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NEAR-SURFACE LEACHING STUDIES OF Pb-IMPLANTED SAVANNAH RIVER WASTE GLASS

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INTRODUCTION

Ion implantation into simulated nuclear waste glasses is a rapid means of producing near-surface energy deposition similar to that produced by α -recoil nuclei after long storage times (typically $10^3 - 10^6$ years). For example, Dran, Maurette, and Petit¹ used 200 keV Pb-ion implantations in glass at a fluence of $5 \times 10^{12}/\text{cm}^2$ to produce surface damage. This fluence is equivalent to approximately 2×10^{18} alpha-decays/ cm^3 which corresponds to approximately 10^6 years storage for glass containing Savannah River Plant (SRP) defense high-level waste (DHLW). These authors¹ found that this fluence value corresponded to a critical fluence (Φ_c) for enhanced etching (a factor of 20 increase as inferred by step-height changes) for several silicate glasses when etched in a NaCl solution at 100°C. This critical fluence value also corresponds very well with the fluence at which significant overlap of individual ion tracks occurs. In a subsequent paper,² Dran and his colleagues at Orsay have examined the etching problem in greater detail for a wide variety of glasses and etching conditions and have shown that the leaching of implanted glasses is a complex process and that the overall rate of dissolution depends upon the form of the hydrated layer and its swelling and subsequent removal. The rates at which these various steps occur determines the kinetics of the release of the glass constituents to the solution. Recently, Primak³ has also observed etch rate increases due to ion implantation using a variety of inert gas ions along with D^+ ions. The increases he observed, however, were approximately 7 times smaller than those observed by Dran, et al.¹ The reported increase in etch rate has drawn the attention of the Harwell group,⁴ who have observed that significant increased leaching rate increases have not been noted in their glasses doped internally with alpha emitting actinides even when the α -decay dose exceeds that produced by a Pb-fluence of Φ_c . For example, a glass doped with Pu-238 has been under observation for an alpha decay dose of $> 5 \times 10^{18}$ decays/ cm^3 . Based on weight loss measurements,

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the etch rate increased by a factor of <2. Similarly, preliminary measurements of the leach rate of ion implanted SRP waste glass based on solution analyses indicate no increase in leach rate up to doses equivalent to 3×10^{20} α -decays/cm³.⁵

The present experiments with SRP simulated nuclear waste glass implanted with Pb ions (see the Experimental Section), used RBS and ERD to follow in detail the changes in composition which occur in the near-surface region upon leaching in deionized water at 90°C. Analyses of the leach solutions were made in an attempt to correlate the actual leach rates with the observed near-surface compositional changes. These experiments show that radiation damage can cause changes in the composition of the near-surface of the leached glass. We also find that a critical fluence is reached where abrupt changes of the surface elemental composition occur as a result of leaching. This fluence is near the value observed by both Dran, et al.¹ and Primak.³ Solution analyses were not made for all the leaching experiments. However, those analyses which were made indicate that the amount of material actually leaving the glass is not significantly increased as a result of the radiation damage.

EXPERIMENTAL

Compositions of the frit and simulated DHLW are shown in Table I. The frit is currently the reference proposed by SRP to immobilize all the DHLW currently stored at SRP. Glasses were prepared by melting a dry mix (72 wt % frit and 28 wt % simulated waste) at 1150°C for at least three hours. To attain homogeneity, the glasses were then crushed and remelted at 1150°C. They were finally annealed at 500°C for 1 hour. Samples were then cut and polished for irradiation. Static leach tests were made using deionized water at 90°C. The surface area to leachate volume ratio (SA/V) was 0.05 cm⁻¹. Analyses for dissolved Si, Li, B and Na were made using inductively coupled plasma spectroscopy (ICP). Similar results were observed for both acidified and nonacidified leachates.

TABLE I
Composition of Reference Frit 131 and Simulated Defense
High-Level Waste (TDS-3A)^a

Frit Component (wt %)	Simulated Waste Component (wt %)
SiO ₂ (57.9), B ₂ O ₃ (14.7), Na ₂ O (17.7) Li ₂ O (5.7), MgO (2.0), TiO ₂ (1.0) La ₂ O ₃ (0.5), ZrO ₂ (0.5)	Fe ₂ O ₃ (47.3), MnO ₂ (13.6), zeolite (10.2), Al ₂ O ₃ (9.5), NiO (5.8), SiO ₂ (4.1), CaO (3.5), Na ₂ O (3.1), coal (2.3), Na ₂ SO ₄ (0.6)

^aGlass mix (dry basis) is 72 wt % frit and 28 wt % waste.

