WSRC-RP-89-26

# APPLICATION OF THE HYDRATION THERMODYNAMIC MODEL FOR GLASS DURABILITY UNDER SATURATED TUFF REPOSITORY CONDITIONS (U)

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# APPLICATION OF THE HYDRATION THERMODYNAMIC MODEL FOR GLASS DURABILITY UNDER SATURATED TUFF REPOSITORY CONDITIONS

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## ABSTRACT

The effects of tuff repository groundwater on glass dissolution and surface layer formation was examined utilizing the hydration thermodynamic model. A 28 day MCC-1 monolithic durability test was performed on the following glasses: $SiO_2$, obsidian, basalt, medieval window glasses, frit glass, and simulated nuclear waste glass. Silica dissolution was compared with the pH corrected free energy of hydration and shown to have the theoretical slope, ln(1/2.303RT), in agreement with MCC-1 tests using deionized water. X-ray diffraction and scanning electron microscopy identified clays of the saponite family and carbonates, on the glass surfaces leached in tuff groundwater.

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## 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 [1,2]. 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 long-term durability can be accurately modeled [1].

Figure 1. Title slide. A thermodynamic approach originated by Newton and Paul and modified by Jantzen and Plodinec to include waste components has been selected to quantify the durability of Defense Waste Process Facility (DWPF) waste glass [3-9]. The approach models glass durability as functions of glass composition and durability [2-7]. This current study evaluates the performance of waste glasses and several analogs (natural glasses, medieval window glasses, etc.) in a simulated Tuff environment.

Figure 2. Objectives. The effects of three parameters on glass durability were studied. These include: glass composition and solution pH; groundwater composition and ionic strength; "back reaction" precipitation. Glass composition and solution pH are discussed initially.

Figure 3. Tetrahedron. Silica is the primary component of waste glass and the fundamental structural unit is the $(SiO_4)^{-4}$ tetrahedron, which consists of a central $Si^{+4}$ ion surrounded by four $O^{-2}$ ions. This shape (essentially a four sided pyramid) is determined primarily by the size and charge of the respective ions.

Figure 4. Glass Polymerization. The degree to which the $SiO_4$ tetrahedrons are interconnected varies among silicates. Section (a) is a two-dimensional representation of a crystalline form of silica, crystobalite. There is consistent short-range (individual tetrahedrons) and long-range (the connected rings of tetrahedrons) order in this structure. Section (b) is a representation of vitreous silica. The basic tetrahedral unit is largely unchanged; however, there is a lack of long-range order due to the randomness of the angles connecting the tetrahedrons. This is normally brought about by cooling from a melted state faster than the tetrahedrons can arrange themselves. Section (c) shows the structure of Cesium silicate. The much larger $Cs^+$ ions modify the $(SiO_4)^{-4}$ network, breaking up Si-O-Si bonds that connect the tetrahedrons.

Figure 5. Soda-Silica Glass. Sodium oxide is a very common component in glass (10% of SRS waste glass); its primary function is to modify the Si-O-Si network. By breaking these bonds, soda reduces the high melting and processing temperatures necessary for pure silica. The oxygen ions connected to only 1 silicon ion are said to be non-bridging oxygens, while those connected to 2 silicon ions are known as bridging oxygens. Ions that break up the silicate network are called network modifiers; examples of which are alkali, alkaline earth, and divalent transition metal ions.

Figure 6. Soda-Boric Glass. Boron oxide is another component of waste glass. Like silica, $B_2O_3$ forms a glassy network, though the structural units are planar $(BO_3)^{-3}$ triangles. The addition of small amounts of soda to $B_2O_3$ glass results in the formation of $(BO_4)^{-4}$ tetrahedrons; with a $Na^+$ ion adding the extra charge needed for this geometry.

Figure 7. Free Energy of Hydration. Glass dissolution can mechanistically be modeled as a combination of ion exchange and matrix dissolution reactions [1,5,11,12]. In glasses where hydrated amorphous surface layers form, 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 [1,5]. The hydration thermodynamic approach also includes the effects of solution pH on matrix dissolution [1,5-9].

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 $(SiO_4)^{-4}$ network are considered to be released to the solution by ion exchange with protons in the water. The unpolymerized $(SiO_4)^{-4}$ associated with these species is released to the solution by matrix dissolution. An equation expressing these two mechanisms is given as follows:

$$Na_2SiO_3 + 2H^+ \qquad H_2SiO_3 + 2Na^+ \tag{1}$$

Dissolution of the highly polymerized $(SiO_4)^{-4}$ network, not associated with the network breaking or intermediate ions, is expressed by the following equation:

$$SiO_2 + H_2O \qquad H_2SiO_3 \tag{2}$$

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:

$$Fe_2O_3 + 3H_2O \qquad 2Fe(OH)_3 \tag{3}$$

Figure 8. Calculated $\Delta G$. This approach assumes that the glass is a mechanical mixture of orthosilicate and oxide components 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 [1,5,6,9,10,13]. 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

$$G_{hyd} = \sum x_i \cdot ( G_{hyd})_i \qquad (4)$$

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

Figure 9. Corrosion Mechanisms. Glass dissolution begins with ion exchange between alkali and hydrogen ions. This reaction hydrates the glass surface, forming a gel layer of more stable species (glass network). The dissolution of the matrix is the rate determining step in the overall reaction. As the reaction progresses, the solution becomes saturated and precipitation of certain species results. These species interact with the oxides, hydrides and hydroxides of the gel layer and may form protective surface layers. [14].

Figure 10. Dominant Mechanism. The glass composition (silica and alkali content) and pH of the solution determine which corrosion mechanism is most likely. High silica glasses (vycor, pyrex, etc.) are highly polymerized and ion exchange is the most prevalent reaction. Poorly durable glasses with little silica and large amounts of alkali dissolve quickly, forcing the pH to increase into regions where silica dissolution is accelerated. Most glasses, including waste glass are somewhere in-between, and either mechanism may be prevalent, depending on the state of the reaction.

Figures 11, 12. pH Effect. Several studies have shown the effect of pH on the leaching of silicate glasses. It is shown that above a pH of 9-10 the corrosion rate of silicate glasses is greatly increased [15]. Also, certain low silica and waste glasses have higher corrosion rates at low pH values as well [15].

Figures 13, 14, 15. $SiO_2$ Stability. 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:

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

Similar equations are given elsewhere for the pH dependent dissociation of $H_3BO_3$ [1,8-11].

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 $G_{hyd}$ is the theoretical slope, ln(1/2.303RT), of Grambow's glass dissolution model [1,5-9,16,17,18]. The model maintains that the dissolution of all silicate-based glasses can be described by the activity diagrams for the dissolution of amorphous silica.

Figures 16. Glass Compositions. The compositions of the eight glasses tested are given in Figure 16.

Figure 17. MCC-1 Test. Since glass dissolution was being examined for groundwater-dominated, saturated repository environments, all the glasses were leached in duplicate by the MCC-1, groundwater dominated, 28 day durability protocol [19]. All the leachates were analyzed by Inductively Coupled Plasma (ICP) and Atomic Absorption (AA) spectroscopy. All the pH values in brine were corrected for the liquid junction potential by means of an HCl titration.

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 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 [1].

Figure 18. Leach Test Results. 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 PBB-3), were found to be defined by the same linear equation as glasses leached in deionized water (Figure 18). The slope of this line is the theoretical slope, ln (1/2.303RT), for glass dissolution controlled by the dissolution of amorphous silica [1,13,20,21,22,].

