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by

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XPS AND ION BEAM SCATTERING STUDIES OF LEACHING IN SIMULATED WASTE GLASS CONTAINING URANIUM*

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ABSTRACT

Glass samples (consisting of 2 mole % UO_3 dissolved in a number of complex borosilicate simulated waste glasses including Battelle 76-68) were leached for varying times in distilled water at 75°C. The glass surfaces were examined before and after leaching using x-ray photoemission spectroscopy and back-scattered ion beam profiling. Leached samples showed enhanced surface layer concentrations of several elements including uranium, titanium, zinc, iron and rare earths. An experiment involving the leaching of two glasses in the same vessel showed that the uranium surface enhancement is probably not due to redeposition from solution.

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33½ x 52 picas working size
30 x 47 picas final size

3/SC

INTRODUCTION

Critical evaluation of the various proposals for the emplacement of radioactive waste in geological repositories must, to a large extent, be based on an understanding of radionuclide release from high level waste (HLW) forms. 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 photoemission 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

X-ray Photoemission Spectroscopy (XPS)

This technique involves irradiating the sample to be analyzed with monoenergetic soft x-rays. (In this study the Al K_α line, $h\nu = 1486.6$ eV, was used.) The kinetic energy (K.E.) of photoemitted electrons is measured and the binding energy (B.E.) of the electrons in the sample is inferred from energy conservation via the relation, $B.E. = h\nu - K.E.$ The region of the sample analyzed is limited by the escape depth of the electrons (typically ~ 30 Å). Elemental compositional analysis is performed by measuring the intensity of electrons emitted from characteristic atomic core states. More detailed chemical and physical information comes from measurements of 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 electron energy analyzer. A neutralization filament is used for preventing charge buildup on insulating samples. The system also included a sample fracture mechanism for exposing fresh surfaces under high vacuum (~ 10^{-10} torr) conditions allowing spectra to be taken which are characteristic of bulk unleached glasses.

Ion Beam Spectroscopy (IBS)

In order to develop models for the mechanisms involved in leaching, it is often important to be able to interpret XPS results in light of compositional variations over a broader depth range. One might then be able to judge whether the detailed bonding information inherent in the XPS technique was representative of the entire gel layer or just the immediate surface (perhaps a surface layer laid down by redeposition from solution).

Analysis by this technique is accomplished by bombarding the sample with alpha particles accelerated to a fixed energy (typically 2.9 MeV) and energy analyzing the backscattered particles. Most of the observed particles have undergone a single, large-angle, elastic scattering event. For a given detection angle, the particle retains a fixed fraction of its kinetic energy in this scattering depending only on the ratio, R, of the mass of the scattering nucleus to the mass of the alpha particle. This fraction, known as the kinematic factor is given by

$$K = \left[\frac{(R^2 - \sin^2\theta)^{1/2} + \cos\theta}{R + 1}\right]^2 .$$

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. 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 Å.

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

The compositions of the simulated waste glasses used in this study are given in Table 1. Samples of 7668, 3008, and 76-101 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 alcohol. Leaching was performed in individual polypropylene containers at 75°C. After drying, those samples which were to be examined by ion backscattering were coated with ~ 200 Å 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 energy axis associated with a given elemental profile may be thought of as an approximate depth scale.

Figure 1 shows data on the 76-101 + 2 mole % UO_3 glass. The profile 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 Å). 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.

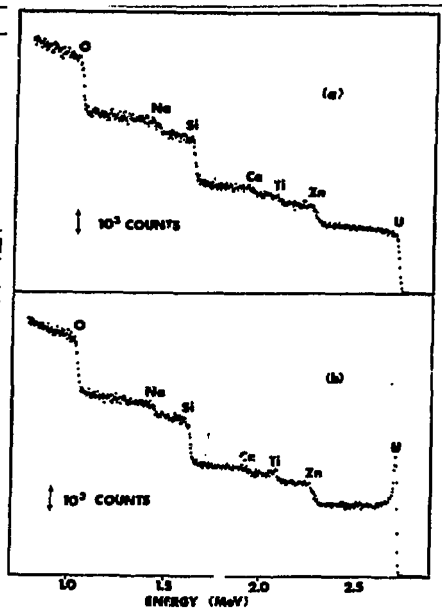

Fig 1. IBS profiles of 76-101 + 2% UO_3 (a) before (b) after leaching for 1 day at 75°C in distilled water.

