**PREDICTION OF RADIOACTIVE WASTE GLASS DURABILITY BY THE
HYDRATION THERMODYNAMIC MODEL: APPLICATION TO SATURATED
REPOSITORY ENVIRONMENTS**

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ABSTRACT

The effects of groundwater chemistry on glass durability were examined using the hydration thermodynamic model. The relative durabilities of SiO_2 , obsidians, basalts, nuclear waste glasses, medieval window glasses, and a frit glass were determined in tuffaceous (J-13) groundwater, basaltic (GR-4) groundwater, WIPP-A brine, and Permian-A brine using the monolithic MCC-1 durability test. For all the groundwaters, the free energy of hydration, calculated from the glass composition and the final experimental pH, was linearly related to the logarithm of the measured silica concentration. The linear equation was identical to that observed previously for these glasses during MCC-1 testing in deionized water. The slope defined is the theoretical slope, $\ln(1/2.303RT)$, for glass dissolution controlled by the dissolution of amorphous silica.

In the groundwater-dominated MCC-1 experiments, the pH values for all the glasses tested appeared to be buffered by the groundwater-precipitate chemistry. The superposition of the linear equation for the groundwaters and deionized water experiments occurred because the hydratic thermodynamic model accounts for dissolution as a function of solution pH. The behavior of poorly durable glasses demonstrated that the silica release is a function of the ionic strength of the solution. The ionic strength, in turn, reflects the effect of the groundwater chemistry on the pH. Using the hydration thermodynamic model, nuclear waste glass durability in saturated repository environments can be predicted from the glass composition and the groundwater pH.

INTRODUCTION

Determination of glass durability as a function of glass composition is significant to the development of durable glasses for nuclear waste disposal. The long radioactive half-lives of fission products and actinides in high-level nuclear wastes require that they be isolated from the biosphere for 10^3 to 10^5 years. The isolation technique selected for defense high-level waste produced at the Savannah River Site (SRS) is immobilization in borosilicate glass and subsequent emplacement in a geologic repository [1]. The intrusion of groundwater into and passage through a repository, is the most likely mechanism by which radionuclides may be removed from the waste glass and carried to the biosphere. Thus, it is important that nuclear waste glasses be stable in the presence of groundwaters for very long periods of time and that the long-term durability can be accurately modeled.

Although it is impossible to directly demonstrate the 1000 year stability of a nuclear waste glass, the existence of natural glasses, such as obsidians, basalts, or tektites, which are millions of years old, demonstrate that glasses can be formulated which will survive geologic environments. Similarly, synthetic glasses of known longevity or performance, such as medieval window glasses, can also demonstrate the potential long-range performance of nuclear waste glass.

To quantify the relative durabilities of nuclear waste glasses as a function of composition, their performance relative to natural and ancient glasses (whose long-term performance is known) was investigated [2-8]. The thermodynamic approach of Newton and Paul [9], which expresses glass durability as a function of glass composition, was modified to include complex multicomponent nuclear waste glasses [2-3] and the effects of solution pH [4-6].

The hydration thermodynamic model [2-8] was applied to experimental laboratory results for over 300 glasses in deionized water (MCC-1 28 day tests). Although equilibrium was probably not achieved in these short-term laboratory tests, the use of equilibrium thermodynamics was found to furnish a quantitative frame of reference for the relationship between the glasses and the aqueous environment on both historic and geologic time scales.

The thermodynamic model was shown to be applicable to a wide variety of glasses [2-8,10] in various environmental conditions including the successful prediction of hydration rind dating on obsidians [11]. The hydration thermodynamic model has also modeled the response of waste glasses and historical glasses during in-situ burial experiments. Correlations have been observed between laboratory (MCC-1 28 day) and in-situ (2-5 year) experiments [8,10].

It was also demonstrated [6-8] that the thermodynamic approach for glass durability could be combined with the thermodynamic approach used by Pourbaix [12] and Garrels [13] to describe the effects of natural aqueous environments (solution pH and Eh) on glass. The construction of Pourbaix diagrams for glass dissolution was shown to conceptually unify the dissolution behavior of glasses in natural environments [6-8].