The superposition of the theoretical slope for glass dissolution in deionized water and in the groundwaters occurs because the - $G_{hyd}$ accounts for the effect of final leachate pH on the glass durability. For all the glasses tested in brine and GR-4 the final leachate pH did not change from the initial leachant pH. This decreased the calculated $G_{hyd}$ values for poorly durable glasses, e.g. frit 131 [1]. In turn, lower Si releases were measured. This is indicated by the arrows in Figure 1 which lead from the $G_{hyd}$ for poorly durable frit 131 in deionized water (pH = 11.06) to the $G_{hyd}$ for the same frit in the silicate groundwaters (pH = 9.56 for J-13, 9.75 for GR-4) [1].

Figure 19. pH vs. $NL_{Si}$. A strong correlation between the final leachate pH and the ionic strength was observed for the frit 131 glass in the four groundwaters investigated (Figure 19). Since the leachate pH reflects the effect of the groundwater-precipitate chemistry on the glass dissolution, modeling glass dissolution with the ( $G_{hyd})_{pH}$ term accounts for the effects of the secondary phase formation [1].

Figure 20. Objectives. The effects of groundwater composition ionic strength on glass durability were examined.

Figure 21. Ionic Strength. The total ionic strength of a solution is determined by the concentration and valence of all present ions; the calculation (as per Berner) is shown in Figure 21 [23].

Figure 22. Groundwater Composition. The composition of the four groundwaters tested is shown in Figure 22.

Figure 23. $I_{[t]}$ vs. $NL_{[i]}$. The ionic strength of J-13 and GR-4 was 0.0231 and 0.0315, respectively. The values for WIPP-A and Permian brine were 6.984 and 11.297. 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 23). 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 [1].

Figure 24. Objectives. The effects of "back reaction" precipitation on glass durability were examined.

Figure 25. Precipitate Schematic. The various crystalline precipitates found on the leached glass surfaces included calcium carbonate and a lithian-saponitic clay [1]. Figure 25 shows a hypothetical view of the cross-section of a leached glass sample.

Figure 26. Surface Species Present. The tri-octahedral smectite clay, hectorite (a lithium saponite of the composition $Li_xMg_{6-x}Si_8O_{20}(OH)_4 \cdot xNa^+$) 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 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 (Figure 26). In the frit 131 glass, which contains La, the smectite phase was enriched in this component (Figure 26). 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 [1,24].

No crystalline precipitates were observed on the durable glasses, $SiO_2$ and obsidian, in either of the silicate (J-13 or GR-4) groundwaters studied (Figure 26). 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 $Na_3Ca_6(PO_4)_5$ formed on the only K- and $PO_4$- containing glass (ESF 151) [1].

The $CaCO_3$ and Ca-smectite clays are the phases predicted 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 [25,26]. 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 [1].

Figure 27. $I_{[t]}$ vs. pH. The initial pH of J-13, GR-4, WIPP-A, and Permian PBB-3 groundwaters were 7.4, 9.7, 6.5, and 6.3, respectively (see Appendix I)[1]. 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 to 9.56, but not to the 11.06 values measured for deionized water.

Figure 28. Conclusions. By modeling reactions from glass oxide/silicate to stable aqueous or hydrated species, it is possible to predict the effects of each component on glass/groundwater equilibrium. Therefore, the hydration thermodynamic approach accounts for the ion exchange, matrix dissolution, and hydrated amorphous precipitation mechanisms occurring during glass dissolution [1].

The ionic strength, $I_{[t]}$, of the groundwater influences the solubility of species [27] and the cation adsorption properties of hydrous surfaces [28,29]. Interactions between the glass and the initial groundwater effect the $I_{[t]}$ and the pH of the final leachate. Since the $I_{[t]}$ and the pH of the leachates are functions of the precipitation reactions, inclusion of the experimentally determined solution pH in the $G_{hyd}$ calculation provides for the functional dependence of the dissolution rate on the precipitation [1].

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 relation 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 [1].

In summary, superposition of the linear equation for glass durability in groundwaters and deionized water experiments occurs because of the inclusion of the experimentally determined solution pH in the free energy of hydration model. Since the final $I_{[t]}$ and the pH of the leachates are functions of the precipitation reactions, inclusion of the final solution pH in the free energy model provides the functional dependence of the dissolution rate on the secondary precipitation.

Therefore, the hydration free energy model

- can be used to compare glass durability in deionized water and in repository groundwaters.
- mechanistically accounts for the observed suppression of glass dissolution in saturated groundwater tests [30,31].

## ACKNOWLEDGEMENT

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# Application of the Hydration Thermodynamic Model for Glass Durability Under Saturated Tuff Repository Conditions

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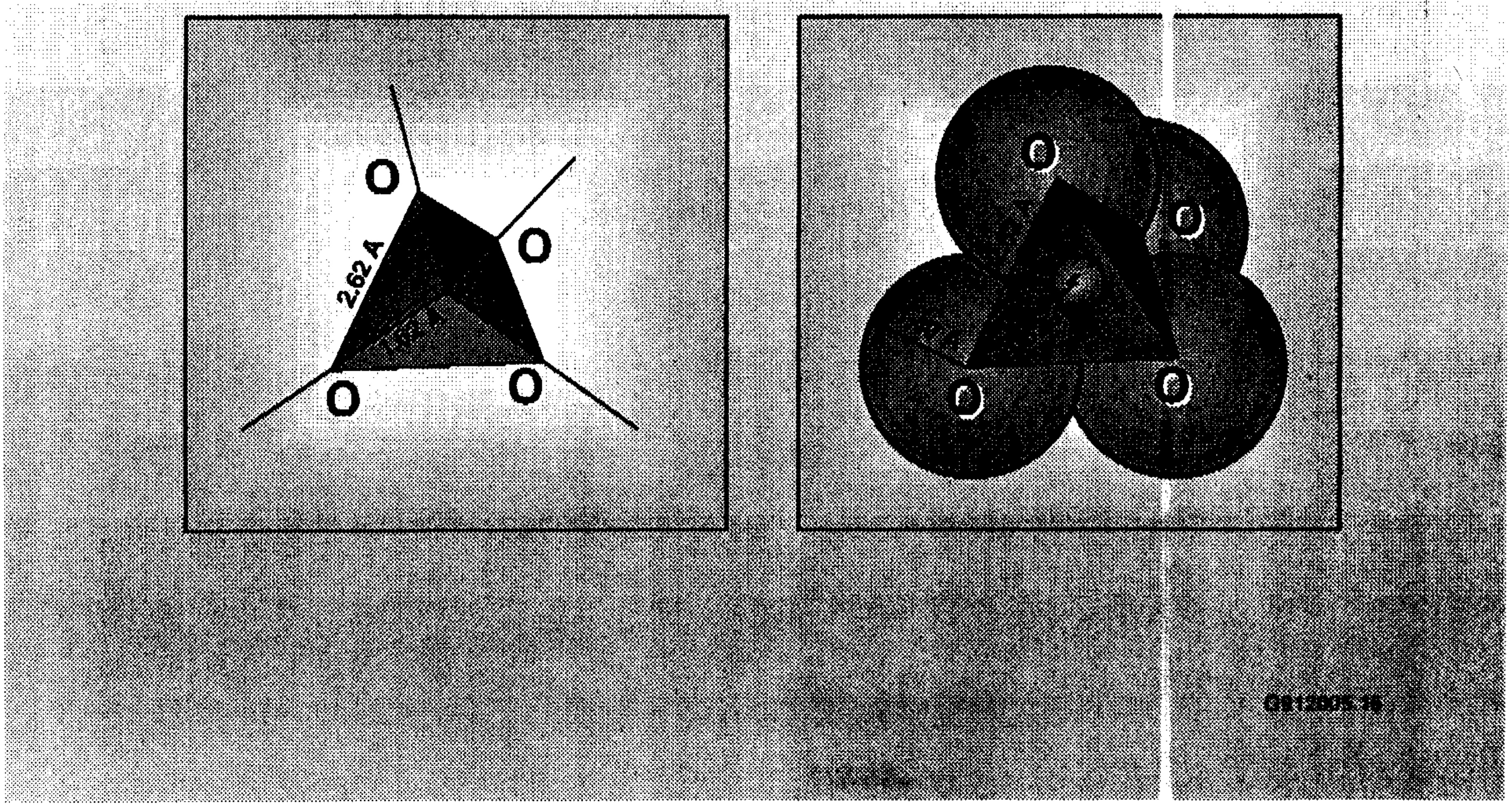
# Objectives

