

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161, phone: (800) 553-6847, fax: (703) 605-6900, email: orders@ntis.fedworld.gov online ordering: <http://www.ntis.gov/ordering.htm>

Available electronically at <http://www.doe.gov/bridge>

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062, phone: (865) 576-8401, fax: (865) 576-5728, email: reports@adonis.osti.gov

TECHNICAL DIVISION
SAVANNAH RIVER LABORATORY

DPST-84-658

ACC. NO. 196196

CC: W. R. Stevens, III, SRL, 773-A
R. B. Ferguson, 773-A
E. J. Hennelly, 773-41A
W. R. Cornman, 773-41A
G. L. Pine, 773-41A
N. E. Bibler, 773-A
D. F. Bickford, 773-A
A. R. Jurgensen, 773-A
B. G. Kitchen, 773-41A
G. G. Wicks, 773-A
PMC File, 773-A
SRL Records (4), 773-A

September 5, 1984

TO: M. J. PLODINEC

SRL FILE
RECORD COPY

FROM: C. M. JANTZEN *cmj*

EQUILIBRATION OF LEACHANTS WITH BASALT
ROCK FOR REPOSITORY SIMULATION TESTS

INTRODUCTION AND SUMMARY

In a nuclear waste repository in basalt, the groundwater will have a low redox potential (Eh) which may affect the leach rate of SRP waste glass. Accurate laboratory simulations of conditions in a basalt repository must maintain low Eh values throughout the course of the experiment. In this report, important parameters affecting the ability of basalt to maintain appropriate Eh-pH conditions are examined, in particular basalt type and groundwater simulation.

The principal results demonstrate that:

- o Groundwater simulations must be deoxygenated and equilibrated with crushed basalt to maintain basalt repository conditions during leaching experiments.
- o Equilibration of crushed basalt with one of the simulated groundwater compositions (GR-4) reached the expected Eh-pH conditions of a basalt repository; the other simulated groundwater (GR-3) did not. Thus GR-4 is recommended for all further tests simulating conditions in a repository in basalt.

- o Simulated basalt groundwaters equilibrate faster at higher rock surface area to solution volume (SA/V) ratios.

DISCUSSION

Three geologic formations are being considered for the first high-level waste repository in the United States - tuff, salt, and basalt. Of these, the groundwater in a basalt repository is expected to be the most strongly reducing with an oxidation potential, or Eh, of $-0.40 \pm 0.05V$ [1,2]. Many recent attempts at laboratory simulation of low Eh have not fully addressed possible experimentally induced interactions. The use of hydrazine [3], or of a redox-active metal [4,5] in an oxygenated system, may cause interactions that will not occur in a basalt repository, where no hydrazine or oxygen are present. The presence of iron species in solution precludes the use of a potentiostat for Eh stabilization [6,7]. Hydrothermal experiments can achieve low Eh but often use temperatures higher than those expected for defense waste glass. Moreover, higher temperature interactions may not be representative of the reactions occurring at lower temperatures. Purging the solution with an Ar-4% H_2 gas mixture in the presence of a palladium catalyst can be used to lower solution redox potentials but measurements of only $-0.12V$ have been reported [8].

The use of redox-active solids in deoxygenated solutions to stabilize low redox potentials was, therefore, examined. The iron-bearing phases in basalt yield redox-active species in solution which give stable Eh measurements. Because the Fe^{2+}/Fe^{3+} redox couple dominates the controlled laboratory experiments, it was assumed that the electrode measurements were controlled by this redox couple.

In this study the interactions between crushed Umtanum basalt and deionized water or simulated basalt groundwaters were examined. Two Grande Ronde groundwater simulations representative of the candidate repository horizons were examined, GR-3 and GR-4 (Table I). The latter, GR-4, is lower in sulfate and more representative of the actual groundwater analyses given in Table I. Equilibration of rock and solution was examined as a function of (1) rock surface area to solution volume ($SA/V \text{ cm}^{-1}$); (2) residence time (t in hours); and (3) solution composition. Compositional variation of the basalt as a function of size was also examined to ensure that equilibration was a function of rock surface area and not of rock compositional variation. Subsequent reaction of solutions equilibrated with Umtanum basalt, a repository horizon, with Pomona* basalt rock cups was also examined.

* Pomona basalt is not one of the candidate repository horizons but is chemically similar (Table XI) and more readily available than than Umtanum basalt.

EXPERIMENTAL

The experimental cell consisted of a one and one-half liter Pyrex® vessel and lid filled with leachant. The vessel was placed on a hot plate (Figure 1) in a glove box continually purged with 99.999% argon. The leachants were deoxygenated with an argon (99.999%) sparge* before any redox-active solid was added. Continuous monitoring of Eh and pH at temperature was achieved using a 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 stirrer bar and continuous argon sparging maximized solution homogeneity during measurement. The Pt electrode must be periodically cleaned with 1 micron diamond paste to minimize poisoning of its surface [11]. The measured electrode potential was calibrated with Zobell solution (potassium ferrocyanide) at room temperature [11].

Solution analyses were done by inductively coupled plasma (ICP), ion chromatography (IC) and atomic absorption (AA). Comparative solution analyses were made between filtered and nonfiltered samples and between acidified and nonacidified samples. Solids were analyzed by both HCl/HF bomb dissolution and Na₂O₂ dissolution followed by ICP, IC, and AA analyses.

