WSRC-MS-99-00591

Surface Studies of Nuclear Waste Glasses

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This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

Introduction

GLASS is the matrix of choice of every major country involved with long-term management of high-level radioactive waste (HLW). There are many reasons why glass is preferred [1]. Among the most important considerations is the ability of glass structures to accommodate and immobilize the many different types of constituents present in HLW, and to produce a product that not only has excellent technical properties, but also possesses good processing features [2,3]. Glass is also the material of choice for immobilization of a wide range of other potentially hazardous materials. The single most important property of waste glass is that it possesses good chemical durability and hence, the ability to retain hazardous species when subjected to a wide range of environmental leaching conditions [4].

Among the important objectives of national and international waste management programs is the ability to understand the leaching process of complex waste glasses and ultimately, to model corrosion behavior. Modeling information is needed to predict long term performance and subsequent reliability. Essential to this task is to characterize leaching of these systems. There has been much fine work performed in the glass field on characterization of leaching of simple glasses, generally 2 or 3 component systems. HLW glass systems are more complex and generally contain 40 to 50 different elements along with special considerations such as radiation effects. In order to better understand the leaching behavior of complex glass systems, an integrated study approach is often used to characterize reacted glasses. In this approach, a variety of surface analytical tools are used to characterize leached surfaces and coupled with bulk studies and solution analysis. Each tool provides important information on the chemistry or structure of species of interest in and through leached surface layers. The integrated study approach and the various analytical tools and techniques often used to characterize surface layers and interfaces in nuclear glasses are depicted schematically in Figure 1, along with sampling depths [5].

Figure 1. Analytical Tools Used for Integrated Study Approach of Leached Glasses

Surface Layers

Surface layers have been observed on a wide array of nuclear glass systems and under a wide range of conditions. These layers are generally complex and often, contain a variety of crystalline and non-crystalline phases as well as a series of sublayers, which can be characterized and more fully understood using the integrated study approach. The chemistry, morphology, density and general characteristics of the layers are a strong function of the chemistry of the glass and leaching conditions. The leached glass surface layers can be very important as protective layers, resulting in an already durable glass product exhibiting improved durability with time. While some systems exhibit significant benefits of protective surface layers under specific conditions, other systems and other conditions can produce surface layers that provide much less protection to the glass underneath and in some cases, no protection at all. Surface layers observed in various nuclear waste glass systems all fall within the 5 cases as defined and described by Hench [6]. In Figure 2, surface layers representative of U.S. waste glasses leached under selected conditions are summarized [7].

Figure 2. Typical Leached Layers and Elemental Profiles for SRS HLW Waste Glass

Leached Layers Observed in Field Tests

The WIPP/SRL Materials Interface Interactions Tests [MIIT] represents the largest and most cooperative in-situ testing program of nuclear waste glass systems in the international waste management community [8]. It is a joint effort designed, coordinated and managed by the Savannah River Site in Aiken, South Carolina along with Sandia National Laboratories in Albuquerque, New Mexico, and sponsored by the U.S. Department of Energy. MIIT involves the field testing of almost 2,000 simulated or non-radioactive waste forms and waste package components from around the world buried in the salt site at the Waste Isolation Pilot Plant (WIPP) in Carlsbad, New Mexico. This 5-yr. burial program involves participation by academia, federal and national laboratories along with leading scientists from around the world, including France, Germany, Belgium, Japan, Sweden, the United Kingdom, and the United States. Among the main objectives of this effort, is to understand and ultimately, be able to predict the long term performance of nuclear waste glasses in realistic repository environments. Analyses and assessment of a wide range of international waste glass systems and package components studied in the MIIT program are documented elsewhere [9-11].

Post-Test Analyses of SRS Defense Waste Glass. Based on surface and bulk studies along with solution analyses, the performance of the U.S. SRS 165/TDS waste glass has been very good. In general, there are two distinct regions noted on leached nuclear glasses; an outermost precipitated layer and a inner glass reaction zone.

Precipitated and Glass Reaction Zones. Precipitated and glass reaction zones were analyzed and measured as a function of time and other relevant conditions by Tacca and Wicks [11]. The outermost layer consists mainly of precipitated salt phases and includes crystalline as well as amorphous regions as determined by SEM, EDX and wide angle x-ray diffraction [WAXD]. These phases were attributed to the brine and salt precipitates that form on the glass surface during the MIIT leaching tests conducted in the salt environment at WIPP. There are two important points to note concerning the glass reaction region underneath the precipitated layers; 1) the amount of interaction of the glass with surrounding brine environment, as measured by the intrusion of Mg and Cl from the brine into the glass, is very low and 2) the rate of interaction decreases with increasing time. These observations indicated that the chemical durability of the glass is very good and actually can become better with increasing time.

