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CHEMISTRY AND GLASS LEACHING AS RELATED
TO THE NNWSI REPOSITORY SITE

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The Effect of Gamma Radiation on Groundwater Chemistry and Glass Leaching as Related to the NNWSI Repository Site

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Introduction

The volcanic tuff beds of Yucca Mountain, Nevada, are currently being evaluated by the Nevada Nuclear Waste Storage Investigations (NNWSI) project as a repository for the permanent storage of high-level nuclear waste.¹ A complete evaluation of the site requires an understanding of the complex physical processes expected to occur in the repository and a description of how the interaction of these physical processes will affect repository performance. In addition, the evaluation must consider changing conditions that will exist as the waste ages and the level of radioactivity decreases.

One issue that has a direct influence on the performance of the repository, especially during the initial 300-1000 year containment period is the effect of penetrating gamma radiation. It is during this period that the radiation levels will be most intense, with the initial dose rate being $\sim 5 \times 10^4$ rad/hr for commercially generated waste and $\sim 5 \times 10^3$ for the waste produced by the Defense Waste Processing Facility. The composition of the groundwater will be affected by both direct radiolysis and by dissolution of radiolytic products that form in the gas phase. Changes in groundwater chemistry could affect corrosion of the metal components of the waste package, as well as the durability of the waste form in the event of premature failure of the container. Physical damage to the solid components of the waste package as a result of gamma radiation is not expected to adversely affect performance.

To address the effect of ionizing radiation on groundwater chemistry and waste form durability, NNWSI is performing an extensive set of experiments as a function of dose rate (2×10^5 , 1×10^4 , 1×10^3 , and 0 rad/hr). The results of the tests done at 2×10^5 rad/hr have been reported,^{2,3,4,5} while the 1×10^3 and 0 rad/hr tests are in progress.⁶ This paper presents an overview of the results of the tests done at 1×10^4 rad/hr and discusses the relevance of these tests to repository conditions. An interpretation of the results relating to the manner by which the glass waste form corrodes is presented elsewhere. A complete discussion of the effect of gamma radiation on groundwater chemistry and waste form durability will be presented when the series of experiments are complete.

Background

Previous studies^{8,9} indicate that when moist air is subject to gamma radiation several competing reactions occur. The most important of these is the production of nitric acid which, if liquid water is present, will dissolve in solution. The rate of nitric acid production has been quantified by Burns⁸ and is a direct function of, in part, the dose rate, time of irradiation, gas composition, and the ratio of the volume of gas to the volume of liquid (R).

The effect of nitric acid production on groundwater chemistry and glass reaction is more difficult to project. When experiments were done in deionized water, the pH quickly became more acidic leading to accelerated corrosion of the glass.^{9,10} However, in NNWSI groundwater (J-13) in the presence of tuff, the system is buffered by bicarbonate and by the leaching of alkalis (Na^+ , Li^+ , Cs^+) from the glass. The overall effect of these processes at a dose rate of 2×10^5 rad/hr (total dose up to 2.7×10^8 rad) was to retard glass reaction compared to the non-irradiated experiments.³

As the dose rate is lowered to 1×10^4 rad/hr (total dose up to 4.4×10^7 rads), of interest is how will the reduced production of nitric acid effect the solution chemistry balance, i.e., with less acid production will the effect of alkalis exceed that of acid production, thereby promoting a "pH excursion" and more rapid glass reaction?

Experimental

A. Test Matrix

Tests were done to study the effect of radiation on the groundwater, groundwater in the presence of tuff, and glass durability with and without tuff present. All the tests were done in 304L stainless steel vessels.

The tests done without glass were also used to correct the solution concentration in the glass containing tests and in this respect function as "blanks". The test matrices were:

- (1) two glass disks in preequilibrated J-13 water (EJ-13), $SA/V = 0.3 \text{ cm}^{-1}$, $R = 0.3$;
- (2) two glass disks in EJ-13 with a polished tuff core wafer, $SA/V = 0.3 \text{ cm}^{-1}$, $R = 0.3$;
- (3) EJ-13, $R = 0.3$; and
- (4) EJ-13 with a polished tuff core wafer, $R = 0.3$.