INTERACTIONS BETWEEN BASALT AND DEIONIZED WATER

Deionized water is a more aggressive leachant than silica saturated simulated groundwater. Hence, laboratory control of the solution Eh (oxidation potential) was first attempted with crushed basalt and deionized water. Crushed Umtanum basalt was found [12,13] to be most effective at setting or controlling the Eh at negative values. Basalt SA/V ratios of <10 cm⁻¹ have little effect on Eh equilibration in deionized water but larger ratios affect the Eh dramatically, and make it a strong function of rock residence time in solution [12].

Eh values of -0.42V at a pH of 8.44 were reached with deoxygenated deionized water and crushed Umtanum basalt in 20 to 120 hours at 60°C depending upon the SA/V of the basalt in the leachant (Tables II and III). Replicate experiments with deionized deoxygenated water and crushed Umtanum basalt confirmed the results shown in Figure 2. These values compare favorably to the -0.40V at pH 9.1 ± 0.5 calculated [2] for a basalt repository at 70°C, but never measured in situ due to sampling difficulties associated with field measurements [11,14]. The calculated Eh and pH values for the BWIP repository groundwater are shown by the cross on Figure 1. The vertical bar shows the range of Eh values actually measured for BWIP groundwaters [15].

* The purity of the argon is a critical parameter.

The crushed Umtanum basalt interactions with deionized water produce a colloidal suspended material [13]. The unacidified solution analyses whether filtered or not filtered did not approach the composition of either GR-3 or GR-4 groundwaters (Table IV). The solutions were not analyzed in the acidified condition. Dissolution of the colloidal material, identified as a mixture of $Fe_{0.47}Mg_{0.53}SiO_3$ and $Na_{0.33}Ca_{0.66}Al_{1.8}Si_{2.2}O_8$ [13], by acidification would have altered the equilibrated solution composition to be more representative of a Grande Ronde groundwater. The solution is silica saturated with respect to the Grande Ronde (GR-3) composition.

INTERACTIONS BETWEEN BASALT AND SIMULATED GR-3 GROUNDWATER

Since crushed basalt in deoxygenated deionized water achieved the Eh and pH calculated by the Basalt Waste Isolation Project (BWIP) for a basalt repository [2], similar experiments were attempted with a simulated groundwater composition recommended by BWIP (GR-3, see Table I) [14,15]. Even with SA/V ratios as high as 20 cm^{-1} and residence times as long as 144 hours at 60°C , the calculated Eh and pH values achieved with deionized water could not be achieved with GR-3 (Table V).

The simulated Grande Ronde groundwater is pH-adjusted in the air-saturated condition, as suggested by Jones [9]. As the crushed basalt is added, the pH decreases from 9.2 to 8.6 while the Eh decreases as shown by the solid symbols in Figure 2. The open symbols on Figure 2 show the Eh-pH trends delineated from the crushed rock-deionized water experiments. Difficulty in the laboratory measurement may be due to the presence of sulfate in the GR-3 groundwater composition and/or nonequilibrium between the groundwater composition and the basalt. There is independent data that the latter may actually be responsible [16].

Analysis of the groundwater after equilibration with basalt showed enrichment in Ca, Mg, Na, Li, Ni, and Pb (Table VI). Alkali contamination could be due to leakage from the KCl reference electrode used during in-situ Eh measurement. Silica is undersaturated in the rock equilibrated GR-3 solution (Table VI).

INTERACTIONS BETWEEN BASALT AND SIMULATED GR-4 GROUNDWATER

A low sulfate simulated groundwater composition (GR-4) was then supplied by the Basalt Waste Isolation Project (see Table I or Ref 10) at our request. Equilibration of GR-4 with crushed Umtanum basalt (SA/V approximately 10 cm^{-1}) at 60°C achieved an Eh of -0.34V at a pH of 9.4 after 90 hours residence time (Figure 2). Adding additional basalt or allowing residence times of up to 216 hours only changed the Eh to -0.36V at a pH of 9.5 (Table VII). These values compare favorably with the -0.40V oxidation potential at $\text{pH } 9.1 \pm 0.5$ calculated for the basalt repository at 70°C [2].

Analysis of the unacidified groundwater after equilibration with the crushed rock showed increases in Al, B, Ca, Li, and Na (Table VIII). The rock equilibrated solution was oversaturated with respect to silica. Acidification of the unfiltered equilibrated groundwater enhanced the concentrations of these elements further suggesting that they are indeed a finely dispersed colloidal material. These solutions apparently change with time as the acid slowly digests the colloidal material. The filtered samples have the same elemental concentrations whether acidified or not acidified (Table VIII).

Additional interactions of the equilibrated GR-4 groundwater with monolithic Pomona basalt (rock cups) at 90°C for 672 hours [17] decreases the silica, iron, and aluminum concentrations in solution (Table VIII). Concentrations of B, Ca, and Mg are increased dramatically while alkali concentrations remain the same. The intergranular amorphous phase of the basalt is highly reactive [18] and preferential leaching of this rock component is likely responsible for these variations in solution chemistry.* Alternatively, solution-solid surface interactions could be dominating.