In this study the relative durability of SiO_2 , Hanford basalt, obsidian, two medieval window glasses from the European Science Foundation (ESF), frit 131 glass not containing simulated SRS waste, and 131 and 165 waste glasses containing only sludge are evaluated using hydration thermodynamics. The experimental laboratory results (MCC-1 28 day tests) for these 8 glasses in deionized water, tuffaceous (J-13) groundwater, basaltic (GR-4) groundwater, WIPP-A brine, and Permian-A brine are compared.

KINETIC VS. THERMODYNAMIC GLASS DISSOLUTION MODELS

The durability of a glass is a function of both its kinetic and thermodynamic stability in an aqueous environment [14-15]. Kinetic models have been applied to the time dependent corrosion of glasses [15-22], waste glasses [20-21], and crystalline silicates [18,22]. These models mathematically describe ion exchange, diffusion, and protective layer formation in the form of time-dependent master equations. Kinetic models describe the leaching behavior of a given glass but they do not predict which of a given group of glasses will be most durable.

Chemical thermodynamics has also been used to predict the stability of vitreous silicates [14-15,12,23] and crystalline silicates [12-13,24-25] in aqueous environments. Application of chemical

thermodynamics does not require determination of the time-dependent kinetics of the leaching processes, but provides an ontological approach to glass durability based on the thermodynamic stability of the reactants (e.g. glass) to the products formed during leaching or weathering, e.g. silicic acid, cations or complexes in solution, and/or precipitates.

The relationship between the kinetic and thermodynamic aspects of glass durability was shown experimentally to relate to the relative contributions of glass composition and imposed test conditions [26]. The kinetic rate laws described by Lasaga [22] and Grambow [27] include expressions for the forward dissolution of the solid (glass or mineral species) and expressions for the precipitation of aqueous species or complexes from solution. These master rate equations model the change in solution concentration as a function of time in terms of the kinetic SA/V term, the temperature dependence of the dissolution, and the activity of the H^+ ion (pH) up to and including equilibrium conditions. Although different assumptions are made by Lasaga [22] and Grambow [27] the final rate laws derived are similar [26]. These rate laws are also analogous to expressions derived for mineral dissolution utilizing the progress variable approach and transition state theory [28]. Because the activity-pH diagrams provide the fundamental correlation between minimum solubility of a species in solution and the free energy [6,13,29], the approaches of Lasaga [22] and Grambow [27] mathematically describe the experimentally determined relations between durability, kinetic $(SA/V) \cdot t$, and the thermodynamic ΔG_{hyd} [26].

THE HYDRATION THERMODYNAMIC MODEL

Glass dissolution can mechanistically be modeled as a combination of ion exchange and matrix dissolution reactions [4,14,16]. In glasses where hydrated amorphous surface layers form (Figure 1), additional equations expressing the surface contribution can be included. The hydration thermodynamic approach models the relative contribution of each of these three mechanisms as a function of the glass composition [4]. The hydration thermodynamic approach [4-10] also models the effects of solution pH on the glass dissolution.

Network breaking (e.g. alkali, alkaline earth, Fe^{2+} , Mg^{2+} , etc) and intermediate glass structural species (e.g. Pb^{2+}) associated with the unpolymerized glass $(\text{SiO}_4)^{-4}$ network are considered to be released to the solution by ion exchange with protons in the water. The unpolymerized $(\text{SiO}_4)^{-4}$ associated with these species is released to the solution by matrix dissolution. An equation expressing these two mechanisms is given as follows:

Dissolution of the highly polymerized $(\text{SiO}_4)^{-4}$ network, not associated with the network breaking or intermediate ions, is expressed by the following equation:

Dissolution of Fe_2O_3 , Al_2O_3 , Nd_2O_3 , TiO_2 and other species which form hydroxides or hydrates that participate in surface layer precipitation reactions are written as follows:

This approach assumes that the glass is a mechanical mixture of orthosilicate and oxide components [4,5,8,9,27] and that the overall free energy of hydration of a glass is the sum of the free energies of the hydration reaction types given in equations 1, 2, and 3. The contribution of each mechanism toward the calculation of the overall glass durability is the weighted hydration free energy of that component species in the glass. The formalism is

$$\Delta G_{\text{hyd}} = \sum x_i \cdot (\Delta G_{\text{hyd}})_i \quad (4)$$

where $(\Delta G_{\text{hyd}})_i$ is the free energy change of the most stable hydration reaction of component i at mole fraction x_i .

