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CONTROL OF OXIDATION POTENTIAL FOR  
BASALT REPOSITORY SIMULATION TESTS

by

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## CONTROL OF OXIDATION POTENTIAL FOR BASALT REPOSITORY SIMULATION TESTS

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### ABSTRACT

Borosilicate waste glass durability in simulated repository environments can be assessed by use of static tests in leach vessels fabricated of the representative geomedium. Control of the oxidation potential during the test simulates a basalt repository environment. Under very anoxic conditions (i.e. at negative Eh values), the interactions between basalt and SRP waste glass in silica-saturated basaltic groundwaters are the same as those of basalt and groundwater when no waste glass is present. The lack of significant leaching of ions from the waste glass and the lack of any significant changes in either the leached surfaces of glass or basalt under anoxic conditions suggests that the components of this system are at equilibrium when oxygen is absent.

### 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 can be important in determining its equilibrium solubility and its rate of release from the waste form. Moreover, the adsorption and migration of multivalent elements in geologic media are highly dependent upon the redox states of elements dissolved in the groundwater. Because long-lived hazardous nuclides such as Tc, Am, or Np are less soluble in the reduced state, reducing groundwaters could limit the release of these species.

Of the geologic formations considered for high-level waste repositories in the United States (tuff, salt, and basalt), the basalt groundwater is expected to be the most strongly reducing with an oxidation potential, or Eh, of  $-0.40 \pm 0.05V$  [1,2]. Waste form leach tests have not, to date, addressed leaching under low-Eh repository conditions [3,4]. Thus, methods to control the Eh in the laboratory without the use of chemical additives were developed [5,6] to accurately determine glass performance in a basalt repository environment.

In this study, the results of the first set of static leach tests of defense waste glass under conditions specific to a nuclear waste repository in basalt are presented. Durability of defense waste glass under conditions relevant to a basalt repository can be assessed accurately only when interactions between waste glass, stainless steel, and basalt rock are examined in simulated groundwater in the absence of oxygen.

### EXPERIMENTAL

Equilibration of simulated groundwaters with crushed rock under deoxygenated conditions provides an anoxic, low Eh solution to be used as a leachant for testing waste package component interactions [6]. The deoxygenated experiments are contained in a glove box continuously purged with 99.999% argon (Figure 1). The iron-bearing species in basalt yield redox-active species in solution which give stable Eh measurements. Because the

$\text{Fe}^{2+}/\text{Fe}^{3+}$  redox couple dominates the controlled laboratory experiment, it was assumed that the electrode measures this redox couple [5,6]. Experimentation in a controlled laboratory can thus achieve the anoxic values calculated for crystalline repositories but not measured in the field due to problems with oxygen contamination.

Simulated basaltic groundwater [7] was equilibrated with crushed basalt. Crushed Umtanum basalt had previously been found [5,6] to be most effective at setting or controlling the Eh at negative values and it is representative of the candidate repository Grande Ronde formations. Basalt SA/V ratios of approximately  $10 \text{ cm}^{-1}$  at  $60^\circ\text{C}$  are achieved in approximately 90 hours with deoxygenated GR-4 groundwater. The Eh and pH of the rock-equilibrated solution was monitored in-situ. Replicate experiments with deoxygenated GR-4 groundwater and crushed Grande Ronde basalts confirmed that Eh values of  $-0.34$  to  $-0.40\text{V}$  at pH values of 9-10 can be achieved repeatedly. These values compare favorably to the Eh values of  $-0.40\text{V}$  at  $\text{pH } 9.1 \pm 0.5$  calculated for a basalt repository at  $70^\circ\text{C}$  [2].

