X-RAY PHOTOEMISSION SPECTROSCOPY AND ION BACKSCATTERING

ANALYSIS OF LEACHED SIMULATED WASTE GLASS CONTAINING UO$_3$

MASTER

by

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ABSTRACT

UO_3 has been dissolved into several complex boro-silicate glasses including Battelle simulated waste glasses 76-68, 3008, and 76-101. The glass surfaces were examined before and after leaching using x-ray photoemission spectroscopy and backscattered ion beam profiling. Samples leached in distilled water showed enhanced surface layer concentrations of several elements including uranium, titanium, zinc, iron and rare earths. For the case of uranium in 76-101, a simple experiment involving leaching two glasses in the same container showed that this surface enhancement is probably not due to redeposition from solution. Similar samples behaved quite differently when leached in a pH = 3.5 nitric acid solution, showing a surface layer high in SiO_2.

INTRODUCTION

Complex borosilicate glasses appear to be viable media for long-term immobilization of radioactive waste products, but the detailed mechanisms of HLW leaching from these glasses and the factors influencing the chemical species being leached are, as yet, incompletely understood. The mechanisms are especially important if one wants to use leaching parameters derived from relatively short-term testing to model and predict long-term leaching behavior.

This study examines chemical and physical changes occuring at or near the borosilicate glass surface upon leaching, using x-ray photo-emission spectroscopy (XPS), and ion beam scattering (IBS). The objective is to develop sufficient understanding of the leaching process to be able to provide a scientific basis for the formulation of actinide and fission product release models.

We have chosen to examine a number of complex silicate glasses containing dissolved UO_3 including Battelle simulated waste glasses 76-68, 3008, and 76-101.

EXPERIMENTAL METHODS AND MATERIALS

X-RAY PHOTOEMISSION SPECTROSCOPY (XPS)

Surface analysis by this technique is accomplished by energy analyzing electrons photoemitted from the near surface region (~30 A) when a sample is irradiated with monoenergetic x-rays (we use the Aℓ K$_\alpha$ line at 1486.6 eV). Useful chemical and physical information comes from measurements of line positions, intensities, line widths (and detailed line shapes), absolute and relative line shifts, doublet splittings, satellite line structure and splitting, etc. The system used in this study was a PHI model 548 spectrometer which has been installed in a glovebox. The system employs a cylindrical mirror analyzer and includes a neutralization filament for preventing charge buildup on insulating samples and a sample fracture mechanism for

exposing fresh surfaces under high vacuum ($\sim 10^{-10}$ torr) conditions allowing spectra to be taken which are characteristic of bulk unleached glasses.

ION BEAM SPECTROSCOPY

Analysis by this technique is accomplished by bombarding the sample with alpha particles accelerated to a fixed energy (typcally 2.9 MeV) and energy analyzing the backscattered particles. The observed particles have undergone a single, large-angle, elastic scattering event. For a given angle, the particle losses a fixed fraction of its kinetic energy in this scattering depending only on the relative mass of the alpha particle and the scattering nucleus. Thus, all particles scattered from like atoms at the sample surface have the same energy. Most particles, however, are scattered from atoms at various distances beneath the surface. These particles have lost an additional amount of energy roughly proportional to the distance traveled through the sample. Thus, for a uniform sample the spectra appear as an overlapping series of energy steps (one for each element) with the distance from the edge of the step indicative of the depth in the sample at which the elastic scattering took place. Generally, the spectra are readily interpretable as concentration profiles of the individual elements that have been shifted in energy and superposed. Typical distances analyzed are thousands of angstroms with resolutions of ~ 500 A.

Some of the features of Rutherford scattering spectrometry make its use in looking at actinides in complex glasses particularly attractive. In a complex glass such as 76-68, the large number of components means the elemental edges are rather close, making determination of individual profiles difficult at best. However, actinide atoms, being substantially heavier than the other elements present, have step edges above and separated from those of the other components making profiling rather straightforward. In addition, the cross section for scattering from a nucleus goes as Z^2 so that actinides are observable in lower concentrations than the lighter atoms.

SAMPLE PREPARATION

Samples of 7668, 3008, and 76-101 obtained from Battelle were powdered, mixed with 2 mole % UO_3 powder, and remelted. Samples cut from the glass ingots were cut to appropriate shape, polished and cleaned with ethyl alchol. Leaching was performed in individual poly-propylene containers at 75°C. After drying, those samples which were to be examined by ion backscattering were coated with ~ 200 A of carbon to minimize surface charging during ion bombardment. Unleached control samples were polished, cleaned, and carbon coated in a similar manner. Rod shaped XPS samples were also prepared for fracture under ultrahigh vacuum conditions.