The reacted glass surfaces were investigated in more detail by other analytical techniques, including Fourier Transform Reflection Spectroscopy [FTIRRS], by Clark, Zoitos and co-workers at the University of Florida [13], and by Secondary Ion Mass Spectroscopy, by Lodding et. al. of Chalmers University in Sweden [14]. FTIRRS showed that the disruption to the glass structure was very small even after leaching for two years in WIPP while SIMS provided one of the most detailed tools for mapping individual elements throughout leached layers of the burial glasses. SIMS showed that the precipitated layer actually consists of two individual layers and the reaction zone of the glass consists of at least three individual leached layers [15]. The SIMS technique is discussed in more detail by Lodding elsewhere [16]. By combining studies of SEM, EDX, FTIRRS, WAXD, TEM, EMP, and most importantly, SIMS, a composite picture of leaching of the SRS waste glass in WIPP was developed and is summarized in Figure 3 [8]. Each of the various precipitated and reacted glass layers are discussed below:

- Outermost Precipitated Salt Layer; The outermost precipitated layer was studied and characterized by Vernaz of the CEA in France [17], Harker of Rockwell International [18], Ewing then at the University of New Mexico

[19] and SRL. Both amorphous as well as highly crystalline phases were observed, including $MgCl_2$, KCl, $CaSO_4$, NaCl, and a variety of mixed silicates, along with additional minor phases. The layer was generally very heterogeneous and varied considerably in thickness. The chemistry of the layer was dominated by large amounts of Mg and Cl derived from the surrounding brine, along with other components such as Ca, Na, S, and Si. The salt layer, which was formed primarily as a result of the geologic environment and not from leaching the glass, is expected to effect subsequent glass leaching.

- Precipitated Glass Layer; Immediately adjacent to the glass surface and under the outermost precipitated salt layer, is a thin, precipitated glass layer. This layer formed when elements from the glass were leached and precipitated in this region. The layer is more uniform than the salt precipitated layer and characterized by large amounts of elements from the brine, including Mg and Cl, along with Si. This layer is also relatively depleted in elements such as Al, Zr, and Fe, which are generally the least leachable species within the glass. This observation along with ratios of other components present, morphology and subsequent brine analysis of leachate, show that this is a precipitated region and not a selectively leached part of the original glass.

- Major Depletion Zone; Directly under the precipitated layers is where glass begins and represents a major deletion zone in the outermost glass surface. Here major components of the glass are depleted in this area. The region is further characterized by the intrusion of major brine components such as Mg. The original glass surface, the interface, is located in this region.

- Gradient Zone; Below the major depletion zone is the gradient zone, which is characterized by depletion of alkali and alkali earth components of the glass and enrichment in the main brine component, Mg. One of the most interesting features of this zone is the presence of a potassium peak. The distance from the interface or glass surface to the potassium peak in the zone, represents the main reaction front of the glass after interacting with the surrounding environment.

- Diffusion Zone; This innermost glass leached layer is believed to be similar to the gel layer which initially forms on simple glasses during leaching. The zone is characterized by depletion in Li from the glass and enrichment of H from the solution. The thickness is consistent with diffusion calculations of these components in the bulk glass.

Figure 3. Schematic Representation of Surface Layers on SRS Waste Glass after Burial in WIPP

Brine Analyses. The MIIT program is the only in-situ testing effort of this type which allows solution analyses to be obtained and subsequently, correlated with surface studies. Brine analyses were performed on leachates from selected boreholes containing SRL 165/TDS waste glass undoped and glass doped with Eu and Yb as chemical tracers. After measuring concentrations found in solution, leach rates were calculated based on sample characteristics and testing conditions. In addition to assessing glass performance in the field, the solution analyses were used to define the original position of the glass surface in more detail. Analyses were performed by Macedo and co-workers at the Catholic University of America and are summarized elsewhere [20].

There are several important observations that can be made from these data. First, the leaching behavior of SRL glass is very similar to other important international waste glass compositions used in this study. This includes the Japan- Switzerland- Sweden [JSS] composition. This observation was predicted by the compositional ternaries discussed elsewhere [21]. Next, the actual leach rates are very low, generally less than 1 g/m^2-day. This is noted based on both brine analyses and by calculations of SIMS profiles, even for very mobile and non-radioactive species such as Li. Finally, if one takes into account the geometry of the stored waste, leaching depths can also be calculated and related to the Nuclear Regulatory Commission release rate criteria [10 CFR Part 60]. For the MIIT tests, both solution analyses as well as independent surface studies, showed release rates of species of interest of less than one part in 100,000 for all elements investigated, thus far [20, 22, 23].

Based on characterization studies, such as those discussed briefly above, and as a result of many other investigations conducted over the past 30 years, both qualitative and quantitative glass leaching models have been developed to explain observed leaching behavior and the effects of surface layers on the leaching process. In one approach, a simplified 3-stage corrosion process based on glass structural changes has been postulated for nuclear waste glasses involving 1) interdiffusion, 2) matrix dissolution and 3) the effects of surface layer formation [24]. This concept and other modeling efforts are described in detail elsewhere [1].

Summary

The random network structure of glass provides a unique matrix that is particularly suited for incorporation and subsequent immobilization of potentially hazardous radioactive and non-radioactive materials. Based on all data currently available, including characterization studies and leaching tests, the performance of a wide variety of waste glass systems and their ability to retain hazardous species is excellent, when tested under realistic conditions, as determined by many studies performed by many different investigators in many different countries. In addition to possessing outstanding chemical durability, the durability of nuclear waste glasses generally improves with increasing time. This behavior has been observed not only in laboratory tests, but in actual field experiments conducted with simulated U.S. HLW glasses buried in Sweden, Belgium, the United Kingdom and the United States.

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