The Effects of the Following On Glass Durability:

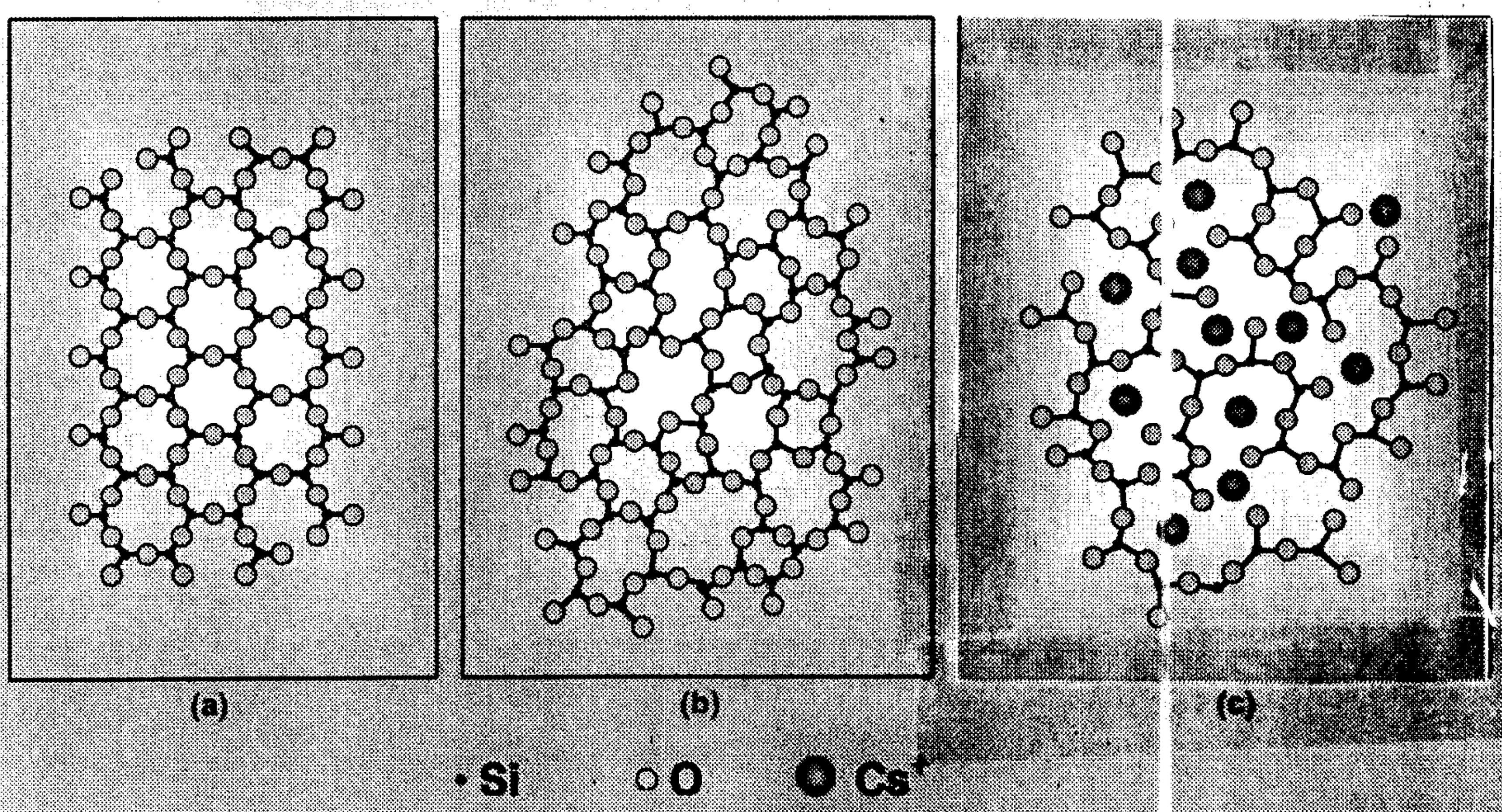
- Glass Composition and Solution pH
- Groundwater Composition and Ionic Strength
- "Back Reaction" Precipitation