Reproducible compositions of GR-4 with crushed Umtanum basalt can be achieved when the solutions are filtered whether acidified or not acidified (Table IX). The resulting compositions are not as reproducible as the unfiltered and unacidified samples (Table X).

The colloidal material appears to be rich in iron and silica, perhaps a ferrous iron silicate [13]. The presence of this colloid stabilizes the low redox potentials needed to simulate basalt repository conditions.

VARIATION OF BASALT COMPOSITION WITH PARTICLE SIZE

Since a variety of basalt sizes were used throughout this study, the potential of basalt composition change with particle size was investigated. In particular, since the intergranular glassy phase was found [13,18] to be the most reactive basalt component, there was concern that this glassy material might be softer than the remaining basalt matrix phases. The reactive component could then potentially fractionate into the finer mesh sizes.

Both Pomona and Umtanum basalts were crushed and sized into the fractions used in the solution/rock equilibration studies. Solids analyses of the various sizes were compared to each other and to whole rock analyses found in the literature (Table XI). No chemical variation as a function of size was observed.

* Independent data from BWIP suggests that the intergranular glass increases concentrations of Si, Al, and K in the solution [19].

CONCLUSIONS

Basalt repositories are anticipated to be mildly to strongly reducing and the presence of free oxygen will be limited. Redox-active solids such as crushed basalt must be used to control the oxidation potential of waste glass leachants during laboratory experimentation under basalt repository conditions.

Iron is present in the basalt in the ferrous and ferric state which readily allows stable and reproducible laboratory measurements of the oxidation potential with platinum electrodes [12,13]. The redox species must be present in sufficient concentrations to be measured reliably. Their concentration, in turn, is a function of SA/V of the redox-active basalt leachant system and the residence time of the redox-active solid-leachant interaction. Basalt composition does not change with size.

Crushed Umtanum basalt in contact with GR-4 simulated groundwater was found to be the most reactive material, and was able to maintain the Eh at negative anoxic values. Eh values of -0.42V at a pH of 8.44 can be reached with deoxygenated deionized water and crushed basalt in 20 to 120 hours depending on the SA/V of the basalt in the leachant. These values compare favorably to the -0.4V at pH 9.1 calculated for a basalt repository at 70°C.

Equilibration of the high sulfate GR-3 simulated groundwater with crushed basalt did not achieve the environmental conditions expected for a basalt repository. The low sulfate GR-4 simulated groundwater readily achieved the basalt repository Eh and pH after 90 hours residence time with crushed Umtanum basalt. Values of -0.34V at pH of 9.4 were reproducible. The chemistry of the rock-equilibrated GR-4 groundwater was also found to be reproducible.

CMJ/pmc
Att
#16

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 Radionuclide Solubility in a Nuclear Waste Repository Located in Basalt," EOS Trans. Amer. Geophys. Union, 62, 1065, 1981.
3. P. F. Salter, L. L. Ames, and J. E. McGarrah, "The Sorption Behavior of Selected Radio Nuclides on Columbia River Basalts," RHO-BWI-LD-48, August 1981.
4. G. L. McVay and C. Q. Buckwalter, "Effect of Iron on Waste Glass Leaching," J. Am. Ceram. Soc. 66, 170-174, 1983.
5. C. Q. Buckwalter and L. R. Pederson, "Inhibition of Nuclear Waste Glass Leaching by Chemisorption," J. Amer. Ceram. Soc. 65, 431-436, 1982.
6. D. Rai, R. J. Serne, D. A. Moore, and R. W. Stromatt, "Electron Transfer Method of Controlling Eh During Adsorption of Multivalent Elements By Geologic Media," PNL-SA-6766, 1978.
7. A. M. Giblin, B. D. Batts, AND D. J. Swaine, "Laboratory simulation Studies of Uranium Mobility in Natural Waters," Geochim. Cosmochim. Acta., 45, 699-709, 1981.
8. A. E. Norris, "Fission Product Release," ONWI/SUB/79/E511-01200-11, 1979.
9. T. E. Jones, "Reference Material Chemistry Synthetic Groundwater Formation," RHO-RE-SR-5, 1982.
10. Letter, M. J. Smith to M. J. Plodinec, "Reference Grande Ronde Groundwater #4," October 4, 1983.
11. D. Langmuir, "Eh-pH Determination," R. E. Carver (ed), Procedures in Sedimentary Petrology, Wiley Interscience, N.J., 597-635, 1979.
12. C. M. Jantzen, "Effects of Eh (Oxidation Potential) on Borosilicate Waste Glass Durability," Advances in Ceramics, 8, Nuclear Waste Management, Am. Ceramic Soc, Columbus, OH, 385-393, 1984.
13. C. M. Jantzen, "Methods of Simulating Low Redox Potential (Eh) for a Basalt Repository," DP-MS-83-59, November 1983.

