

MASTER

MECHANISM FOR ELEVATED TEMPERATURE LEACHING*

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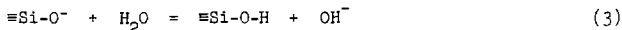
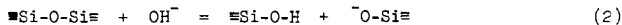
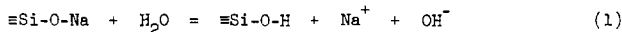


ABSTRACT

Long-term, elevated temperature leaching and subsequent electron microprobe analysis of simulated waste glass and ceramic materials have been completed. A cyclic leaching pattern was found in all systems over a 20-month period. It appears that the leaching of mobile ions by simple diffusional processes is modified by more complex chemical interactions. The release of immobile ions is primarily a function of their chemical interactions in the matrix which suggests that these ions may be complex species when released into solution. A mechanism is proposed which incorporates these ideas and the cyclic phenomenon observed.

INTRODUCTION

The leaching process of a simple soda-silica glass can be represented by Equations 1-3.¹ The removal of Na⁺ from the



glass surface results in a depletion layer containing a Na⁺ concentration gradient. This provides the impetus for diffusion of Na⁺ from the interior of the glass to the depleted zone. Note

*This work supported by the United States Department of Energy (DOE), under Contract DE-AC04-76-DP00789

**A DOE Facility.

that Equations 1-3 suggest that the silicate matrix is included in all leaching processes of glass--the hydrated depth is termed the gel or leach layer and is itself solubilized at some rate.

The inclusion of additional elements in a glass is tantamount to compounding the leaching processes, e.g., in soda-lime-silica glasses, the formation of calcium silicate can act as a barrier to inhibit the diffusion of Na^+ .¹ In a complex system such as vitrified nuclear waste, the leaching behavior of elements may be quite complicated due to interactions of the elements with each other, with the matrix, with the gel layer, H^+ or with OH^- ions. These interactions can include ion-exchange, metathetical reactions, precipitation, complexation and polymer formation. The relative importance of the interactions depends on the physical form of the materials, leachant, temperature, exposure time, composition, and other physical variables. Thus, long-term leaching studies are of paramount importance since they can indicate the relative importance of specific mechanisms and mechanism changes as a function of time. The present work is an initial step toward gaining understanding of the basic leaching processes.

EXPERIMENTAL

Monolithic forms of two zinc borosilicate glass samples, one prepared at Battelle Northwest (BNW) and one prepared at Sandia Laboratories (SIA) using 73-1 glass frit, and one hot pressed sodium titanate waste pellet (STW) containing ca. 10 w/o zeolite, underwent soxhlet leaching tests for 20 months. The STW pellet was primarily a ceramic, but did contain a small amount of a dispersed amorphous silica phase due to the inclusion of zeolite. All three samples contained nominally 25 w/o simulated high-level calcined waste with a composition similar to that proposed for the Allied General Nuclear Services fuel reprocessing plant planned in Barnwell, SC. Tc, Pm, and transuranics (TRU) were not included. Each sample was leached in a quartz soxhlet apparatus² using deionized water (300 mL), maintained at boiling temperature. The leachant was changed monthly. An identical soxhlet apparatus containing only deionized water was run in parallel as a blank. The total amounts of Cs, Sr, Na, Mo, Zn and Si in the leachant were determined by atomic absorption spectroscopy.

Initial homogeneity of the samples was assured by scanning the total widths several times of unleached, freshly polished surfaces of identical samples with an electron microprobe for the elements Cs, Sr, Gd, Pd and U. Except for Pd which had agglomerated into islands of the metal throughout the samples, less than 5% variation was found within each sample for these elements.

At the conclusion of the leaching, the samples were sectioned,

mounted and polished and the distribution of selected elements in the gel layer was determined by electron microprobe analysis. Both quantitative analysis and pictorial distributions were obtained.

RESULTS AND DISCUSSION

From about the second month of leaching on, the glass samples (SIA, BNW) displayed a reddish-brown "skin" on their surfaces which periodically sloughed inhomogeneously, generally reexposing the glass surface. The primary elemental composition of this layer in order of decreasing concentration as determined by emission spectroscopy is: Al~RE>Zr>Fe>U>Mo>Cr~Ca. These elements generally are considered as immobile elements, i.e. those which do not diffuse or diffuse very slowly. There was no "skin" formation or sloughing observed on the ceramic sample (STW).

The cyclic leaching pattern is not a new phenomenon and has been reported previously.³⁻⁶ Figs. 1 and 2 serve to demonstrate its characteristics in this study. Concentration maxima of immobile elements, e.g. U, RE, Si, Mo, in the leach solution generally precede the maxima of mobile elements, e.g., Na, Cs, Sr, by up to one month whereas the concentration minima are temporally coincident. This cyclic phenomenon was observed for all three samples although it was somewhat subdued for the ceramic sample (STW). This might be due to the much lower silicate content (10 w/o) in the ceramic sample as opposed to the glass samples and/or because the silicate phase is not continuous in the ceramic sample, but is dispersed throughout the ceramic phase.

