THE EFFECTS OF GAMMA RADIATION ON GROUNDWATER CHEMISTRY
AND GLASS REACTION IN A SATURATED TUFF ENVIRONMENT

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ABSTRACT

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The Nevada Nuclear Waste Storage Investigations project has completed a series of experiments that provide insight into groundwater chemistry and glass waste form performance in the presence of a gamma radiation field at 90°C. Results from experiments done at 1×10^3 and 0 R/hr are presented and compared to similar experiments done at 2×10^5 and 1×10^4 R/hr. The major effect of radiation is to lower the groundwater pH to a value near 6.4. The addition of glass to the system results in slightly more basic final pH, both in the presence and absence of radiation. However, there is essentially no difference in the extent of glass reaction, as measured by elemental release, as a function of dose rate or total dose, for reaction periods up to 278 days.

INTRODUCTION

The Nevada Nuclear Waste Storage Investigations (NNWSI) project has been evaluating the volcanic tuff beds of Yucca Mountain, Nevada, as a possible repository site for the permanent storage of nuclear waste. As a part of the site characterization program, we have been studying the effects of penetrating gamma radiation on the interaction of components relevant to a repository in a tuff environment [1,2,3]. The purpose of these experiments is to produce data applicable to projecting the release of radionuclides from the waste glass and to determine if radiation produces measurable effects on the chemistry of the groundwater or the glass performance. Experiments have been performed at 2×10^5 Roentgen/hour [1] (R/h) and 1×10^4 R/h [2] in our laboratory previously. The present experiments were performed at exposure rates of 1×10^3 R/h and 0 R/h.

The need for such analyses arises from the unique conditions anticipated in the tuff repository due to the fact that the suggested repository horizon lies above the water table in the unsaturated zone. It is expected that the repository will remain dry during the first 300 to 1000 years after waste emplacement when significant gamma fields would be present. Low gamma fluxes will still be present 1000 years after emplacement when the groundwater is more likely to directly contact the waste. It is therefore important to understand the effects of radiation on the glass performance at these low exposure rates. While the exposure rates used in these experiments are much higher than those expected in the repository during the isolation period (times 1000 years or more after emplacement), they do produce measurable effects which are useful in guiding future experiments designed to more closely simulate the repository conditions where the effects of radiation may not be easily measured.

REVIEW OF POSSIBLE RADIOLYTIC PROCESSES

Past work has shown that the irradiation of moist air produces nitric acid, nitrous oxide, and ozone, as well as several short-lived species [4]. The irradiation of a two-phase air-water system without CO₂ has been

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218

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found to produce nitric acid in the liquid phase [7,8]. If the air-to-liquid volume ratio is large, then even small irradiation doses will significantly increase the acid concentration of the initially pure water. An equation describing this behavior has been developed by Burns et al. [9]. It has also been found that irradiation of unbuffered deionized water in contact with an air atmosphere that contains CO₂ results in the production of formic and oxalic acids as well as nitric acid [10,11].

The corrosion rates of both metals and glasses in pure water have been found to be increased by radiolytically produced nitric acid [12,13]. NNWSI J-13 groundwater contains many dissolved species, some of which have been found [5] to react with radiation-produced radicals. These species include HCO₃⁻, CO₃²⁻, NO₃⁻, and Cl⁻, in addition to dissolved O₂ and CO₂ gases. Furthermore, HCO₃⁻, along with dissolved CO₂, is a well-known buffer (pK_a ~ 6.4 at 90°C [3]). The radiation chemistry of such a groundwater solution would be expected to be quite different from that of high-purity water.

The solid phases expected to be present in the repository might also have significant effects on the radiation chemistry of a solution in contact with them. For example, dissolved iron from the canister material is a catalyst for the decomposition of radiolytically produced H₂O₂ [14], as is manganese oxide, which is present in fractures in the tuff as well as in defense waste glass. In addition, feldspars in the tuff have been found to ion exchange with H⁺, leading to a buffering of the solution and weathering of the feldspars to clays [15]. Austenitic steels, the NNWSI reference alloy system for the waste packages, have been found to produce ferric containing colloids in irradiated high-purity water [16]. It is important to include these repository-relevant materials in experiments of radiation effects.

EXPERIMENTAL

These experiments were not designed to simulate the repository environment, but rather to measure the effect of penetrating gamma irradiation on the groundwater chemistry and component interactions relevant to a tuff repository. The experiments involved placing two disks of synthetic waste glass (each glass having a surface area of about 2.5 cm²) along with a wafer of topopah spring tuff (surface area about 10 cm²) in a 304 L stainless steel vessel. NNWSI J-13 groundwater which had been prereacted with pulverized tuff at 90°C for 14 days (referred to as EJ-13 water) was used as the leachant. The volume of EJ-13 added to a experiment was varied to maintain a gas-to-leachant volume ratio near 0.3 and a glass surface area to leachant volume near 0.3 cm⁻¹. The vessels were sealed using a silicone rubber gasket and compression fitting. The experimental assembly was identical to that used in previous experiments [1,2].