REFERENCES, cont'd

14. D. R. Runnells, and R. RR. Lindberg, "Geohydrologic Exploration Using Equilibrium Modeling: A critical Analysis of Eh and pE," Assoc, Geochem. Cosmochim. Symposium, Helsinki, Finland, 1983.
15. 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.
16. 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," Geochemical Behavior of Disposed Radioactive Waste, ACS Symp, 246, 229-247, 1984.
17. C. M. Jantzen and G. G. Wicks, "Basalt Repository Simulation Tests: Effects of Eh (Oxidation Potential) on Borosilicate Waste Glass Durability," DPST-84-566, 1984.
18. C. M. Jantzen, "Comparative Reactivity of Waste Glass and Candidate Repository Basalts for Oxidation Potential Control," in preparation.
19. D. L. Lane, M. J. Apted, C. C. Allen, and J. Myers, "The Basalt/Water System: Considerations for a Nuclear Waste Repository," RHO-BW-SA-320P, November 1983.

TABLE ICOMPOSITION OF GRANDE RONDE
GROUNDWATERS (in mg/L)

| <u>Component</u> | <u>Rocky Coulee*</u> | <u>Cohasset*</u> | <u>Umtanum*</u> | <u>GR-3 Synthetic (ref 9)</u> | <u>GR-4 Synthetic (ref 10)</u> |
|---------------------------------|----------------------|------------------|-----------------|---------------------------------------|--|
| Na | 373.8 | 336.8 | 354.9 | 358 | 334 |
| K | 25.3 | 13.9 | 9.39 | 3.43 | 13.0 |
| Ca | 2.9 | 2.2 | 1.63 | 2.78 | 2.2 |
| Mg | <0.1 | <0.1 | <0.1 | 0.03 | --- |
| Si | 34.6 | 44.6 | 47.7 | 76.2 | 45 |
| F | 20.0 | 20.0 | 18.2 | 33.4 | 19.9 |
| Cl | 507 | 405 | 451 | 312 | 405 |
| SO ₄ | 1.4 | 4.2 | 1.7 | 173 | 4.0 |
| (CO ₃) _T | 92.6 | 115 | 98.8 | 65.8 | --- |
| PH | 8.77 | 9.71 | 9.45 | 9.77 | 9.96 |

* From borehole RRL-2

TABLE IICRUSHED UMTANUM BASALT AND DI WATER AT 60°C
(Not in Glove Box)

| <u>Scenario</u> | <u>Time Duration Cumulative (hrs)</u> | <u>Eh (volts)</u> | <u>pH</u> |
|--|---|-------------------|-----------|
| Air Saturated | Initial | +0.6 | 5.6 |
| 99.999% Ar Purge | 6 | +0.2 | 6.9 |
| Umtanum Basalt Crushed 15 g <100 mesh | 8 | -0.05 | 7.0 |
| Umtanum Basalt Crushed 15 g <100 mesh | 15 | -0.20 | 7.5 |
| Umtanum Basalt Crushed 15 g <100 mesh | 34 | -0.40 | 8.6 |

TABLE IIICRUSHED UMTANUM BASALT IN DI WATER AT 65°C

(In Glove Box)

| <u>Scenario</u> | <u>Time Duration Cumulative (hrs)</u> | <u>Eh (Volts)</u> | <u>pH</u> |
|---|---|-------------------|-----------|
| No Heat Ar Purge in vessel Ar Purge in glovebox | Initial | +0.6 | 5.78 |
| No Heat Ar Purge in vessel Ar Purge in glovebox | 75 | +0.13 | 7.46 |
| Added 15 g 100-200 Mesh Basalt | 75.5 | -0.28 | 8.46 |
| | 100 | -0.37 | 8.46 |
| Added 15 g 200-325 Mesh Basalt | 101 | -0.34 | 8.41 |
| Stirrer Bar Off | 123 | -0.42 | 8.44 |
| | 130 | -0.41 | 8.49 |

TABLE IV

CRUSHED UMTANUM BASALT AND DI WATER AFTER 22 HOURS

| Element | Recipe† for GR-3 mg/L | Not Acidified | | | |
|-----------------|-----------------------------|----------------------------|---------------------------|---|-----------|
| | | Gravity Settle (cloudy) | Filtered Soln <0.45 μm | Residual in ppt mg/L moles | |
| Al | -- | 7.00 | 0.04 | 7. | 16. |
| B | -- | 0.40 | 0.32 | -- | -- |
| Ca | 2.76 | 7.60 | 3.68 | 4. | 6. |
| Fe | -- | 12.20 | 0.43 | 12. | 13. |
| K | 3.43 | KCl Probe | KCl Probe | KCl Probe | KCl Probe |
| Li | -- | 0.10 | 0.10 | -- | -- |
| Mg | 0.032 | 7.3 | 1.66 | 6. | 15. |
| Mn | -- | 0.13 | 0.003 | -- | -- |
| Na | 363. | 4.5 | 3.67 | 1. | 2.5 |
| Si | 36. | 38.0 | 16.06 | 22. | 47.5 |
| Sr | -- | 0.05 | 0.03 | -- | -- |
| Ti | -- | 0.40 | -- | -- | -- |
| F | 33.4 | <0.1 | <0.1 | Fe _{0.47} Mg _{0.53} SiO ₃ | |
| Cl | 310. | KCl Probe | KCl Probe | +Na _{0.33} Ca _{0.66} Al _{1.8} Si _{2.2} O ₈ | |
| SO ₄ | 173. | 0.98 | 1.17 | | |

* Had achieved measured Eh of - 0.41 volts at pH of 8.46.