The reactants in Equations 1 and 2 are H_2SiO_3 . The solubility of silica increases rapidly at pH values >9.5 due to dissociation of silicic acid. Therefore, an additional contribution to the hydration free energy, based on the dissociation constants of silicic acid was calculated as follows:

$$(\Delta G_{\text{hyd}})_{\text{pH}} = 1.364 \left[-\log \left(1 + \frac{10^{-10}}{10^{-\text{pH}}} + \frac{10^{-21.994}}{10^{-2\text{pH}}} \right) \right] \quad (5)$$

Similar equations are given elsewhere for the pH dependent dissociation of H_3BO_3 [7-11].

The hydration free energy calculates the relative role of amorphous silica dissolution as modified by gel surface layer formation. The slope of glass durability versus ΔG_{hyd} [4-8] is the theoretical slope, $\ln(1/2.303RT)$, of Grambow's glass dissolution model [27,30,31]. The model maintains that the dissolution of all silicate-based glasses can be described by the activity diagrams for the dissolution of amorphous silica.

EXPERIMENTAL

The compositions of the eight glasses and the four simulated groundwaters studied are given in Appendix I. Since glass dissolution was being examined for groundwater-dominated, saturated repository environments, all the glasses were leached in duplicate by the MCC-1 28 day durability protocol [32]. All the leachates were analyzed by Inductively Coupled Plasma (ICP) and Atomic Absorption (AA) spectroscopy.

The glass monoliths were dried at 90°C for 1 hour to remove adsorbed water but not structural H_2O . The surfaces were examined by X-ray Diffraction (XRD) analysis on a Phillips vertical diffractometer with CuK_α radiation. For maximum sensitivity, the solid surfaces were examined at low kilovoltage settings and slow goniometer speeds with each analysis taking between 12-18 hours to complete. The solids were

also examined by Scanning Electron Microscopy (SEM) with Energy Dispersive Analysis by X-ray (EDAX) capability. The analyses determined by EDAX were used in conjunction with the XRD analyses to confirm the identification of surface precipitates.

RESULTS

Hydration Thermodynamic Model in Saturated Groundwater Environments

The experimentally determined release properties of the eight glasses leached in silicate groundwaters (tuffaceous J-13 and basaltic GR-4) and in brines (WIPP-A and Permian-A), were found to be defined by the same linear equation as glasses leached in deionized water (Figure 2). The slope of this line is the theoretical slope, $\ln(1/2.303RT)$, for glass dissolution controlled by the dissolution of amorphous silica [27,31-32].

The superposition of the theoretical slope for glass dissolution in deionized water and in the groundwaters (Figure 2), occurs because the pH values for all the glasses tested was "buffered" at a constant pH by the groundwater chemistry and/or by the precipitation of secondary species. Buffering of the leachates decreased the calculated DG_{hyd} values for poorly durable glasses, e.g. frit 131. In turn, lower Si releases were measured. This is indicated by the arrows in Figure 2 which lead from the ΔG_{hyd} for poorly durable frit 131 in deionized water (pH = 11.06) to the ΔG_{hyd} for the same frit in the silicate groundwaters (pH = 9.56 for J-13, 9.75 for GR-4).

The Effects of pH and Ionic Strength

The initial pH of J-13, GR-4, WIPP-A, and Permian-A groundwaters were 7.4, 7.7, 6.5, and 6.8, respectively (see Appendix I). For most of the glasses examined, the pH of the leachant did not change appreciably from the initial pH values within the sensitivity of the pH measurement technique. For the poorly durable frit 131 glass, the alkali leaching from the glass did drive the pH of J-13, GR-4, and WIPP-A groundwaters to 9.56, 9.75, and 7.31, respectively, but not to the 11.06 values

measured for deionized water. This enabled the following evaluations to be made:

- (1) the effect of the $(\Delta G_{\text{hyd}})_{\text{pH}}$ term for a glass of the same base composition in groundwaters of varying pH
- (2) the effect of the ionic strength of varying groundwaters on the glass durability
- (3) the relationship between the ionic strength and the pH of the groundwater.

