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BRINE CHEMISTRY EFFECTS ON THE DURABILITY OF A
SIMULATED NUCLEAR WASTE GLASS*

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ABSTRACT

The effects of various solution chemistry parameters on the alteration and leaching characteristics of a copper borosilicate simulated waste glass have been determined under hydrothermal conditions. Results are presented which demonstrate that leachant salinity, volume/glass surface area ratio, pH, cation content, and dissolved SiO_2 concentration effects are important. A brief explanation of these results is given which is based on ion exchange and solution saturation equilibria.

INTRODUCTION

The leaching process generates the source for radionuclide dispersal which makes the study of the chemical durability of nuclear waste forms in geologic isolation environments an essential portion of the technological basis of radioactive waste management. It has been shown in previous studies that a number of experimental and environmental parameters affect the wasteform leaching process [1,2,3,4]. Of particular importance to a bedded salt and subseabed site specific study is the effect of possible wide variations in leachant chemistry on chemical durability. Sources of chemical variations in the leachant include any or all of the following: (1) Repository Site. Leachant compositions can range from a saturated NaCl brine solution to a number of saturated Na/K/Mg chloride brines in bedded salt to the unsaturated Na/K/Mg chloride containing

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seawater in subseabed sediments [5]; (2) Leachant volume to waste-form surface area ratio (V/SA). The mechanism of leachant intrusion (i.e. thermal migration versus a flooding accident in bedded salt) can affect the V/SA ratio which in turn influences the concentration of solubilized products; (3) Dissolved SiO_2 concentration. The presence of geologic materials and canister backfill materials (clays and quartz) will increase the concentration of dissolved SiO_2 in solution; and (4) Radiation. The steady-state concentration of gamma radiolysis products (H_2 , H_2O_2 , Cl_2 , OCl^-) is a function of solute concentration [6].

The results of a study investigating the effects of the above four solution chemistry factors on the leaching characteristics of a copper borosilicate simulated waste glass in hydrothermal brine environments will be presented in this paper. An explanation of the results will be given which is based on ion-exchange and solution saturation equilibria. It should be noted that the maximum anticipated interface temperature for waste glass under inundated bedded salt repository conditions is less than 150°C [7]. A temperature of 250°C was used exclusively in this study in order to both overtest the waste glass durability and to accelerate the leaching reactions. A more complete description of current repository environments is given in Reference 5.

EXPERIMENTAL

A copper-titanium borosilicate glass frit (#199), obtained from the Battelle Pacific Northwest Laboratory, was melted with a simulated Barnwell type oxide waste to form the waste glass studied. The glass/waste composition was 30% waste oxides, 37% SiO_2 , 9.8% B_2O_3 , 8.4% Na_2O , 21% K_2O , 2.1% CaO , 6.3% TiO_2 , 1.1% Al_2O_3 , and 3.1% CuO .

The majority of the experiments were conducted in high pressure one liter 4130 steel autoclaves. The solution and 3 mm cubes of the waste glass were sealed inside a gold capsule. When a large solution excess was desired, 1-liter and 4-liter stainless steel and Hastelloy C-276 autoclaves were used.

Two saturated chloride brines, denoted as Brine A and Brine B, along with seawater and deionized (DI) water were used as the basic leach solutions in this study. The two saturated brines are representative of solutions which may be encountered in bedded salt environments and their detailed composition and origin is given in Ref. 5. Basically, Brine A contains high concentrations of Na/K/Mg chloride (107 g/l, 57 g/l, 138 g/l, respectively), whereas Brine B contains predominately NaCl (290 g/l). Seawater is an unsaturated chloride brine containing a moderate concentration of MgCl_2 (5 g/l). Other solutions used were variations of the above four.

Waste glass durability was assessed using a combination of weight loss measurements, solution analyses and a leached layer characterization. The sample weight loss was successfully used as a method of determining the extent of glass matrix alteration by measuring the final weight after the leached layer had been mechanically removed. Solution analyses were performed using atomic absorption, flame emission, and induction-coupled-plasma emission spectroscopy. Selected leached layers were characterized on the electron microprobe (EMP).

RESULTS

A very important experimental parameter is the solution volume to waste glass surface area (V/SA) ratio. The dramatic dependency of matrix alteration and cesium solubility on V/SA ratio is shown in Table I. Cesium solubilization was used as a measure of leachability because previous studies have shown cesium to have both the highest leach rate of all the simulated radionuclides and to be least involved in the solid alteration product reactions [1, 3,4]. From the data shown in Table I, one can conclude that reaction products, if allowed to concentrate, will significantly retard both the corrosion and leaching reactions. In an effort to both understand this retardation and the effect the presence of geologic and backfill materials will have, experiments were conducted with varying amounts of colloidal silica added. The colloidal silica served as a source for silicic acid in the high temperature water (solubility of amorphous silica in 250°C water is 2 g/l). The effect of dissolved SiO₂ on waste glass durability is shown in Table II. The solution composition was varied by changing the chloride cations used. The influence of cation additions and leachant composition is shown in Table III. To determine the effect of radiation, glass waste was leached at 90°C for 79 days in the four standard leach solutions in the presence of gamma radiation from a 10⁷ rads/hr ⁶⁰Co source. Identical experiments were performed outside the gamma source for comparative purposes. The production of radiolysis products in the brine solutions increase the oxidizing potential of the solution which might increase the extraction of species such as uranium which need to be oxidized. It was found, however, that the presence of radiation did not cause a detectable change in either matrix alteration or cesium and uranium solubilization. The effects of radiolysis represent the chief unknowns presently and will continue to be studied.