RESULTS

Ion backscattering spectra of three different glass compositions before and after leaching for one day in distilled water at 75°C are shown in Figures 1-3. The figures represent raw data in the form of counts as a function of backscattered alpha particle energy. Because of the slow and smooth behavior of the energy loss rate dE/dx as a function of energy, the horizontal scale may be thought of as an approximate depth scale. (The offset between the oxygen and silicon profile edges corresponds to ~ 2 μ.)

Figure 1 shows data on the 76-101 + 2 mole % UO_3 glass. The pro-file edges of all of the elemental components of the glass except boron (and any hydrogen left after leaching) are apparent. Two features of the spectra are noteworthy. First, there is very little change in the sodium profile after leaching. This is in sharp contrast to a series of soda-lime-silicate and soda-alumina-silicate glasses examined in an earlier study. Second is a substantial enhancement of the titanium and uranium concentrations near the glass surface. The uranium peak is about 1.7 times as high as the level in the bulk glass and appears to be no broader than the energy resolution of the technique (equivalent

to ~ 500 A). The relative enhancement of the titanium at the surface may be as great but the smaller titanium signal is obscured by the statistical noise.

Figure 2 shows profiles of 3008 + 2 mole % UO_3 glass. Titanium and uranium show concentration enhanced surface layers comparable to those in the 76-101 based glass. Zinc also shows surface enhancement not readily apparent in the 76-101 based glass. Iron and nickel present in the 3008 based glass do not yield individual resolvable profiles but the composite Fe + Ni profile does show surface enhancement.

Figure 3 shows profiles of 76-68 + 2 mole % UO_3 glass. The composition of this glass is quite complex and only the most prominent profile edges are noted. Many edges are weak and obscured but Fe + Ni
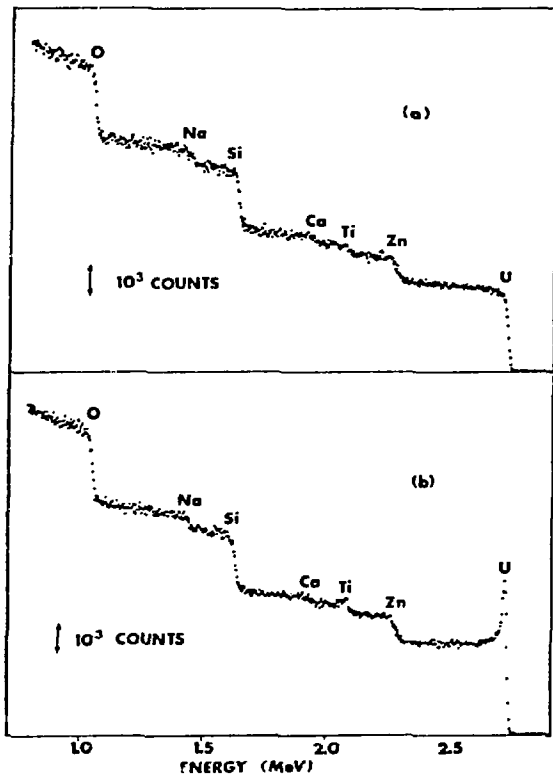

FIGURE 1. IBS profiles of 76-101 + 2% UO_3 (a) before (b) after leaching for 1 day at 75°C in distilled water.
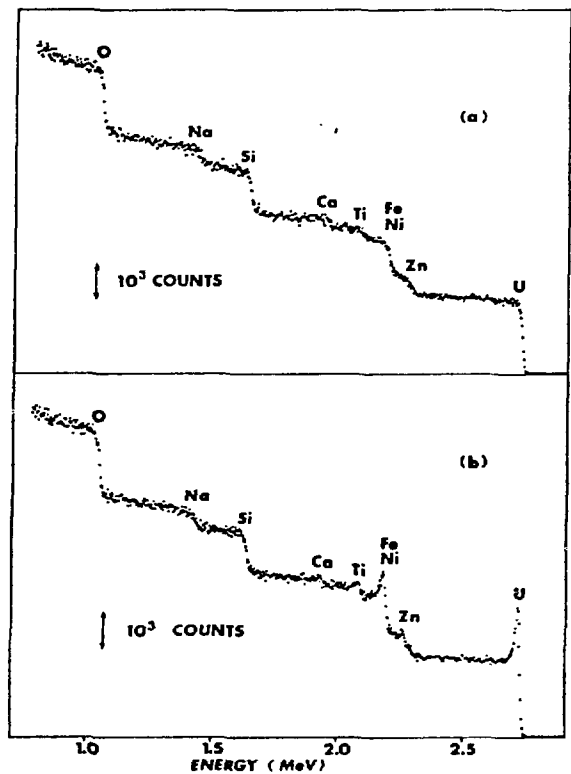
FIGURE 2. IBS profiles of 3008 + 2% UO_3 (a) before (b) after leaching for 1 day at 75°C in distilled water.