† Jones 1982 (ref 9).

TABLE VCRUSHED UMTANUM BASALT AND GR-3 GROUNDWATER INTERACTIONS

| <u>Scenario</u> | <u>Time Duration Cumulative (hrs)</u> | <u>Eh (volts)</u> | <u>pH</u> | <u>Temp (°C)</u> |
|--|---|-------------------|-------------|------------------|
| Air saturated Grande Ronde groundwater | 0 | +0.36 | 9.2 | 45 |
| 45 to 60 g BWIP basalt crushed at 80-100 mesh (SA/V approximately 0.6 to 1 cm ⁻¹) with Ar purge in Grande Ronde groundwater. | 5 | +0.22 | 9.4 | 45 |
| 80 to 125g BWIP basalt crushed at 80-100 mesh (SA/V approximately 1 cm ⁻¹) with Ar purge in Grande Ronde groundwater. | 20 | +0.15 | 9.43 | 45 |
| 30g BWIP basalt (SA/V approximately 7 cm ⁻¹) <200 mesh with Ar purge in Grande Ronde groundwater. | 2 | +0.04 | 8.75 | 60 |
| 60g BWIP basalt <200 (SA/V approximately 20 cm ⁻¹) mesh with Ar purge in Grande Ronde groundwater. | 1 144 | -0.04 -0.08 | 8.59 8.6 | 60 60 |

TABLE VI
GRANDE RONDE 3 GROUNDWATER ANALYSES

| <u>Element</u> | <u>Recipe†</u> <u>mg/L</u> | <u>As Made</u> | <u>In Deaerated water with</u> <u>Basalt at SA/V 20 cm⁻¹</u> <u>144 Hours/60°C</u> |
|-----------------|-------------------------------|----------------|---|
| Al | -- | 0.651 | 0.17 |
| Ca | 2.76 | 13.2 | 33.8 |
| Fe | -- | <0.01 | 0.05 |
| K | 3.43 | KCl Probe | KCl Probe |
| Li | -- | 0.031 | 2.03 |
| Mg | 0.032 | 0.054 | 3.27 |
| Mn | -- | <0.01 | 0.11 |
| Na | 363. | 368.0 | 738. |
| Ni | -- | <0.05 | 0.31 |
| Pb | -- | <0.03 | 0.49 |
| Si | 36*. | 37.3 | 22.6 |
| Sr | -- | 0.364 | 0.27 |
| Ti | -- | <0.003 | 0.02 |
| F | 33.4 | -- | -- |
| Cl | 310. | KCL Probe | KCl Probe |
| SO ₄ | 173. | -- | -- |

* Calculated from amount of Na₂SiO₃·9H₂O given in Jones 1982 (ref 9).

† Jones 1982 (ref 9).

TABLE VIICRUSHED UMTANUM BASALT - GR4 GROUNDWATER INTERACTIONS

| <u>Condition</u> | <u>Time Duration Cumulative (hrs)</u> | <u>Eh (volts)</u> | <u>pH</u> | <u>Temp (°C)</u> |
|--|---|-------------------|-----------|------------------|
| Air Saturated Grande Ronde Groundwater GR4 | 0 | +0.50 | 9.9 | 25 |
| Ar Purge | 3 | +0.35 | 9.9 | 50 |
| 15g Umtanum Basalt Crushed 200-325 Mesh | 1 | -0.04 | 10.0 | 50 |
| 30g Umtanum Basalt Crushed 200-325 Mesh | 1 | -0.2 | 10.0 | 50 |
| 30g Total Umtanum Basalt Crushed 200-325 Mesh | 90 | -0.34 | 9.4 | 65 |
| Added 15g <325 Mesh Basalt | 216 | -0.36 | 9.5 | 65 |

TABLE VIII

GRANDE RONDE 4 GROUNDWATER ANALYSES IN CONTACT WITH UMTANUM BASALT

| Element | Recipet Mg/l | As Made | Not Acidified† | | Acidified‡ | | Not Acidified§ | |
|---------|-----------------|---------|-------------------------------|---------------------|-------------------------------|---------------------|-------------------------------|--------------------|
| | | | Gravity Settle (cloudy) | Filtered <0.45µm | Gravity Settle (cloudy) | Filtered <0.45µm | Gravity Settle (cloudy) | Settle (cloudy) |
| Al | -- | 0.07 | 1.99 | 1.24 | 3.41 | 1.30 | 0.07 | 0.07 |
| B | -- | -- | 0.94 | 0.93 | 0.92 | 0.90 | 2.52 | 2.52 |
| Ca | 2.2 | 1.79 | 5.69 | 5.36 | 8.70 | 7.18 | 63.26 | 63.26 |
| Fe | -- | <0.01 | 0.69 | 0.07 | <u>4.91</u> | 0.06 | 0 | 0 |
| K | 13.0 | 13.9 | KCl Probe | KCl Probe | KCl Probe | KCl Probe | KCl Probe | KCl Probe |
| Li | -- | <0.005 | 0.29 | 0.29 | 0.29 | 0.29 | 0.14 | 0.14 |
| Mg | -- | 0.01 | <0.01 | <0.01 | <u>0.50</u> | 0.04 | 28.63 | 28.63 |
| Mn | -- | <0.01 | 0.04 | 0.02 | 0.09 | 0.02 | 0.07 | 0.07 |
| Na | 334 | 370 | 487.75 | 464.62 | 451.13 | 460.76 | 467.7 | 467.7 |
| Si | 45 | 45.6 | 104.5 | 100.9 | 101.4 | 96.3 | 66.18 | 66.18 |
| F | 19.9 | 17.7 | 25.8 | 28.45 | 22.2 | 25.0 | 11.3 | 11.3 |
| Cl | 405 | 364 | KCl Probe | KCl Probe | KCl Probe | KCl Probe | KCl Probe | KCl Probe |
| SO | 4.0 | 4.97 | 12.6 | 12.2 | <0.05 | <0.05 | 55.1 | 55.1 |