3

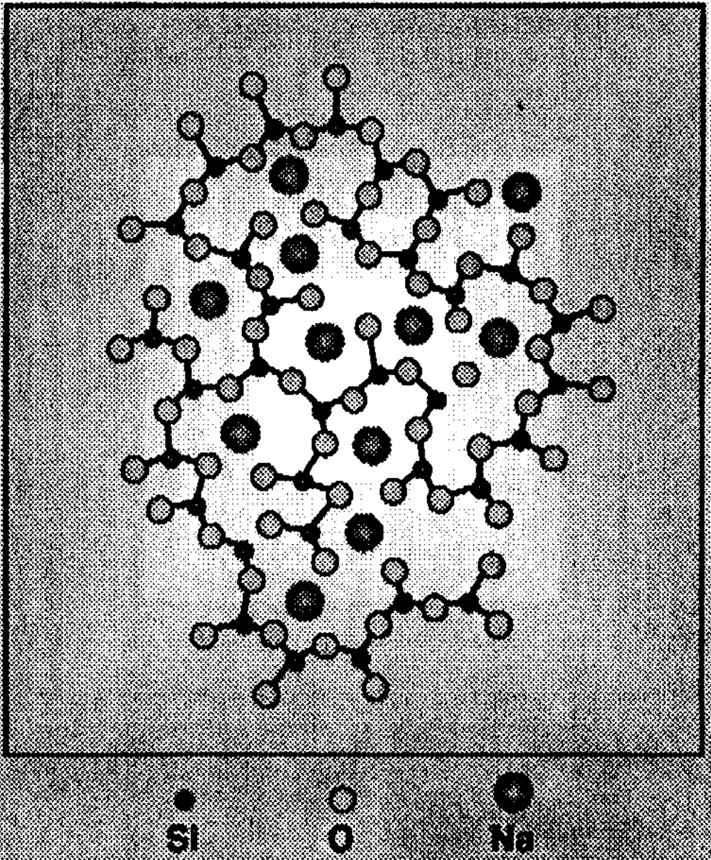


3

# Glass Polymerization



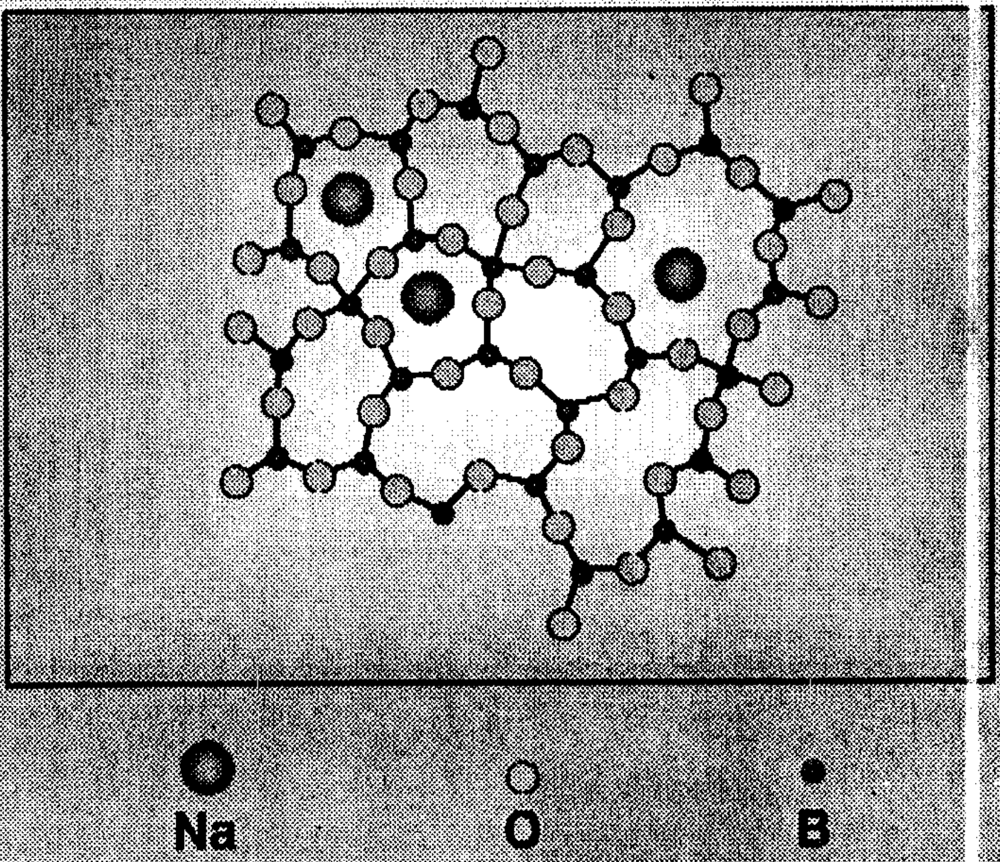
# Schematic Representation of the Structure of Soda-Silica Glass (In Two Dimensions)



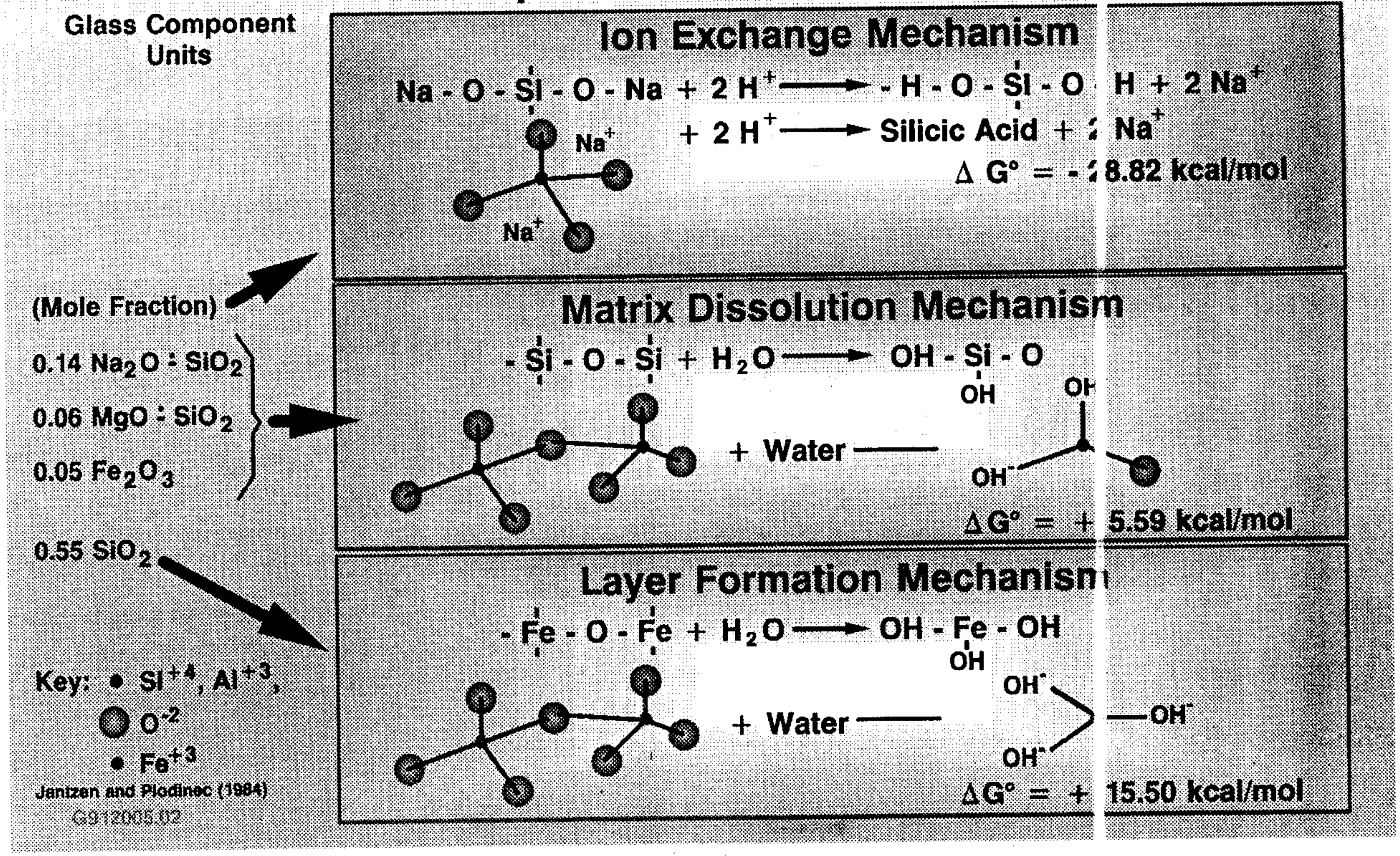
G912005.18

5

# Schematic Representation of the Structure of a Soda-Boric Oxide Glass of Low Soda Content (In Two Dimensions)



# Free Energy of Hydration for a Simple Glass Composition



Glass Component Units

(Mole Fraction)

0.14 $Na_2O : SiO_2$

0.06 $MgO : SiO_2$

0.05 $Fe_2O_3$

0.55 $SiO_2$

Key: ● $Si^{+4}$, $Al^{+3}$, ● $O^{-2}$ ● $Fe^{+3}$

Jantzen and Plodinec (1984)