enhancement is still clear. The rare earths are not individually distinguishable but their composite profile, designated Ce, Nd on the figures, show surface enhancment. The uranium enhancement in Figure 3 is similar to that in the other glass compositions.

The effects of leaching on the XPS spectra of these glasses were also very pronounced. Moreover, because the depth examined by the XPS technique is approximately an order of magnitude smaller than the depth resolution of IBS profiling, the two probes complement each other very well in providing information on the depth and makeup of the layer affected by leaching.

Figure 4 shows 500 electron volt wide XPS spectra of 76-101 + 2% UO_3 glass for a freshly fractured surface (top) and after leaching in distilled water at 75°C for progressively longer periods. The intensity of a particular core line is proportional to the cross-section for photoemission from that core state times the concentration of that atomic species. The relative cross-sections can be determined by examination of the unleached sample which should be representative of the known bulk glass composition. For a given spectrum, concentrations can then be normalized to sum to 100%, thus determining the surface composition at different leach times. With this procedure, we find progressive enhancement in TiO_2 and UO_3 and, to a lesser extent, in ZnO as leach time increases (to 33%, 15%, and 18%, respectively). Necessarily, the SiO_2 concentration is reduced (to ~ 30%). In the earliest stages of leaching, there is an initial increase in SiO_2 presumably due to the even more rapid loss of Na and B.

The enhancement of U and Ti as seen by XPS is substantially greater than the peak enhancement as seen on the IBS profiles. The reason for this is that the IBS profile can only give the enhancement factor averaged over its depth resolution. The surface peaks in the true U and Ti profiles must be considerably narrower than the IBS profiles show and at
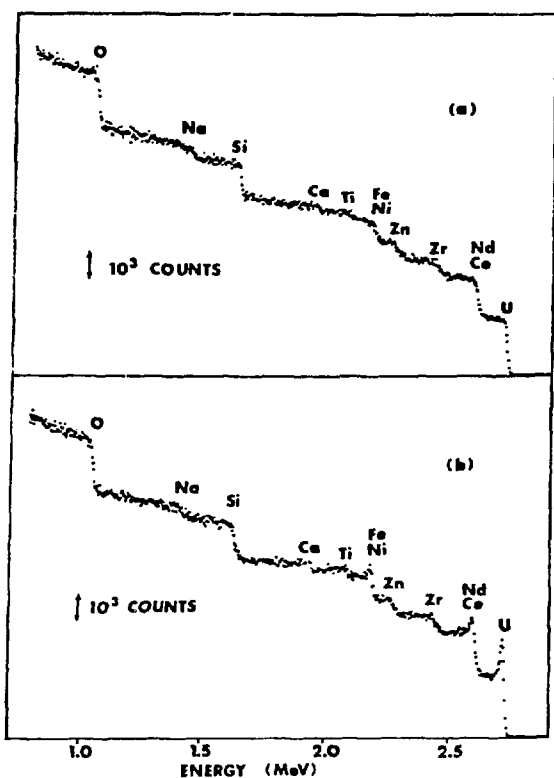
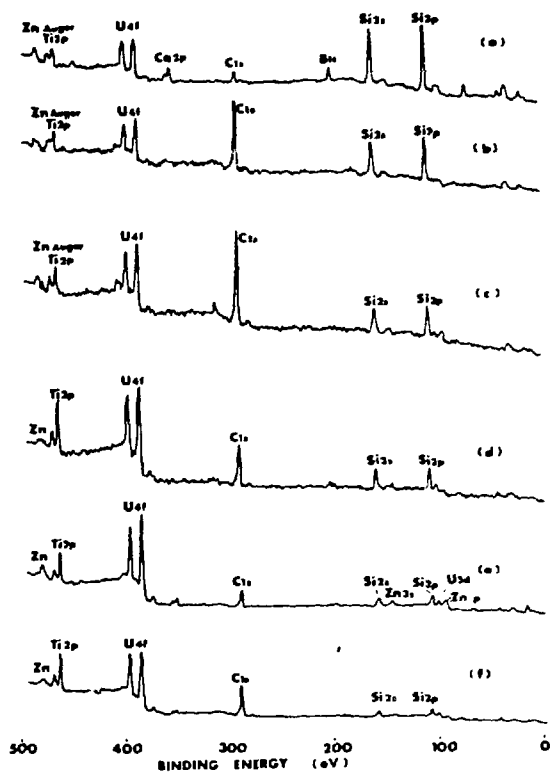FIGURE 3. IBS profiles of 76-68 + 2% UO$_3$ (a) before (b) after leaching for 1 day at 75°C in distilled water.