Equilibration of GR-4 with crushed Umtanum basalt (SA/V approximately  $10 \text{ cm}^{-1}$ ) at  $60^\circ\text{C}$  achieved an Eh of  $-0.34\text{V}$  at a pH of approximately 10 after 90 hours residence time. This equilibrated groundwater was used to evaluate the interactions between basalt and simulated SRP waste glass under anoxic, static (MCC-1) conditions. Three rock cup vessels [8] inside Teflon® leach vessels were filled with pretreated GR-4 and kept in an oven at  $90^\circ\text{C}$  in the argon glovebox (Figure 1). Two of the rock cup vessels contained simulated SRL-165 waste glass polished to a 600 grit finish. One rock cup vessel did not contain glass and was used as an anoxic standard or blank. Two other rock vessels were filled in the environmental chamber and sealed in Parr bombs. These were removed from the environmental chamber and placed in an oven in air at  $90^\circ\text{C}$ . Likewise, two more rock cup vessels inside Teflon® leach vessels were filled inside the chamber and subsequently placed in a  $90^\circ\text{C}$  oven in air (Figure 1). The glass SA/V was  $0.1 \text{ cm}^{-1}$  and the test duration was 28 days.

Solutions were analyzed in triplicate by inductively coupled plasma (ICP), ion chromatography (IC), atomic absorption (AA), and a Scintrex UA-3 analyzer. The leachates were analyzed acidified and nonacidified but not filtered. The glass and rock surfaces, and precipitates, were examined by scanning electron microscopy and by electron microprobe.

## INTERACTIONS BETWEEN SRL-165 WASTE GLASS, BASALT, AND SIMULATED GROUNDWATER

Interactions between defense waste glass and basalt in contact with pre-equilibrated low Eh ( $-0.34\text{V}$ ) GR-4 simulated groundwater vary as a function of the final oxidation potential (Eh) of the solution. Of the seven tests described above, the one anoxic test that contained only basalt and simulated groundwater was used as an anoxic standard or blank in order to determine the background concentration of elements leaching out of the rock when no waste glass was present.

In six of the seven tests, negative oxidation potentials were successfully maintained for 28 days inside the rock leaching vessels (Table I). The annular space outside the rock cup was completely oxidized (Eh =  $+0.4\text{V}$ ) in the test at  $90^\circ\text{C}$  in air. Oxidation of the solution in the annular space was anticipated for the test at  $90^\circ\text{C}$  in air as the Teflon® outer leach vessels are not airtight. The oxidation state of the solution in the annular space in the vessels in the environmental chamber remained anoxic (Eh =  $-0.27$  to  $-0.29\text{V}$ ). The Parr bombs do not have an annular space and so no similar evaluation could be made.

The tests carried out in the environmental chamber were the most successful at maintaining the low Eh conditions inside the rock vessels (Table I). None of the solutions inside the rock cup ever reached the

oxidation potential of the solution saturated with air ( $E_h \geq +0.4V$ ). All of the solutions changed from an initial pH of 10.15 at ambient temperature to a final pH near neutral regardless of whether waste glass was present or not.

Analyses of the groundwater solution inside the rock cup (in contact with glass) can be correlated with the final  $E_h$  of the solution (Figures 2-3). Anoxic conditions decrease the concentration of redox elements in solution (Figure 2). The concentrations under very reducing conditions are the same as the blank, e.g. when no glass is present. The scatter in the uranium data is due to the low concentrations present. At these low concentrations, errors of  $\pm 10$  ppb are expected. Anoxic conditions also appear to decrease the release of the alkali indicator element lithium from the glass (Figure 3). For the glass matrix elements silicon and boron (Figure 3), there is little or no apparent release of these elements within experimental error. Note that for boron the entire span of the experimental data is only 1 ppm and no trends can be delineated. There is no change in the measured concentration of these elements when acidified according to MCC-1 procedures [9]. Samples re-analyzed at 1 month intervals after acidification showed no change. Acidification was not slowly dissolving any colloidal material in the leachate.

The normalized mass losses for U, B, and Li at an oxidation potential of  $-0.4V$  after 28 days are 0.19, 0.23, and 0.22  $g/m^2$ , respectively. In terms of an annular release rate, these values are  $5 \times 10^{-7}$ ,  $6.0 \times 10^{-7}$ , and  $6.0 \times 10^{-7} \text{ yr}^{-1}$ .