G912005.02

## Ion Exchange Mechanism

Na - O - Si - O - Na + 2 $H^+$ ⟶ - H - O - Si - O - H + 2 $Na^+$

+ 2 $H^+$ ⟶ Silicic Acid + 2 $Na^+$

Δ G° = - 28.82 kcal/mol

## Matrix Dissolution Mechanism

- Si - O - Si + $H_2O$ ⟶ OH - Si - O

OH

+ Water ——

Δ G° = + 5.59 kcal/mol

## Layer Formation Mechanism

- Fe - O - Fe + $H_2O$ ⟶ OH - Fe - OH

OH

+ Water ——

ΔG° = + 15.50 kcal/mol

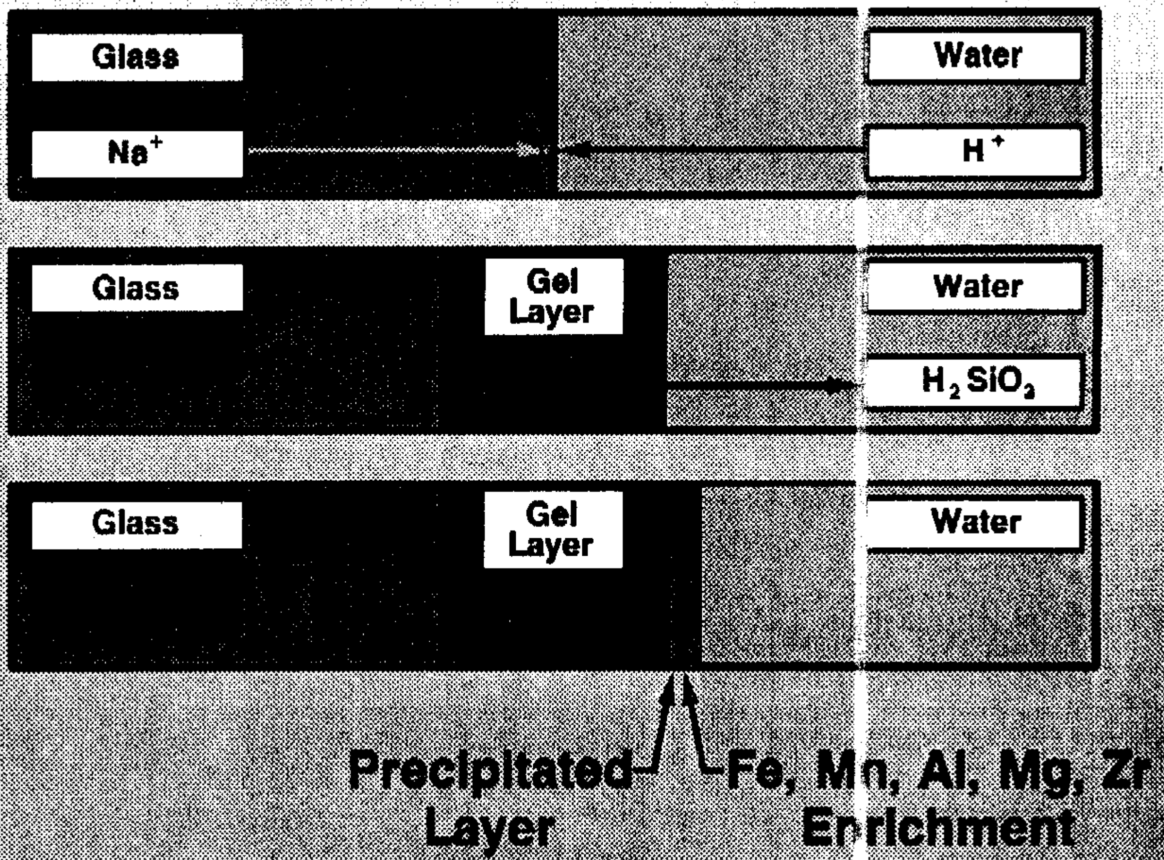
# After Newton and Paul (1980)

Table 1. Calculation of the Free Energy of Hydration of a Glass

| Compound | ΔG° | ΔG° Per Mole of Glass |
|---|---|---|
| $Na_2O \cdot SiO_2$ | - 28.815 | 0·14 X - 28.815 = - 4.034 |
| $MgO \cdot SiO_2$ | - 13.888 | 0·06 X - 13.888 = - 0.833 |
| $Fe_2O_3$ | + 15.50 | 0·05 X + 15.50 = + 0.775 |
| $SiO_2$ | + 5.590 | 0·55 X + 5.590 = + 3.075 |
| | | Total, R = - 1.017 Kcal/mole |

G912005.04

# Glass Corrosion Mechanism



**Ion Exchange**

**Matrix Dissolution**

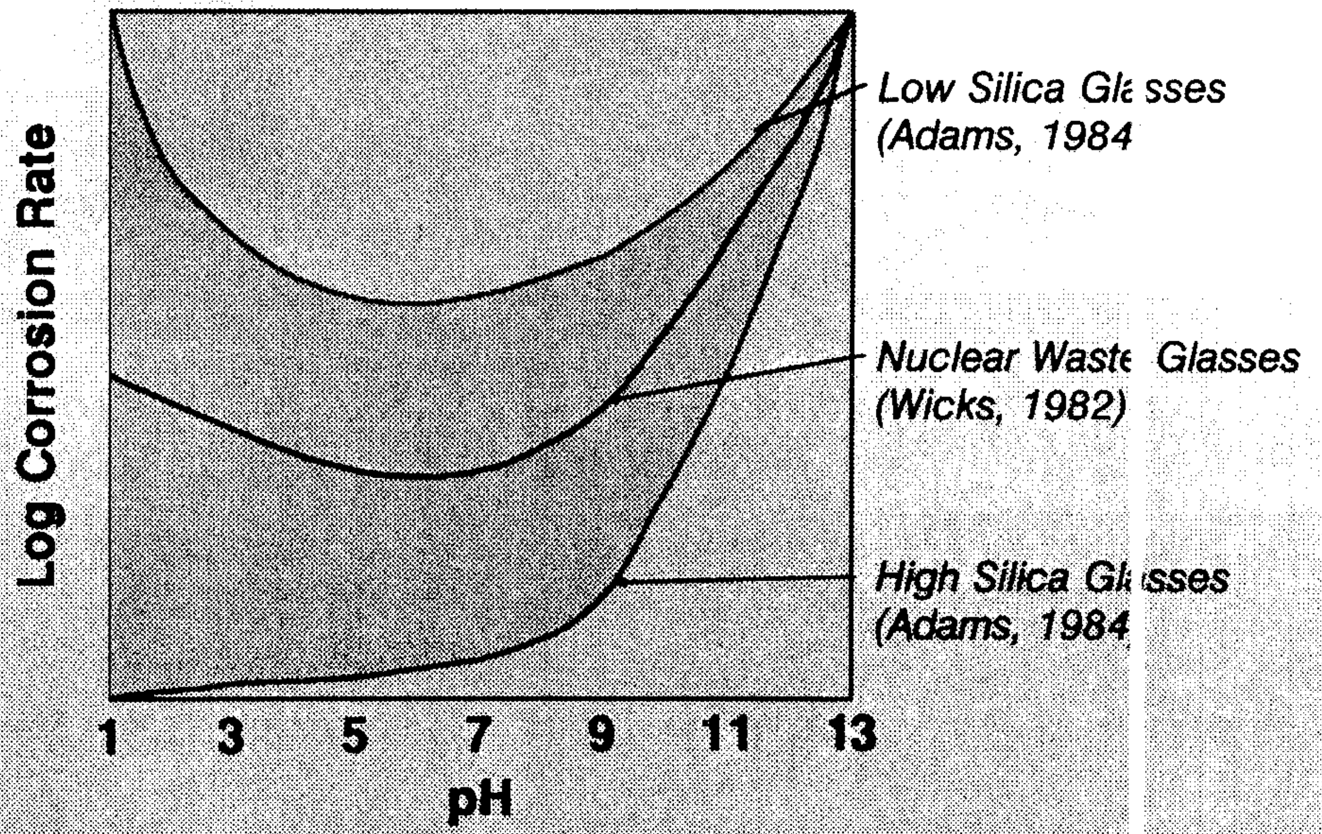
**Protective Layer Formation**

Jantzen and Plodinec (1984)