FIGURE 4. XPS spectra of 76-101 + 2% UO$_3$ (a) unleached, after leaching for (b) 1 hr (c) 3 hrs (d) 6 hrs (e) 1 day (f) 3 days at 75°C in distilled water.

least as high as the enhancement observed in the XPS spectra. Information from both techniques is valuable in studying the evolution of the leaching process; IBS to give the integrated excess U or Ti in the entire surface region, and XPS to give detailed compositional and chemical information about the 20-30 Å layer right at the glass-solution interface.

Surface enhancement could result from selective leaching or by redeposition from solution. An experiment was performed to determine which mechanism was responsible for the uranium enhancement in the 76-101 based glass. Two glass samples (one plain 76-101 and one containing

UO$_3$) were placed in the same polypropylene container with ~ 2 ounces of distilled water and leached at 75°C for 24 hours as before. Gentle agitation was provided every few hours. If the uranium was being dissolved and redeposited it should be detectable on both glass surfaces. XPS examination of the plain 76-101 glass did not reveal any uranium present indicating that the observed enhancement was due to selective leaching of other components and not redeposition from solution.

Figure 5a and b show XPS spectra of 76-68 + 2% UO$_3$ glass fractured in vacuum and leached for one day in distilled water at 75°C respectively. As the number of components increases, identification of many features in the spectra becomes more difficult. The relative surface concentrations of U, Si, Ti and Zn seem to be similar to the 76-101 based glass. Zr shows substantial surface enhancement (rather ambiguous in the IBS profile). The Fe + Ni profile peak in the IBS spectrum would appear to be predominantly Fe from the XPS data.

Some recent leaching studies conducted by Dr. Gary McVay of Battelle PNL suggest that the significant effects observed when leaching is performed under gamma irradiation are due, at least in part, to radiolysis of air in the presence of water yielding HNC$_3$. By examining leached samples with ESCA in combination with ion sputtering, they observed elemental profiles of Nd, Zn, Si, Na, Fe, and Ti in HNO$_3$ leached 76-68 glass which were similar to results on a gamma-irradiated deionized water leached sample.
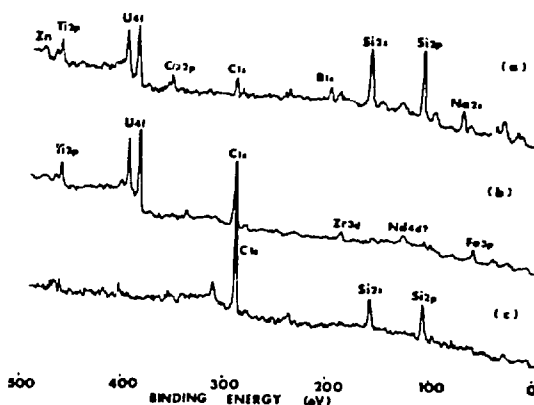
We leached samples of 76-101 + 2% UO$_3$ and 76-68 + 2% UO$_3$ glasses in HNO$_3$ (pH = 3.5) for one day at 75°C. Figure 5c shows the XPS spectrum of the HNO$_3$ leached 76-68

FIGURE 5. XPS spectra of 76-68 + 2% UO$_3$ (a) unleached; leached for 1 day at 75°C in (b) distilled water (c) HNO$_3$ (pH = 3.5).

based glass. The immediate surface is silica rich. (The C 1s peak is due to surface contamination which was quite large on this sample.) The uranium 4f signal is absent. Some Ti is still present but the signal is smaller than in the water leached sample.

