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EFFECTS OF Eh (OXIDATION POTENTIAL) ON BOROSILICATE WASTE GLASS DURABILITY*

by

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ABSTRACT

Solid state materials can be used to control the oxidation potential (Eh) of waste glass leachants. These materials are chosen based on known Eh-pH relations for redox species in the presence of dissolved silica. Experiments under oxidized conditions have enabled evaluation of waste glass durability in the presence of waste package components which affect Eh.

INTRODUCTION

Radioactive waste glasses contain many elements which are redox active, i.e. can occur in more than one redox state. The valence state of an ion, in particular technetium and the actinide elements, can be important in determining the equilibrium solubility and the rate of dissolution of the waste form. Moreover, the adsorption and migration of multivalent elements in geologic media are highly dependent upon the distribution of the redox states in the groundwater. This is particularly important for repositories in which the groundwaters are expected to be anoxic.

In the United States three types of geologic formations are being examined as potential high-level waste repositories. These include the basalt formations at Hanford, tuff at the Nevada Test Site and salt formations in several states. Tuff in the saturated

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zones and salt formations are expected[1] to be mildly anoxic (Eh = 0.0 and -0.1 volts, respectively) while the basalt is expected[1,2] to be strongly anoxic (Eh = -0.45 ±0.05 volts).

Waste-form performance evaluated in the laboratory has, to date, not addressed waste form performance under anoxic repository conditions.[3,4] Since technetium and actinide solubilities* are strong functions of temperature, Eh, pH and water chemistry, these variables must be simultaneously examined in order to evaluate any synergistic effects between the waste-form and the groundwater chemistry.

Synergistic effects between waste-form and waste-package components must also be considered as a function of groundwater chemistry. This is of particular concern when one or more of the waste package components is known to affect or control the Eh. Two pertinent examples are the potential use of crushed basalt as a backfill material in a basalt repository[5] and the use of iron (or low carbon steel) as a canister material. Dissolution of the intergranular glassy phase in basalt is believed to control the Eh-pH relations in solution[2] since it contains a redox active phase, e.g. ferrous iron-silicate glass. The leaching of waste glass under oxic conditions in the presence of basalt may, therefore, be different than the leaching of glass in the presence of basalt under anoxic conditions. Likewise, the presence of iron[6] or any metallic species[7] in a laboratory waste-form performance test may cause different synergistic effects under oxic and anoxic conditions. Therefore, a systematic examination of the effect of various waste package components (e.g. metal canister materials, basalt backfill and waste glass) on solution Eh was undertaken as a first step toward the assessment of the synergistic effects between waste-form and waste-package components under repository conditions.

Eh MEASUREMENT AND VERIFICATION

Oxidation-reduction reactions can be thought of as reactions which involve the transfer of oxygen or the transfer of electrons. Since many redox reactions do not involve molecular oxygen directly it is more convenient to consider redox reactions as electron transfers.[8] Even if molecular oxygen were involved,

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* Actinide solubilities are greatly reduced at low Eh values due to the stabilization of the insoluble +(IV) oxidation state relative to the +(VI) oxidation states: actinide solubility decreases with decreasing pH because of the destabilization of actinide-hydroxyl complexes at low pH.[2]

kinetic problems* complicate the use of oxygen activity as a thermodynamic variable at low temperatures. At high temperatures the oxygen activity (fugacity) is a more convenient parameter to use.[8]

Since the redox reactions are electron transfers, an electron potential, p_e, can be described[8] so that

$$p_e = 1/n \log K_{eq} + 1/n \log \frac{\text{(activity product oxidized species)}}{\text{(activity product reduced species)}}$$

where n = the number of electrons transferred during the reaction.

When described in terms of the free energy of the reaction and measured relative to the potential of a hydrogen half cell reaction the electrode potential, Eh, in volts is

$$Eh = E^o + \frac{0.059}{n} \log \frac{\text{(activity product of oxidized species)}}{\text{(activity product of reduced species)}}$$

where E^o = standard electrode potential (the Eh the cell would have if all the chemical species involved were in their standard states)

$E^o = \Delta G^o / n\mathcal{F}$

ΔG^o = standard free energy of reaction

$\mathcal{F}$ = Faraday constant, 23.06 kcal per volt gram equivalent

The p_e and Eh are related by

$$p_e = \frac{\mathcal{F}}{2.303RT} Eh$$

Since an absolute potential cannot be measured, the potential difference between a measuring electrode whose voltage is a

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*There is no correlation between the measured Eh and dissolved oxygen (DO) concentration. The reaction,

$$\frac{1}{2} O_2 + 2H^+ + 2e^- = H_2O$$

which represents the upper stability limit of water, is too slow to control measured Eh.[9]

function of the electron activity and a reference electrode is measured. A platinum measuring electrode provides an inert means of transferring electrons to or from solution[8] and the potential difference is measured relative to a calomel or silver/silver-chloride reference electrode.[9]

