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WASTE GLASS PERFORMANCE IN CRYSTALLINE REPOSITORY ENVIRONMENTS

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THE ROLE OF GROUNDWATER OXIDATION POTENTIAL AND RADIOLYSIS ON WASTE GLASS PERFORMANCE IN CRYSTALLINE REPOSITORY ENVIRONMENTS

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ABSTRACT

Laboratory experiments have shown that groundwater conditions in a granite repository will be as reducing as those in a basalt repository. Chemical analysis of the reduced groundwaters confirmed that the Fe^{2+}/Fe^{3+} couple controls the oxidation potential (Eh). The reducing groundwater conditions were found to decrease the time-dependent release of soluble elements (Li and B) from the waste glass. However, due to the lower solubility of multivalent elements released from the glass when the groundwaters are reducing, these elements have significantly lower concentrations in the leachates.

Gamma radiolysis reduced the oxidation potential of both granitic and basaltic groundwater in the absence of both waste glass and oxygen. This occurred in tests at atmospheric pressure where H_2 could have escaped from the solution. The mechanism for this decrease in Eh is under investigation but appears related to the reactive amorphous precipitate in both groundwaters. The results of these tests suggest that radiolysis may not cause the groundwaters to become oxidizing in a crystalline repository when abundant Fe^{2+} species are present.

INTRODUCTION

The Savannah River Laboratory is investigating the performance of nuclear waste glass under conditions representing potential repository environments. For crystalline rock repositories, such as granite and basalt, the groundwaters are expected to be reducing, e.g., have negative oxidation potentials (Eh). The object of the current study was to assess the effect of groundwater oxidation potential on waste glass durability and to evaluate the effect of radiolysis on the oxidation potential.

Anoxic Leaching

The oxidation potential of the groundwater has a large effect on multivalent elements in the waste glass. The adsorption and migration of these elements in geologic media are often highly dependent upon their oxidation states in the groundwater. Because long lived nuclides such as Tc, Pu, Np, and U are less soluble in the reduced state, reducing groundwaters can be beneficial for repository performance. The rate of release of soluble elements from the glass under anoxic conditions is a better measure in determining whether the actual leaching kinetics are slower in reduced groundwaters.

Previous studies have demonstrated that oxidizing leachants are more aggressive than reducing solutions and increase the release of multivalent elements from nuclear waste glasses. White et al. [1] showed that in anoxic solutions Tc concentrations (from dissolution of simulated defense waste reference glass) were lower than in oxic solutions. However, these experiments were carried out in deionized water with a palladium scrubber and at pH extremes of 3 and 11. Peters and Diamond [2] reported that Np is leached less by a factor of 10, while Pu and U are leached less by a factor of 2 to 5 from simulated commercial high-level waste glass (PNL 76-68) at oxidation

potentials of 0 to +0.1 V compared to leaching rates in air-saturated (+0.3 V) solutions. Similar results were achieved in both deionized water and in simulated brines. Apted and Myers [3] and Coles and Apted [4] examined the behavior of simulated commercial high-level waste glass (PNL 76-68) in basaltic groundwaters at between 200-300°C. The elements Na, Mo, Ca, B, and Sr were leached at one-half the level observed in oxic groundwaters [3]. Technetium was released from the anoxic solutions a factor of 4 less than in the oxic solutions [4]. Although the oxidation potential was not measured in these experiments, the Eh was inferred to be reducing since the system was closed and contained crushed glass, crushed basalt, and solution. Jantzen and Wicks [5] examined the durability of defense waste glass (SRL 165) in basaltic groundwaters after 28 days at oxidation potentials between +0.23 and -0.30 V. The redox sensitive elements Fe, Ni, and Mn appeared to be released by a factor of 4 to 12 less under anoxic conditions while the U concentrations were barely above the analytic detection limit for all tests. These trends can be attributed to the lower solubility of the reduced species of these elements since there was little change in the leachability of the glass matrix elements B and Si. However, all of these elements, except U, appear in the rock-equilibrated water and trends of silicon and boron release are difficult to discern. In basaltic groundwater, the only reliable indicator element that is released from the waste glass is lithium. Lithium appeared to have concentrations in the reducing groundwaters less by a factor of 3 than in the oxidizing groundwaters after 28 days [5].