Implants were made with an Accelerators, Inc., implanter (15 - 250 keV). Single energy implants (207 keV) and multiple-energy (40-250 keV) Pb-implants were made; the single implants were made because of the previous experimental work by others^{1,2} and experimental simplicity. The multiple-energy implants were made to approximate a uniformly damaged near-surface region. Fluences for the multiple energy implants were chosen⁶ so that the total energy deposition approximated that for 3×10^{18} , 3×10^{19} , and 3×10^{20} α -decays/cm³. These are referred to as "low," "medium," and "high" dose implants throughout this paper. Some samples were also implanted with H to a fluence of 1×10^{16} H/cm² at either 100 keV or 45 keV. These H implants were used as a marker for monitoring the depth of compositional changes and material removal rates at the glass surface.

The near-surface elemental concentrations were determined by Rutherford backscattering spectrometry (RBS) and elastic recoil detection (ERD). For RBS, the probe particle was 2.8 MeV He⁺ and the angle between surface normal and the incident beam was set at 55° for high resolution (~ 50 Å). For elastic recoil detection (ERD),⁷ 12 MeV C³⁺ was used to determine the position of the 100 keV hydrogen marker which initially was at a depth of ~ 1 μ m. Hydrogen and lithium profiles were obtained using 20 MeV Si⁴⁺ as the ERD probing beam.

RESULTS

Our results can best be presented and discussed in terms of the type of implantation (multiple or single energy) and the leaching times (5, 6 or 1.5 hours).

A. Multiple Energy Implantation Followed by 5 and 6 Hr Leach Tests

For these experiments, three samples were implanted (on both sides) each to different doses (low, medium, and high fluence) which are equivalent to 3×10^{18} , 3×10^{19} and 3×10^{20} α -decays/cm³. The glasses along with an unimplanted sample were then leached by two 5-hour tests and then three 6-hour tests for a cumulative leach time of 28 hours. Leach rates for Si, B, Li, and Na were measured by solution analysis. The results are plotted in Figure 1 as a function of equivalent α -decays/cm³. Based on solution analyses, no evidence for significant enhanced leaching due to implantation is observed in the data shown in Figure 1. If enhanced leaching occurred, it should be especially apparent in the first leach test where the leaching occurred primarily in the implantation-damaged surface. For a leach rate of 1 g/m²d, approximately 800 Å is leached in 5 hours, which is approximately the range of the highest energy Pb ions used in the implantation. In the first leach test, the maximum difference for any leach rate based on any of the four elements is within a factor

of two of the respective leach rates for the unimplanted glass. No trend with radiation fluence is evident even though the largest two fluences exceed the equivalent α -decay dose produced by the Φ_c determined by Dran, et al.¹ In the second leach test, where some of the damaged layer is probably still being leached, the variation in the leach rates is still less than a factor of 2. Results of the fifth leach test are somewhat scattered also but indicate no effect of implantation. These results may display scatter because of the

Figure 1. Leach rate in deionized water vs. equivalent α -decays/cm³ for 5 leach tests of Pb-ion implanted SRP-DHLW glass. Leach rates are based on 4 elements dissolved in the leachate: $\bullet$, Si; $\blacksquare$, B; $\blacktriangle$, Li; $\blacklozenge$, Na ($T = 90^\circ\text{C}$, $SA/V = 0.05 \text{ cm}^{-1}$, $\rho = 2.7 \text{ g/cm}^3$).

Fig. 2. RBS yield vs. recoil energy

Fig. 3. ERD yield (H, Li) vs. depth.

instability and partial flaking off of the surface layer formed by the previous four leach tests.

After the fifth leach test, the RBS and ERD spectra of these four glasses were measured (Figures 2 and 3). The spectra indicate that implantation followed by leaching results in compositional changes in the near-surface of the leached glasses. Leaching at 90°C of the unimplanted glass produced surface peaks of Fe and/or Ni and of Nd (Figure 2). These distributions are 2.5 ~ 3 times the bulk values and peak ~ 200 Å from the surface and extend ~ 1000 Å into the sample. In addition, the Si and O edges show erosion to a depth of ~ 4000 Å due to a loss of $\sim 4 \times 10^{16}$ Si/O atoms/cm². As seen from the data in Figure 2, the surface compositions of the implanted glasses after leaching differ for "low," "medium," and "high" Pb-fluence levels.