G912608.03

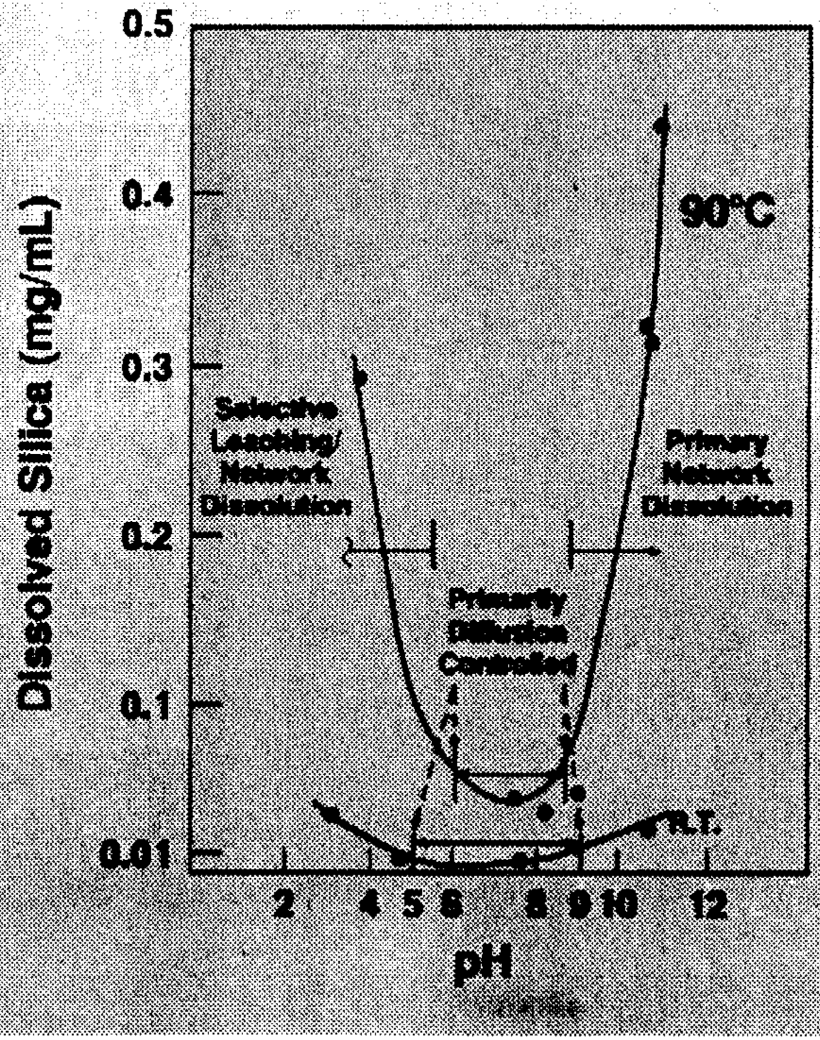
# Dominant Leaching Mechanism

| Dominant Reaction | Alkali/Silica | Silica | pH |
|---|---|---|---|
| Ion Exchange | Low | High | <9-10 |
| Combination | High | Low | <9-10 |
| Matrix Dissolution | Very High | Low | >9-10 |


Log Corrosion Rate
1
3
5
7
9
11
13
pH
Low Silica Gl sses
(Adams, 1984
Nuclear Waste Glasses
(Wicks, 1982)
High Silica Gl sses
(Adams, 1984

G912005.01

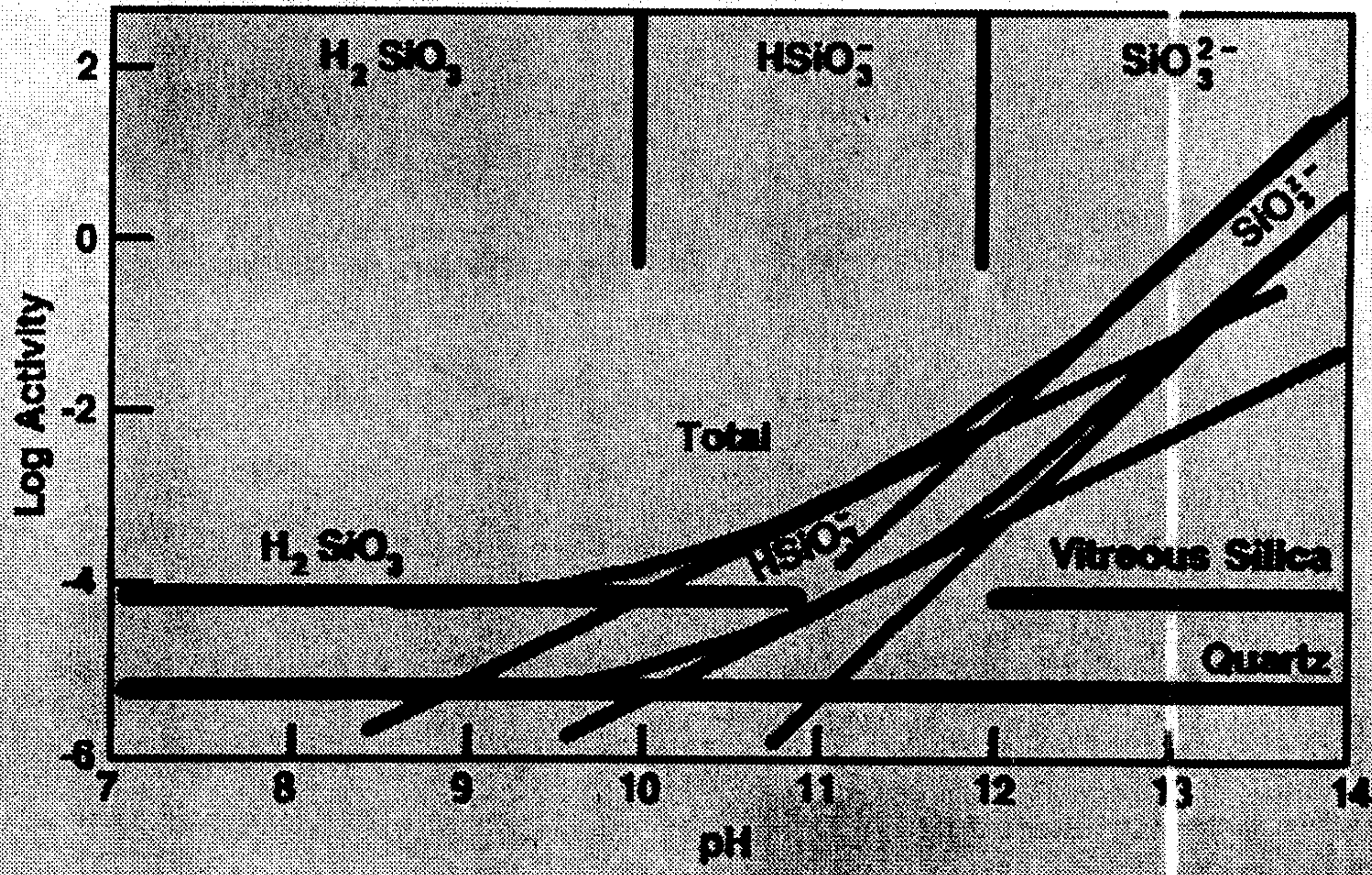
# Effect of pH on Leaching of SRS Waste Glass



Wicks, et al–1982

G912005.11

# Stability Diagram of Quartz and Vitreous Silica In Aqueous Solution at 25°C



G912005.20

$$H_2SiO_3 \rightleftharpoons HSiO_3^{-} + H^{+}$$

$$H_2SiO_3 \rightleftharpoons SiO_3^{=} + 2H^{+}$$

$$\Delta(\Delta G\ \text{hydration}) = 1.364\ \left[-\log\left(1 + \frac{10^{-10.00}}{10^{-pH}} + -\frac{10^{-21.994}}{10^{-2pH}}\right)\right]$$