Effects of Radiolysis

Since groundwater is mostly water, its radiolysis should dominate the effects of radiation. Radiolysis of water forms equivalent amounts of oxidizing and reducing species. Oxidizing species are H_2O_2 molecules, and $\cdot OH$ and possibly $\cdot HO_2$ radicals depending on the type of radiation. Reducing species are H_2 molecules, thermalized hydrated electrons, and H atoms [6]. If these species all remain in the radiation field, a steady state is quickly achieved and there is no net change in the redox properties of the water. It has been postulated [7] that in a repository H_2 will escape, leaving an excess of oxidizing species. As a result of this, the multivalent radionuclides could be oxidized and become more soluble. Recently, Neretnieks [8,9] has modeled the effect of an oxidizing front caused by radiolysis in the flowing groundwater of a repository in granite. The movement of such an oxidizing front is postulated to decrease the retention of redox active radionuclides in the repository.

EXPERIMENTAL

The release of soluble components from defense waste glass (SRL 165) was determined in basaltic groundwater (GR-4) and in granitic groundwater (Stripa). Groundwater samples were equilibrated with rock and reduced before the leaching tests began. An x-ray amorphous precipitate, possibly a colloid, enriched in Fe^{2+} was identified in both groundwaters. The Fe^{2+} precipitate has a high surface area and is possibly the reactive species controlling the solution redox. The precipitate reactivity and the role of Fe^{2+} during radiolysis were studied. The change in oxidation potential due to groundwater radiolysis in the absence of the waste form and in the absence of air was determined. The Eh of the reduced groundwaters was measured after irradiation by Co-60 gamma rays. Various gas volumes were used in the irradiation vessels in order to simulate H_2 volatilization from the solution, as had previously been predicted for a repository environment.

The experimental cell for laboratory equilibration of simulated silicate groundwater with crushed rock consists of a 2-liter glass reaction vessel on a hot plate. The apparatus is enclosed in a glove box purged with 99.999% argon gas. The reaction vessel is filled with simulated groundwater solution and sparged with the ultrapure argon while heating to about 70°C. For determination of the relative reactivity of the various solids as a function of reaction time and solids surface area, continuous Eh and pH measurements were made at 70°C. The details of this procedure are described elsewhere [5,10].

Solid-solution residence times necessary to establish reducing groundwater conditions are about 90-120 hours depending on solids reactivity and particle size [11]. When the exact (SA/V)(t) parameter has been established for a particular solid and simulated groundwater, new solutions are equilibrated without continuous Eh and pH monitoring. Continuous monitoring is undesirable because of the considerable in-leakage of KCl from the measuring probes at 70°C. Oxygen concentrations are too low to be detected with a dissolved oxygen sensor.

The Eh and pH of rock-equilibrated leachants are measured in the reaction vessel after the specified solid-solution residence time. Aliquots are measured at the initiation and completion of the leaching or irradiation experiments. Aliquot Eh measurements are stable but introduce errors of +0.1 V. This may be attributed to the inhomogeneous distribution of the reactive precipitate. All measurements are made in the ultrapure argon atmosphere. The amorphous precipitate was not filtered from the rock equilibrated solutions during the leaching experiments. The radiolysis experiments were carried out with unfiltered samples.

Teflon® (Du Pont) leach vessels containing simulated SRP waste glass were filled with rock-equilibrated groundwaters to evaluate the interactions of glass and anoxic groundwaters under static MCC-1 conditions in the absence of rock. The solution was kept at 70°C during filling to minimize any temperature effects on silica saturation. All the vessels were filled in the environmental chamber. Duplicate 7-, 14-, 21-, and 28-day samples were left in an oven in the environmental chamber while a duplicate set of samples were removed to an oven in an oxidizing (air) environment for the same length of time. Although the vapor space in these vessels was filled with argon gas, the samples removed to the oxidizing environment exchanged air for argon in less than 1 hour.

The leachants, leachates, and irradiated solutions were analyzed for both cations and anions. Cations were determined by inductively coupled plasma induced spectroscopy and anions were determined by ion chromatography. The concentration of Fe²⁺ was determined spectrophotometrically using 1,10-phenanthroline as the indicator [12]. Analysis of standard Fe²⁺ solutions gave a molar absorptivity of 12×10^3 at 508 nm, in good agreement with published values [12]. Preparation of the solutions for spectrophotometric analysis was performed in an argon atmosphere with deaerated reagents to prevent air oxidation of the Fe²⁺. Total Fe was measured by plasma-induced spectroscopy. All solutions were acidified with either H₂SO₄ or HNO₃ to dissolve any colloid present prior to analysis.