The glass surfaces which were toward the top of the leach vessel were covered with a fine grey precipitate. The lower surfaces did not have any precipitate cover. Examination of the upper surfaces by electron microprobe and scanning electron microscopy revealed that this precipitate was only loosely attached. In areas where the precipitate surface was broken away, the original polishing scratches in the glass surface from sample preparation before leaching could be observed. The precipitate was found to be rich in Ca, Mg, Al, and Si suggesting that it was suspended particles of  $Na_{0.33}Ca_{0.66}Al_{1.8}Si_{2.2}O_8$  that was in the pre-equilibrated groundwater as reported previously [6]. No glass leached layer was observed by electron microprobe (minimum resolution 0.2  $\mu m$ ).

Examination of the lower leached surfaces (leached under the more oxidizing conditions) by electron microprobe and scanning electron microscopy showed some etching of the original polishing marks. There was no evidence of etching or leaching in the samples in the very anoxic groundwater in 28 days. In cross section, no leached layer was observed with the electron microprobe.

Lastly, the surfaces of the rock leach vessel were examined by scanning electron microscopy. In the more oxidized case, the interstitial glass in the rock had been etched away and some fine needle shaped phase redeposited. In the anoxic groundwaters, there was little or no deterioration nor any reprecipitation on the rock surfaces. Energy dispersive x-ray analysis of the oxic and anoxic rock surfaces showed that the surface exposed to oxygenated groundwater was enriched in iron.

## INTERACTIONS BETWEEN SRL-165 WASTE GLASS AND SIMULATED GROUNDWATER

Since no significant interaction occurred between the waste glass, basalt rock, and simulated groundwater when oxygen was absent, the components of the system appeared to be at equilibrium. SRL waste glasses contain approximately 12 wt% iron comparable to basalt. The SRL glass has a ratio of ferrous to ferric iron ( $Fe^{2+}/Fe^{3+}$ ) of approximately 0.48 [10], while basalts are more enriched in ferrous iron. The results for equilibration of

GR-4 groundwater with rock were, therefore, compared to GR-4 groundwater interactions with SRL-165 waste glass (Figure 4). Eh-pH values for GR-4 groundwater and basalt are -0.34V at approximately 10 pH while the values for interaction of GR-4 groundwater and waste glass are - 0.39V at approximately 9.5 pH at 60-65°C (Figure 4). These values represent the calculated equilibrium Eh-pH for a basalt repository at 70°C [2] which is superimposed on Figure 4.

## CONCLUSIONS

Basalt repositories are expected to be mildly to strongly reducing and the presence of free oxygen will be limited. Redox-active solids such as crushed basalt can be used to control the oxidation potential of waste glass leachants during laboratory experimentation. Iron present in the solution from the basalt is in both the ferrous and ferric states which readily allows stable and reproducible measurements [6].

The interactions between basalt and waste glass in simulated basalt repository groundwater (GR-4) demonstrates that solution concentrations under very anoxic conditions were nearly the same as those of basalt and groundwater when no waste glass was present. The lack of significant changes in solution concentrations and the lack of any significant changes in the glass surfaces after leaching under low-Eh conditions suggest that minimal leaching has occurred in 28 days. The basalt rock surfaces also remained unaltered under these conditions in contrast to the results obtained with oxygenated groundwaters.

No significant interactions occur among the rock, the glass, and the solution when oxygen is absent. This implies that under deoxygenated conditions the components of this system are nearly at equilibrium. This is supported by the findings that crushed SRL-165 waste glass alone in deoxygenated basaltic groundwater imparts the same Eh and pH to the solution as crushed basalt.

