

PERFORMANCE OF BOROSILICATE GLASS, SYNROC AND SPENT FUEL AS NUCLEAR WASTE FORMS

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ABSTRACT

Presently, there are three prominent waste forms under consideration for the disposal of high-level waste: Borosilicate glass and Synroc for high-level radioactive waste from fuel reprocessing and spent fuel as the waste form for non-reprocessed fuel. Using the present experimental data base, one may compare the performance of these three waste forms under repository relevant conditions. In low water flow regimes and at temperatures less than 100°C, the fractional release rates of all three waste forms are low, on the order of $10^{-7}/d$ or less, and may decrease with time. Under these conditions, the three waste forms behave similarly. At elevated temperatures or in high flow regimes, the durability of borosilicate glass will be much less than that of Synroc, and thus, for certain disposal schemes (e.g., deep burial) Synroc is preferable. All predictions of the long-term behavior are based on the extrapolation of short term experimental data, we point out that appropriate and useful natural analogues are available for each of these waste forms and should be used in the performance assessment of each waste form's long-term behavior.

INTRODUCTION

This paper is a partial summary of a more detailed discussion (1) of nuclear waste forms, the method by which they can be compared, and the extrapolation of their long-term chemical durability. The principal purpose of this discussion is to emphasize the diverse characteristics on performance assessment, and to suggest the application of natural analogues to the validation of performance assessment results.

During the ten years between 1975 and 1985, there was a substantial effort in the United States, Canada, Europe and Australia to investigate alternatives to the then and now standard nuclear waste form, borosilicate glass, for high-level radioactive waste. This was a period of active research and controversy during which waste forms were compared and ranked, despite the fact that important data were incomplete or even missing. Now, half decade later, the research has waned, and nuclear waste form properties are of little interest. Some programs have continued (e.g., Synroc development at Lucas Heights in Australia), but most ended with the decision in the United States to solidify defense nuclear waste in borosilicate glass and the subsequent construction of the Defense Waste Processing Facility (DWPF). More recently, as a result of national policies in various countries, spent fuel has become an important waste form for commercially generated nuclear waste. Spent fuel, i.e., irradiated UO_2 in a metallic cladding, is not a designed or tailored waste form, and its properties vary with fabrication and irradiation history. Investigations on the properties of spent fuel began in the late 70's and continue at a moderate level.

At present, the waste form is often not considered an important barrier to radionuclide migration from a repository. A common conclusion of performance assessments of repository behavior is that orders of magnitude variation in the properties of the waste form (most importantly the

corrosion rate) have no significant effect on the final calculated dose-to-man. Many experts maintain that a well-designed geologic repository will successfully isolate radionuclides from the biosphere. Nevertheless, the ideal performance of geologic barriers depends on a complex interaction of geologic, hydrologic, geochemical and geophysical variables. The performance assessment is technically complex and largely incomprehensible to the general public. The validation of large scale, site-specific repository systems over long periods of time offers little hope of convincing success. In contrast, the prediction of the long-term behavior of a nuclear waste form is a more tractable problem. Given specific repository conditions (i.e., flow rate, solution composition, temperature, etc.) the chemical durability of the waste form over long periods of time can be evaluated on a physico-chemical basis, and perhaps validated by careful comparison to appropriate natural analogues (2). Finally, although borosilicate glass has become the standard waste form for reprocessing waste, one should not be so complacent as to believe that additional work is not necessary. In fact, important developments have already occurred. The development of a full scale non-radioactive production plant for Synroc and the detailed characterization of this multiphase ceramic waste form is an excellent example. There are plans to build a pilot plant on a technical scale for the production of highly radioactive Synroc in the USSR and to demonstrate disposal of Synroc in the deep underground.

HIGH-LEVEL RADIOACTIVE WASTE FORMS

Nuclear waste forms use one or more of three principles for the containment of radionuclides:

1. Radionuclides may be dispersed at the atomic level through an aperiodic solid (glass). The aperiodic atomic array provides for a wide range of sizes and coordination geometries so that this single phase may accommodate the full range of atoms contained in the

waste. Borosilicate glass is the most prominent of such waste forms.