The Si released to solution for frit 131 in the varying groundwaters is shown in Figure 3a as a function of the ΔG_{hyd} calculated from the glass composition and the measured solution pH. For the four groundwaters and the deionized water, a linear trend is observed indicating that the $(\Delta G_{\text{hyd}})_{\text{pH}}$ term adequately models the effects of solution pH on glass dissolution for complex groundwaters.

The ionic strength of the silicate groundwaters was calculated as outlined in Berner [33]. The values for J-13 and GR-4 were 0.0231 and 0.0315, respectively. The values for WIPP-A and Permian brines were 6.984 and 11.297, respectively. The Si and the B released to solution from frit 131 were found to be logarithmic functions of the ionic strength of these four groundwaters despite the widely varying chemistry (Figure 3b). The data for deionized water did not appear to fit the observed dependence of the ionic strength on the glass durability for this poorly durable glass.

The buffering of the groundwater pH for the frit 131 glass experiments was determined to be a direct function of the ionic strength in the four groundwaters investigated (Figure 3c). Since the groundwater pH reflects the effect of the groundwater-precipitate chemistry on the pH, modeling the pH with the $(\Delta G_{\text{hyd}})_{\text{pH}}$ term accounts for the differences in the ionic strength of the leachants.

The Significance of the Crystalline Precipitates Identified

Tuffaceous J-13 and Basaltic GR-4 Groundwater

The tri-octahedral smectitic clay, hectorite (a lithium saponite of the composition $\text{Li}_x\text{Mg}_{6-x}\text{Si}_8\text{O}_{20}(\text{OH})_4 \cdot x\text{Na}^+$) was identified on the lithium containing glasses (the 131 and 165 waste glass and the frit 131 glass) in both J-13 and GR-4 groundwater. Saponite (15A) was identified on the surface of the basalt which contains no Li. These silicious phases were primarily found to be enriched in Ca, Fe, Mg, Al, and Ti (Table 1). In the frit 131 glass, which contains La, the smectite phase was enriched in this component (Table 1). The formation of these smectites from silica enriched solutions in the presence of Fe and Mg at near boiling temperature is consistent with their known synthesis [34].

No crystalline precipitates were observed on the durable glasses, SiO_2 and obsidian, in any of the silicate (J-13 or GR-4) groundwaters studied (Table 1). For the poorly durable ESF medieval window glasses, the precipitates identified on the glass surfaces by XRD analysis were dominated by the interactions of the glass species with carbonate and bicarbonate in the groundwater. CaCO_3 formed on the Ca rich ESF medieval window glasses while KOH and $\text{Na}_3\text{Ca}_6(\text{PO}_4)_5$ formed on the only K and PO_4 containing glass (ESF 151).

The CaCO_3 and Ca-smectite clays are the phases predicted [35] to form in J-13 water in the presence of SRS glasses at 90°C by the EQ3/EQ6 geochemical modeling code which is based on transition state theory [28]. However, the CaCO_3 was found to be enriched in Mn rather than Mn forming a secondary pyrolusite phase (MnO_2) as predicted by EQ3/EQ6.

WIPP-A Brine

In the WIPP-A brines, carbonate and magnesium chloride phases dominated the surface chemistry of the frit 131 glass, the waste glasses, and the basalt. In the WIPP-A brines, hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) dominated the surface chemistry of all the

glasses except the high K and PO_4 containing ESF 151 glass (Table 1). The hydromagnesite was enriched in Mg, Ti, and Al.

Amorphous or poorly crystallized Mg-Cl deposits were also identified in all the glasses leached in WIPP-A brine. A Mg-Fe enriched CaCO_3 phase, ankerite, was identified by XRD on the surface of the SRS 165 waste glass. $\text{Na}_3\text{Ca}_6(\text{PO}_4)_5$ was identified by XRD on the surface of the PO_4 rich ESF 151 glass in WIPP-A brine.

