical amorphization temperature. Such correlations, applied to complex ceramic systems, might help tailor better waste forms.

Microporous silicotitanates and niobates have been proposed as ion exchangers with very strong selectivity of cesium over sodium and of strontium over calcium. They thus can capture the short-lived isotopes of Cs and Sr and then be calcined to form refractory ceramics that sequester these elements. Thermochemical studies of the ion-exchange process and the formation of dense perovskites from the open frameworks suggest that the initial selectivity depends more on kinetic factors than on a thermodynamic preference for Cs over Na or Sr over Ca, but the dehydrated dense phases are indeed thermodynamically stable.[36,37]
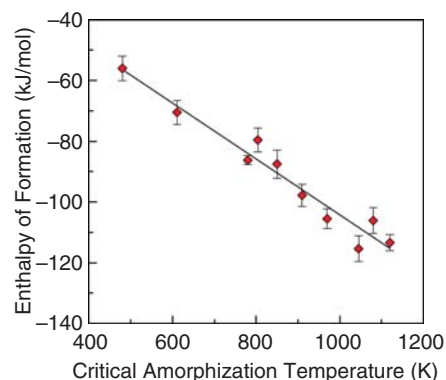

Figure 4. Linear correlation between enthalpy of formation from oxides and critical amorphization temperature for rare-earth titanate pyrochlores. Data from Reference 34.

Radiation Effects

Self-radiation from radionuclide decay can affect microstructural evolution, phase stability, and thermodynamic properties in waste forms. The principal sources of radiation in HLW are β decay of the fission products (e.g., ^{137}Cs and ^{90}Sr) and α decay of the actinide elements (e.g., U, Np, Pu, Am, and Cm). β decay produces energetic β particles (~0.5 MeV), low-energy recoil nuclei, and γ-rays; whereas α decay produces energetic α particles (4.5–5.5 MeV), energetic recoil nuclei (70–100 keV), and some γ-rays. These particles and γ-rays interact with solids primarily through energy transfers to electrons through ionization processes, producing electron–hole pairs, or to

atomic nuclei through elastic collisions, displacing atoms to produce defects. In general, β decay of the short-lived fission products is the primary source of radiation (and heat generation) from HLW during the first 600 years of storage. Because of the long half-lives of the actinides and their daughter products, α decay is dominant at longer times.

In addition to energy transfer, the particles emitted in radioactive decay are often readily accommodated in complex glasses but can have a significant chemical effect on crystalline waste forms. The principal source of transmutations in HLW is β decay of the relatively abundant fission products ^{137}Cs and ^{90}Sr. Transmutation of these two elements is accompanied by changes in both ionic radius and valence. Cs^+ decays to Ba^{2+} with a decrease in ionic radius of 20%, and Sr^{2+} decays to Y^{3+}, which, in turn, decays to Zr^{4+} with a final ionic radius decrease of 29%.[38] One way to mitigate the effects of such transmutations is through the use of multiple cation waste forms with one or more variable-valence cations.[39] In addition, helium atoms, formed by α particles capturing two electrons, are also produced in actinide-bearing waste forms and must be accommodated. For high actinide loadings, the He concentrations can become quite high (several atomic percent) and difficult to accommodate within both glass and ceramic structures.

Based on decades of radiation-effects research on nuclear waste forms,[15,16] only radiation effects from actinides and the fission products Cs and Sr are expected to be of major concern. Because the waste streams for some advanced nuclear energy systems are intended to separate actinides from Cs and Sr, radiation effects can be considered separately.

Radiation Effects in Actinide Waste Forms

Self-radiation damage in glasses and ceramics containing short-lived actinides, namely, ^{238}Pu and ^{244}Cm, was an area of active research for several decades; thus, radiation effects from α decay in many glasses and crystalline phases of interest are fairly well known.[15–17] In glass waste forms, the effects of α decay are generally small at the ambient temperatures expected over the decay times for actinides.[15] At low doses (less than 10^{17} α decays/g), there is an increase in stored energy associated with the formation of defect centers in the glass structure. As the dose increases, more global rearrangements of the glass network occur and are manifested as volume expansions or compactions that saturate at doses on the

order $(2–3) \times 10^{18}$ α decays/g. The maximum volume expansions or compactions from α-decay damage are only on the order of 1%. At extreme doses (greater than 8×10^{18} α decays/g), helium bubble formation has been observed, which can lead to loss of mechanical integrity at extremely long times. Given the small changes in stored energy, structure, and volume, glasses generally do not exhibit significant changes in chemical durability.