Two glasses based on the composition of Savannah River Laboratory (SRL) 165 black frit were studied. One was doped with uranium, cesium, and strontium, referred to as SRL U glass, and the other was doped additionally with ²³⁷Np, ²³⁹Pu, and ²⁴¹Am, referred to as SRL A glass. Experiments were also run using ATM-1c and ATM-8 glasses to verify that the radiation effects measured were not novel to SRL 165 type glasses. The results of these experiments will be presented elsewhere. Finally, experiments were performed which contained EJ-13 water but no glass. These experiments were useful in measuring the effects of radiation on the groundwater alone. These experiments were also used as blanks to determine the background levels of the leachate for experiments with glass.

All experiment types were run in duplicate, both with and without a tuff wafer, at 1 x 10³ R/h and 0 R/h. The irradiated experiments were placed in a 90°C oven in the gamma radiation facility at ANL which

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includes a retractable ^{60}Co source. Dosimetry had been performed inside an empty vessel in the oven and the appropriate adjustments made to produce an exposure rate of 1×10^3 R/h. The nonirradiated experiments were run in a 90°C oven in our laboratory. Exposure times varied from 14 to 280 days.

At the termination of an experiment the vessel was cooled to near room temperature before opening. The analysis of the vessel contents has been described previously [1]. This includes analyzing the leachate pH, the concentration of various anions (ion chromatography), cations (ICP and fluorescence), and released dopants (α -counting). Analyses of the total dissolved carbon and organic carbon were also performed. The glass disks were measured for weight change. The reacted surfaces of the glasses were analyzed using various surface analytical techniques (including SEM/EDS, SIMS, NRS, AES, XPS, and ion microprobe). The tuff surfaces were likewise analyzed.

The released actinides may dissolve into solution, adhere to colloidal material in the leachate, adsorb to the stainless steel vessel surfaces, or adsorb or precipitate onto the glass or tuff surfaces. Since the glass and tuff were removed from the vessel prior to leachate analysis, detection of actinides on these surfaces will occur during surface analyses. The remaining actinides were analyzed using three different samples. An aliquot of the leachate was analyzed without further treatment. This aliquot contained both dissolved and pseudo-colloidal actinides and will be referred to as the "unfiltered" aliquot. A second sample of the leachate was filtered through a 50 A filter which removed most of the colloidal fraction. An aliquot of the filtrate was analyzed for dissolved actinides. Finally, the leachate was acidified to a pH near 1 with HNO_3 and allowed to stand in the vessel for about 20 hours at 90°C . This dissolved all pseudo-colloidal and adsorbed actinides. An aliquot of this acid-washed solution, which represents the total amount of actinides, was analyzed.

SELECTED RESULTS AT 1×10^3 R/h and 0 R/h

The leachate pH values for the experiments without glass are shown in Fig. 1a. The original leachant had a pH value near 7.8. The symbols represent the average of duplicate experiments, which differed typically by only a few percent. The nonirradiated experiments, which are shown by the open symbols, appear to become slightly more basic with time both for the tuff-present (square symbols) and tuff-absent (circular symbols) experiments. The leachate pH values in the irradiated experiments were lower than that of the original leachant. This is due to the radiolytically produced nitrogen acids dissolved in solution. The pH of these experiments never dropped below 6.4, however, because of the high bicarbonate concentration in EJ-13 water (~ 120 ppm) which, along with dissolved CO_2 , successfully buffers the leachate to pH values above 6.4.

Figure 1b shows the pH values of the leachates of experiments which contained SRL U glass. Behavior similar to the experiments without glass is seen, namely that the nonirradiated experiments have slightly higher pH values than the original leachant and the irradiated experiments are slightly acidified. The experiments with glass are slightly more basic than the experiments without glass of the same duration, presumably due to the depletion of protons from the solution during ion exchange with leachable glass components, such as Li and Na. The pH values of the SRL glass-containing experiments are about 0.2 to 0.5 pH units higher than the corresponding no-glass experiments.

A good measure of the extent of glass reaction is provided by the normalized mass losses, wherein the amount of a species in the leachate is normalized to its concentration in the original glass and to the exposed

Ebut

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Figure 1. Leachate pH values for experiments performed with (a) EJ-13 only, (b) EJ-13 + SRL U glass: ○ without tuff at 0 R/h; □ with tuff at 0 R/h; ● without tuff at 1E3 R/h; ■ with tuff at 1E3 R/h plotted vs. reaction time.

surface area of the glass. Such normalization allows direct comparison of the releases of various elements and the total glass weight loss. The normalized elemental mass losses of B, Li, Na, Si, and U and the normalized glass weight loss for SRL U glass are plotted against the reaction time in Fig. 2(a-e) and Fig. 3. These plots are interesting in that there appears to be no obvious influence of radiation on the leachate levels of the glass components. The values for the nonirradiated experiments, shown by the open symbols, are not distinguished from those of the irradiated experiments even though the leachate pH values differed by nearly 2 units.