Permian Basin Brine #3

The carbonate, sulfate, and chloride chemistry of the Permian basin brine (PPB3) dominated the surface chemistry of precipitates observed on the eight glasses. Hydrotalcite, $(\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O})$, anhydrite (CaSO_4), and magnesium-oxychloride $(\text{Mg}_2(\text{OH})_5\text{Cl} \cdot 4\text{H}_2\text{O})$ were identified on the ESF glasses, frit 131 glass, the two SRS waste glasses, and on the basalt (Table 1). No crystalline precipitates were observed on the durable SiO_2 and obsidian glass.

For the least durable frit 131 glass, the pH of the Permian brine decreased from 6.8 to 5.8 over the 28 day duration of the test. This may be due to the buffering of the pH by the precipitating carbonate species (hydrotalcite).

DISCUSSION

The hydration thermodynamic approach models the ion exchange, matrix dissolution, and the continuous hydrated amorphous precipitation occurring in the gel layer of a glass (Figure 1). The interactions of the dissolution products of reactions, such as Equations 1-3, with anions in the groundwater is not specifically modeled. However, the precipitation of these secondary species is not continuous over the monolith surface in water-dominated experiments as shown by Harker [36] and others. Therefore, in saturated repository environments, the dissolution rate may be affected more by the continuous hydrated amorphous precipitation occurring in the leached gel layer than by the secondary species precipitating.

The ionic strength of a solution can influence both the solubility of species [37] and the cation adsorption properties of hydrous surfaces [38,39]. Since the ionic strength and the pH of the leachates are functions of the precipitation reactions, inclusion of the experimentally determined solution pH in the ΔG_{hyd} calculation provides for some functional dependence of the dissolution rate on the precipitation. The relationship between pH and ionic strength may also explain why increased ionic strength appears to depress glass dissolution [40] and decreases the surface H^+ concentration of the glass [41].

The leachate concentrations are in equilibrium with the precipitating secondary species. For glasses in J-13 groundwater, a Li-Ca rich smectite clay (hectorite) and CaCO_3 were the two dominant species found on the glass surfaces (Table 1). Ca clays (smectites and clinoptilolite) are the secondary phases identified by EQ3/EQ6 as controlling the solution composition of J-13 well water during reactions with Topopah Tuff at 150°C [42] while CaCO_3 is one of the primary controlling mineral phases. Similarly, CaSO_4 and carbonate phases like hydromagnesite and hydrotalcite were observed on the glass surfaces leached in WIPP and Permian brines (Table 1). CaSO_4 phases (gypsum, anhydrite, and polyhalite), magnesite, and magnesium silicate phases have been identified as the phases controlling brine composition in the WIPP repository environment [43]. Therefore, the leachate pH appears to be determined by equilibrium between the groundwater and the secondary precipitates, where the secondary precipitates are ion-exchanged derivatives of the original equilibrium between the groundwater and the host rock mineralogy. Hence, the pH of the leachates is buffered by this equilibrium in much the same manner that the original groundwater pH is controlled by equilibrium with the repository host rock mineralogy [42,44-45]. For groundwater-dominated repository scenarios, the hydration thermodynamic model can therefore predict glass durability from glass composition and groundwater pH.

CONCLUSIONS

- The thermodynamic approach can model the observed suppression of glass dissolution in groundwaters [46,47].
- Nuclear waste glass durability in groundwater-dominated saturated repository environments can be predicted from the glass composition and the groundwater pH by the hydration thermodynamic model.
- The groundwater ionic strength reflects the buffering capacity of the groundwater chemistry and/or the buffering due to the precipitation of secondary species.
- Modeling the pH effect on glass durability with the $(\Delta G_{\text{hyd}})_{\text{pH}}$ term accounts for the differences in the ionic strength of the leachants.