† 216 hours at 60°C.

§ Additional 672 hours at 90°C with monolith of Pomona basalt.

TABLE IX

REPRODUCIBILITY OF GRANDE RONDE 4 GROUNDWATER ANALYSES IN CONTACT WITH UMTANUM BASALT
(Solutions Are Filtered)

| Element | Recipe mg/L | As Made | 216 hrs Residence Time* | | As Made | 192 hrs Residence Time† | |
|-----------------|----------------|---------|-------------------------|-----------------------|---------|-------------------------|-----------------------|
| | | | Filtered No Acid | Filtered With Acid | | Filtered No Acid | Filtered With Acid |
| Al | -- | 0.07 | 1.24 | 1.30 | -- | 0 | <0.25 |
| B | -- | -- | 9.3 | 9.00 | -- | 2.30 | 2.28 |
| Ca | 2.2 | 1.79 | 7.79 | 7.18 | 1.83 | 1.90 | 2.93 |
| Fe | -- | <0.01 | 0.46 | 1.69 | -- | 0.10 | 0.25 |
| K | 13.0 | 13.9 | KCl Probe | KCl Probe | 14.9 | KCl Probe | KCl Probe |
| Li | -- | <0.005 | 0.29 | 0.29 | -- | 0.22 | 0.22 |
| Mg | -- | 0.01 | -- | 0.02 | -- | -- | -- |
| Mn | -- | <0.01 | -- | 0.04 | -- | -- | -- |
| Na | 334 | 370 | 464.6 | 460.8 | 331.7 | 540.0 | 547.1 |
| Si | 45 | 45.6 | 100.9 | 96.3 | 45.7 | 93.2 | 87.1 |
| F | 19.9 | 17.7 | 28.5 | 25.0 | 16.6 | 24.0 | 30.0 |
| Cl | 405 | 364 | KCl Probe | KCl Probe | 377 | KCl Probe | KCl Probe |
| SO ₄ | 4.0 | 4.97 | <0.05 | <0.05 | 5.07 | <0.05 | <0.05 |

* January 1984.

† April 1984.

TABLE X

REPRODUCIBILITY OF GRANDE RONDE GROUNDWATER ANALYSES
IN CONTACT WITH UMTANUM BASALT
 (Solutions Not Acidified and Not Filtered)

| <u>Element</u> | <u>Recipe mg/L</u> | <u>As Made</u> | <u>Gravity† Settle (cloudy)</u> | <u>As Made</u> | <u>Gravity§ Settle (cloudy)</u> |
|-----------------|------------------------|----------------|---|----------------|---|
| Al | -- | 0.07 | 1.99 | -- | 0.57 |
| B | -- | -- | 9.4 | -- | 2.22 |
| Ca | 2.2 | 1.79 | 5.69 | 1.83 | 2.05 |
| Fe | -- | <0.01 | 0.69 | -- | 0.81 |
| K | 13.0 | 13.9 | KCl Probe | 14.9 | KCl Probe |
| Li | -- | <0.005 | 0.29 | -- | 0.22 |
| Mg | -- | 0.01 | <0.01 | -- | <0.05 |
| Mn | -- | <0.01 | 0.04 | -- | <0.01 |
| Na | 334 | 370 | 487.75 | 331.7 | 611.7 |
| Si | 45 | 45.6 | 104.5 | 45.7 | 92.4 |
| F | 19.9 | 17.7 | 25.8 | 16.6 | 30.0 |
| Cl | 405 | 364 | KCl Probe | 377 | KCl Probe |
| SO ₄ | 4.0 | 4.97 | 12.6 | 5.07 | <0.05 |

† 216 hours at 65°C.

§ 192 hours at 65°C.