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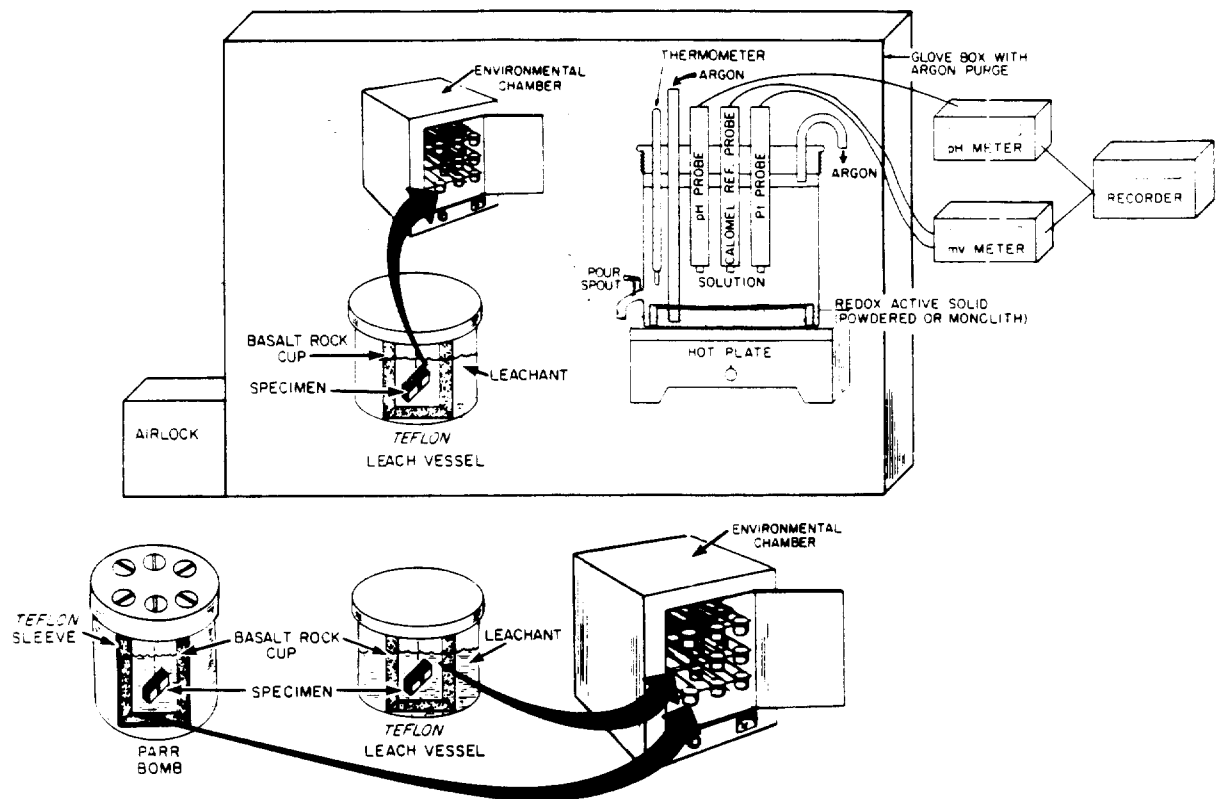


FIGURE 1. Experimental design. All leach vessels including the Parr bombs filled inside glove box.