Each matrix was run at 90°C for periods of 14, 28, 56, 91, and 182 days. Duplicate samples were run for each time period and when possible, MCC-1 protocol was followed. Detailed procedures used in testing have been presented by Bates.³

B. Test Components

The components used in this test are of the same type as used in previous testing except for the following:

- (1) groundwater. Although the same water equilibration procedures have been used in each set of tests, the groundwater composition varies slightly. The EJ-13 composition used in the present tests ($\mu\text{g}/\text{mL}$) is Al, <0.10 ; B, 0.14; Ca, 11.92; Fe, <0.01 ; Li, 0.046; Mg, 0.96; Na, 45.23; Si, 30.7; Sr, 0.043; U, <0.001 ; F^- , 2.45; Cl^- , 7.70; NO_3^- , 8.35; NO_2^- , <0.2 ; $\text{SO}_4^{=}$, 18.60, and $\text{pH} = 7.61$.
- (2) tuff. Polished tuff core wafers were used in the present experiments instead of crushed tuff. This was done to allow the interaction of actinide elements with the tuff to be studied via ion microprobe analysis.

C. Sample Description

Test matrices (1) and (2) were done with two different glass types.

These were:

- (1) Savannah River Laboratory (SRL) 165 black frit to which uranium, cesium, and strontium had been added. This is referred to as SRL U glass.
- (2) SRL U glass to which ^{237}Np , ^{239}Pu , and ^{241}Am had been added. This is referred to as SRL A glass.

The composition of these glasses are essentially constant through the entire set of radiation experiments.⁶

D. Analyses

At the completion of each test, the solutions were cooled to room temperature and analyzed for pH, cations (inductively coupled plasma spectroscopy, ICP), anions (ion chromatography, IC), uranium (atomic fluorescence, AF), radionuclides (γ and α counting), and dissolved gases (Van Slyke, GC). The solid test components were measured for weight change and were analyzed

by scanning electron microscopy and associated energy dispersive X-ray analysis (SEM/EDS), secondary ion mass spectroscopy (SIMS), nuclear resonance profiling, and ion microprobe.

Results

These tests have resulted in an extensive collection of data. In this paper selected results are presented stressing changes in solution chemistry, the behavior of actinides and glass matrix elements, and profiles of reacted glass surfaces.

A. Solution Analyses

The variation of solution pH with time is shown in Figure 1 for the tests done without tuff. The effect of tuff was to produce slightly more acidic solutions through 56 days, but essentially the same after 182 days. All of the tests showed the same pH trend, e.g., gradually increasing acidity through 91 days with an actual reversal of the trend at 182 days.

The pH reversal in the glass containing tests could be explained by alkali release from the glass, but the same trend is also observed in the non-glass containing tests. The most likely explanation is an experimental artifact resulting in the loss of acid volatiles from the system. Slight weight losses were observed in the 182-day tests (~ 0.2 gm), that can be attributed to leakage from the vessels. Leakage would result in the loss of CO_2 and air (N_2) from the gas phase. This would reduce the amount of bicarbonate in solution and also result in less nitric acid being produced. Dilution of the gas phase is also suggested by the reduced amount of dissolved O_2 and N_2 in solution after 182 days when compared to the other test periods. Without the gas dilution it would be expected that the pH in the "blank" experiments would stabilize at ~ 6.4 , which is the carbonic acid-bicarbonate equilibrium pH at 90°C .¹¹

When glass is present, the pH values are always more basic than the corresponding "blank" experiments and there is little difference between the SRL U and SRL A experiments. This suggests that alkali release from the glass is affecting the solution chemistry. The most dramatic effect of subtle pH changes is observed as the amount of each actinide detected in solution decreases by up to a factor of 10 as between the 91 and 182 day tests.

In most experiments the concentrations of Cl^- , F^- , and SO_4^{2-} are virtually unchanged from the original EJ-13 water. The amount of fixed nitrogen is predicted to increase with continuing irradiation, but the amount of increase, ~30 nanomols after 182 days, is within the experimental precision. The concentration of fixed nitrogen species is shown in Table 1. While only NO_3^- is present in the initial EJ-13 water, NO_2^- is formed due to radiolysis and by the reduction of NO_3^- by the test components. Glass and tuff are particularly effective in promoting the reduction of NO_3^- .

In a few experiments the amount of fixed nitrogen is lower than the EJ-13 value, sometimes being less than the analytical detection limits. In these experiments the concentrations of F^- and SO_4^{2-} are also lowered, while the concentration of Cl^- is elevated.