TABLE XI

CHEMICAL COMPOSITION†† OF COLUMBIA RIVER BASALTS

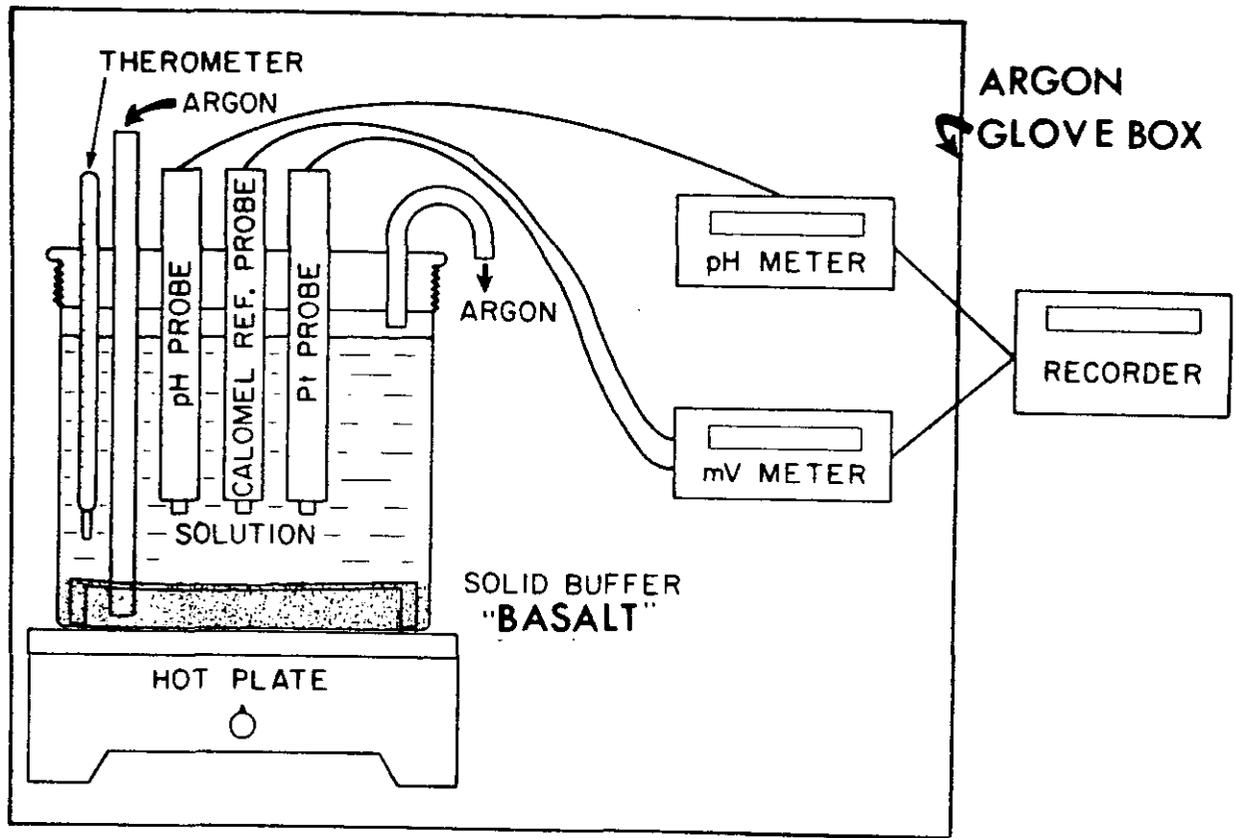
| Oxide | RUE-1 (Umtanum)* (Wt%) | Umtanum Flow† (Wt%) | Flow E Basalt† (Wt%) | Pomona Basalt† (Wt%) | Pomona (Wt%) | | | | Umtanum (Wt%) | | | |
|--------------------------------|------------------------------|---------------------------|----------------------------|----------------------------|--------------|-----------------|-----------------|--------------|---------------|-----------------|-----------------|--------------|
| | | | | | >100 Mesh | 100-200 Mesh | 200-325 Mesh | <325 Mesh | >100 Mesh | 100-200 Mesh | 200-325 Mesh | <325 Mesh |
| SiO ₂ | 54.66 | 56.26 | 53.99 | 52.12 | 50.83 | 50.99 | 50.50 | 48.28 | 54.40 | 55.06 | 52.79 | 58.96 |
| Al ₂ O ₃ | 13.48 | 13.77 | 13.89 | 15.12 | 15.43 | 15.81 | 15.49 | 16.19 | 14.03 | 14.65 | 14.08 | 15.24 |
| FeO | 10.07 | 11.71 | 12.28 | 11.19 | 12.81 | 12.44 | 12.88 | 14.84 | 15.45 | 14.45 | 16.74 | 9.67 |
| Fe ₂ O ₃ | 3.62 | — | — | — | — | — | — | — | — | — | — | — |
| MnO | 0.24 | 0.20 | 0.20 | 0.19 | 0.20 | 0.19 | 0.19 | 0.24 | 0.24 | 0.22 | 0.24 | 0.15 |
| CaO | 7.19 | 7.25 | 8.42 | 9.99 | 10.99 | 11.08 | 10.65 | 10.29 | 7.58 | 7.73 | 7.48 | 8.62 |
| MgO | 3.73 | 3.37 | 4.35 | 7.00 | 6.64 | 6.28 | 7.00 | 5.93 | 3.62 | 3.41 | 3.25 | 4.17 |
| NiO | — | — | — | — | 0.06 | 0.08 | 0.14 | 0.54 | 0.14 | 0.16 | 0.15 | 0.10 |
| Na ₂ O | 2.90 | 3.34 | 1.20 | 2.13 | 1.37 | 1.48 | 1.65 | 2.21 | 2.40 | 2.33 | 2.88 | 1.79 |
| K ₂ O | 1.60 | 1.64 | 3.41 | 0.46 | — | — | — | — | — | — | — | — |
| TiO ₂ | 2.17 | 2.07 | 1.94 | 1.57 | 1.68 | 1.65 | 1.51 | 1.48 | 2.14 | 2.00 | 2.38 | 1.31 |
| P ₂ O ₅ | 0.34 | 0.39 | 0.31 | 0.24 | — | — | — | — | — | — | — | — |

* M. J. Apted and J. Myers, "Comparison of The Hydrothermal Stability of Simulated Spent Fuel and Borosilicate Glass In A Basaltic Repository," (RHO-BW-ST-38P, July 1982).