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Table 1. Precipitates Identified on Leached Glass Surfaces

Glass	DI Water *		GR-4 Groundwater**		J-13 Groundwater**		WIPP-A Brine**		Permian Brine**	
	XRD		XRD	SEM	XRD	SEM	XRD	SEM	XRD	SEM
ESF 151	Alpha KOH (a) CaCO ₃ (c) X-SiO ₂ (b) Ca ₂ SiO ₄ (d)		Alpha KOH (a) CaCO ₃ (c) Na ₃ Ca ₆ (PO ₄) ₅ (f)	CaCO ₃ with Mg and Mn	Alpha KOH (a) CaCO ₃ (c) Na ₃ Ca ₆ (PO ₄) ₅ (f)	CaCO ₃ with Mg and Mn	Na ₃ Ca ₆ (PO ₄) ₅ (f)	Ca, P rich phase Mg, Cl phase	Hydroxalite (k) CaSO ₄ (l) Mg-oxychloride(m)	Mg, Ca, Cl rich phase
ESF 149	CaCO ₃ (c)		CaCO ₃ (c)	CaCO ₃ with Mn	CaCO ₃ (c)	CaCO ₃ with Mn clay with Mg, Al, Si	Hydromagnesite(l) enriched in Mg, Si, Ti, and Al Mg, Cl phase		Hydroxalite (k) Mg-oxychloride(m) Mg, Cl phase	CaSO ₄
Frit 131	Li ₂ CO ₃ (e) Hectorite (?) (g)		Hectorite (a) Li saponite of the smectite family(g)	enriched in Ca, Mg, and Ti	Hectorite (a) Li saponite of the smectite family(g)	enriched in Ca, Mg, and La	Hydromagnesite(l) enriched in Mg, Si, Ti, and Al Mg, Cl phase		Hydroxalite (k) CaSO ₄ (l) Mg-oxychloride(m)	Mg, Al, Cl rich phases
SRS 131	amorphous		Hectorite (a) Li saponite of the smectite family(g)	enriched in Ca, Fe, and Al	Hectorite (a) Li saponite of the smectite family(g)	enriched in Ca, and Mg	Hydromagnesite(l) enriched in Mg, and Al Mg, Cl phase		Hydroxalite (k) CaSO ₄ (l) Mg-oxychloride(m)	Mg, Al, Fe, Cl rich phases
SRS 165 Black Frit	amorphous		Hectorite (a) Li saponite of the smectite family(g)	enriched in Ca, Fe, and Al	Hectorite (a) Li saponite of the smectite family(g)	enriched in Ca, Mg, and Al	Hydromagnesite(l) enriched in Mg, Ankerite - a Ca, Mg and Al Fe Carbonate (j) Mg, Cl phase		Hydroxalite (k) CaSO ₄ (l) Mg-oxychloride(m)	Mg, Fe, Cl rich phases
Hanford Basalt			Saponite (Ca Smectite) (h)		Saponite (Ca Smectite) (h)		Mg, Cl phase Hydromagnesite		Hydroxalite CaSO ₄ Mg, Cl phase	
Obsidian	minor Spinel		minor Spinel	Spinel no surface	minor Spinel	Spinel no surface	Mg, Cl phase Hydromagnesite		minor Spinel Mg, Al, Cl phases	Spinel
SiO ₂	amorphous		amorphous	no surface	amorphous	no surface	Hydromagnesite(i) Mg, Al and Si rich (poorly crystalline)		amorphous Mg, Cl phase	Mg, Cl phase

* MCC-3/90 days, ** MCC-1/28 days

(a) JCPDS 21-645, (b) JCPDS 16-380, (c) JCPDS 05-586, (d) JCPDS 14-35, (e) JCPDS 22-141, (f) JCPDS 11-236, (g) JCPDS 25-1385, (h) JCPDS 13-86, (i) JCPDS 25-513, (j) JCPDS 12-88, (k) JCPDS 14-191 or 35-965, (l) JCPDS 37-1496, (m) JCPDS 12-122 or 7-420

Figure 1. Schematic of the mechanisms involved during glass dissolution in saturated environments, e.g. ion exchange and matrix dissolution, coupled with hydrated amorphous surface layer formation and "back reactions" involving precipitation from solution (after reference 36).

