THE EFFECT OF RADIOLYSIS ON LEACHABILITY OF PLUTONIUM AND AMERICIUM FROM
76-101 GLASS*

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ABSTRACT

One aspect of the leachability of actinide-bearing glass which has not been adequately addressed is the effect of radiolysis of the system (glass-water) on the amount of actinides liberated from the glass. In the present study, we have investigated the leaching of plutonium and americium from 76-101 glass samples (containing 2 mole % plutonium) in the presence of a one megaRad/hour gamma-radiation field. The presence of the radiation field was found to increase the leaching rate of both plutonium and americium by a factor of five. Speciation studies of the plutonium in the leachate indicate that the plutonium is present predominantly in the higher oxidation states, Pu(V) and Pu(VI) and that it is significantly associated with colloidal particles. Examination of the glass surfaces with X-ray photoemission spectroscopy, XPS, both before and after leaching was carried out; these studies showed lower surface concentrations of plutonium in the samples of glass leached in the radiation field.

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INTRODUCTION

Previous studies [1] designed to evaluate the effects of radiation on leachability of solid matrices involved loading high specific activity radionuclides into the candidate waste form and leaching with the appropriate leachant. These experiments simulated the radiation damage which would occur within the solid waste form in the first 1000 years of its lifetime. The general conclusion was that such effects produced only minimal change of leach rate.

However, one aspect of the effect of radiation on the in situ integrity of glass which has not been adequately addressed is the effect of radiolysis of the surrounding water on glass leachability. In a previous study, we have determined that plutonium in environmental solutions undergoes oxidation-reduction cycles in a gamma radiation field [2]. Plutonyl ion, PuO_2^{++} , is a considerably more soluble species than the Pu(IV), PuO_2 presumed to be present in the glass matrix. The purpose of the present study is to determine whether the radiolytic oxidation of plutonium in solution can enhance its leachability from Battelle 76-101 glass [3].

EXPERIMENTAL

Glass samples containing 2 mole percent $^{239}\text{PuO}_2$ were prepared from a standard 76-101 glass frit. The initial (plutonium containing) glass was crushed, ground, remelted, and finally annealed in a platinum boat. The procedure was repeated several times to insure uniformity of plutonium distribution throughout the

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glass sample. The glass slug was then cut into wafers 7 mm x 1 mm x 11 mm (and in a second preparation 5 mm x 1 mm x 14 mm) by a diamond saw using ethanol as a coolant.

In accordance with the MCC-1 static leach test guidelines, the glass wafer was suspended by a teflon line in a quartz vessel containing 40 ml of triply distilled water. The surface area to volume ratios (SA/V) was thus 0.060 cm^{-1} for the 7 mm wafer and 0.044 cm^{-1} for the 5 mm wafer. Sample and leachant preparation were conducted in a nitrogen atmosphere.

The glass samples were leached for one hour, six hours, and twenty-four hours in a one megaRad/hour gamma radiation field ^{60}Co . We estimate a maximum temperature rise of 5 degrees C in the 24 hour irradiation. A duplicate experiment was done in each case without the influence of the radiation. At the conclusion of each leach period, the glass wafer was removed to prevent redeposition of the solubilized plutonium onto the glass. The pH of one sample of the leachates from each leach period was determined by means of a glass electrode and pH meter. Duplicate one milliliter samples of leachates were taken for radiochemical assay both by liquid scintillation and gas flow proportional counting techniques. Alpha pulse height analysis of counting plates was also carried out to determine the isotopic and elemental composition of the leachates.

To complement the information obtained by analysis of the leaching solutions, X-ray photoemission spectroscopy (XPS) was used to examine the glass surface before and after leaching. XPS is a surface sensitive (20-30 Å) spectroscopic technique that provides quantitative compositional data by monitoring the intensity of photoemitted electrons from atomic core states when a sample is illuminated with monochromatic X-rays. In addition, information on the oxidation state of many elements can be obtained by measuring small changes in the binding energies (chemical shifts) of these core levels.