15

|  | SiO2 | Obsidian | Basalt | 165 BF | ESF 149 | ESF 151 | 131 Stage 1 | Frit 131 |
|---|---|---|---|---|---|---|---|---|
| $Al_2O_3$ | 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 |  |
| $Fe_2O_3$ |  |  |  | 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 | 2.696 |  |
| $Na_2O$ | 0.032 | 1.434 | 2.664 | 11.011 | 0.101 | 5.005 | 13.980 | 17.700 |
| $Li_2O$ |  |  |  | 5.005 |  |  | 4.218 | 5.700 |
| NiO | 0.085 |  | 0.146 | 0.901 |  |  | 1.008 |  |
| $SiO_2$ | 96.647 | 73.175 | 51.302 | 55.055 | 57.403 | 56.050 | 45.942 | 57.900 |
| $Cr_2O_3$ | 0.066 | 0.000 | 0.025 |  |  |  |  |  |
| $B_2O_3$ | 0.796 | 0.032 | 0.044 | 7.207 |  |  | 10.884 | 14.700 |
| SrO | 0.006 |  | 0.039 |  |  |  | 0.051 |  |
| $ZrO_2$ | 0.003 | 0.054 | 0.024 | 0.701 |  |  | 0.370 | 0.500 |
| $TiO_2$ | 0.008 | 0.862 | 2.333 |  | 0.202 | 0.200 | 2.078 | 1.000 |
| $K_2O$ |  | 5.043 | 0.482 |  | 14.452 | 7.207 |  |  |
| $Cs_2O$ |  |  |  |  |  |  | 0.062 |  |
| $P_2O_5$ | 0.030 | 0.091 | 0.504 |  |  | 3.904 |  |  |
| $La_2O_3$ |  |  |  |  |  |  | 0.370 | 0.500 |
| BaO |  | 0.044 |  |  |  |  |  |  |
| PbO | 0.047 |  |  |  |  | 0.711 |  |  |
| SUM | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

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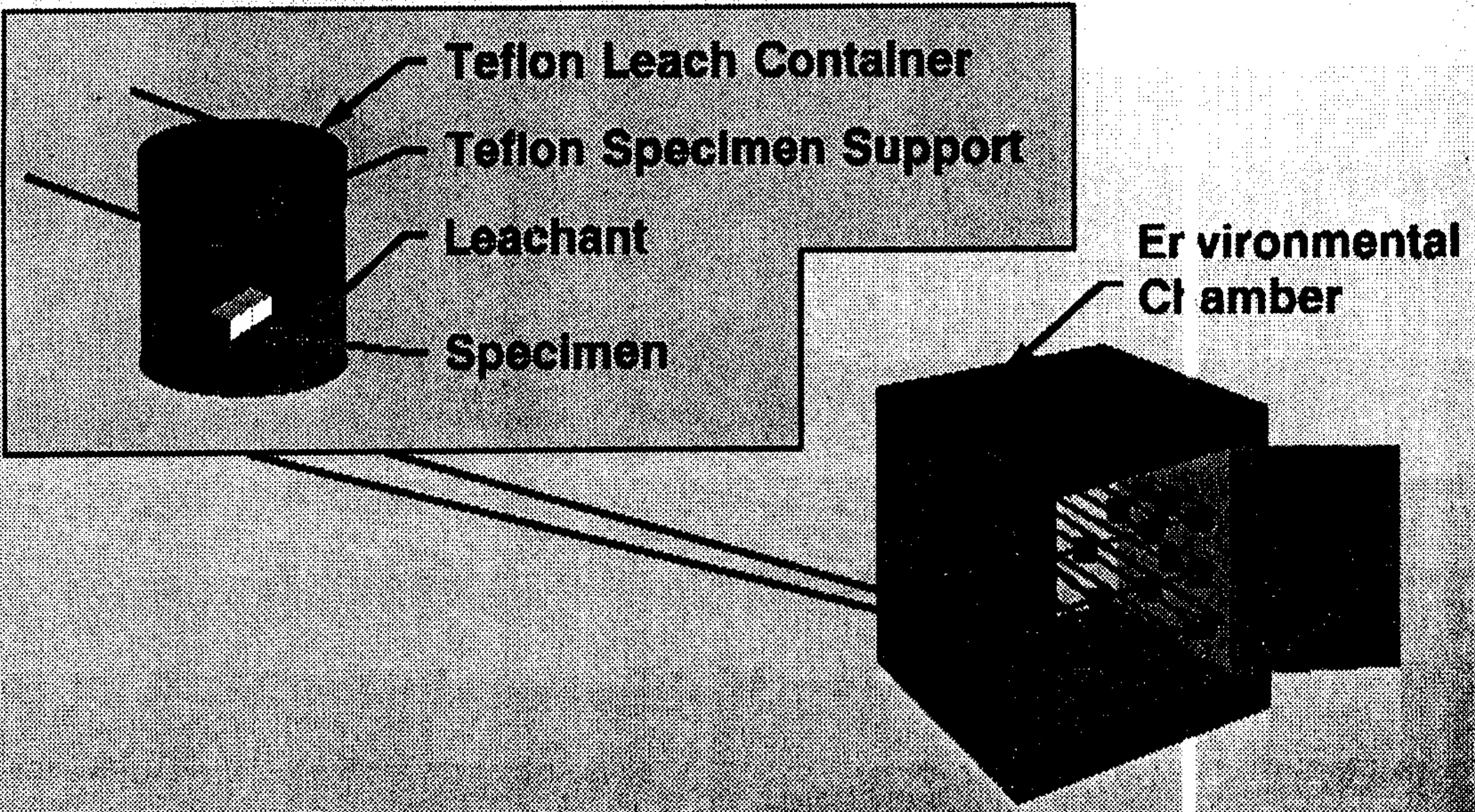
# Materials Characterization Center (MCC)
# Leach Test Description