Under oxidizing conditions (high Eh) in the pH environment of the anticipated repositories, the platinum electrode is in an aqueous environment above the calculated platinum-oxygen couple[10] and easily becomes contaminated. In natural environments such as stagnant or reducing waters where oxygen has been replaced by other electron acceptors, the platinum electrode can respond to other redox systems and give mixed potentials. Likewise, sulfur must be absent to avoid Pt-S interactions.[10] These conditions are often not met in the natural environment and hence Eh measurements in the field are difficult and almost always suspect.[11]

Anoxic conditions below the $Pt-O_2$ couple, in the absence of sulfur and with known redox reactions can be achieved in simulated laboratory experiments. Since many redox processes are very slow in reaching equilibrium and a meaningful Eh cannot be defined for non-equilibrium systems, known singular redox couples were investigated with Pt electrodes and the results compared to calculated equilibrium Eh-pH diagrams.[12]

When the ferric-ferrous couple is present in either oxygenated or anoxic waters Eh measurements are stable and reproducible.[9] In acidic oxygenated water, the ferric-ferrous couple has a high redox capacity and therefore gives reproducible measurements. At pH values greater than 4, anoxic waters can be in equilibrium with dissolved ferrous iron and solid ferric oxyhydroxides which produce stable and reproducible Eh measurements at aqueous ferrous iron concentrations as low as 0.6 ppm.[13] The reaction

$$Fe^{2+} + 3H_2O = Fe(OH)_3 + 3H^+ + e^-$$

is catalyzed by a layer of ferric oxyhydroxide which forms on the surface of the platinum electrode during Eh measurement[14] and, hence, Eh measurements which are consistent with the activities of the iron species present can be achieved.[9]

In poorly-poised systems the concentration of redox-active species is low and Eh measurements drift. In well-poised systems the redox capacity is large, e.g. greater than 10^{-5} M[8], and Eh measurements are reproducible. Therefore, Eh was measured as a function of residence time of the solid in the aqueous media and as a function of the ratio of the surface area of the solid to the volume of solution. This assumes that the concentration of redox-active species released by the solid is a function of the reactivity parameters, time and surface area.

EXPERIMENTAL

The experimental cell consisted of a one-liter Teflon® (Du Pont) leach vessel filled with leachant and placed on a hot plate (Figure 1). The leachants were deoxygenated with an argon sparge before any redox active solid was added. Continuous at temperature monitoring of Eh and pH was achieved by the Pt measuring electrode, calomel reference electrode and a pH electrode. The temperature of the experiment is limited by the maximum temperature (80°C) of the electrodes. Temperature was measured with a thermometer. A Teflon® floating stirring bar and continuous argon sparging maximized solution homogeneity during measurement. The Pt electrode was periodically cleaned with 1 micron diamond paste to minimize poisoning of its surface.[9] The measured electrode potential was calibrated with Zobell solution (potassium ferro-ferricyanide) at room temperature.[9]

The metallic, waste glass, and repository rock systems investigated under oxic and deoxygenated conditions are indicated in Table I. Deionized water and balsaltic groundwater (GR3) were used as leachants. Iron filings, lead shot, Hanford Umtanum basalt and SRL 165 waste glass were used as redox active solids. For the metallic iron-SRL 165 waste glass interactions under oxygenated conditions, comparative MCC-1 tests were run at 70°C. The surface area-volume ratio of the glass and ductile iron were kept the same as previously described by McVay and Pederson.[7]

TABLE I

Systems Examined

Solid	Solution	Condition
Metallic Iron*	Deionized Water	Deoxygenated
Metallic Lead*	Deionized Water	Deoxygenated
SRL 165 Waste Glass**	Deionized Water	Deoxygenated
Umtanum basalt**	Deionized Water	Deoxygenated
Umtanum basalt**	GR3 Groundwater	Deoxygenated
Iron + SRL 165 Waste Glass*	Deionized Water	Oxygenated

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* Eh measured as a function of residence time.