The calculated mass of Pu in the unfiltered and acid-washed fractions are shown in Fig. 4a,b for the nonirradiated and irradiated experiments, respectively. The solubility of plutonium is small at the pH values of these experiments. The experiments without tuff show negligible unfiltered plutonium, whereas the experiments with tuff show an increase in unfiltered plutonium with time for both the nonirradiated and, to a lesser extent, irradiated experiments. The total amount of plutonium, which is mostly adsorbed on the stainless steel, increases with time for both experiments with and without tuff. The experiments without tuff showed similar releases for the irradiated and nonirradiated experiments. With tuff present, the nonirradiated experiments show greater release than the irradiated experiments. Tuff appears to have a similar effect on the release of some other glass constituents, notably those elements expected to be released through matrix dissolution. The normalized weight loss in Fig. 3 also shows higher glass reaction in the presence of tuff. Elements expected to be released by diffusional control, such as lithium in Fig. 2b, do not show a strong dependence on the presence or absence of tuff.

COMPARISON WITH RESULTS OBTAINED USING HIGHER DOSE RATES

The leachate pH values of the experiments run at 1×10^3 R/h are very similar to the pH values of previous experiments run at 2×10^5 R/h and 1×10^4 R/h. The leachate pH values of selected experiments are plotted

E2b2

Z24

Z210

Figure 2. Normalized elemental mass losses for (a) boron, (b) lithium, (c) sodium, (d) silicon, and (e) uranium plotted vs. reaction time for experiments with EJ-13 + SRL U glass: ○ without tuff at 0 R/h; □ with tuff at 0 R/h; ● without tuff at 1E3 R/h; and ■ with tuff at 1E3 R/h.

Figure 3. Normalized weight loss of EJ-13 + SRL U experiments: ○ without tuff at 0 R/h; □ with tuff at 0 R/h; ● without tuff at 1E3 R/h; and ■ with tuff at 1E3 R/h plotted vs. reaction time.

Figure 4. Mass of plutonium in the unfiltered aliquot of experiments: ○ without tuff and □ with tuff, and the mass of plutonium in the acid-washed solution of experiments: ● without tuff and ■ with tuff irradiated at (a) 1E3 R/h and (b) 0 R/h plotted vs. the reaction time.

as a function of the total exposure (which is simply the exposure rate times the exposure time) in Fig. 5a,b. The symbols represent experiments of similar exposure times. The pH of all irradiated experiments without glass (Fig. 5a) became acidified to near 6.4. The original leachant pHs varied between 7.6 and 8.1. Notice that the pH values for the irradiated experiments remained near 6.4 for total exposures greater than 1E6 R to the highest total dose attained, about 269E6 R. The diagonal line in Fig. 4 represents the negative log of the amount of nitric acid (or H^+) expected to be produced under these test conditions according to the equation of Burns et al. [9] as a function of the total exposure. This HNO_3 would be expected to determine the pH after a total exposure of about 10^4 R. The horizontal line represents the pK_a of the $HCO_3^-/CO_2(aq)$ buffer

Expt
Z26
Z210

Figure 5. Leachate pH values for experiments (a) with EJ-13 only, and (b) with EJ-13 + SRL A glass plotted vs. the log of the total exposure dose for reaction times of: ▲ 28 days; ● 56 days; ◆ 91 days; ■ 181 days; and ▼ 278 days. Nonirradiated experiments are plotted at log total dose value of zero for convenience. The diagonal lines represent the amount of H^+ expected to be produced in the vessels from the equation of Burns et al. [9]. The horizontal lines at pH 6.4 represent the pK_a of the CO_2/HNO_3^- buffer at $90^\circ C$.

at $90^\circ C$. The HCO_3^- in EJ-13 water is seen to successfully buffer the leachate to a $pH > 6.4$ for all total exposures attained. In fact, the concentration of HCO_3^- in EJ-13 water is sufficient to neutralize the acid produced by ten times the highest total exposure of these experiments.

The normalized weight loss of SRL A glass is plotted vs. the reaction time in Fig. 6a,b for experiments with and without tuff. Again, radiation does not seem to affect the extent of glass corrosion, although the presence of tuff has an accelerating influence, according to the weight loss data.