Electron microprobe studies of the leached samples identified the presence of a discrete gel (leach) layer in the glass samples, but none for the ceramic sample. Because of this, a definitive leaching mechanism for the ceramic sample has not been formulated and further studies are in progress. Therefore, the following discussion concerns only the glass samples (SIA, BNW).

Elemental distributions were determined across the gel layers several times at different locations by the electron microprobe with consistent results. When compared to unleached glass, several conclusions can be made. Figs. 3 thru 8 are from the BNW glass which is used as an example. (a) Fig. 3: the gel (leach) layer appears to be porous in nature, (b) Fig. 4: there are distinct, continuous linear zones where Na, Fe, Zn and perhaps P are concentrated. Since Na, Zn and P have some diffusion mobility, these layers suggest that there are diffusion barriers formed in the gel layer. The Na-Fe-Zn-P layers, once formed, may themselves become diffusion barriers, (c) Fig. 5: mobile elements (Na, K, Cs, Sr) are depleted in the leach layer (Na is shown in Fig. 4 and is depleted except in the Na-Fe-Zn-P layers), (d) Fig. 6: the relative concentrations of immobile elements (Zr, U, RE) are enhanced in the leach layer, (e) Fig. 7: matrix elements do not exhibit identical behavior,

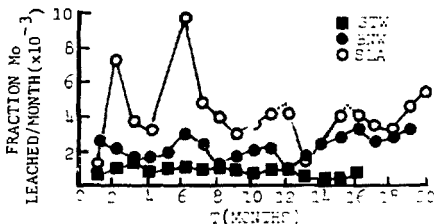


Figure 1. Soxhlet Leaching of Mo From Glasses (SLA, BWA) and Ceramic (PTX) Leached With 25 w/c Waste Oxide Simulant.

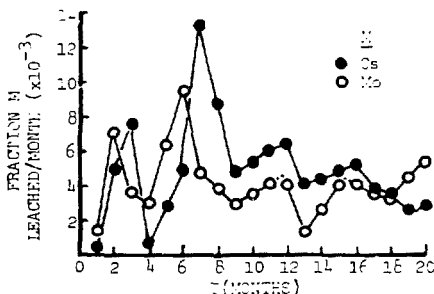


Figure 2. Comparison of Soxhlet Leaching of Mobile (Cr) and Immobile (Co) Elements from Class (SLA) Loaded with 25 w/c Waste Oxide Simulant.

i.e., the relative concentration of Al is decreased, but approximately constant in the leach layer, Si definitely decreases toward the outer edge of the gel layer, and Zn generally decreases except in the thin barrier zones as shown in Fig. 5. Note that these results indicate the solubilization of the silicate matrix as suggested in Equations 1-3, (f) Fig. 8: in the leach layer, Mo is depleted, probably due to the formation of soluble MoO_4^{-2} species, and Cr is depleted only in the outer half of the leach layer. This latter result may indicate a species change from an insoluble chromium compound to a soluble CrO_4^{-2} species. The fact that this change occurs at a Na-Fe-Zn-P barrier may or may not have significance.

The following leaching mechanism is consistent with the experimental results. The leachant reacts with the fresh glass surface to form siliceous gels initially releasing both mobile and immobile ions into solution. The immobile ions form hydroxides or other insoluble species in the gel layer which prevents their rapid diffusion or solubilization. They remain to produce a porous framework as the siliceous gels dissolve away. Mobile ion diffusion becomes increasingly inhibited because the effectiveness of diffusion barriers in the gel layer is continually enhanced by the formation of contiguous secondary diffusion barriers, e.g., the Na-Fe-Zn-P layers. Eventually, the leach layer becomes strained as the siliceous matrix is dissolved and the immobile ions accumulate in insoluble form. The leach layer begins to lose physical integrity with the matrix, possibly at a Na-Fe-Zn-P interface and begins to slough off. Thus, the total immobile ion concentration in the leachant begins to increase and reaches a maximum approximately when the sloughing process is complete and then begins to decrease as a "new" gel layer begins to form. In the sloughing process, the diffusion barriers are removed, or at least decreased, and mobile ions can diffuse more freely, thereby increasing the concentration of mobile ions in the leachant. After the sloughing process is complete, new diffusion barriers are being established and the concentration gradient is being decreased as a new gel layer is formed, thereby causing a decrease in the mobile ion leaching. The cycle then is repeated.

The introduction of immobile elements into solution is by a sloughing process of material composed of insoluble compounds with subsequent solubilization. This suggests that the immobile ion species in solution may be complex in nature rather than a simple ion. Scheffler et al.⁴ have shown this to be the case for plutonium. The point to be made is that the chemical nature of these species must be known in order to describe their transport through geomeia.