** Eh measured as a function of both SA/V and residence time.

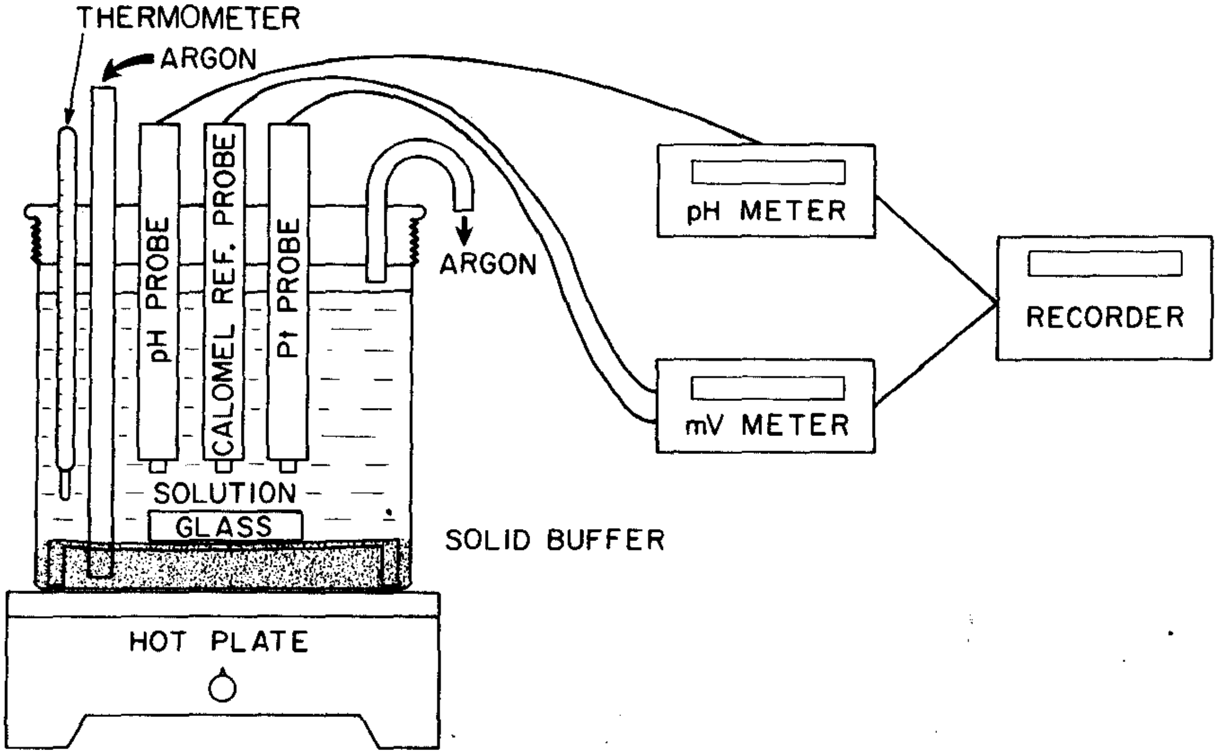

FIGURE 1. Experimental design for Eh measurement in deoxygenated leachants

RESULTS

Iron and Deoinized Water

Deoxygenating deoinized water by sparging with argon at 50°C for 14 hours lowers the Eh from the air-saturated value (t initial) of +0.6 volts to +0.2 volts. Deionized water is a poorly poised solution and a stable measurement is difficult to achieve. The observed changes in Eh and pH are plotted in Figure 2a. The shaded area of this "environmental" Eh-pH plot represents the values of natural waters that contain more than 0.01 ppm dissolved oxygen. It is readily apparent that 0.01 ppm dissolved oxygen contamination* can cause very high Eh measurements.

After 14 hours of Ar sparging, 15 g of iron powder were added. The Eh immediately began to fall and after 4 hours a potential drop to −0.3 volts was achieved. This value is about 80% of the value calculated from equilibrium thermodynamics for the Fe°/Fe^{2+} couple in water.[12]

Lead and Deionized Water

Leachant deoxygenation with argon for 20 hours with subsequent addition of 15 g of lead shot lowered the Eh to −0.13 volts. This Eh is within 90% of the calculated equilibrium value for metallic lead going to Pb^{2+} in solution.[15]

SRL 165 Waste Glass and Deionized Water

Deionized water was degassed with argon using a gas disperser and times as short as 30 to 45 minutes were found to give acceptable Eh measurements. After initial deoxygenation, 15 g of SRL 165 waste glass cubes with an SA/V of 0.02 cm^{-1} and a measured Fe^{2+}/Fe^{3+} ratio of 0.48 were added. Even after 12 hours of dissolution the Eh was only lowered to about +0.08 volts and the pH raised to 7.6 (Figure 2b). An additional 50 g of waste glass cubes were added but this only increased the effective SA/V to 0.07cm^{-1}. After 24 hours the Eh was close to zero (+0.02) while the pH had increased to 8.0.

The SA/V parameter was increased by adding 14 g of crushed SRL 165 waste glass which had been sieved between 100 and 200 mesh so that the effective SA/V was 2.0 cm^{-1}. After 24 hours dissolution this had little additional effect on the Eh but increased the pH to 8.83, but after 40 hours the Eh dropped to −0.17 at a pH of 9.48. The experiment was repeated with 15 g of SRL 165 waste glass crushed to less than 325 mesh (an effective SA/V of about 5.5 cm^{-1}) and the same Eh and pH values were obtained after 24 hours (Figure 2b).