Numerous studies have also been performed on the effects of α decay in single-phase ceramics, multiphase ceramics, and glass ceramics containing short-lived actinides.[16] These include studies on Synroc,[40] pyrochlore-based ceramics,[16,17,41] murataite-based ceramics,[42] and celsian glass ceramic.[43,44] The swelling in Synroc exceeded 6%. The swelling in the glass ceramic was projected to saturate at about 0.5%. Single-phase ceramics that have undergone self-damage from short-lived actinides generally exhibit a crystalline-to-amorphous transformation with accompanying volume changes that range from about 5% to more than 18%.[16] Only a few new studies of radiation effects in ceramics incorporating short-lived actinides have been performed in the past decade.[41,42,45,46]

Extensive fundamental studies of radiation effects in identical or similar ceramics have been performed using ion-beam irradiation.[16–18,47,48] One outcome of this research has been the discovery of a radiation-tolerant class of ceramics, zirconate pyrochlores, that can readily accommodate actinides and remain structurally unaffected by self-radiation damage for millennia.[49–51] However, these zirconate pyrochlores do require higher processing temperatures than the titanate pyrochlores currently being considered.

Accelerated test methods for α-decay effects in ceramics using short-lived actinides and ion-beam irradiation have been validated in comparisons with natural mineral data, as shown in Figure 5, under conditions where the recovery kinetics is negligible.[17,50,52,53] Based largely on ion-beam studies integrated with computer simulation models, a fundamental understanding of radiation damage processes in these materials is emerging, and validated predictive models are being developed, as illustrated in Figure 6. However, data obtained at much lower dose rates using actinides are also needed over a range of temperatures to develop and validate models that are scalable for broad ranges of time, temperature, and dose rates.

Radiation Effects in Cs/Sr Waste Forms

In some advanced closed-fuel-cycle concepts, the separation of Cs and Sr into a separate waste stream provides an opportunity to immobilize these high-heat-generating radioisotopes into waste forms for interim storage over several hundred years. Because of desired high waste loadings, Cs/Sr waste forms will be subject to significant self-heating (up to 1000°C) and high ionization and transmutation rates but low displacement doses [<0.01 displacements per atom (dpa) over 1,000 years]. The cumulative ionization dose projected for Cs/Sr waste forms is
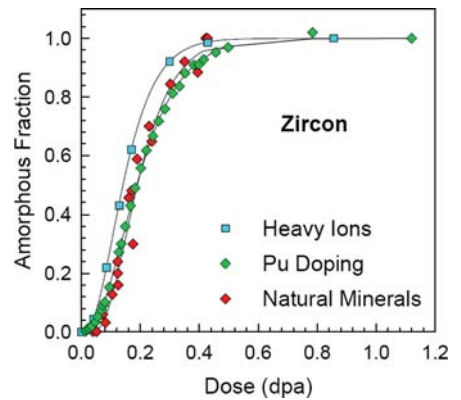
Figure 5. Radiation-induced amorphization in zircon showing similar dose-dependent behaviors over a large range of temporal scales: minutes for heavy ions, decades for Pu doping, and 5.5×10^8 years for natural minerals. Data from References 47 and 48. *Note:* dpa is displacements per atom.
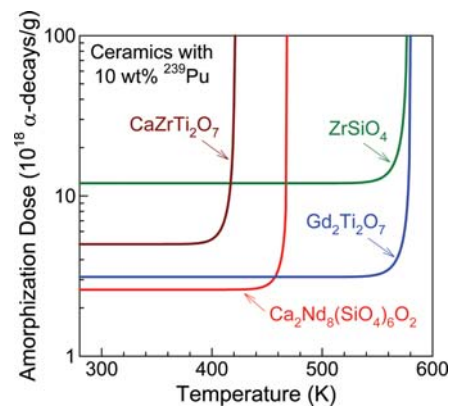
Figure 6. Predicted amorphization dose as a function of temperature for different ceramics containing 10 wt% ^{239}Pu. Adapted from References 17, 52, and 53.