Irradiations were performed with a Co-60 gamma ray source. The dose rate to the solutions was 10⁵ rad/hr as determined by the Fricke dosimeter. Temperature during the irradiation was 30°C. The rock-equilibrated solutions for irradiation were placed in 316 SS vessels while in the argon glovebox. The Parr vessels containing Teflon® gaskets were sealed and irradiated in a Co-60 source. Oxidation potential measurements on identical solutions and vessels stored in the absence of radiation confirmed that the vessels did not leak during the irradiation. After being irradiated, each vessel was returned to the glovebox where it was opened and the solutions were prepared for analysis.

RESULTS AND DISCUSSION

Equilibrated Stripa and Grande Ronde Groundwaters

Simulated Stripa granitic groundwater (Table I) was equilibrated with crushed Stripa granite from borehole No. 13. The Eh/pH changes as a function of time (Figure 1) are very similar to those reported for Grande Ronde groundwater in the presence of crushed Umtanum basalt [5]. The final at temperature Eh value for the granitic groundwater was -0.45 V at a pH of 8.8. The granite was more reactive than basalt achieving a lower Eh in about 70 hours rather than 90-120 hours for basalt (Table I). The oxidation potential of the granitic groundwater equilibrated in the laboratory was lower than either field measurements or calculated values reported by Wickberg et al. [13] for the Stripa repository (Figure 1).

Reproducible Eh and pH values for Grande Ronde-4 groundwater with Umtanum basalt have been in the -0.34 to -0.40 V range at pH values between 9.1 and 10.1 [5,11]. The rock-equilibrated GR-4 groundwater used in this study had an Eh value of -0.40 V at a pH of 9.1 at 65°C (Table I) which compares exactly to Eh values of -0.40 V at pH of 9.1 ± 0.5 calculated for a basalt repository at 70°C [14].

Both the granite and basalt equilibrated groundwaters contained a precipitate. Table I summarizes the differences between the starting groundwater compositions and the rock-equilibrated solutions. Acidified and unacidified rock-equilibrated solutions were analyzed to determine the chemical contribution of the precipitate phases. This is particularly important because previous work [11] had demonstrated that the precipitate phases in rock-equilibrated basaltic solutions could take as long as three months to dissolve after the solutions were acidified according to MCC-1P procedures [15]. In the unfiltered and acidified solutions, Fe^{2+} was definitely detected by spectrophotometric analysis. Ferrous iron appears to amount to 20-70 percent of the total Fe present. The presence of Fe^{2+} confirms that it is the Fe^{2+}/Fe^{3+} couple that is being measured, and that the Fe^{2+} is controlling the groundwater Eh.

TABLE I. Final Compositions of Reduced Groundwaters Equilibrated with Rock and Unfiltered

	<u>Stripa Granitic Groundwater</u>			<u>Grande Ronde Basaltic Groundwater</u>		
	<u>Recipe*</u>	<u>Not Acidified</u>	<u>Acidified***</u>	<u>Recipe**</u>	<u>Not Acidified</u>	<u>Acidified***</u>
Cations (ppm)						
Na	65	112	102	334	408	382
K	3.9	N.A.	N.A.	13	N.A.	N.A.
Si	12	17	15	45	72	68
Ca	18	5.8	8.4	2.2	2.8	4.5
Mg	4.3	0.082	0.25	-	0.26	0.6
Li	-	0.047	0.044	-	0.05	0.04
B	-	1	0.98	-	2	2
Al	-	0.56	0.62	-	0.77	1.7
Fe(total)	-	0.09	1.0	-	1.0	6.9
Fe^{2+}	-	N.D.	0.69	-	0.32	1.2
Anions (ppm)						
F	-	0.4	N.A.	20	24	21
Cl	70	156	N.A.	405	475	558
SO_4	9.6	13	N.A.	4	7	<12
HCO_3^-	123	N.A.	N.A.	120	N.A.	N.A.
pH (T°C)		8.2 (25°C)	8.8 (75°C)	9.4 (25°C)	9.1 (65°C)	
Eh (T°C)		+0.30 (45°C)†	-0.45 (75°C)††	+0.30 (45°C)†	-0.40 (65°C)‡	

* Lars Werme - personal communication

** GR-4 composition

N.A. = not analyzed

N.D. = not detected

*** Acidified with either HNO_3 or H_2SO_4 .

† Reading after sparging with Ar for 2 hours

†† After 70 hours equilibration

‡ After 90 hours equilibration

Role of Amorphous Precipitates in Reducing Groundwaters

To determine the role of the precipitate phases in the rock-equilibrated solutions, samples were analyzed after being filtered through 0.45 micron filters. Since the precipitate is inhomogeneously distributed in the solution, large volumes (about 500 mL) were filtered. After filtration, both the starting solution and the filtrates were acidified and analyzed. The filtrates were lower in Al, Ca, total Fe, Fe^{2+} , Mg, Si, and sometimes Na or K.