The release of selected cations is shown in Figure 2. The relative release of the major cations is the same in all experiments and is consistent with the pattern $\text{Li} \geq \text{Na} \geq \text{B/U} \geq \text{Si}$. However, less than 2 g/m² separates the Li and Si values after 182 days. The release of these cations may be slightly greater for the SRL A glass than the SRL U glass, but the differences fall within the estimated error of the measurements. Also, the release is slightly greater in the experiments containing tuff.

The normalized leach rates for Li, Na, B, U, and Si decrease with time and show no indication of reversing this trend. For these five elements

Table 1. Concentration of Fixed Nitrogen Species

		NO GLASS			SRL U			SRL A		
		concentration ^a			concentration ^a			concentration ^a		
		NO ₂ ⁻	NO ₃ ⁻	Total	NO ₂ ⁻	NO ₃ ⁻	Total	NO ₂ ⁻	NO ₃ ⁻	Total
EJ-13	14	68.5	67.7	136.2	102.7	37.4	140.1	104.4	40.0	144.4
	28	65.2	74.8	140.0	107.6	36.3	143.9	125.0	37.6	162.6
	56	62.0	53.2	115.2	100.0	38.7	138.7	100.0	36.3	136.3
	91	<4.4	<4.8	<9.2 ^b	91.3	45.2	136.5	75.0	36.3	111.3
	182	57.0	78.7	135.7	123.9	43.6	167.5	125.7	18.2	143.9
EJ-13 + Tuff	14	97.8	44.8	142.6	112.6	41.1	153.7	115.9	35.2	151.1
	28	60.4	30.3	90.7 ^b	110.9	47.3	158.2	117.4	60.5	177.9
	56	71.7	37.1	108.8	60.9	62.9	123.8	75.0	45.2	120.2
	91	109.8	44.4	154.2	<4.4	<4.8	<9.2 ^b	104.4	45.2	120.2
	182	97.8	49.7	147.5	102.8	48.4	151.2	52.2	12.1	64.3 ^b

^aThe concentrations are the average of duplicate tests, nano moles/mL, NO₃⁻ in EJ-13 is 134.7 nano moles/mL.

^bIn some tests the chloride concentration has increased and the fixed nitrogen has decreased.

a reasonable parabolic function fits the data through 91 days, but the release for each element is lower than projected by parabolic kinetics at 182 days. The deviation is smallest for Li followed by B and Na. In all cases the reaction rate is greater when tuff is present in the test.

The normalized releases for transuranic elements are given in Table 2. Each value is an average of duplicate tests. The precision was better for Am and Pu than for Np due to degradation of the alpha spectrum in the Np energy range. These data indicate that the release of Pu and Np increases through 91 days and actually decreases after 182 days, whereas the release of Am and U, in most tests, is still increasing after 182 days. Also, the release of transuranic elements is larger when tuff is present in the tests, most likely due to the slightly more acidic pHs in the tuff-containing tests.

B. Component Analyses

The normalized mass losses for the glass disks are shown in Figure 2. The trend reinforces the observation drawn from the solution analyses that the extent of reaction increases steadily through 91 days as a function of $t^{1/2}$, but then slows after 182 days.

Similar reinforcement of the solution analyses trends was found using surface analytical methods. SEM analysis indicated that through 56 days there was very little change in the appearance of the glass surface, but that by 182 days precipitate formation was occurring and analcime was identified on the surface.

SIMS profiles were taken of one sample for each time period. The same relative elemental profiles were noted for each time period, with increasing depletion of leached components as the reaction time increased. The 91-day profile is shown in Figure 3. Na, Li, and B are all depleted

Table 2. Concentration, Normalized Transuranic Release, and pH Values for Tests Containing SRL A Glass