† P. F. Salter, L. L. Ames, and J. E. McGarran, "The Sorption of Selected Radionuclides on Columbia River Basalts," (RHO-BWI-LD-48, August 1981).

†† All data normalized to 100%.

FIGURE 1: The Experimental Design



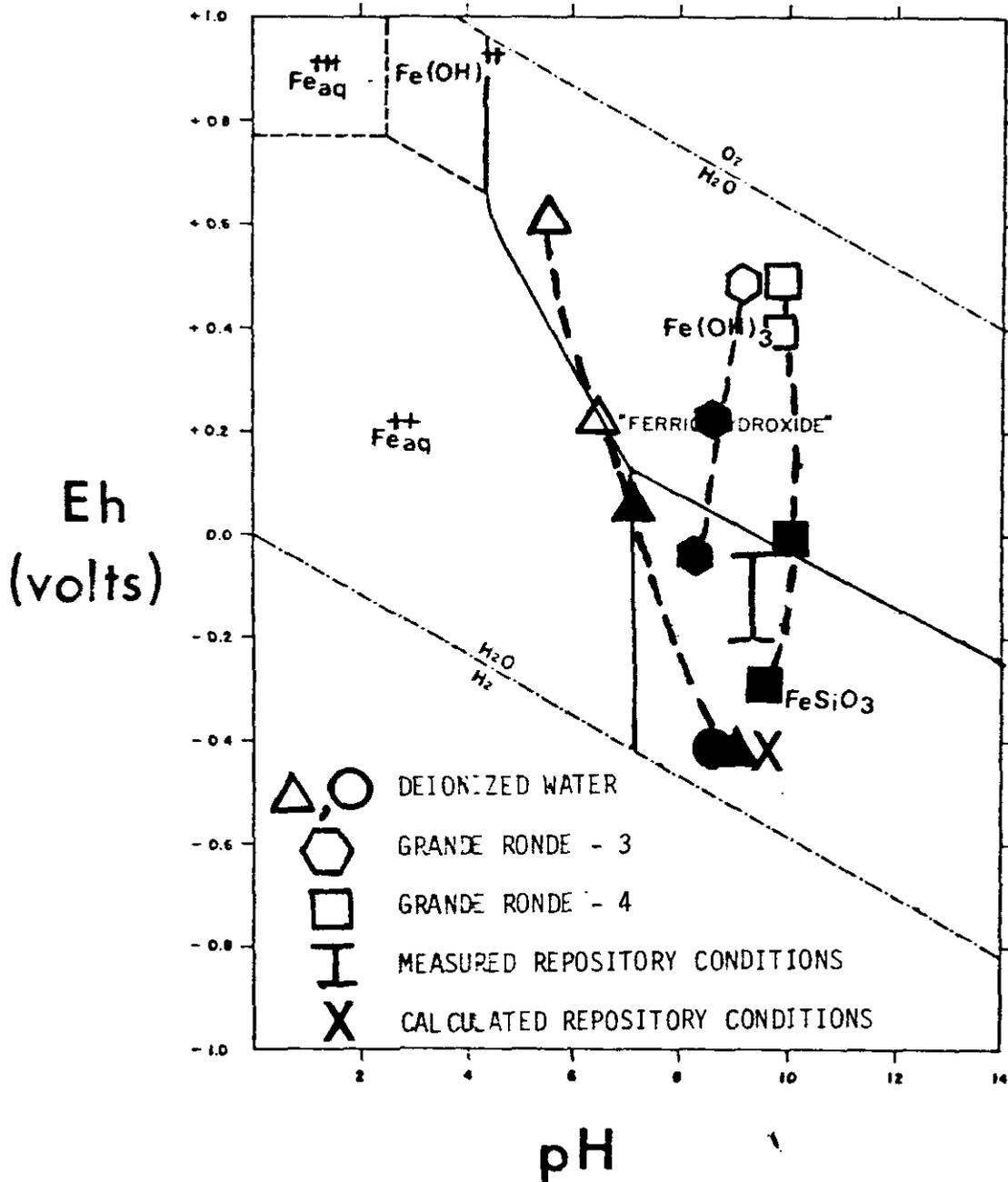


FIGURE 2: Eh-pH changes measured (+0.05V) for deoxygenated deionized water and Umtanum basalt (triangles) and the Eh-pH changes measured for deoxygenated GR-3 and GR-4 simulated basaltic groundwater (hexagons and squares respectively). The X represents the calculated Eh and pH values for the basalt repository groundwater (Ref. 2) and the vertical bar represents the range of Eh values actually measured for the BWIP groundwaters (Ref. 15). SA/V = 10 cm^{-1} (<100 mesh). The open symbols represent Eh conditions achieved by argon sparging only.