The filter papers contained several grams of material. It was dried at 90°C for 1 hour and then analyzed by x-ray diffraction. For basalt, a crystalline feldspar of the $\text{NaAlSi}_3\text{O}_8$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$ type was identified. For granite, a K-Ca rich feldspar, a Ca rich iron pyroxene and a chlorite phase were identified. A mass balance subtracting out the alkali, alkaline earth, aluminum, and silicon associated with the crystalline phases suggested that a residual x-ray amorphous precipitate rich in Fe, Mg, and Si with some Ca was present for granite as well as basalt [10].

Interestingly, an amorphous precipitate of the same composition had been found for GR-4 groundwater or deionized water that had been equilibrated with an SRL 165 waste glass. The glass had an $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of 0.5. The SRL waste glass had achieved Eh and pH values similar to those of basalt rock [5]. These final Eh and pH values are given in Table II. The residual (Fe + Mg)/Si ratio of the amorphous precipitate for GR-4 groundwater equilibrated with basalt and SRL 165 waste glass is 2.6, and for Stripa groundwater equilibrated with granite is about 3.6.

The significance of the Fe^{2+} silicate colloid is apparent on the Eh-pH diagram (Figure 1). All the final Eh-pH values for basalt, granite, and SRL waste glass fall in the thermodynamically calculated stability field for FeSiO_3 . Jacobs and Apted [14] and others [16] had suggested that dissolved Fe^{2+} glass in basalt mesostasis was in equilibrium with amorphous silica and secondary magnetite in the repository environment, implying that the quartz-pyroxene-magnetite (QPM) equilibrium controls the groundwater Eh in the stability field of FeSiO_3 .

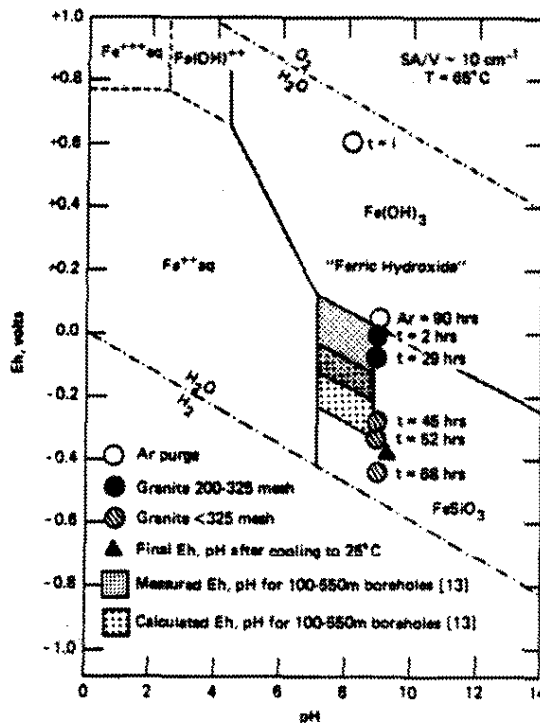
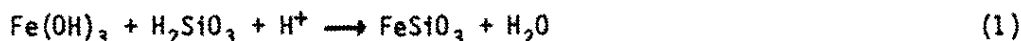


FIGURE 1. Stripa Granite/Granitic Groundwater Interactions

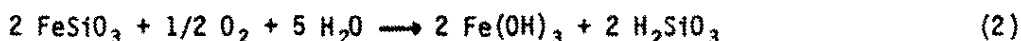
Although borosilicate waste glass is an Fe²⁺ glass, granite does not contain an Fe²⁺ intergranular phase. Recent studies by White et al. [17,18] have demonstrated that the driving force behind cation-electron mass transfer and aqueous reduction reactions is the oxidation of in situ Fe²⁺ iron on or beneath crystalline solid surfaces, e.g., reduced iron minerals act as electron donors. Moreover, White [18] demonstrated that O₂ uptake rates for basalt and magnetite in aqueous solution are comparable. Magnetite is a major Fe²⁺ phase in basalt and granite but not in waste glass. However, the redox active species, Fe²⁺, is common to all the solids and thus they all achieve the same Eh and pH values in either simulated groundwater or deionized water (Table II).