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* Ultrapure argon (99.999%) must be used for degassing.

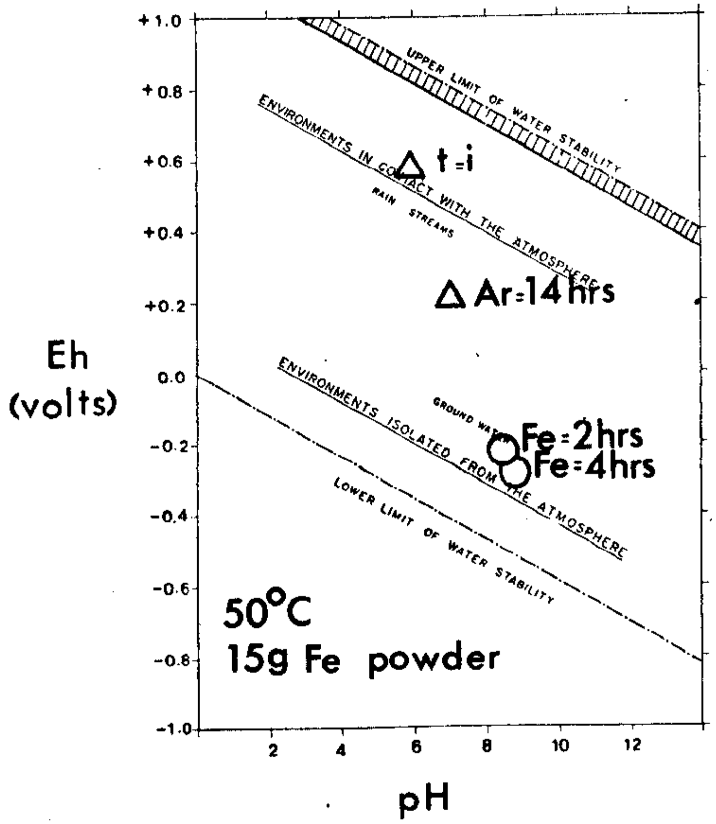

FIGURE 2a. Eh-pH changes measured for deoxygenated deionized water with 15 g of iron powder as a function of residence time

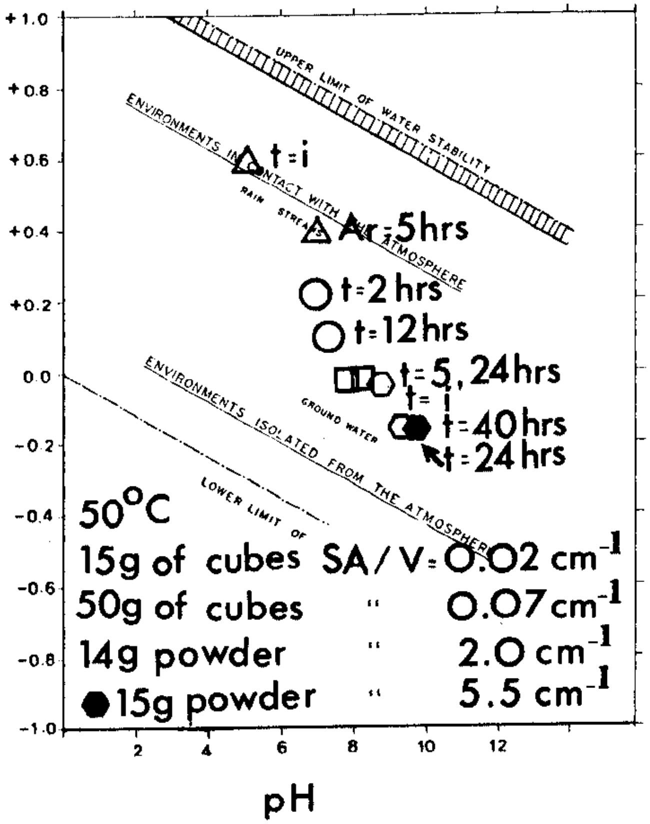

FIGURE 2b. Eh-pH changes measured for deoxygenated deionized water with SRL 165 waste glass as a function of residence time, surface area of the glass and volume of leachant

Umtanum Basalt and Deionized Water

Umtanum basalt is one of the potential repository materials and, therefore, the control of Eh as a function of time and SA/V were examined. Basalt cylinders totaling 150 g at an effective SA/V of 0.2 cm^{-1} dropped the Eh of deoxygenated deionized water to +0.09 volts after 14 hours of rock-water interaction. The leaching cell was opened, additional basalt cylinders added to give an SA/V of 2.0 cm^{-1} and the solution deoxygenated. After 64 hours contact the Eh and pH at 50°C were the same as obtained at the lower SA/V (Figure 3a).