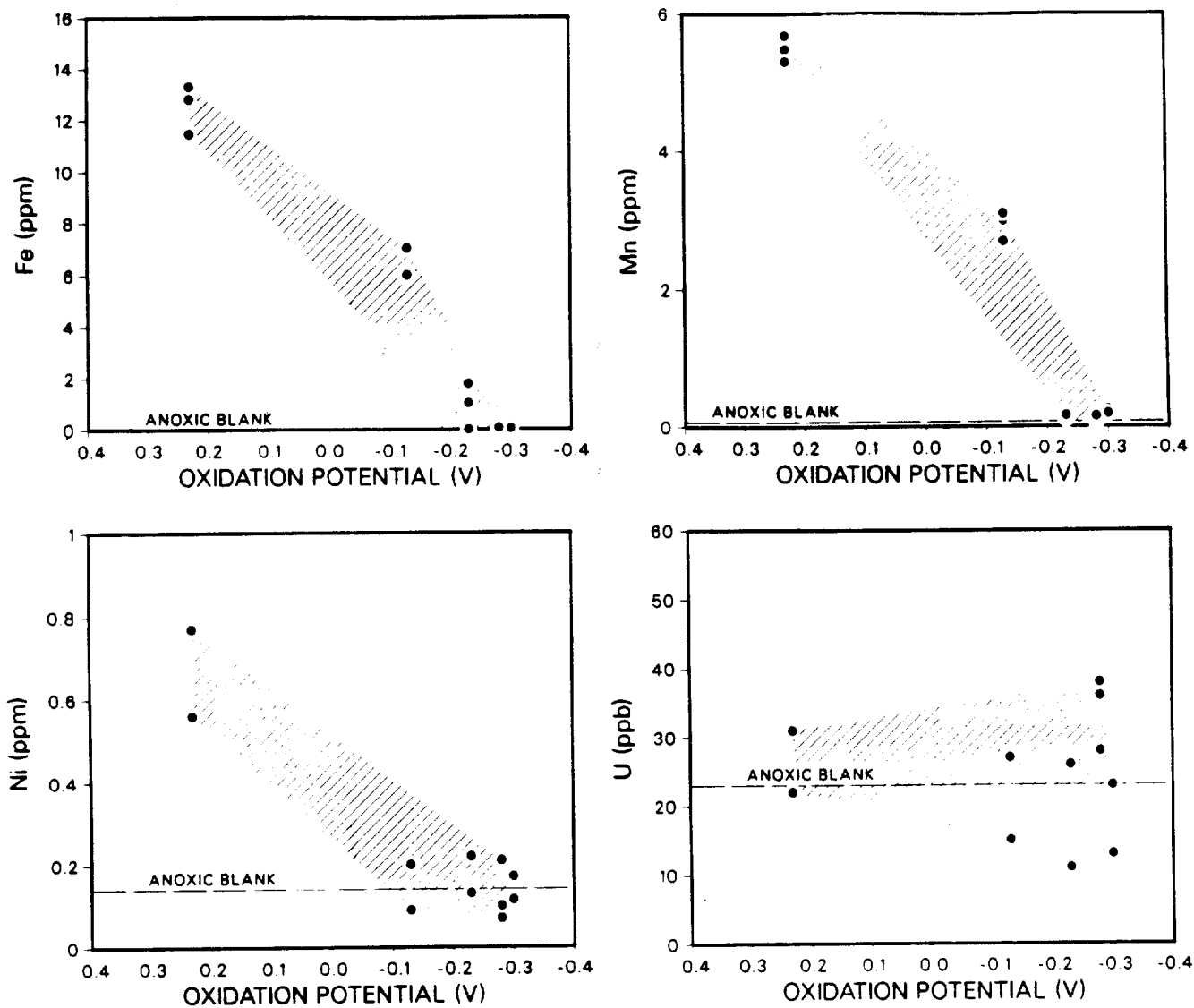


FIGURE 2. Concentrations of redox sensitive elements leached from the glass as a function of oxidation potential, Eh.