shown in Figure 7 as a function of storage time, along with the doses expected for current commercial HLW glasses. At these high ionization doses and temperatures, many materials undergo decomposition, phase separation, and bubble formation under electron-beam irradiation on laboratory time scales. Whether similar processes occur when dose rates are orders of magnitude lower requires careful investigation. However, such studies are limited by the time scales required to achieve desired dose levels using existing capabilities, as indicated in Table II. Electron-beam interactions are similar to those of β particles and the fast electrons produced by γ interactions, but their dose rates are significantly higher than the 10^4–10^5 Gy/h expected in Cs/Sr waste forms. Available γ sources have dose rates that are too low to achieve the necessary dose levels, and doping with short-lived isotopes, such as [134]Cs, is limited because of self-heating to low dopant levels, making it impossible to achieve the necessary doses. Only electron beams or highly ionizing ion beams (such as protons or helium) offer the capability to study radi-ation effects over the ionizing dose range of interest. Developing predictive models and validating such an approach will require a more fundamental understanding of ionization effects and the coupling of electronic excitations to atomic dynamics than currently exists.[54]

The additional self-radiation effect in Cs/Sr waste forms is that associated with high transmutation rates at high temperatures. The use of short-lived isotopes might be the only way to experimentally investigate the stability and response of these waste forms to the large changes in valence states and ionic radii, but such studies are challenging and have been somewhat inconclusive in the past.[38] Advanced computational methodologies might provide the only avenue to explore this issue.

Chemical Durability

Chemical durability is an important technical performance property of waste forms in groundwater environments. Leaching provides a physical measure of how well waste forms can retain radionuclides if exposed to water in a repository setting. Whereas thermodynamics can give the equilibrium states, kinetic information is needed to understand rates of leaching, especially in open systems. An advantage of waste forms based on mineral analogue phases is that the mineral phases can be shown to have survived for several hundred million years or more in wet, thermal geologic environments. As such, they demonstrate durability on a time scale longer than that required by regulators, albeit for low radionuclide loadings and slightly different compositions. More importantly, an understanding of the chemical durability of these specific mineral compositions and structures should lead to predictive models of durability for a broader range of compositions and structure types.

For leach testing, many institutions worldwide have developed different protocols, and it is often difficult to compare the diverse data presented in the litera-ture. The most commonly used tests include those developed by the Materials Characterization Center (MCC-1) in the United States, the Soxhlet test used in Europe, the MCC-3 Test using powdered samples, and more recently the Product Consistency Test (PCT) developed at Savannah River. The temperature of testing is most frequently 90°C but can range from room temperature to 200°C, and leaching times can extend from a few days to several years. The essential role played by the composition of the waste form is taken into account in expressing leaching as normalized by dividing the concentration measured in the leachate for any given component by its fraction in the waste form. For highly soluble elements that leach congruently, such as boron, lithium, and sodium in glasses, the normalized concentration truly reflects the waste-form durability. Other elements will display their percolating role, that is, the capability to slow the loss of the more mobile species, such as alkali and boron in glasses. The variation in size of the waste-form samples tested and the volume of leachant used is also corrected by dividing the normalized concentration by the ratio of the surface area (SA) of sample exposed to the solution volume, V, (SA/V, in m^{-1}). In this case, the leaching is expressed in grams per square meter per day (g m^{-2} day^{-1}) as is presented in Figure 8 for U release from a borosilicate glass.[55] In addition, the leach rate itself can depend on SA/V, particularly at high SA/V ratios where the concentration of leached elements can build up in solution. The self-diffusion rates of radioisotopes in the waste form can also affect elemental leach rates by changing the local surface concentration exposed to water.
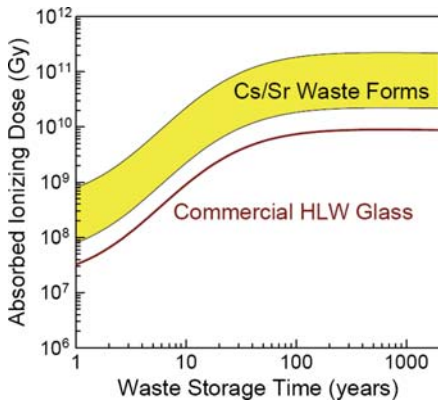

Figure 7. Predicted absorbed dose for commercial high-level waste (HLW) glasses[15] and for potential waste forms to immobilize Cs and Sr in some advanced closed-fuel-cycle concepts.