2. Radionuclides are fixed at specific atomic sites in periodic crystalline solids. Some structures (e.g., monazite) have a number of different atomic sites; thus, different nuclides may be incorporated into a single phase. However, the wide diversity of waste compositions usually precludes this possibility, and polyphase assemblages are more common (e.g., Synroc).
3. Radionuclide bearing phases (e.g., calcines) are encapsulated in non-radioactive phases of high chemical durability (e.g., a TiO_2 -matrix).

In contrast to the tailored waste forms, the properties of spent fuel as a waste form are determined by the irradiation history of the UO_2 in the reactor. Radionuclides are distributed among the fuel matrix, precipitated phases (e.g., metallic Pd-Ru-Rh-Tc-Mo particles), grain boundaries and voids such as cracks or the fuel sheet gap.

Presently, there are three prominent waste forms: Borosilicate glass and Synroc for high-level radioactive waste from fuel reprocessing and spent fuel as the waste form for non-reprocessed fuel. We describe the state of knowledge of the chemical durabilities and performance of these waste forms.

PERFORMANCE OF BOROSILICATE GLASS, SYNROC AND SPENT FUEL

Borosilicate Glass

The properties of borosilicate glasses have been reviewed in detail by Lutze (3). Typical borosilicate glasses for LWR high-level radioactive waste are composed of 40-50 SiO_2 , 15 B_2O_3 , 30-40 others (e.g., Na_2O , Al_2O_3 , CaO , etc.) and 10^{-15} waste oxides (numbers in weight percent). Production temperatures are 1050-1150°C. The chemical durability of borosilicate glass has been tested under almost all conceivable conditions and, in some cases, for periods of several years. Tests at high temperatures, above 250°C (4), have demonstrated that under these conditions borosilicate nuclear waste glasses are rapidly devitrified. At lower temperatures, <100°C, these glasses are chemically more durable, and the corrosion rate is dominated by either the intrinsic properties of the glass or by the composition of the surround solution. In deionized water at high water flow rates (1 L/h), the glass corrodes at a constant maximum rate, the "forward rate" of reaction. The forward rate for borosilicate nuclear waste glass is on the order of 1 gm-2d-1 at 90°C. At a groundwater flow rate of 10^{-4} L/h (150 L of glass), the corrosion rate is independent of flow rate and is small, in the order of 10^{-3} gm-2d-1, compared with the forward rate. At intermediate flow rates, the glass corrosion rate varies linearly with the flow rate.

The corrosion rate of borosilicate nuclear waste glass decreases with increasing silica concentration in the leachate, and approaches a saturation value. Long-term corrosion does not cease at silica saturation in a static or slow flow system, but is governed by a constant or decreasing long-term rate (typically 10^{-3} gm-2d-1 at 90°C) that controls the alteration of a borosilicate nuclear waste glass.

Grambow et al. (5) completed a performance assessment which considered conditions in a granitic repository with flowing water. Glass blocks of "Cogema" size (150 L in a steel canister) were assumed to be fractured (increase in the surface area is ten times the geometric surface area). The corrosion temperature was 90°C and was kept constant. Three alternative cases are considered which demonstrate the range of potential glass performance as measured by its degree of chemical alteration. Glass alteration is a measure of glass/water reaction determined by the release of the soluble element boron into solution.

In case 1, glass alteration was assumed to be determined by the forward rate of reaction. This is a hypothetical limiting case, valid only in an infinite volume of water. Complete alteration occurs within 100 years at 90°C. Alteration will be much slower under realistic repository conditions (Case 2). In Case 2, a fraction of only $10^{-3}\%$ of the glass block is altered before reaching silica saturation. Using a flow rate of 1 L/yr and a constant long-term corrosion rate of 0.003 gm-2d-1, 1% of the block is altered after 500 years. Complete alteration will not be reached until after 10^{+4} years. This is still a conservative estimate, as the corrosion rate may decrease with time. In Case 3, the long-term corrosion rate is assumed to be zero. This is a limiting case to the extent that further alteration of the glass can only occur as a result of flow, i.e., transport of silica away from the reacting system. At a water flow rate of 1 L/yr/canister a fraction of 1% is altered after 10^{+3} years and 100% after 10^{+6} years. The flow rate determines the rate of glass alteration even if the long-term rate is not zero but too small to replace the losses of silica from the reacting system.