The observed Eh and pH values of Table II lie between the QPM equilibrium boundary suggested by Jacobs and Apted [14] at 65°C and the Fe₃O₄-Fe₂O₃ boundary [19]. Although the magnetite in basalt and granite may be the redox active phase dissolving, magnetite is metastable relative to FeSiO₃ in a system saturated with respect to amorphous silica. Thus the equilibrium diagram is expected to be controlled by the Fe₂O₃-FeSiO₃ couple [19]. However, Drever [20] suggests that initial precipitation of species in an aqueous system would be amorphous and have a higher free energy than the anhydrous species. Hence the Fe(OH)₃-FeSiO₃ boundary plotted in Figure 1 represents the equilibrium of Fe(OH)₃ in the presence of SiO₂ glass.

The measured Eh and pH values from Table II for basalt, granite, and SRL glass-equilibrated solutions are lower than either the Fe(OH)₃-FeSiO₃ boundary or the Fe₂O₃-FeSiO₃ couple. However, the half reaction for Fe(OH)₃ in the presence of silicic acid



has a negative free energy of reaction in agreement with the data of White et al. [17] for quantitative reduction of aqueous Fe³⁺ and H⁺ concurrent with loss of oxygen in solution. It is assumed that FeSiO₃ and Fe(OH)₃ species are amorphous and highly reactive precipitates and that an aqueous activity for these species can be estimated from the known Fe²⁺ and Fe³⁺ concentrations (Table I). This yields a Fe(OH)₃-FeSiO₃ metastable couple parallel to the couple drawn on Figure 1, but passing through the measured Eh and pH values. Calculation of the pO₂ for the complete metastable reaction including the oxygen contribution is



The K_{sp} and the analytic concentrations suggest a calculated pO₂ of 10⁻⁶⁶ atm in agreement with the 10⁻⁷⁰ atm value calculated from the measured Eh and pH. This agreement thus supports the hypothesis that an amorphous reactive ferrous silicate precipitate formed by reacting Fe²⁺ species in saturated silica solutions establishes and maintains the reduced groundwater oxidation potentials of crystalline repository groundwaters.

TABLE II. Eh and pH for Solutions Equilibrated with Redox Solids*

Initial Solution	Redox Solid					
	Basalt Rock		Granite Rock		SRL 165 Glass	
	Eh (V)	pH	Eh (V)	pH	Eh (V)	pH
GR-4 water	-0.4	9.1	-	-	-0.39†	9.5†
Deionized water	-0.42**	8.4**	-	-	-0.38	9.0
Stripa water	-	-	-0.45	8.8	-	-

* Measurements taken with mixtures were in the range 60° - 80°C

** Reference 10

† Reference 5

Effect of Eh on Glass Leaching

The time-dependent leaching of the soluble elements Li and B from SRL 165 waste glass under oxic and anoxic conditions is shown in Figure 2. Lithium releases could be accurately determined for both the Stripa and Grande Ronde groundwater but B releases could only be determined for the Stripa groundwater. The B concentration in the basalt equilibrated groundwater solution was too high and no changes were detected due to glass dissolution. This was also true for Na, Si, and other cations in the solutions. Results in Figure 2 are the averages of duplicate experiments. The error bars indicate the range of the results. The pH of the oxic and anoxic solutions remained the same during the experiments. This occurs because the leachants are dominated by the groundwater chemistry.

Leaching was consistently lower in the low Eh solutions by a factor of about 2. Thus reducing groundwaters have only a small effect on the durability of the glass per se. However, other studies have shown that low Eh significantly lowers the concentration of many redox active elements. This is apparently due to solubility rather than increased durability of the glass.