Deionized water at 60°C was Ar sparged for 6 hours and 15 g of crushed basalt (<100 mesh) added through an opening in the top of the vessel. After 2 hours the Eh dropped to about 0.0 volts. Addition of another 15 g of crushed basalt gave an effective SA/V of 5 cm^{-1} in 1500 ml of water. An additional 15 grams gave an SA/V of 10 cm^{-1} and after 7 hours the Eh was lowered to -0.2 volts. Crushed basalt was continually added in 15 g amounts. At an SA/V of 15 gm^{-1} the Eh dropped to -0.35 at a pH of about 8.75 after 19 hours contact between the sparged water and the basalt (Figure 3b).

Duplicate and triplicate experiments with deionized deoxygenated water and crushed Umtanum basalt confirmed the results shown in Figure 3b and Figure 3c. Crushed basalt (15 g) of 100 to 200 mesh lowers the Eh to -0.28 after 75 hours of rock-solution contact but an additional 15 g of 200-325 mesh powdered basalt brought the solution Eh to -0.34 volts at 8.41 pH after 25 hours and to -0.42 volts at pH 8.44 after an additional 20 hours. These values compare favorably to the -0.40 volts at pH 9.75 calculated for a basalt repository but never measured in situ due to sampling difficulties associated with field measurements.[9,11]

Basalt SA/V ratios of <10 cm^{-1} had little effect on Eh equilibration in deionized water but larger ratios affected the Eh dramatically, and made it a strong function of rock-solution residence time. Basalt compositional variation as a function of mesh size was investigated. No variation was observed by wet chemical analysis of the rock. Since no redox couple other than Fe^{2+}/Fe^{3+} existed in this controlled laboratory experiment, it was assumed that the electrode measurements were controlled by this redox couple.

Umtanum Basalt and Grande Ronde Groundwater

Since crushed basalt in deoxygenated deionized water achieved the calculated Eh and pH of the Basalt Waste Isolation Project repository[2] after 20 to 120 hours (depending on the SA/V) at

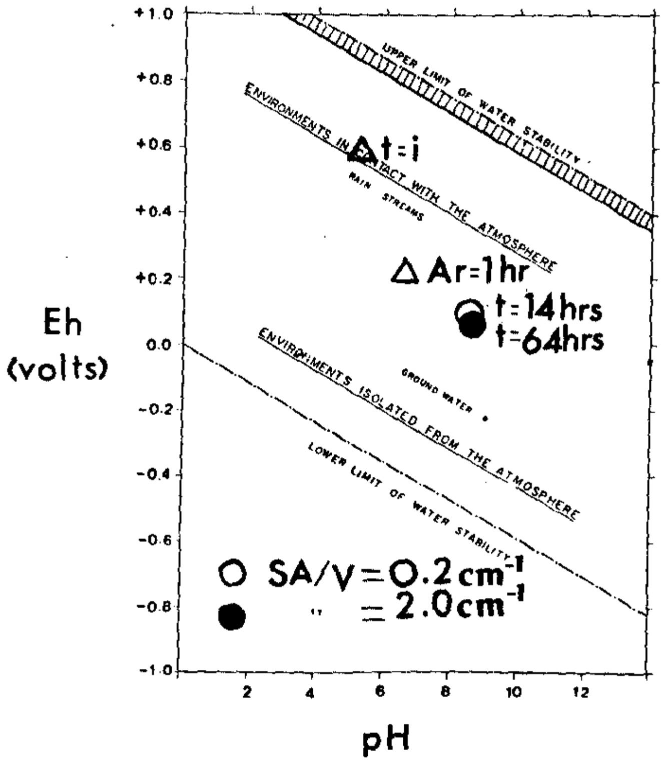

FIGURE 3a. Eh-pH changes measured for deoxygenated deionized water and Umtanum basalt at low SA/V as a function of time