Further studies will be necessary to characterize the diffusion barriers, the effect of time between leaching changes, the effect of leachant composition, and the effect of temperature. Characterization of the species produced through leaching of a wasteform should also be considered.

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ACKNOWLEDGMENT

The authors express their appreciation to P. F. Hlava, Sandia Laboratories, for the electron microprobe work and to J. K. Johnstone, Sandia Laboratories, for informative discussions.

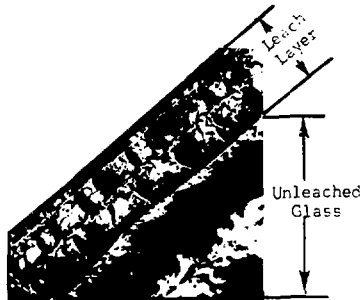


FIGURE 3. SCANNING ELECTRON MICROSCOPY PHOTOMICROGRAPH OF GLASS AFTER 20 MONTHS SOXHLET LEACHING. LEACH LAYER AND UNLEACHED GLASS ARE DENOTED. Scale: _____ = 5 μ .

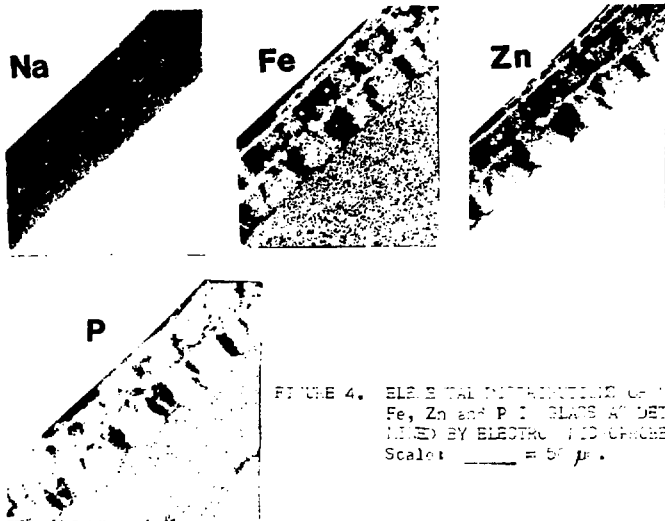


FIGURE 4. ELEMENTAL DISTRIBUTIONS OF Na, Fe, Zn and P IN GLASS AS DETERMINED BY ELECTRON MICROSCOPY. Scale: _____ = 50 μ m.



FIGURE 5. ELEMENTAL DISTRIBUTIONS OF MOBILE IONS IN GLASS AS DETERMINED BY ELECTRON MICROSCOPY. Scale: _____ = 50 μ m.

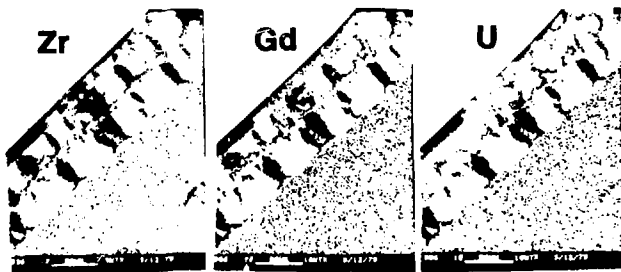


FIGURE 6. ELEMENTAL DISTRIBUTIONS OF MOBILE ELEMENTS IN GLASS AS DETERMINED BY ELECTRON MICROSCOPE.
Scale: _____ = 50 μ m.

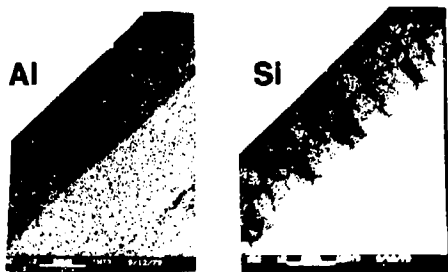


FIGURE 7. ELEMENTAL DISTRIBUTION OF MATRIX ELEMENTS IN GLASS AS DETERMINED BY ELECTRON MICROSCOPE.
Scale: _____ = 10 μ m.

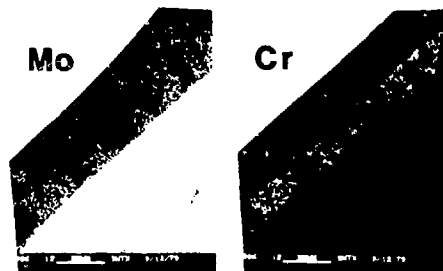


FIGURE 8. ELEMENTAL DISTRIBUTION OF IMMOBILE AND ION FORMING ELEMENTS IN GLASS AS DETERMINED BY ELECTRON MICROSCOPE.
Scale: _____ = 50 μ m.