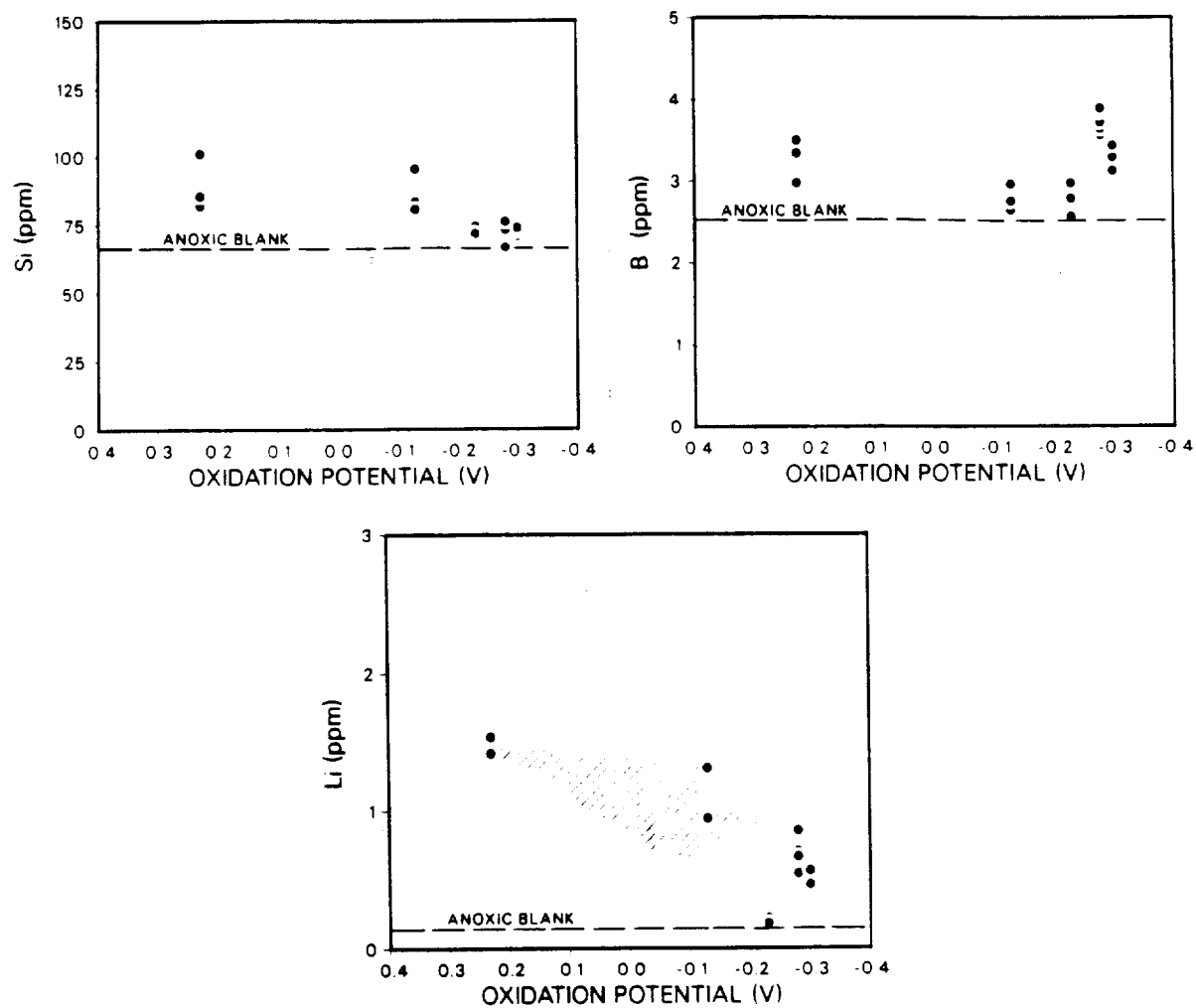


FIGURE 3. Concentrations of glass matrix elements and the alkali indicator element Li which is leached from the glass as a function of oxidation potential, Eh.