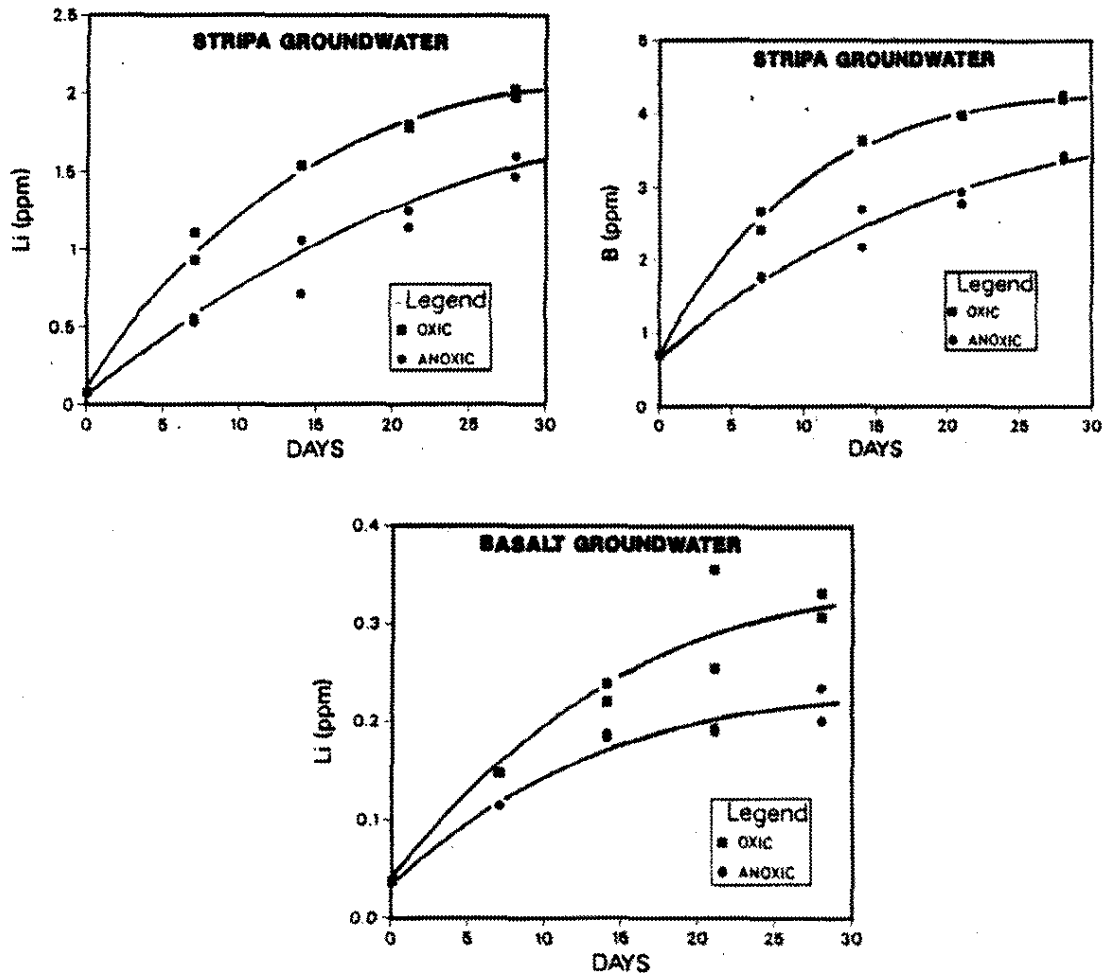


FIGURE 2. Time Dependent Release of Li and B from SRL Waste Glass in Reduced and Oxidized Groundwaters

Effect of Radiation of Low Eh Groundwater Solutions

Results of irradiating samples of the reducing groundwaters in the absence of air or glass in sealed vessels with Co-60 gamma rays for 20 hours are shown in Table III. In contrast to predictions of recent models of groundwater radiolysis [7,21], the solutions did not become oxidizing as a result of accumulation of H_2O_2 . As indicated in Table III, radiolysis caused the solutions to become more reducing, i.e., the Eh decreased for both solutions. Ten other samples of the groundwaters were irradiated for various times ranging from 5 to 20 hours. In all cases, the Eh decreased to approximately -0.5 V. As shown in Table III, the concentrations of soluble anions and cations in the groundwaters did not change significantly as a result of radiolysis. Apparently, radiolysis of the Teflon® gasket at these total doses was not producing sufficient F^- ions to change their concentration in the groundwater. The total Fe concentrations of the solutions were different because different amounts of Fe containing particulates were removed from the stock solutions for each test.

To determine if Fe was being leached from the vessels during radiolysis and whether this may cause the solutions to become more reducing, samples of Ar saturated deionized water were irradiated in the stainless steel vessels and the total amount of Fe was analyzed. Increases in Fe concentration due to radiolysis were less than 0.02 ppm; thus, it appears that only small amounts of Fe were leached from the steel vessels. In these irradiation tests with deionized water, radiolysis did cause the Eh of the water to decrease from ~0.0 V to -0.1 V although the solutions were not well poised. This decrease is less than that observed with the groundwaters (Table III).

The effect of gas volume over the solution was investigated to see if a larger free volume, which would allow more H_2 to escape from the solution, would cause the solution to become oxidizing. In all the above tests, the gas volume was only one-tenth the solution volume; thus H_2 could not readily escape the solution. In two other tests, the gas volume relative to the solution volume was increased by a factor of 10. Again, radiolysis caused the Eh to decrease for both the granitic and basaltic groundwater to -0.5 V after only 5 hours irradiation. The reason for the decrease in Eh is not immediately apparent, but it may be due to a change in the Fe^{2+}/Fe^{3+} ratio. In these initial experiments, the change in this ratio due to radiolysis could not be determined because the ratio in the solution before radiolysis was not accurately known. The stock solutions were not stirred while sampling and results for total Fe in the stock solutions were not reproducible due to inhomogeneous distribution of the amorphous precipitate.