The presence of tuff is seen to have a prominent effect on the distribution of Pu between the pseudo-colloidal and adsorbed on the stainless steel fractions. Figures 7a,b plots the ratio of the total amount of Pu (mostly adsorbed on the steel) to the amount of pseudo-colloidal Pu (plus the dissolved Pu) against the reaction time. When tuff is present, the ratio remains near 10:1 for all dose rates and reaction times. When tuff is not present, the ratio is seen to increase with time.

It may also be argued that the slope of the ratio vs. time plot decreases with increasing dose rates, although the differences are small. It is thought that the influence of tuff is through production of colloids to which Pu adheres. In the absence of a tuff wafer, the amount of colloidal material in the EJ-13 water is quickly saturated with Pu. The presence of a tuff wafer provides a source of fresh colloidal material. This effect seems to diminish with increasing dose rates, suggesting a pH control of the tuff wafer's ability to produce these colloidal materials. Therefore, while the glass reaction, as measured by normalized elemental release, does not appear to be sensitive to pH differences of about 2 units, the effect of tuff on the system does, with the effect decreasing as the pH decreases.

Figure 6. Normalized weight loss of SRL A glasses reacted with EJ-13 (a) with tuff, and (b) without tuff irradiated at: ▲ 2E5 R/h; ■ 1E4 R/h; ● 1E3 R/h; and ◆ 0 R/h plotted vs. the reaction time.

Figure 7. Plot of log of the ratio of the "acid washed" and "unfiltered" plutonium fractions vs. reaction time for EJ-13 + SRL A experiments irradiated at: ▲ 2E5 R/h; ■ 1E4 R/h; ● 1E3 R/h; and ◆ 0 R/h (a) with tuff and (b) without tuff.

REPOSITORY RELEVANCE AND CONCLUSIONS

These experiments incorporated many of the components expected to be present in a repository in tuff rock into the experimental design, but were not intended to simulate predicted repository conditions. The results are used to identify changes in the component interactions which may be attributed to a gamma radiation field. Any noticeable trends will be used in designing more repository-relevant experiments. The differences between the current experimental conditions and the actual repository include, in part: (1) that the gamma field present in the repository

will be much weaker, only a few R/h 1000 years after emplacement, (2) that the repository is an open system allowing interchange of gas and groundwater, (3) that the ratio of gas to liquid will be substantially greater in the repository. This will allow the pH to become very acidic in small droplets of groundwater, as the amount of HCO_3^- may be insufficient to buffer the solution. (4) The amount of tuff surface contacting the groundwater, air, glass, and steel will be much greater in the repository. This may have a significant effect on the removal of adsorbable species from the groundwater and release of materials into the groundwater by the tuff rock.

These differences and other uncertainties surrounding the repository design make the repository a difficult case to analyze. Nevertheless, the interactions incorporated into the present experiments should be representative of the repository, and the main application of the present work suggests that:

- (1) Nitrogen in the air will be fixed and then dissolve as acids in the available liquid. The pH of the liquid will drop as a result of these acids. The pH will be buffered to values above 6.4 by the bicarbonate in the NNWSI groundwater (~120 ppm) and dissolved CO_2 . The present experimental configuration produced about 2.6×10^{-6} moles of H^+ (using the equation of Burns et al. [9]) in the experiment with the greatest exposure. The buffering capacity of the EJ-13 leachate in the experiments is about 32 μmoles (16 mL of 120 ppm HCO_3^-), more than 12 times that required to neutralize the produced acid. The buffering capacity may be overcome in the actual repository where thin films of water may condense on the waste form and be exposed to irradiated moist air. This would allow the pH to decrease below a value of 6.4. The solubility of actinide species in this film would be increased at lower pH values, but transport away from the glass would be unlikely in the absence of a fluid phase.
- (2) The extent of glass reaction, as measured by the leachate concentrations of glass components, does not appear to be strongly influenced by the exposure rate or total exposure. The mechanism of glass reaction, a knowledge of which is necessary to make long-term projections, may, however, differ in the presence and absence of radiation. Further analyses of the reacted glass surfaces are required to assess whether or not the current results are useful in projecting glass performance. The effects of pH values below 6.4 have not been investigated. It is not unlikely that the glass performance in acidic leachants could be different than the glass performance at higher pHs.
- (3) The amount of Pu in unfiltered groundwater appears to be a function of the dose rate and the presence of tuff. This is an important factor because radionuclides can be transported away from the near-field environment only if they remain suspended or dissolved in solution. Since most of the Pu could be removed by filtration through 50 A filters, most of the Pu is thought to exist as pseudo-colloids.

While further analyses of the experimental components and complete data sets are required to fully assess the effect of gamma radiation on groundwater chemistry and glass waste form performance [17], the results presented suggest that future research be focused on repository-relevant dose rates and larger ratios of gas to liquid.

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