For the low-level implant, the major difference in RBS spectra, relative to the leached unimplanted sample, is that the Fe/Ni and Nd surface peaks are reduced by about 65%. For the medium Pb-fluence, leaching at 90°C reduces the near-surface Fe/Ni level from $\sim 6 \times 10^{19}$ /cm³ to 4×10^{19} /cm³. The removal depth is >3000 Å. However, the surface Fe/Ni peak is enhanced about 25% and extends to greater depth (~ 1500 Å). The Nd surface peak is also broadened and has a shoulder near the expected depth (~ 800 Å) of the implanted Pb. Si and O both show greater losses than in the reference material with the additional loss coming from the ion-implanted layer. Rough calculations show ~ 1400 Si/O atoms removed per incident Pb ion which is reasonable for the average number of displacements in the collision cascade. Release of these displaced atoms apparently occurs for critical energy deposition values as discussed below for single-energy implants. The alkali content for the medium- and high-Pb fluence levels has also been significantly altered. This is especially true for Li (Figure 3) which is removed from depths >3000 Å. Na is also preferentially removed from the implanted region but the effect is not as well defined (Figure 2). Extensive hydration (Figure 3) is not seen to accompany the Li loss which probably indicates substantial removal of the gel layer. Some loss of H could also have occurred due to a longer time interval between leaching and scattering measurements than was the case for the single-energy implants of (B) below. Leaching of the high-level Pb implant results in an RBS spectrum almost identical to that for the leached unimplanted sample. ERD measurements, however, show loss of Li as was observed for the medium-dose implant. On the basis of the ERD spectra for the medium and high fluence and the RBS spectra for the medium Pb-implant, Pb-ion fluences equivalent to

α -decay doses on the order of $10^{19}/\text{cm}^3$ produce significant changes in the near-surface composition of leached SRP glass.'

B. Single Energy Implantation Followed by Four 1.5 Hr Leach Tests

To obtain information at various stages of damage and/or leaching, experiments were performed using single energy implants (207 keV Pb) at fluences of 5×10^{11} - 1×10^{16} ions/ cm^2 . These glasses were also implanted with 100 keV H ions as a depth marker at $\sim 10,000$ A. Leach rates were determined after each of four 1.5 hr leach tests at 90°C . Again, the leach rates based on Si, B, Li and Na, did not vary by more than a factor of 2 to 3 over the entire fluence range. Values of the leach rates agreed with those determined in the earlier tests (nominally $1 \text{ g/m}^2\text{d}$, see Figure 1) even though the leach times were very short. A significant decrease in the Na leach rate was observed for all the glasses as the cumulative leach time increased. Figure 4 shows this decrease for the two unirradiated glasses and two irradiated glasses. The decrease in leach rate for Na as well as that for Fe, Ni and other elements in unirradiated glass has also been noted by Altenhein, et al.⁸ Apparently, Na very near the initial surface of the glass is easily removed. From the data in Figure 4, it is clear that for these short leach times, the glasses implanted to Pb-ion fluences of 1×10^{14} and $1 \times 10^{16}/\text{cm}^2$ are leaching similarly to the unirradiated glass. This result was also confirmed by the RBS and ERD spectra (not shown). Enhancement of Fe/Ni, Nd and Li at the surface were observed along with Na and Si depletion.

Measurement of the depth of the H marker by ERD using C^{+3} ions indicated that the marker had not moved even though Si and other elements were being leached from the surface. This could occur because the gel layer containing Fe, Ni, etc., largely remains and the net energy loss is primarily due to lower Z components which do not contribute significantly to the ERD measurement of the marker depth. The movement of other species into the near-surface region may also partially compensate by replacing the leached atoms in solution. A Si removal rate of $1 \text{ g/m}^2\text{d}$ infers removal on the order of 200 A per 1.5 hr test for a total of 1200 A. Altenhein, et al.⁸ have speculated that the enhancement of Fe, Ni and other elements may form a protective layer by forming insoluble oxides and hydrates.

C. Additional 10 Hr. Leach Test of Single-Energy Implanted Glasses

All the samples discussed above were leached an additional 10 hrs. Unfortunately, it was not possible to obtain solution analysis of these leachates. Figures 5-7 compare the RBS spectra and the ERD profiles for the implanted samples after the 10 hr leach to those for unimplanted material.