Figure 6 shows these results more clearly on the 76-101 based glass. The HNO_3 leached surface, (c), appears to be mostly SiO_2 with some Ti present in sharp contrast to the water leached result in (b).

Figure 7 shows the IBS profile of the HNO_3 leached 76-68 + 2% UO_3 glass. (Unfortunately, a technical mishap prevented our obtaining the results on the 76-101 based glass.) The interpretation of some of the features is complicated by the number of components present. Nonetheless, several points can be made. Both Ti and Fe show very large surface enhancements. The U edge shows depletion below bulk values to a depth of at least several hundred angstroms but there appears to be structure within this depleted region. There is a broad peak near where the Zr edge should exist but this could be due to contributions from several elements. Na shows a deep depleted region. Finally, the Si signal is enhanced in a surface layer several hundred angstroms deep.
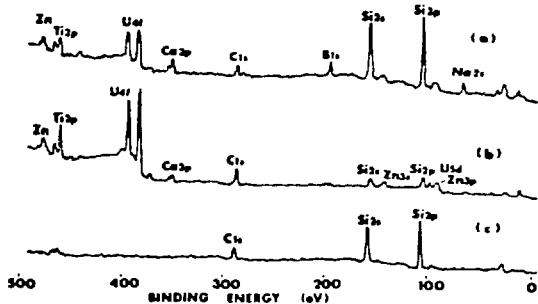

FIGURE 6. XPS spectra of 76-101 + 2% UO_3 (a) unleached; leached for 1 day at 75°C in (b) distilled water (c) HNO_3 (pH = 3.5).
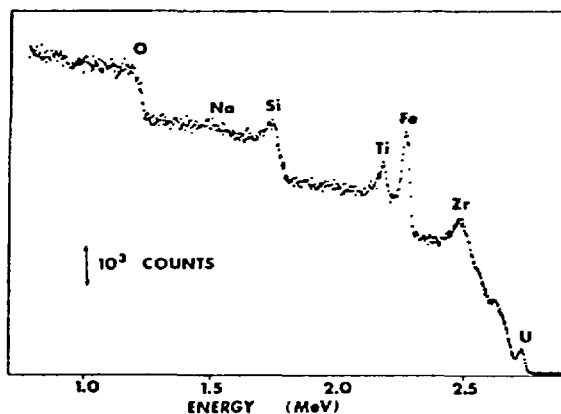
FIGURE 7. IBS profile of 76-68 + 2% UO_3 leached 1 day at 75°C in HNO_3 (pH = 3.5).

CONCLUSIONS

The surface composition of 76-101, 3008, and 76-68 simulated waste glasses containing UO_3 have been examined before and after leaching. Distilled water leaching in all of the glasses was characterized by the removal of Si, B, and Na from the surface region leaving a surface layer enhanced in Ti, Zn, Fe, the rare earths, and U. These results (except U enhancement) are in accord with the ESCA/ion sputtering profiles obtained at PNL. In the HNO_3 leached glasses, on the other hand, we find the surface becoming Si rich, while U (and probably the rare earths) are depleted. The very large Ti and Fe concentration enhancements, which extend to several hundred angstroms, imply removal of many of the other glass components from thicknesses several times this great. Apparently the surface layers of TiO_2, ZnO, UO_3, etc. in the water leached glasses acted as passivating films hindering continued leaching.

In an earlier IBS and XPS leaching study of Al_2O_3 in $Na_2O \cdot 3SiO_2$ glasses, we found the addition of Al_2O_3 to drastically affect Na removal from the glass, apparently by inhibiting ion exchange at the surface since Al_2O_3 addition actually increases Na diffusion constants (Terai 1969). Recent Basic Energy Sciences sponsored XPS work within our group has revealed systematic effects in the bonding of Na in $Na_2O \cdot 3SiO_3$ based glasses as various glass matrix forming and modifying components are added. We plan to extend this approach to gain an understanding of the function of the various glass components in 76-101 glass.

Past experiences has proved that physical and chemical information obtained on U systems cannot always be applied to Np, Pu, and Am. Future work will be extended to include 76-68 and 76-101 glasses incorporating the higher actinides.

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