TABLE III. Effect of Radiation on Reduced Stripa and Basalt Groundwaters*

	Stripa		Basalt	
	Unirradiated	Irradiated	Unirradiated	Irradiated
Eh (V)	-0.28	-0.48	-0.23	-0.48
pH	9.5	8.5	10.1	10.1
Cations (ppm)				
Na	106	103	441	429
Li	0.030	0.034	0.043	0.052
B	1.0	1.0	2.2	2.1
Si	17	16	73	71
Ca	6.2	6.1	3	3.3
Fe (total)	0.29	1.34	1.2	1.4
Fe ($^{2+}$)	N.D.	0.84	0.57	0.83
Anions (ppm)				
F	0.4	1.0		
Cl	181	217		
SO_4	18	13		

* Irradiated 20 hr at 10^4 rads/hr. Solution to gas volume = 0.1 V = 31°C
Final samples acidified with H_2SO_4 before cation analysis.

Two tests were performed to confirm the observed decreases in Eh with irradiation. In the first test, a sample of an irradiated solution which had a measured Eh of -0.45 V was exposed to air and the Eh was measured again. In a matter of minutes, the Eh increased to +0.37 V, the value for oxygenated groundwaters. In the second test, a deaerated sample of the standard Zobell solution was irradiated for 65 hours. The Eh decreased from +0.43 V to -0.46 V. This solution is an equimolar solution of ferro- and ferri-cyanides at neutral pH. For the test the pH was adjusted to 9.5 to correspond to that for a basalt groundwater. Radiolysis also caused the pH to decrease to 8.8, probably because of the hydrolysis of Fe ions released from the CN^- complexes. The irradiated solution was very blue, and a precipitate of Prussian Blue was observed. These tests confirmed that the Eh decreases which were observed were definitely due to radiolysis.

Changes in oxidation potential due to radiolysis have been measured in another system. This was an acidic nuclear process solution containing large concentrations of fission products [22]. The dose rate to the solution (primarily from fission product beta particles) was 1.5×10^5 rad/hr. In this solution, which initially had all the Fe in the +2 state, the Eh increased from +0.55 V to +1.0 V in only 10 minutes. Prior to this 10 minute period, however, the Fe^{2+} concentration decreased linearly from 0.018 M to 0.0005 M in 8 hours while there was little change in Eh. Thus, it appears that with appropriate changes in the Fe^{2+}/Fe^{3+} ratio the Eh can change rapidly. In the experiments reported in this study, the total Fe concentration was very low; thus, the change in the Fe^{2+}/Fe^{3+} ratio even though small, may have caused a significant change in the Eh at low radiation doses.

The stability of Fe^{2+} in neutral solutions during irradiation has been demonstrated by Matthews [23]. In his tests, the solution was a deaerated solution of $FeSO_4$ at pH -6. Radiolysis caused the Fe^{3+} concentration to increase until a steady state was reached at a Fe^{2+}/Fe^{3+} ratio of 0.42. The calculated H_2 concentration in solution was 3.4×10^{-5} M corresponding to a H_2 partial pressure of only 40 torr above the solution. In these solutions, it was postulated that the Fe^{2+} and Fe^{3+} ions were associated with a colloid and that this colloid did not hinder the reactivity of the ions. The Eh of the final solution after steady state was reached was not measured. Based on the Fe^{2+}/Fe^{3+} ratio, the Eh was probably negative. In the experiments of Matthews [23], H_2O_2 was being produced as a molecular product by the radiolysis of water. Apparently, this production did not cause complete oxidation of Fe^{2+} to Fe^{3+} .

To measure the pressure changes during irradiation, two aliquots of basalt groundwater were irradiated in stainless steel vessels attached to pressure transducers. Both the pressure and temperature were monitored. As shown in Figure 3, the pressure above each increased linearly after an initial rapid rise due to the temperature change caused by gamma ray heating. The total pressures in the two tests were different due to different initial Ar pressures. As with the other tests, the Eh for both solutions decreased from -0.3 to -0.5 V. The observed pressure increases due to radiolysis were ~30 torr. Careful analysis of the composition of the gas after the tests indicated that the pressure increases were due solely to the production of H_2 . No other gases were formed by the radiolysis. The G value for the production of H_2 for both tests was 0.64 ± 0.03 molecules/100 eV. This value is somewhat larger than 0.45, the value for the molecular yield of H_2 from gamma ray radiolysis of water [6]. Perhaps some of the aqueous electrons produced in the bulk of the solution are recombining to form H_2 but this appears unlikely based on the relative rate constants for the various reactions involved [6]. It does appear that H_2 escapes from the solution during radiolysis, but even with this occurring, the Eh of the solution decreases rather than increases. More experiments need to be performed before these observations can be fully explained.