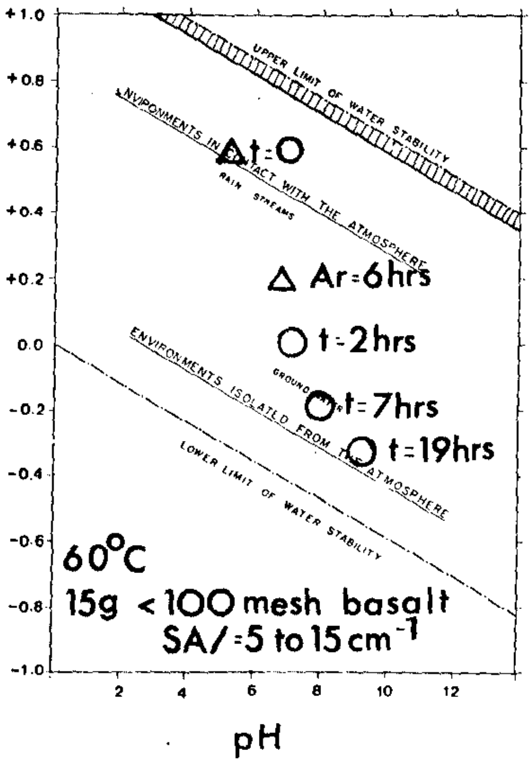

FIGURE 3b. Eh-pH changes measured for deoxygenated deionized water and Umtanum basalt at high SA/V as a function of time

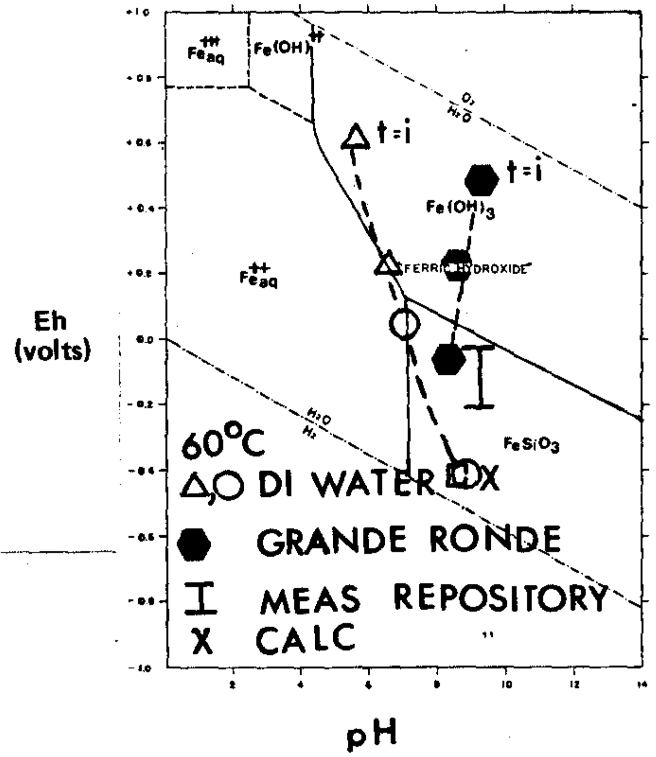

FIGURE 3c. Eh-pH changes measured for deoxygenated deionized water and Umtanum basalt from Figure 3b (open symbols) and the Eh-pH changes measured for deoxygenated GR3 simulated basaltic groundwater (solid symbols). The X represents the calculated Eh and pH values for the basalt repository groundwater (Reference 2) and the vertical bar represents the range of Eh values actually measured for the BWIP groundwaters (Reference 17).

60°C, a similar experiment was attempted with deoxygenated Grande Ronde Groundwater (GR3).[16] Even with SA/V ratios as high as 28 cm^{-1} and residence times as long as 144 hours at 60°C, the calculated Eh and pH values achieved with deoinized water could not be achieved with GR3 groundwater (Figure 3c).

The simulated Grande Ronde groundwater is pH adjusted in the air saturated conditions as suggested by Jones.[16] As the crushed basalt is added the pH decreases from 9.2 to 8.6 as the Eh decreases as shown by the solid symbols in Figure 3c. The open symbols on Figure 3c show the Eh-pH trends delineated from the crushed rock-deionized water experiment (Figure 3b). The cross shows the calculated Eh and pH values[2] for the repository groundwater while the vertical bar shows the range of Eh values actually measured.[17] Difficulty in the laboratory measurement may be due to the presence of sulfate in the GR3 groundwater composition and/or non-equilibrium between the simulated groundwater composition and the basalt. There is independent data that the latter may be the responsible mechanism.[18]

IRON, SRL 165 WASTE GLASS AND DEIONIZED WATER

SRL 165 waste glass and ductile iron bars were placed in aerated deionized water at 70°C. The SA/V of the glass and the iron were 0.01 cm^{-1}. Continuous Eh monitoring for the first 100 hours demonstrated that the presence of iron was causing the Eh-pH relations of the solution to follow the calculated Fe^{++} (aq)/$Fe(OH_3)$ equilibrium boundary (Figure 4). In Figure 4 the equilibrium boundaries are calculated for 10^{-6} M concentration of iron. Solution analysis revealed the presence of 10^{-7} M iron which moves the equilibrium boundary over to be coincident with the measured Eh-pH values. After 100 hours the pH continued to increase and the Eh of the solution followed the calculated $Fe(OH)_3/FeSiO_3$ equilibrium boundary.