Synroc

Synroc and its chemical durability have been described by Ringwood et al. (6). There are various formulations of Synroc, depending on the composition of the waste stream (e.g., U. S. defense waste versus LWR waste). Synroc C, designed to immobilize LWR waste, consists of hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$), zirconolite ($\text{CaZrTi}_2\text{O}_7$), perovskite (CaTiO_3), rutile (TiO_2), and minor metal alloys. Each of the first three components can accommodate within their structures a range of radionuclides. Hollandite can retain fission products such as Cs, Rb, Ba; zirconolite can retain U, Zr, Np, Pu; perovskite can retain Sr and transuranics such as Np and Pu. The metal alloys will contain Mo and Ru. Waste

loadings can vary over a wide range, typically 10-20 weight percent.

The leachability of Synroc phases is much lower than that of borosilicate glass at temperatures well above 100°C. Synroc does not show a flow rate dependence of its leach rate. Short-term leaching of Synroc appears to be dominated by the dissolution of limited quantities of "non-equilibrium" phases, probably isolated at grain boundaries, that develop in the course of the Synroc production process. The rapid decrease of the leach rate of Synroc with time indicates an early exhaustion of this source. Long-term leaching experiments show that perovskite is the least stable phase, and TiO₂ forms as an alteration product on the Synroc surface.

Three mechanisms control the long-term leaching of Synroc: (a) Base catalyzed hydrolysis of the titanate structure; (b) diffusion-controlled ion-exchange; (c) precipitation and layer formation (7). Levins (6) suggested that the mass loss can be modelled by an equation containing three terms: A near instantaneous release term, a function that accounts for grain boundary diffusion and selective attack on more leachable phases, and a solubility term, describing the release for all elements from Synroc. Titanium is the major matrix element; therefore, TiO₂ solubility could be the limiting factor in the dissolution of the waste form. This approach needs further refinement. The solubilities of the various Synroc phases must be determined. Alteration products which form in the presence of groundwater must be identified. First results have only just recently become available.

Spent Fuel

A detailed review on the properties of spent fuel as a waste form is given by Johnson and Shoesmith (9). Radionuclide release into solution from the gap, grain boundaries, the fuel matrix and the cladding occurs at separate rates and with different rate laws. LWR fuel exhibits an instantaneous fission-gas release from the gap of 1% of the total radionuclide inventory. The fractional release of Cs and I during initial corrosion matches the Xe-gas release. Segregation of fission products at UO₂ grain boundaries provides easy pathways for the access of reactants such as oxygen to the interior of the fuel. Experimental data are often inconclusive as to whether selective fission product release comes from grain boundaries or from dissolution of the matrix and precipitation of alteration products. Nevertheless, there is theoretical consensus that the long-term release of radionuclides from fuel is governed by the dissolution of the UO₂. Under oxidizing conditions, the UO₂ matrix is thermodynamically unstable. U concentrations in solution are constant and are not controlled by the solubility of dissolving UO₂ but by alteration products such as schoepite. The transformation of the matrix to an alteration product will be

accompanied by a release of soluble radionuclides. Only under reducing conditions will the UO₂ matrix become stable, but radiolysis may not allow for reducing conditions. For realistic long-term predictions, fuel matrix dissolution under oxidizing conditions must be treated as an incongruent process, in which the release of soluble elements is accompanied by the corresponding formation of U bearing alteration products at all times. The effective surface area will be between the geometric area and the surface area of individual grains. The difference between these two areas is a factor of 200. The surface area of the reacting UO₂ fuel is not critical if mass-transport of U controls the fractional release rate.