Start
up
14

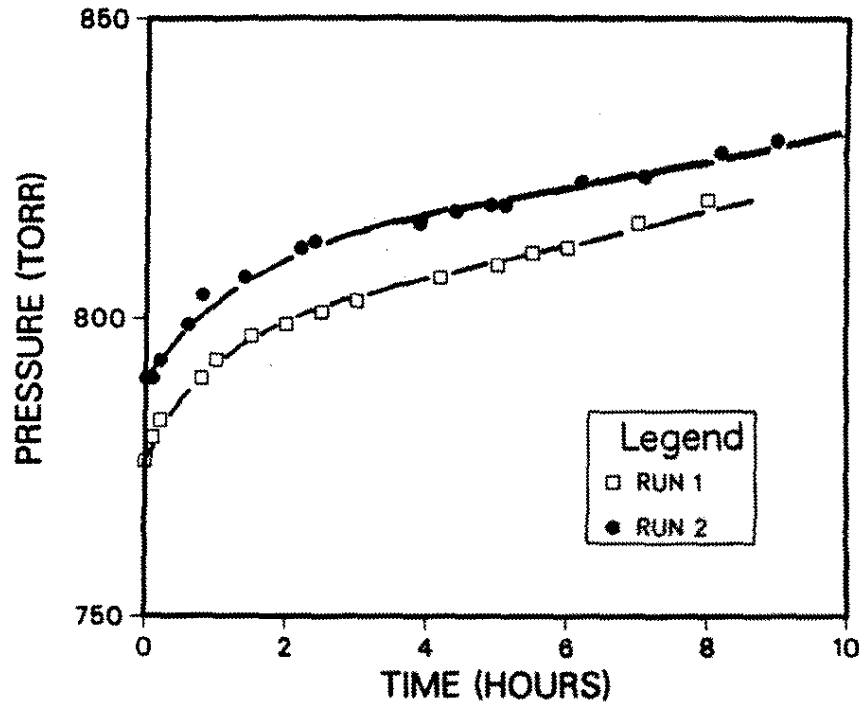


FIGURE 3. Pressure Buildup Inside a Stainless Steel Reaction Vessel from Gamma Irradiation of Reduced Basalt Groundwater

IMPLICATION FOR THE RESULTS TO CRYSTALLINE REPOSITORY PERFORMANCE

The models that have been proposed [7,21] suggest that the reducing groundwaters of crystalline rock repositories will become oxidizing as a result of radiolysis from the waste package. The basic assumption of the models is that H_2 will be transported away from the solution by diffusion and convection leaving an excess of oxidizing species in the solution. The results presented in this study contradict this. These results show that radiolysis causes the solution to be less oxidizing even under conditions where H_2 would be expected to escape from the solution. In a repository, the escape of H_2 would be expected to be hindered by the high lithostatic and hydrostatic pressure. However, it needs to be shown experimentally with solutions actually containing U, Np, Tc, or other redox active radionuclides that oxidation of these species does not take place. For example, if the Fe^{2+} concentration is low and the radionuclide concentration is high, the OH radicals may oxidize the radionuclides rather than Fe^{2+} .

These experiments have to be extended to alpha radiolysis where the yields of H_2 and H_2O_2 are larger than with gamma radiation because of the higher linear energy transfer of alpha radiation. The effects of alpha radiation will be investigated in future experiments. The results of those experiments will be significant to the application of the existing models to repository performance. If the repository groundwaters remain reducing, the most soluble waste glass elements will leach less by a factor of 2 than in oxidizing groundwaters, and the concentrations of redox-sensitive elements will be low due to reduced solubility.



CONCLUSIONS

The data presented in this paper lead to the following three conclusions:

1. Solutions simulating the predicted granite and basalt repository groundwater conditions, including low Eh, can be prepared in controlled laboratory conditions.
2. The major role of Eh in glass leaching is to reduce the solubility of redox-active elements and only slightly improve the durability of the glass. This conclusion is based on the leachability of Li and B from the glass. The solubility of these elements is not affected by the Eh.
3. Radiolysis resulting from gamma and beta radiation from the waste glass may not cause reducing groundwaters to become oxidizing as previously postulated. Alpha radiolysis remains to be investigated.

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