The observed enhancement of waste glass dissolution in the presence of metallic iron[6] is related to the changes in Eh caused by the presence of metallic iron in aerated water. The iron acts as a source for Fe^{++} (aq) and drives the Eh into the region of stability of ferrous iron silicate. The aqueous ferrous iron, therefore, scavenges silica from the solution forming a stable iron silicate precipitate. When the leachant is undersaturated with respect to silica it acts as the driving force for further dissolution of the glass. The presence of iron silicate and iron oxide precipitates was confirmed by drying the 28-day leachant at 90°C and analyzing the solids by x-ray diffraction. The presence of $Fe(OH)_2$, $Fe(OH)_3$ and the $FeSiO_3$-hydrate (greenalite) were confirmed.[2]

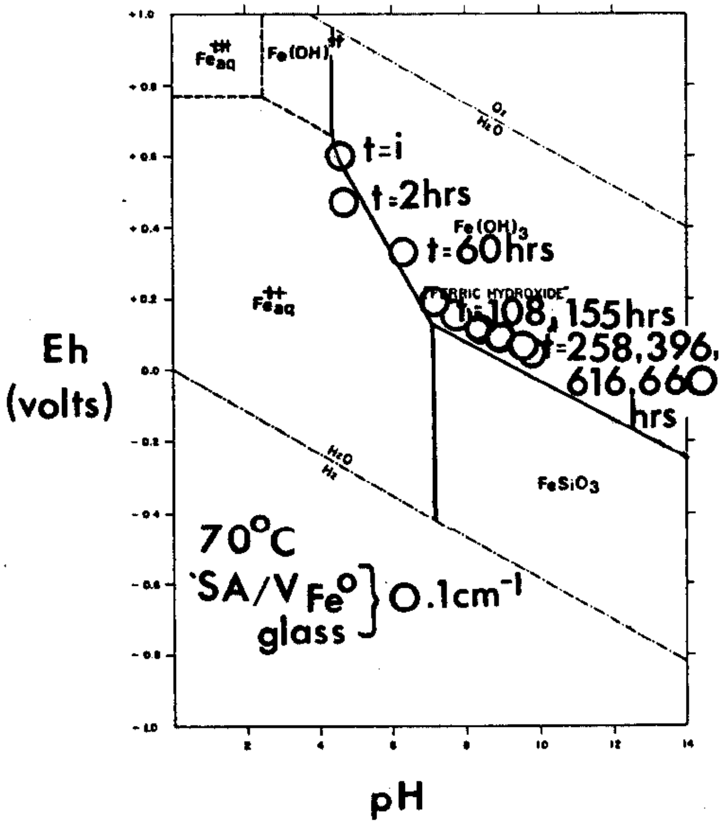

FIGURE 4. Eh-pH changes measured for oxygenated deionized water in the presence of ductile iron and SRL 165 waste glass during a 28-day MCC-1 static leach test. The SA/V of the iron and the glass was 0.1 cm^{-1}.

CONCLUSIONS

Solid state materials can be used to control the oxidation potential of waste glass leachants. Materials in which iron is present in the ferrous and ferric state appear to be most active and readily give stable and reproducible Eh readings when measured with platinum electrodes. The redox species must be present in sufficient concentrations to be measured reliably. Concentration was found to be a function of SA/V of the buffer-leachant system as well as the residence time of the buffer-leachant interaction.

Crushed basalt was found to be the most reactive material to set or control the Eh at negative anoxic values. Eh values of -0.42 volts at a pH of 8.44 can be reached with deoxygenated deionized water and crushed basalt in 20-120 hours depending on the SA/V of the basalt-leachant. These values compare favorably to the -0.4 volts at pH 9.75 calculated for a basalt repository but never measured in situ due to sampling problems during field measurement.

Crushed basalt in deoxygenated deionized water is more reactive than crushed basalt in simulated basaltic groundwater. Anticipated repository Eh and pH values cannot be achieved during crushed basalt-groundwater interactions. This may be a function of the groundwater chemistry or non-equilibrium of the simulated groundwater with the basalt.

The presence of a metallic component in an oxic laboratory waste-package waste-form interactive test can cause experimentally-induced synergistic effects. Repositories are anticipated to be mildly to strongly anoxic and the presence of free oxygen will be limited. In the case of the synergistic effects between ductile iron and waste glass, i.e. the iron enhances glass leaching and the glass enhances iron corrosion, it is the oxygen which acts as the driving force for supplying aqueous ferrous iron to the solution. The iron drives the Eh into a known Eh-pH stability field for ferrous iron silicate. The aqueous ferrous iron then scavenges silica from the solution and precipitates ferrous iron silicate causing undersaturation of silica in the leachant. This in turn acts as the driving force for further dissolution of the glass. Thus, oxygen is necessary to continually oxidize metallic iron to aqueous ferrous iron. The interrelation of iron with silica is a function of the thermodynamics of the low-temperature aqueous iron-silicate stability and not a function of leaching under anoxic conditions. Any metallic Eh buffer which does not have a stable low temperature metal-silicate stability field, e.g. lead, would be considered a candidate for leaching under simulated anoxic conditions.