Test Type	Period (days)	pH	Americium Concentration ^a			Plutonium Concentration ^a			Neptunium Concentration ^a		
			Unfiltered	Acid Strip	NL	Unfiltered	Acid Strip	NL	Unfiltered	Acid Strip ^b	NL
EJ-13	14	7.48	3.6 E-3	4.43E-2	1.8 E-2	4.56E-2	6.79E-1	4.2E-1	1.39E-2	-	1.33
	28	7.15	3.9 E-3	6.70E-2	2.8 E-2	3.58E-2	8.69E-1	5.4E-1	2.20E-2	-	2.10
	56	6.94	4.5 E-3	1.87E-1	7.6 E-2	5.29E-2	2.60	1.63	3.75E-2	-	3.75
	91	6.81	4.9 E-3	3.21E-1	1.28E-1	7.29E-2	3.59	2.15	4.47E-2	-	4.15
	182	7.25	5.6 E-3	6.38E-1	2.25E-1	3.7 E-3	3.13	1.67	2.95E-2	-	2.66
EJ-13 + Tuff	14	6.86	2.8 E-3	4.54E-2	1.6 E-2	3.16E-2	5.69E-1	3.3E-1	9.2 E-3	-	0.83
	28	6.74	1.58E-2	2.40E-1	9.6 E-2	1.05E-1	1.53	9.3E-1	2.16E-2	-	0.43
	56	6.90	1.46E-2	4.26E-1	1.16E-1	1.32E-1	4.16	1.65	4.78E-2	-	3.07
	91	6.86	2.80E-2	9.63E-1	2.54E-1	5.0 E-1	5.93	2.38	2.62E-2	-	3.86
	182	7.18	3.8 E-3	1.12	3.67E-1	9.5 E-3	4.03	2.02	2.14E-2	-	1.83

^aConcentration is reported as disintegrations/second/100 λ of solution.

^bNo Np could be detected in the acid strip due to overlap from the degraded Pu spectrum.

relative to Si. All three elements are almost completely depleted in the outer region of the reacted glass. Boron shows an abrupt increase in concentration reaching the base glass level, while Na and Li display a "s" shaped profile with Na intensity increasing before Li. Ca and Fe show an enrichment on the surface reaching the base glass level at the depth when B reaches the base glass level.

Hydrogen profiles were also taken of the surface by F. Ryerson, and W. Lanford working at SUNY, Albany.⁶ These profiles show two distinct regions. One, which starts at the glass surface (gel layer), where the hydration concentration is fairly constant at a positive level; and the second which has a "s" shaped appearance (transition zone). The hydrogen profiles match well with the cation profiles obtained with SIMS. However, the layer thicknesses measured by SIMS and nuclear profiling are less than predicted by solution-based depletion depths. This observation, plus the nearly uniform release of many elements usually associated with the glass matrix (actinides, Al) suggests that considerable etching of the glass surface has occurred.

Repository Relevance

Analyses of the "blank" tests indicate that the major changes in the groundwater are:

- (1) rapid lowering of the pH to approximately the 6.4 buffered region.

The pH would be expected to remain at this level unless the buffering capacity of the groundwater was exceeded by acid production, in which case the pH would become more acidic; or nitrogen was depleted in the gas phase, either via radiolysis or dilution with water vapor in which case the pH would become more basic. In the present experiment R was set at 0.3, but in the repository R will vary.

Since the repository is located in the unsaturated zone, R could

attain larger values whereupon the buffering capacity of the limited amount of water may be exceeded.

- (2) variation in the ratio of nitrate to nitrite depending on the presence of materials that promote the oxidation of nitrite. The overall affect on repository performance of varying this ratio is unknown.

Glass would interact with water at the radiation levels in the current experiments only if there were a premature container breach. Under such conditions, it appears that the radiation would impede the dissolution of the glass matrix by buffering the solution pH to near neutral. However, under neutral or slightly acid conditions, the solubility of some species is a strong function of pH. Thus, while the overall glass reaction may be retarded, the release of actinides from the glass via etching may be greater than if the pH were more basic and the actinides were trapped in the reacted layer and were never released.

At radiation levels expected in the NNWSI repository at the end of containment period (<100 rad/hr), gamma radiation might be expected to measurably affect glass performance only if R were large, which would effectively enhance the radiation effect, or if the water remained stagnant for long periods of time and radiolytic products could slowly accumulate in solution and counterbalance the pH excursion caused by glass leaching.

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Fig. 1. Variation of pH with time for the non-tuff containing tests.

Fig. 2. Normalized loss for (a) Li, (b) Na, (c) B, and (d) mass.

Fig. 3. SIMS profile of SRL U glass reacted for 91 days showing lithium (7), boron (11), sodium (23), and iron (56).