Fig. 4. Sodium leach rates vs leach time

Fig. 5. ERD yield vs. depth for 207 keV Pb-implanted samples:
— reference (no implant/leach),
... reference (leached), $\blacksquare$ $5 \times 10^{11}/\text{cm}^2$, $\square$ $1 \times 10^{12}/\text{cm}^2$, $+$ $5 \times 10^{12}/\text{cm}^2$, $\blacktriangle$ $1 \times 10^{13}/\text{cm}^2$, $\times$ $1 \times 10^{14}/\text{cm}^2$, $\circ$ $1 \times 10^{15}/\text{cm}^2$, $\blacklozenge$ $1 \times 10^{16}/\text{cm}^2$.

Fig. 6. ERD yield (Li) vs. depth for 207 keV Pb-implanted samples:
— reference (no implant/leach),
... reference (leached), $\blacksquare$ $5 \times 10^{11}/\text{cm}^2$, $\square$ $1 \times 10^{12}/\text{cm}^2$, $+$ $5 \times 10^{12}/\text{cm}^2$, $\blacktriangle$ $1 \times 10^{13}/\text{cm}^2$, $\times$ $1 \times 10^{14}/\text{cm}^2$, $\circ$ $1 \times 10^{15}/\text{cm}^2$, $\blacklozenge$ $1 \times 10^{16}/\text{cm}^2$.

Fig. 7. RBS yield vs. depth for 207 keV Pb-implanted samples:
... reference (leached), $+$ $5 \times 10^{12}/\text{cm}^2$, $\blacktriangle$ $1 \times 10^{13}/\text{cm}^2$, $\blacklozenge$ $1 \times 10^{16}/\text{cm}^2$.

Each series of spectra show large changes occurring for the same critical fluence in the range $\Phi_c = 5 \times 10^{12}$ to 1×10^{13} 207 keV Pb/cm². This fluence agrees with that observed by Dran, et al.¹ and Primak.³ For this fluence interval, Figure 5 shows the movement of H into the glass to depths greater than 5000 Å from the surface and concentrations an order of magnitude larger than bulk values. Measurements with 12 MeV C³⁺ ERD gave no evidence for the 100 keV H depth marker indicating that the physical surface of the glass had been removed to depths >1 μm by this 10 hr leaching step. The integrated H-distributions for samples where the fluence was Φ_c or greater, is about 3×10^{17} H/cm² compared to about 8×10^{16} H/cm² for those with fluences below Φ_c . Figure 6 shows a sharp loss of Li for fluence levels > Φ_c ; for those with fluences below Φ_c the Li levels are about 8×10^{16} Li/cm² while above Φ_c the level is between 1×10^{14} - 8×10^{15} Li/cm², integrated over the depths indicated on Figure 6. In contrast, it is also apparent that for fluences < Φ_c , near-surface Li concentrations are increased over leached unimplanted reference sample levels.

Figure 7 indicates that for fluences > Φ_c several important changes occur in the RBS spectra. The most apparent change is a large increase in the near-surface concentration of Fe/Ni to depths of ~5000 Å. In addition, the Nd near-surface level increases by more than a factor of 2. It is also clear that the Si near the surface has been eroded severely. If one assumes that all of the Fe/Ni and Nd represent ions from the bulk glass pushed back by the moving surface, then material is removed to depths of ~1.1 μm which is consistent with the loss of the H ion depth marker. The levels of H gained and Li lost are consistent with a picture of H:Li ratio of 2-3 which is consistent with H₂O or (OH₃)⁺ diffusion and exchange.

DISCUSSION

These results clearly demonstrate the existence of a radiation damage effect on near-surface compositional profiles for Pb-ion implantation of this borosilicate nuclear waste glass after leaching. However, a corresponding increase in leach rates measured by solution analysis was not detected. The existence of a radiation damage effect itself is not surprising. It is well known that radiation damage alters many physical properties in glass and, in particular, etching rates in fused silica in dilute hydrochloric acid solution (see, e.g., Webb, et al.⁹). These authors⁹ found an increase in initial etch-rate (0.3% HF solution) of 4-5 for H, C, and O ions implanted in SiO₂ glass. It should also be noted that a maximum occurs in initial etch rate for these ions at about the same energy deposition ($2-4 \times 10^{20}$ keV/cm³) into atomic process.¹⁵