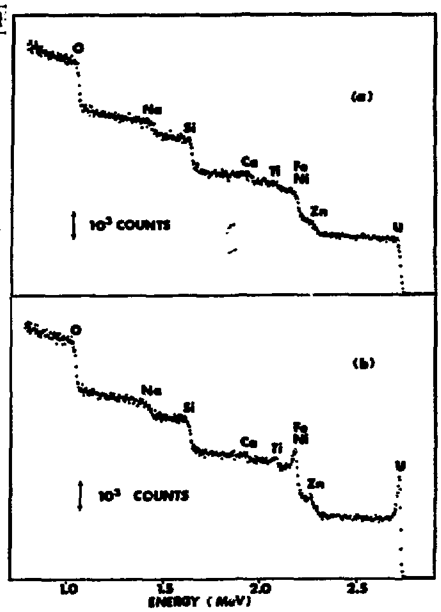

Fig 2. IBS profiles of 3008 + 2% UO_3 (a) before (b) after leaching for 1 day at 75°C in distilled water.

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

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%,

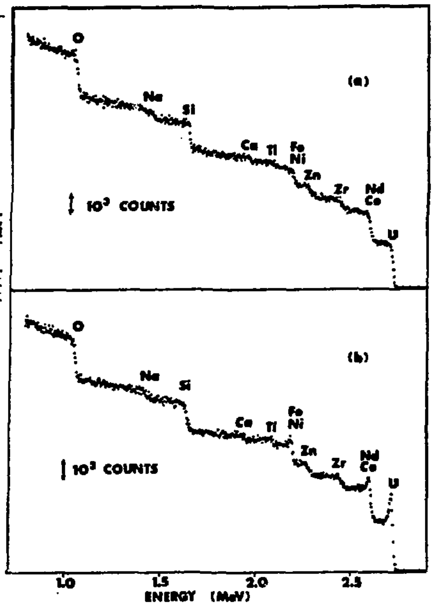

Fig 3. IBS profiles of 76-68 + 2% UO_3 (a) before (b) after leaching for 1 day at 75°C in distilled water.

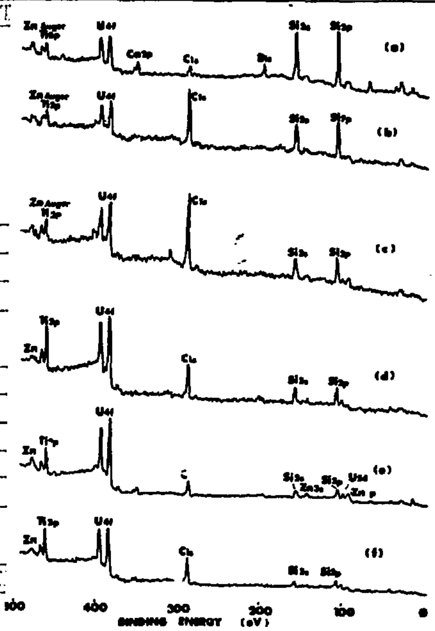

Fig 4. XPS spectra of 76-01 + 2% UO_3 (a) unleached, after leaching for (b) 1 hr (c) 3 hrs (d) 6 hrs (e) 1 day (f) 3 days at 75°C in distilled water.

and 18%, respectively, see Fig. 5). Necessarily, the SiO_2 concentration is reduced. 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 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 6a 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

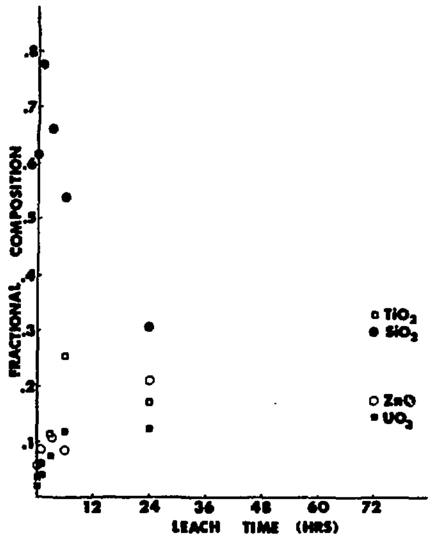

Fig 5. 76-101 + 2% UO_3 glass surface composition vs. leaching time at 75°C in distilled water as determined from data in Fig. 4.

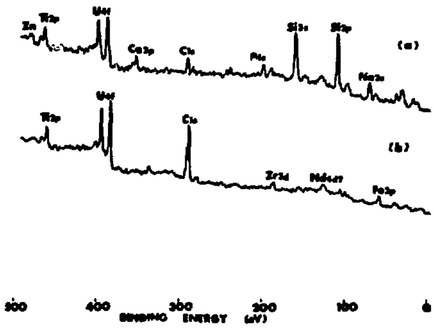

Fig 6. XPS spectra of 76-68 + 2% UO_3 (a) unleached; leached for 1 day at 75°C in (b) distilled water.

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.

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.

The overall similarity in the behavior of the elements common to 76-101 and 76-68, especially uranium, is encouraging. XPS valence state identification in other actinides may rely on the analysis of weak satellite lines which might easily be obscured in the crowded spectra of 76-68. It would be much easier to study actinide behavior in the similar but simpler 76-101 glass.

ACKNOWLEDGEMENTS

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