The following observations concerning leachant chemistry effects based on the data given above: (1) Salinity. As the salt concentration is increased, matrix alteration and Cs solubilization decrease. This effect occurs over a pH range of 0 to 12. (2) pH. Both unsaturated low and high pH solutions produce significant leaching and alteration. However, the addition of 300 g/l NaCl retards cesium extraction in this pH range and alteration only at

Table I. Effect of solution volume to waste glass surface area (V/SA) ratio on % matrix alteration and % cesium solubilized (T = 250°C, t = 28 days)

<u>Leachant</u>	<u>V/SA(cm)</u>	<u>% Altered</u>	<u>% Cs Solubilized</u>
DI Water	0.5	3.6	0.6
DI Water	4.4	16.4	4
DI Water	44	70	18
DI Water	750	100	43
Brine A	4.2	6.6	0.4
Brine A	109	12.6	0.9

Table II. The effect of SiO₂ concentration on waste glass durability (T = 250°C, t = 28 days)

<u>Leachant</u>	<u>V/SA(cm)</u>	<u>SiO₂ added (g/l)</u>	<u>% Altered</u>	<u>% Cs Solubilized</u>
DI Water	4.4	0	16.4	4
DI Water	4.4	0.2	15.5	4
DI Water	4.4	1	6	2
DI Water	4.4	2	3	0.6
DI Water	750	0	100	43
DI Water	750	2	0.1	2
Brine A	4.2	0	6.6	0.4
Brine A	4.2	2	1.0	0.2

Table III. The effect of solution composition on waste glass durability (T = 250°C, t = 28 days, V/SA = 4-5 cm)

<u>Leachant</u>	<u>% Altered</u>	<u>% Cs Solubilized</u>
DI Water	16.4	4.1
Seawater	11.5	4.9
Brine A	6.6	0.4
Brine B	4.6	0.5
100 g/l NaCl	3	0.8
300 g/l NaCl	3	0.4
57 g/l KCl + 243 g/l NaCl	2	0.3
138 g/l MgCl ₂	15	2.5
138 g/l MgCl ₂ + 145 g/l NaCl	9	1.0
pH 0 H ₂ SO ₄	100	49.0
pH 0 300 g/l NaCl	25	4.0
pH 12 NaOH	100	40.0
pH 12 300 g/l NaCl	100	14.0

low pH. (3) Presence of SiO_2 . The presence of dissolved SiO_2 (as Na_2SiO_3 , H_2SiO_4) results in an increase in the waste glass durability. (4) Cation Additions. The effects of Na and K chloride on alteration and cesium release are similar and affect leaching by producing changes in solution salinity. However, additions of magnesium chloride result in significant increases in both matrix alteration and cation release (including Cs, Ca and Sr) by lowering the solution pH and entering into the glass alteration reaction [1]. (5) Radiation. The leaching process is not significantly affected by the presence of high intensity gamma radiation or radiolysis products.

From the above results, solution corrosivity can be expected to increase in the order: saturated KCl/NaCl brine < unsaturated KCl/NaCl brine < saturated MgCl_2 /NaCl brine < unsaturated MgCl_2 /NaCl brine. The various site specific leachants can then be categorized into one of the above basic chemistries.

Leachant chemistry and corrosivity could be altered by the presence of solids in the geologic formation itself. Possible solids which will be encountered in the sites being considered in this study include engineered backfill materials, bedded salt, clays dispersed in bedded salt, and sea sediments. It was shown previously that excess bedded salt does not affect waste glass durability [1]. A mixture of quartz and hectorite (a lithium montmorillonite, $(\text{Mg}, \text{Li})_6 \text{Si}_8 \text{O}_{20}(\text{OH})_4$) is a leading candidate backfill material. The clay found in bedded salt and the deep sea sediments are composed of mixtures of montmorillonites, illites, kaolinites, and other clays. The effect of these solids on the alteration of waste glass in various solutions is shown in Table IV. It was expected that these complex silicate clays would dissolve into the hydrothermal solutions and retard the alteration reactions (similar to additions of SiO_2). This expectation was confirmed only for the sea sediments. The presence of bedded salt clay and hectorite had a large negative or accelerating effect on the alteration mechanism. Magnesium is present in all three clays, yet it was shown in Table III that even extremely high concentrations of MgCl_2 could not produce the alterations caused by the additions of hectorite and bedded salt clay. Additionally, the solution pH remained around 5 to 6 in all of the clay experiments. Thus, the differences in alteration produced by clays and sea sediments must be due to the release from the impurities in the clays of an effective silica complexing species or even a silica network attacking ion such as fluoride. These results point out the existence of a potential wasteform problem in an actual repository if proper backfill materials are not used. This effect is currently being studied in more detail and at more probable lower temperatures.