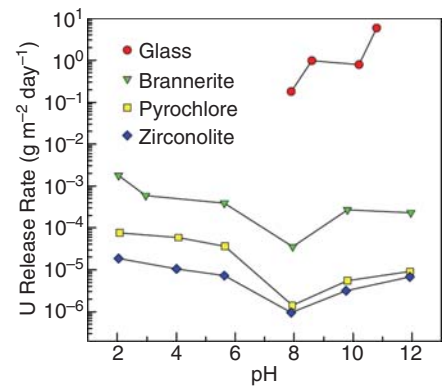

Figure 8. Leach rates for U from a borosilicate glass and several crystalline phases of interest. Data from References 18 and 55.

Table II: Irradiation Techniques, Corresponding Dose Rates, and Equivalent Time Needed To Achieve the Dose Equivalent to 1,000 Years (2×10^{10} to 2×10^{11} Gy) for a Highly Loaded Cs/Sr Waste Form.

Irradiation Technique	Dose Rate (Gy/h)	Irradiation Time (Equivalent to 1,000 Years)
Intense [60]Co γ source	3×10^4	80–900 years
Electron accelerators	10^7–10^8	9–9,000 h
Electron microscopes	10^{11}–10^{13}	2 ms–2 s
Short-lived β emitter	Not feasible	Not feasible

The leach rates for many ceramic phases of interest have been investigated as a function of pH and time. The leach rates[18] for several crystalline phases of interest are also shown in Figure 8 as a function of pH. Using the MCC-1 test at 90°C, the leach rates of U, Np, and Pu from murataite ceramics with 10 wt% UO_2, NpO_2, or PuO_2 were recently found to be 10^{-7} g m^{-2} day^{-1} after seven days,[56] whereas in murataite ceramics with 10 wt% $^{239}PuO_2$ and 0.1 wt% $^{241}Am_2O_3$, the Pu and Am leach rates (MCC-1) at 90°C decreased from an initial value of 10^{-3} g m^{-2} day^{-1} to 10^{-4}–10^{-5} g m^{-2} day^{-1} after 63 days.[57] In the garnet ceramic $Ca_{1.5}GdTh_{0.5}ZrFeFe_3O_{12}$, leach rates (MCC-2, 150°C) of Gd and Th in water were 3×10^{-5} g m^{-2} day^{-1} for Gd and $<10^{-6}$ g m^{-2} day^{-1} for Th.[58]

Whereas experimental leach rates usually decrease upon continued exposure to water, there are reported cases of leach rate enhancements upon exposure to water for periods of a few years, but only for glass in highly alkaline solution (pH > 10).[59] The effect of microorganisms on leach rates could also be an open question for near-surface disposal conditions.

Outstanding Issues

Although the focus of this article has been on glass and ceramic waste forms, some of the more troublesome radioisotopes might require novel approaches. For example, some considerations are being given to a metallic waste form to immobilize Tc and undissolved solids.[60] Likewise, novel immobilization approaches might be required for volatile species, particularly iodine.

When a full safety analysis of an HLW repository is carried out, the stability, radiation resistance, and chemical durability of the waste forms are lost in the uncertainty in the release and migration of the radionuclides. Although this might suggest that detailed attention to waste-form properties and behavior is not very constructive, a higher level of confidence for the safety of future generations is gained by comprehensive measurements of waste-form properties and performance, demonstrated understanding of complex processes and behaviors, and predictive models of performance that can be reliably extrapolated to long time scales. Although the provision of extra barriers such as the waste containers, clay inserts, cementitious repository liners, and rock backfills should provide extra resistance to radionuclides reaching the biosphere, the waste-form durability remains the first barrier in a multibarrier concept allowing for a defense in depth. By contrast, the repository can truly be tested only by a few well-placed drill holes, with cognizance that overreliance on drill holes could cause serious perturbation of the entire repository.

Summary

Careful fundamental scientific studies of waste forms are essential to predicting their long-term behavior. The development of new closed fuel cycles offers both challenges and opportunities to tailor new waste forms for specific waste streams. Experiment and theory at the molecular level, and even the electron level in the case of ionization effects, must be paired with modeling at larger spatial and time scales to predict long-term behavior of proposed waste forms. Much fascinating and important science remains to be done.

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