Although the synergistic effects between the waste-form, waste package components and the groundwater chemistry need to be examined, laboratory experimentation must not produce artificial interactions by failing to monitor anoxic leachants when known redox-active species, e.g. metallic canister components, are present. Possible metal-glass interactions in oxygenated leachants should be predetermined based on the thermodynamically known reactions for metal silica systems at low temperatures. If synergistic interactions are predicted for oxygenated systems then the experiments must be conducted under the anoxic conditions predicted for the repository.

REFERENCES

1. J. E. Mendel. "The Scientific Basis for Long-Term Prediction of Waste-Form Performance Under Repository Conditions." D. G. Brookins (ed), Sci. Basis for Nuclear Waste Management, VI, Elsevier, Publ. Co., New York, 1-7 (1983).

2. G. K. Jacobs and M. J. Apted. "Eh-pH Conditions for Groundwater at the Hanford Site, Washington: Implications for Radio-nuclide Solubility in a Nuclear Waste Repository located in Basalt." EOS Trans. Amer. Geophys. Union, 62, 1065 (1981).

3. D. M. Strachan. "Results from a One-Year Leach Test: Long Term Use of MCC-1." In W. Lutze (ed), Sci. Basis for Nuclear Waste Management, V, Elsevier Publ. Co., New York 181-191 (1982).

4. J. E. Mendel. "Workshop on the Leaching Mechanisms of Nuclear Waste Forms, May 19-21, 1982 Summary Report." PNL-4382, 255 p (1982).

5. D. L. Lane, T. E. Jones and M. H. West. "Preliminary Assessment of Oxygen Consumption and Redox Conditions in a Nuclear Waste Repository in Basalt." RHO-draft (February, 1983).

6. G. L. McVay and C. Q. Buckwalter. "Effect of Iron on Waste-Glass Leaching." J. Am. Ceram. Soc. 66, 170-174 (1983).

7. C. Q. Buckwalter and L. R. Pederson. "Inhibition of Nuclear Waste Glass Leaching by Chemisorption." J. Am. Ceram. Soc. 65, 431-436 (1982).

8. J. I. Drever. "The Geochemistry of Natural Waters." Prentice Hall, N.J., 388 p (1982).

9. D. Langmuir. "Eh-pH Determination." R. E. Carver (ed), Procedures in Sedimentary Petrology, Wiley Interscience, N.J., 597-635 (1979).

10. M. Whitfield. "Thermodynamic Limitations on the Use of the Platinum Electrode in Eh Measurements." Limnology and Oceanography 19 857-865 (1974).

11. D. R. Runnells and R. R. Lindberg. "Geohydrologic Exploration Using Equilibrium Modeling: A Critical Analysis of Eh and pE" to be presented Assoc. Explor. Geochemists, International Assoc. Geodhem. Cosmochim. Symposium, Helsinki, Finland (1983).

12. R. M. Garrels and C. L. Christ. "Solutions, Minerals and Equilibria." Harper & Row, N. Y. 450 p (1965).

13. W. Stumm. "Discussion of Chemical Oxidation and Reduction of Metals and Ions in Solution." In T. E. Larson, B. D. Faust and J. V. Hunter (eds) Principles and Applications of Water Chemistry, John Wiley and Sons, N. Y. 448 p (1967).

14. D. Langmuir. "Geochemistry of iron in a coastal-plain ground water of the Camden, New Jersey area, U.S. Geol. Surv. pp 650-C, C224-C235 (1969).

15. J. P. Hoare. "The Electrochemistry of Oxygen." John Wiley & Sons, 423 p (1968).

16. T. E. Jones. "Reference Material Chemistry Synthetic Groundwater Formation." RHO-RE-SR-5 (1982).

17. T. O. Early, D. R. Drewes, G. K. Jacobs and R. C. Routson. "Geochemical Controls on Radionuclide Releases from a Nuclear Waste Repository in Basalt, Estimated Solubilities for Selected Elements." RHO-BW-ST-39-P (1982).

18. G. F. Vandergrift, D. L. Bowers, T. J. Gerding, S. M. Fried, C. K. Wilbur and M. G. Seitz. "The Interaction of Groundwater and Fresh Basalt Fissure Surfaces and Its Effect on the Migration of Actinides," presented at the 185th National Meeting of the American Chemical Society, in Seattle, Washington (March 21, 1983).