Due to the lack of fundamental understanding of the corrosion mechanisms, the evaluation of the long-term performance must be based on the determination of upper release limits, rather than realistic predictions. A recent comparison of spent fuel corrosion data from nuclear waste management projects in Canada, Sweden and the USA (10) strongly suggests that after 1,000 days typical long-term fractional release rates of soluble radionuclides can be expected to be lower than $3 \cdot 10^{-7}/d$ at 25°C. The extent of radiolytic fuel oxidation is not understood, but, as described recently (10), an upper limit for its effect on corrosion rates can be obtained by assuming the above rate of $3 \cdot 10^{-7}/d$ as resulting exclusively from oxidation of the fuel by radiolysis. The maximum rate of radiolytically enhanced spent fuel corrosion decreases proportionally to the alpha-decay dose (in 1 million years the dose rate decreases by a factor of 1,000).

Evaluation of Waste Form Performance

The evaluation of Synroc, borosilicate glass and spent fuel is based on fractional release data. Release rates in g/m²d, often used for borosilicate glass and Synroc have been recalculated as fractional release rates. For spent fuel there are only fractional release rates available, because the effective surface area of this waste form is unknown. For glass, the effective surface area is typically ten times the geometric surface area. This is the result of fracture upon cooling a Cogema type glass block (108 cm long, 42 cm diameter) below the glass transformation temperature. A factor of ten can also be applied to Synroc, if a 42 diameter and 10 cm high "disc" is produced. Six Synroc discs accommodate the same amount of waste as a Cogema type glass block if a waste load of 13 weight percent and a Synroc density of 4.35 g/cm³ versus 2.75 g/cm³ for glass are considered. Hence, in the conversion of specific rates in g/m²d into fractional release rates Synroc has an effective specific surface area 1.4 times that of the glass.

At high flow rates (90°C, DI water), there is a characteristic difference between borosilicate glass, Synroc and spent fuel. Glass corrodes at a constant rate (on the order

of $1 \text{ gm}^{-2}\text{d}^{-1}$, corresponding to a fractional release from the fractured glass block of $4 \cdot 10^{-5}/\text{d}$) whereas, the leach rate of Synroc and spent fuel decreases with time. After 300 days, e.g., the release rate of Tc for Synroc is $10^{-4} \text{ gm}^{-2}\text{d}^{-1}$ (fractional release of $< 10^{-8}/\text{d}$ for discs of 43 cm diameter and 10 cm height) which is a factor 10^{+4} lower than a typical corrosion rate of nuclear waste glasses under fast flow conditions. For spent fuel (at 25°C) the corresponding rate is $10^{-6}/\text{d}$. There is no data for 90°C .

These striking differences in waste form performance at high flow rates, however, are irrelevant in a repository safety analysis, because there are no flow rates high enough to allow the glass to corrode at a fractional release rate of $4 \cdot 10^{-5}/\text{d}$.

For the more realistic case of low groundwater flow rates, the difference in waste form performance diminishes considerably. The short term release of elements from all three waste forms is qualitatively similar. There is an instantaneous release after which further release proceeds rather slowly. The underlying corrosion mechanisms and the magnitude of the effects are, however, different.

There is substantial experimental evidence that under conditions of low groundwater flow rates, the reaction rates of all three waste forms decrease by many orders of magnitude. The observed fractional long-term rates of matrix corrosion for glass at 90°C and for spent fuel at 25°C are $10^{-7}/\text{d}$ (11). There are no long-term data for spent fuel corrosion at higher temperatures. For Synroc at 90°C the fractional release rate is $10^{-8}/\text{d}$ as under high flow conditions. Considering the experimental uncertainties in the values of these "long-term" rates and the lack of understanding of the respective rate laws, one must tentatively conclude that the long-term behavior of these three waste forms will be the same. Still, this conclusion is restricted to the expected low flow regimes in which the temperature is less than 100°C . Thus, for a waste form whose corrosion rate is much less dependent on temperature or flow rate, as is the case with Synroc, one may anticipate improved performance in repository systems which have higher waste loadings, higher ambient temperatures (deep burial), higher flow rates or in which the time between generation of the waste and disposal is shorter.