Figure 2. Comparison of the hydration thermodynamic data for a "reference set" of glasses tested by the MCC-1 protocol. The equation of best fit and the 95% confidence limits were defined by the MCC-1 data in deionized water. The data for all the groundwaters reverts to the theoretical slope of $\ln(1/2.303RT)$.

Figure 3a. The effect of the $(\Delta G_{hyd})_{pH}$ term for frit 131 in groundwaters of varying pH.

Figure 3b. The effect of the ionic strength of varying groundwaters on frit 131 glass durability.

Figure 3c. The relationship between the ionic strength and the pH of the groundwater for frit 131 glass experiments.

Appendix I

Table A1. Glass and Natural Analog Compositions (Wt. %)

	SiO2	Obsidian	Basalt	165 BF	ESF 149	ESF 151	131 Stage 1	Frlt 131
Al2O3	0.406	12.419	13.384	4.304	4.245	3.904	4.382	
CaO	0.672	1.391	8.668	1.401	21.728	19.017	0.864	
Fe2O3				11.311		0.300	9.145	
FeO	0.910	5.117	15.711				2.469	
MgO	0.147	0.247	4.400	0.701	0.051	3.203	1.481	2.000
MnO	0.145	0.090	0.275	2.402	1.819	0.501	2.695	
Na2O	0.032	1.434	2.664	11.011	0.101	5.005	13.980	17.700
Li2O				5.005			4.218	5.700
NiO	0.085		0.146	0.901			1.008	
SiO2	96.647	73.175	51.302	55.055	57.403	56.050	45.942	57.900
Cr2O3	0.066	0.000	0.025					
B2O3	0.796	0.032	0.044	7.207			10.884	14.700
SrO	0.006		0.039				0.051	
ZrO2	0.003	0.054	0.024	0.701			0.370	0.500
TiO2	0.008	0.862	2.333		0.202	0.200	2.078	1.000
K2O		5.043	0.482		14.452	7.207		
Cs2O							0.062	
P2O5	0.030	0.091	0.504			3.904		0.500
La2O3							0.370	
BaO		0.044						
PbO	0.047					0.711		
ΔG kcal/mole								
Glass	4.964	1.220	-4.054	-4.534	-6.863	-7.270	-6.638	-7.324
GR-4	4.740	0.840	-4.190	-5.000	-6.940	-7.340	-6.820	-8.510
J-13	4.910	1.170	-4.060	-4.710	-6.870	-7.280	-6.700	-8.240
WIPP	4.960	1.210	-4.060	-4.540	-6.870	-7.270	-6.650	-7.330
Permian	4.960	1.220	-4.050	-4.540	-6.860	-7.270	-6.640	-7.320
DI H2O	4.940	1.220	-4.780	-5.040	-7.430	-7.640	-7.890	-11.420

Appendix I (Cont'd)

Table A2. Groundwater Compositions (Molal)

	GR-4	J-13	WIPP A	PERMIAN
Al	-	-	-	-
Li	-	7.2 E-06	3.0 E-03	-
Na	1.45 E-02	1.9 E-03	1.827	1.444
K	3.3 E-04	1.3 E-04	0.768	0.363
Rb	-	-	2.34 E-04	-
Cs	-	-	8.0 E-06	-
Mg	1.6 E-06	7.8 E-05	1.439	2.6304
Ca	5.5 E-05	3.0 E-04	1.5 E-02	0.553
Sr	-	-	5.7 E-05	-
Fe	-	-	3.6 E-05	-
Si	1.6 E-03	2.0 E-03	-	-
Fluoride	1.05 E-03	1.2 E-04	-	-
Chloride	1.1 E-02	1.9 E-04	5.358	7.783
Bromide	-	-	5.0 E-03	5.36 E-02
Iodide	-	-	7.9 E-05	-
Carbonate	4.2 E-04	-	-	-
Bicarbonate	2.0 E-03	2.2 E-03	1.2 E-02	-
Sulfate	4.2 E-05	2.0 E-04	3.6 E-02	5.4 E-02
Borate	-	-	-	-
Nitrate	-	1.5 E-04	-	-
pH	7.7	7.4	6.5	6.8
I[t] $\Sigma(0.5CIZI^2)$	0.0315	0.0231	6.984	11.297

END

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