Speciation of the leached plutonium was studied by two methods. The extent of plutonium absorption on particulates and of plutonium polymer formation was determined by filtration of a sample of the leachates by means of a series of Nucleopore Filters (10 µm - 0.05 µm pore size). Activity in samples of the filtrate was determined in all cases by use of alpha pulse height analysis or gas flow proportional counting. The oxidation state distribution of plutonium in solution was determined by cation exchange chromatography.

Tables I and II summarize the analysis of the leachates and the analysis of the time dependence of the concentration of actinides in the leachates for the unirradiated and irradiated samples respectively. Several points should be made about these data. First of all, the pH of the non-irradiated leachates increases with time because of alkali metals (Na^+ , K^+) leached from the glass. The decrease in pH observed with increased exposure time in the irradiated experiments is due to nitric acid formed from the fixation of the nitrogen in the atmosphere of the leaching experiments [4].

A second point immediately obvious from the kinetic analysis is that plutonium and americium seem to be solubilized from the glass matrix at the same first order rate in the radiation field. The speciation studies indicate that most of the plutonium is present in the higher oxidation states (V and VI) in these leachates. Thus a mechanism involving radiolytic oxidation of Pu cannot be ruled out. The observation of first order kinetics also implies a direct interaction between the metal ions and radiolysis products. The first order rate constant for the irradiated leachates is a factor of 5 higher than that observed for the unirradiated leachate.

XPS RESULTS

There are too many experimental parameters affecting the absolute photoemission intensities. Thus it is not possible to use the absolute peak

intensities from a given core line as an accurate measure of how that element's concentration varies from sample to sample. Quantitatively meaningful information can however, be extracted from the relative photoemission intensities from different core levels within a given sample. A normalization procedure for using this information together with the known bulk composition has been previously reported [5]. Applying that procedure to our photoemission data yields the surface composition given in Table III. The observed surface Pu concentrations are systematically lower on the samples leached in the radiation field. In fact, the unirradiated samples show a somewhat enhanced Pu surface concentration, whereas the irradiated sample surfaces become depleted in Pu, especially those samples leached for only one day. It should be pointed out that the systematics observed in the Pu surface concentration do not necessarily follow from the solution analysis results which show more Pu removed from the irradiated samples. For example, completely congruent dissolution of the glass would leave the surface composition unchanged even if the rate of dissolution were accelerated.

The XPS results indicate that the enhanced removal of plutonium from the glass surface under irradiation conditions results from direct interaction of the plutonium with the radiolysis products (of the water) as suggested by the observed first order kinetics.

The methodology for using XPS chemical shifts to obtain information on Pu oxidation states has been discussed in another paper [6]. Figure 1a shows an XPS spectrum of the Pu 4f core level region of the unleached glass. This sample was fractured in a high vacuum to expose a fresh clean surface representative of the bulk glass. The bulk glass shows that the levels of the spin-orbit split Pu 4f doublet (the primary features at ~ 400 and ~ 425 eV) are further split by 1.8 eV due to the different chemical shifts of two co-existing Pu oxidation states in approximately equal abundance. It has been argued [6] that these states are probably Pu(III) and Pu(IV) with the higher oxidation state at higher binding energy. The corresponding spectra of the samples leached for one day are shown in Figure 1b (unirradiated) and 1c (irradiated). The binding energies of the two states should be measured relative to the Ti $2p_{3/2}$ level (the large peak near 460 eV).

The changes in the relative concentration of Pu and Ti are apparent from the relative peak intensities. In addition, the leached glass spectra show that the lower Pu oxidation state preferentially remains on the surface. A small amount of the higher oxidation state shows up as an unresolved shoulder on the high binding energy side. It is not yet clear whether these results can be explained by different solubilities for the different oxidation states or by redox reactions occurring in the course of leaching.