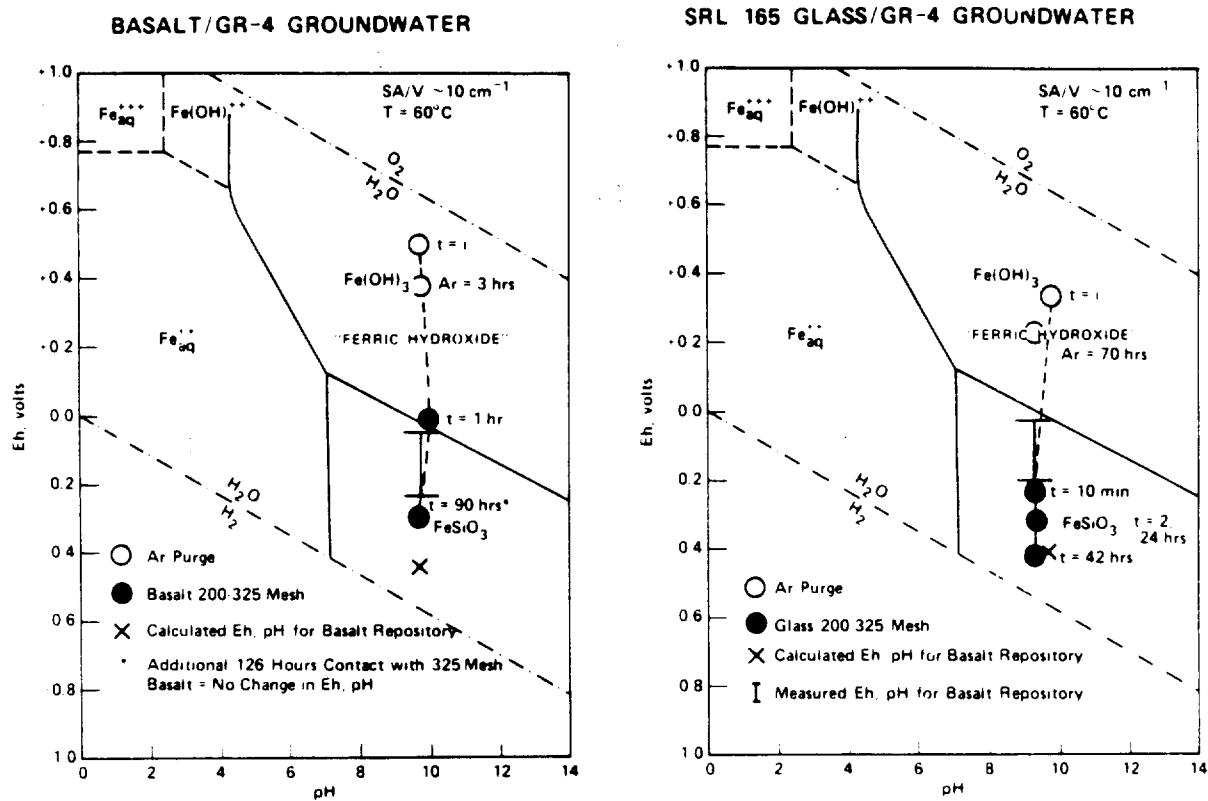


FIGURE 4. The final Eh-pH values achieved when crushed Umtanum basalt or SRL-165 waste glass is reacted with GR-4 groundwater. The vertical bar represents the range of Eh values actually measured for the BWIP repository [11] while the X represents the calculated Eh and pH values [2].

TABLE I. Eh AND pH VALUES FOR REPOSITORY SIMULATION TESTS IN BASALT<sup>t</sup>

TEST	GLASS PRESENT	SOLUTION		IN ROCK CUP		IN ANNULAR SPACE	
		Ehi	pHi	Ehf	pHf	Ehf	pHf
OVEN IN	YES	-0.33	10.15	+0.23*	6.03	+0.4	7.50
OXYGENATED	YES	-0.33	10.15	-0.13**	5.86	+0.39	7.50
ATMOSPHERE							
PARR	YES	-0.33	10.15	-0.28	6.92	NONE	
BOMBS	YES	-0.33	10.15	-0.23	7.25	NONE	
OVEN IN	YES	-0.33	10.15	-0.30	6.85	-0.28	7.36
ENVIRONMENTAL	YES	-0.33	10.15	-0.28	6.80	-0.29	7.56
CHAMBER	NO	-0.33	10.15	-0.27	7.11	-0.27	7.60

\* THIS SAMPLE WAS TILTED AND THERE MAY HAVE BEEN SOME IN-LEAKAGE OF WATER FROM THE ANNULAR SPACE INTO THE ROCK CUP.

\*\* SELF SEALING OF THE ROCK CUP TO ITS LID WAS OBSERVED IN THIS TEST.

<sup>t</sup> ALL MEASUREMENTS AT 25°C.

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