The maximum is followed by a decrease in etch rate with increasing fluence. Similar behavior has been noted for changes in volume, density and refractive index,¹⁰ lateral stress,¹¹ hardness,¹² ion-induced luminescence,¹³ and thermoluminescence¹⁴ for SiO_2 glass. For SiO_2 , the maxima in the induced changes occur for approximately the same energy deposition. These experiments have been discussed in a recent review paper on ion implantation effects in glasses.¹⁵ The decrease in the rate of change of these properties, which is observed after the initial increase occurs at nearly the same energy deposition value and may be due to plastic flow. Such plastic flow results when the compaction of the glass in the implanted region is opposed by lateral tensile stresses in the bulk of the material. In the present experiments, the critical fluence, Φ_c , also occurs at $\sim 2 \times 10^{20}$ keV/cm^2 and may be related to this structural transformation. It should also be noted that the critical Pb-ion fluence corresponds to ion-track overlap for isolated tracks of ~ 45 Å radius. This value is reasonably close to the 25-40 Å radius for isolated Pb-ion tracks seen by Headley, et al.¹⁶ in TEM measurements on Pb-implanted zircon, zirconolite and hollandite. The onset of significant compositional changes appears to occur much more abruptly than in the etching rate experiments of Webb, et al.¹⁰ The sudden sharp compositional changes with Pb-fluence and leaching may reflect the initial high yield stress (and relatively low elasticity) of the glass which must be overcome to initiate plastic flow and consequent increases in leaching rates. In consonance with this view, Dran, et al.² have observed in their experiments with a number of glasses that the more radiation resistant glasses exhibit the sharpest increases in leaching rates.

The ion implantation process itself causes movement of weakly bound modifier ions in the glass structure towards the surface. This is especially the case for alkali ions in alkali silicate glasses and has been noted in earlier work.^{17,18} The driving force for the alkali movement when glasses are bombarded with energetic ions is not fully understood, but may involve electrostatic forces and/or stress fields generated in the material near the end of the ion track.

We should comment on the possible practical implications of our observations. Burns, et al.⁴ have discussed the implantation results of Dran, et al.¹ as noted in the Introduction. The difference in leach rates seems to be a reasonable reconciliation of the wide variations in the leach rates found for the two sets of experiments. As we have already indicated, a possible interpretation of our results could be that the stresses generated in the damaged region may play a significant role in producing enhanced

reaction rates because of a structural transformation of the glass. If this hypothesis should be borne out by further experiments, the implication would be a confirmation of the recognized need for reasonable homogeneity in the nuclear waste glass. Otherwise, the non-uniform α -emitting segments in near-surface regions might make possible the generation of stresses which would allow more rapid dissolution in ground water than is presently measured or anticipated. There is at present no indication from ongoing research on real waste-containing glasses that this effect occurs.

CONCLUSIONS

These experiments on near-surface compositional profiles and solution analyses of Pb-ion implanted SRP nuclear waste glass allow the following conclusions to be made:

- a. Pb-ion simulation of α -recoil damage in SRP glass, followed by leaching in deionized water at 90°C, clearly shows that radiation damage affects near-surface compositional profiles. In particular, large changes were observed in H, Li, Na, Si, Fe/Ni and Nd profiles.
- b. For single energy (207 keV) Pb-implants, a critical fluence, Φ_c , of $5 \times 10^{12} - 1 \times 10^{13}/\text{cm}^2$ was determined for the onset of compositional changes in general agreement with results obtained by Dran, et al¹ and Primak.³
- c. The critical fluence, Φ_c , implies an energy deposition (nuclear processes) of $\sim 2 \times 10^{20}$ keV/cm³. This value corresponds approximately to that for ion-track overlap and to the value observed in many ion-implantation experiments¹⁵ on glass at which observed physical properties begin to change in a manner suggestive of plastic flow or a structural transformation. Such changes could conceivably occur in real waste-containing glasses where segregation of waste has occurred. However, no reports of such an effect in such glasses have yet been noted.
- d. A clear conclusion is that a need exists for further Pb-ion simulation experiments to verify and corroborate these preliminary experiments. In particular, solution analyses are needed to confirm the loss of material by leaching implied by the ERD and RBS measurements at the critical fluence. Although the overall leach rates may not be significantly affected by radiation damage, the compositional changes are sufficiently large as to suggest that phase separation and subsequent crystallization might occur.

- e. Our work indicates that even though the surface compositions are affected, the overall leach rates are not significantly altered by Pb-ion simulation of α -recoil damage. Solution analyses were not made after the 10 hr leach of the single-energy implants which showed loss of material at ϕ_c . It is therefore not known how the leach rate varied. If only slight changes occurred as for the multiple-energy implants, this might indicate that material flaked off or was redeposited from solution on the container walls. The results indicate, however, that the performance of SKS glass in the long-term immobilization of SRP defense high-level waste will not be adversely affected.

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