DISCUSSION

The speciation of the leached plutonium has important consequences for prediction of its tendency to migrate away from a radionuclide repository. The existence of a substantial fraction of the leached plutonium as material absorbed on solid particulates indicates that an important mechanism for plutonium migration in the geosphere may well be particle transport.

The existence of plutonium in higher oxidation states in the leachates implies relatively high solubility. The cation exchange chromatographic results indicate the possibility of either Pu(V) or Pu(VI) as stable plutonium species. This means that the migration of Pu(V) and Pu(VI) should be studied. It also suggests that reducing substances should be incorporated into the backfill materials in the repository.

TABLE I

Raw leach data and kinetic analysis for unirradiated leachate.*

Experiment	Cpm/ml	S.A.	Pu/M/cm ²	pH
24B	144	2.4 cm ²	4.42 x 10 ⁻⁹	7.12
6B	89	2.4 cm ²	2.73 x 10 ⁻⁹	6.35
1B	84	2.4 cm ²	2.58 x 10 ⁻⁹	6.17

First order kinetic analysis:

$$k_1 = 0.02430 (+0.00114) \text{ cm}^{-2} \text{ megaRad}^{-1}$$

$$A_0 = 2.45 \times 10^{-9} \text{ mole/L/cm}^2$$

Linear correlation: 0.99368

* Assume total activity is attributable to plutonium. Initial pH = 5.8.

TABLE II

Raw leach data and kinetic analysis for irradiated leachate.*

Experiment	Cmp ²³⁹ Pu/ml	Cmp ²⁴¹ Am/ml	S.A.	²³⁹ Pu/M/cm ²	²⁴¹ Am/M/cm ²	pH
241-1	5006	1137	2.4 cm ²	6.41x10 ⁻⁸	2.58x10 ⁻¹⁰	3.10
241-2	3797	891	1.8 cm ²	6.48x10 ⁻⁸	2.70x10 ⁻¹⁰	3.33
61-1	842	191	2.4 cm ²	1.08x10 ⁻⁸	4.33x10 ⁻¹¹	3.80
61-2	639	139	1.8 cm ²	1.09x10 ⁻⁸	4.21x10 ⁻¹¹	(6.78)
11	445	101	2.4 cm ²	5.68x10 ⁻⁹	2.29x10 ⁻¹¹	4.79

First order kinetic analysis:

$$A_n = A_0 e^{-kt}$$

<u>Pu</u>	<u>Am</u>
$k_1 = 0.1025 (+0.0038) \text{ (cm}^{-2} \text{ megaRad}^{-1})$	$k_1 = 0.1039 (+0.0032) \text{ (cm}^{-2} \text{ megaRad}^{-1})$
$A_0 = 5.565 \times 10^{-9} \text{ M/cm}^2$	$A_0 = 2.198 \times 10^{-11} \text{ M/cm}^2$
Linear correlation: 0.99876	Linear correlation: 0.99915

* pH = 5.8.

TABLE III
Composition of leached glass surfaces.

Sample	Composition (mole % of Component Oxides)						
	Ti	Pu	Si	Ca	Zn	Na	B
Unleached	3.5	2.0	61.7	3.3	5.7	11.2	12.7
1 Hr. Ref.	4.7	2.9	72.7	4.3	3.9	6.9	4.8
6 Hr. Ref.	3.7	2.5	72.6	3.2	6.3	8.4	3.4
24 Hr. Ref.	3.7	2.9	75.2	2.7	4.4	9.5	1.8
1 Hr. Irr.	4.1	2.4	85.1	1.6	1.1	3.5	2.3
6 Hr. Irr.	4.5	1.4	86.6	2.3	1.0	3.2	1.0
6 Hr. Irr.	4.6	2.1	77.0	4.6	3.8	4.6	3.3
24 Hr. Irr.	2.8	0.4	93.2	0.8	0.4	1.2	1.2

Figure 1. XPS spectra of the Pu 4f core level reg glass; (a) fractured in vacuum; (b) unirradiated water at 25°C; and (c) leached one day in distill presence of a one megaRad/hour

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