At low flow rates and after reaction times much longer than those of laboratory experiments, the long-term corrosion rates may continue to decrease. Finally, the corrosion rates may become controlled by mass transfer of matrix forming elements, i.e., by advective or diffusive transport of Ti, Si or U with the solubility of TiO_2 , SiO_2 or schoepite ($\text{UO}_2(\text{OH})_2\text{H}_2\text{O}$) governing the waste form/solution boundary condition. In this case waste form chemical durabilities would be proportional to the solubility (about 10^{-7} M for TiO_2 , 10^{-3} M for SiO_2 and 10^{-6} M for schoepite) and glass would become by far the least durable product.

However, for the time being, there is no experimental evidence to support this hypothesis.

Matrix dissolution and the precipitation of alteration products are the principal release mechanisms for glass and spent fuel, whereas in Synroc the phases dissolve at different rates. Perovskite is the least stable phase. The release of soluble elements from any of the waste forms is not expected to cease, if, due to solubility constraints of alteration products, the solution concentration of the main matrix forming elements Si, U and Ti, respectively, reach constant values (saturation) in a static or low flow system.

Higher inventories of actinides in spent fuel were sometimes used as an argument in favor of reprocessing waste forms such as glass or Synroc, but in most cases (except perhaps in MgCl_2 brines) actinide release rates were found to be solubility limited and not inventory limited. For example, corrosion tests with spent fuel and with glass in simulated granitic groundwater yield virtually the same solution concentrations of Pu (12), controlled by the solubility of a phase like $\text{Pu}(\text{OH})_4$.

Natural Analogues

The discussion of waste forms has thus far been restricted to an analysis of experimental data a few years in duration. The most interesting question is: "Are there differences among these waste forms that become significant after extended periods of time?" Unfortunately, there will never be an explicit answer to such a question, as the only long-term extrapolation of behavior can come from modelled results. However, one may consider natural systems as providing information on the long-term behavior of materials. This theme, with its advantages and limitations, has been discussed extensively (2, 13), and geochemists have commonly relied on field observations to develop systematic generalizations for corrosion and alteration (e.g., in the case of weathering, Goldich's stability series).

The point in this brief paper can only be that there are appropriate natural analogues for the three types of materials discussed in this paper. Basalt glass and low-silica tektites have been used to study the long-term corrosion processes and products in low-silica borosilicate glasses (2). Most of the primary phases of Synroc -- zirconolite, perovskite and rutile -- occur in the natural environment. In the case of zirconolite, alpha-decay radiation damage effects have also been studied because natural zirconolites contain actinides. The "hollandite" phase in Synroc does not occur naturally, but it is part of a larger class of Ti-oxides which occur in manganese nodules. For spent fuel, there is a considerable literature on the alteration of natural UO_{2+x} under oxidizing conditions (usually at relatively high flow rates). In certain classic localities over fifty uranium oxides and silicates have been identified as alteration products (14). An understanding of the crystal chemistry and elemen-

tal partitioning between these alteration phases is of special interest in modelling the release of radionuclides during the corrosion of spent fuel.

The challenge, not yet met, of natural analogues is to explicitly use them in a systematic performance assessment of nuclear waste forms.

CONCLUSIONS

A quantitative comparison of the performance of the three waste forms cannot be done at this time and is certainly only possible when the details on the long-term corrosion mechanisms for all three waste forms are more firmly established. To this end, we recommend the following as specific research needs:

1. For all three waste forms we must know the long term corrosion mechanism. The extrapolation of this rate over extended periods of time is required by performance assessment, yet at the moment, there is no theoretical basis for this extrapolation. For the borosilicate glass it has been established that corrosion will not cease and is controlled by just such a long term rate.
2. For Synroc, we must arrive at a quantitative understanding of the initial release of material due to corrosion along grain boundaries and of minor soluble phases. In addition, alteration products must be identified, as they can play an important role in determining solubility limits and may also contain and isolate radionuclides.
3. For spent fuel, instantaneous release of radionuclides from between grain boundaries is also of great importance. In addition, we must determine the effect of radiolysis on the oxidation conditions of the corrosion process and identify the long term corrosion products. The latter is exceptionally difficult given the complex mineralogy and crystal chemistry of uranyl silicates and oxides.

Each of the above must be verified (as possible) by comparison to the appropriate natural analogue.

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