Table IV. Influence of the additions of various geologic clays on waste glass alteration. (T = 250°C, t = 28 days, V/SA = 4.2 cm, solution/clay - 4:1)

Clay	Leachant	% Alteration without clay	% Alteration with clay
Hectorite	DI Water	16.4	70
Bedded Salt Clay	DI Water	16.4	46
Sea Sediments	DI Water	16.4	1.7
Bedded Salt Clay	Brine A	6.6	55
Sea Sediments	Seawater	11.5	5.9

DISCUSSION

The mechanism of the dissolution of simple glasses has been extensively studied and need not be presented here except to note a few salient points [8]. First, glass cations (especially alkali ions) are extracted by an ion exchange reaction with H_3O^+ leaving a silica rich phase. The rate of exchange is controlled by the diffusion rates of the ions involved through the leached layer. Hydroxide ions present or produced when H_3O^+ ions are consumed during ion exchange, attack the SiO glass bond resulting in dissolution of the leached layer. The resistance of glass to leaching is then a function of the thickness and integrity of the diffusion limiting SiO_2 rich leached layer and the rate of hydration of the silica. It is believed the chemical durability of glasses increases with divalent oxide additions because these oxides fill microvoids in surface films to form a more impermeable barrier [9].

The glass used in this study is a very complex mixture of various oxides. For discussion purposes, assume the glass is a binary sodium silicate glass which is leached by the following reaction sequence in near neutral solutions:

From the mass action expression for equation (2), it can be shown that

$$\log a_{H_2SiO_3} = \log(K_{eq}) - 2 \log a_{Na^+} - 2pH \quad (4)$$

If it is assumed that the above processes are applicable and the system is at equilibrium, then the results discussed in the previous section can be qualitatively explained as follows: (1) Increases in the salt content in the leachant results in less glass cation ion exchange and less silica dissolution by the retardation of reaction 2 (see equation 4). This result was confirmed with both electron microprobe (EMP) mapping, which showed higher silica, cesium, and sodium content in leach layers produced in brine than in DI water, and by product layer density measurements. The original glass density of 2.18 decreased to 2.0 for a seawater leached layer to 1.4 for a DI water leached layer. Thus, the silica layer forming during DI water leaching is not as compact and protective as the one formed during brine leaching. The solution pH could have a contributing effect here because prior studies have shown that significant SiO₂ dissolution occurs at high pH [8]. DI water leachants maintained a pH of 8-9 and brine leachant pH was 5 to 6. (2) Increases in silica content in solution retard the glass matrix dissolution (reaction 3) which results in a more effective diffusion barrier. (3) Lower solution volume/surface area ratios allow both dissolved alkali and silica concentrations to increase. Increases in Na, Cs, and SiO₂ solution concentrations have been observed with decreases in V/SA ratios. Thus, a combination of the effects of #1 and #2 above retard the reactions as V/SA ratios decrease. (4) The accelerating effect of Mg additions in the leachant is due to the substitution of Mg⁺² in the glass lattice for divalent cations like Ca, Sr, Cu. These divalent ions are not leached in DI water or Brine B. This substitution has been confirmed using the EMP and occurs because it is thermodynamically favorable due to magnesium's high charge to size ratio. Mg content in a Brine A leached layer reached 10-15% of the total constituents. The impermeability of a Mg containing leach layer is not as high as a Ca/Sr layer and therefore the alteration and leaching rates increase as Mg is substituted. The lack of an effect of time on glass durability which has been noticed in other studies is probably due to the saturation and equilibrium effects discussed above [1,4]. Finally, the elements Gd, Ti, Pd, U, La and Mo are not detectably solubilized into high temperature brine solutions.

SUMMARY

The solution chemistry parameters salinity, pH, cation content, volume/exposed surface area and dissolved SiO₂ concentration have been shown to have a significant effect on waste glass durability. 1) Solution corrosivity increases in the order saturated KCl/NaCl brine < unsaturated NaCl/KCl brine < unsaturated MgCl₂/NaCl brine. 2) Additions of alkali ions to the solution retard glass cation

ion exchange. 3) Dissolved SiO_2 in solution improves the impermeability of the leached layer. 4) The presence of Mg decreases glass durability by substituting for divalent oxides like CaO , SrO , and CuO in the glass lattice. 5) The effect of gamma radiolysis products on waste glass durability appears minimal.

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