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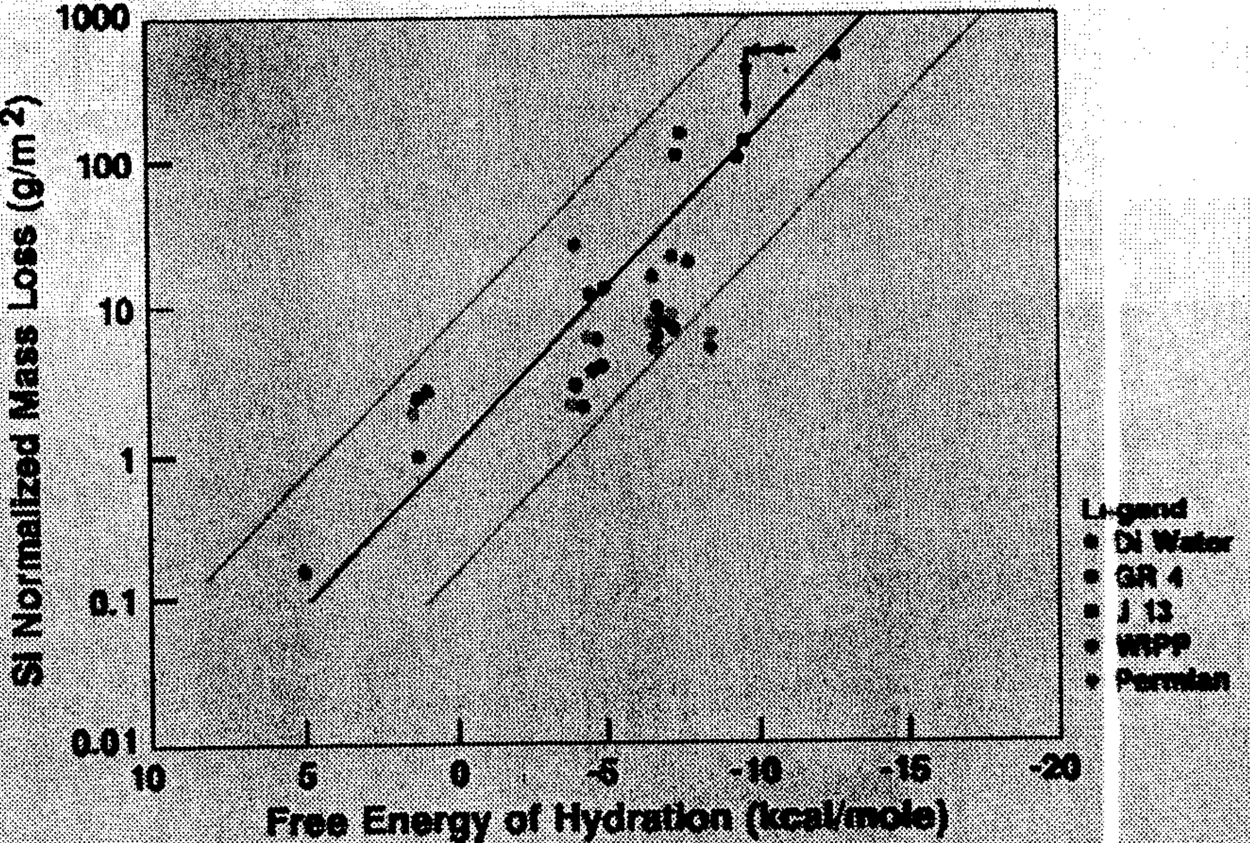
# Free Energy of Hydration for Di Water and Various Groundwaters (MCC-1)



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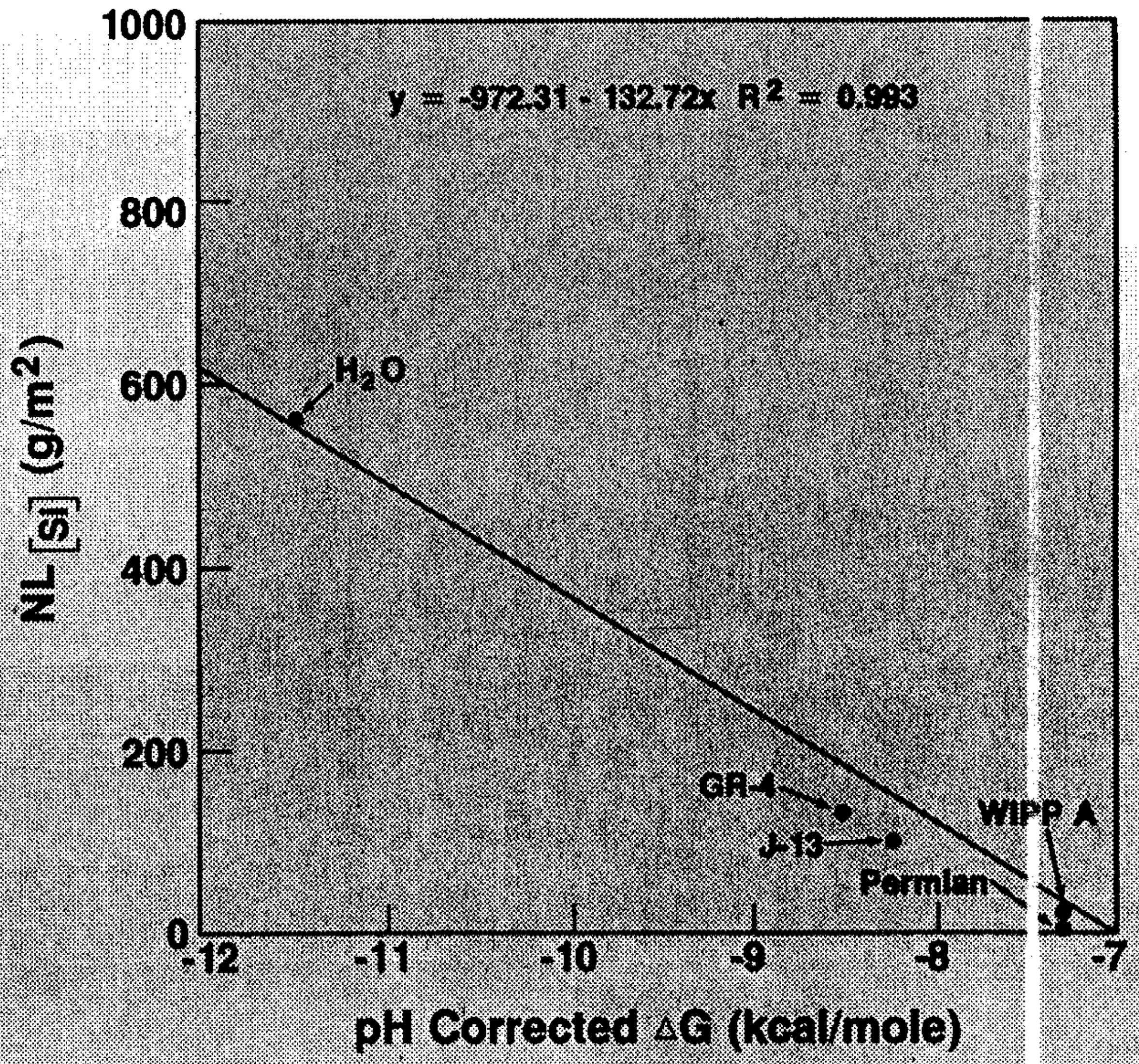
y = -972.31 - 132.72x R 2 = 0.993
1000
800
600
400
200
0
NL [Si] (g/m2)
-12
-11
-10
-9
-8
-7
pH Corrected ΔG (kcal/mole)
H2O
GR-4
J-13
Permian
WIPP A

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# Objectives

The Effects of the Following On Glass Durability:

- Glass Composition and Solution pH
- Groundwater Composition and Ionic Strength
- "Back Reaction" Precipitation

# Total Ionic Strength $I_{[t]}$

$$I_{[t]} = 0.5 \sum C_i Z_i^2$$

$C_i$ = Ion Concentration (molal)

$Z_i$ = Ion Valence

## Groundwater Composition (Molal)

|  | GR-4 | J-13 | WIPP-A | PBB-3 |
|---|---|---|---|---|
| Li |  | 7.2 E-06 | 3.0 E-03 |  |
| Na | 1.45 E-02 | 1.9 E-03 | 1.82 | 1.44 |
| K | 3.3 E-04 | 1.3 E-04 | 0.76 | 0.36 |
| Rb |  |  | 2.34 E-04 |  |
| Cs |  |  | 8.0 E-06 |  |
| Mg | 1.6 E-06 | 7.8 E-05 | 1.43 | 2.63 |
| Ca | 5.5 E-05 | 3.0 E-04 | 1.5 E-02 | 0.55 |
| 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 | 5.35 | 7.78 |
| Bromide |  |  | 5.0 E-03 | 5.36 E-02 |
| Iodide |  |  | 7.9 E-05 |  |
| Carbonate | 4.2 E-04 |  |  |  |
| Biocarbonate | 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 |
| Nitrate |  | 1.5 E-04 |  |  |
| pH | 9.7 | 7.4 | 6.6 | 6.3 |
| $I_{[t]} = 0.5\sum CiZi^2$ | 0.031 | 0.023 | 6.98 | 11.29 |

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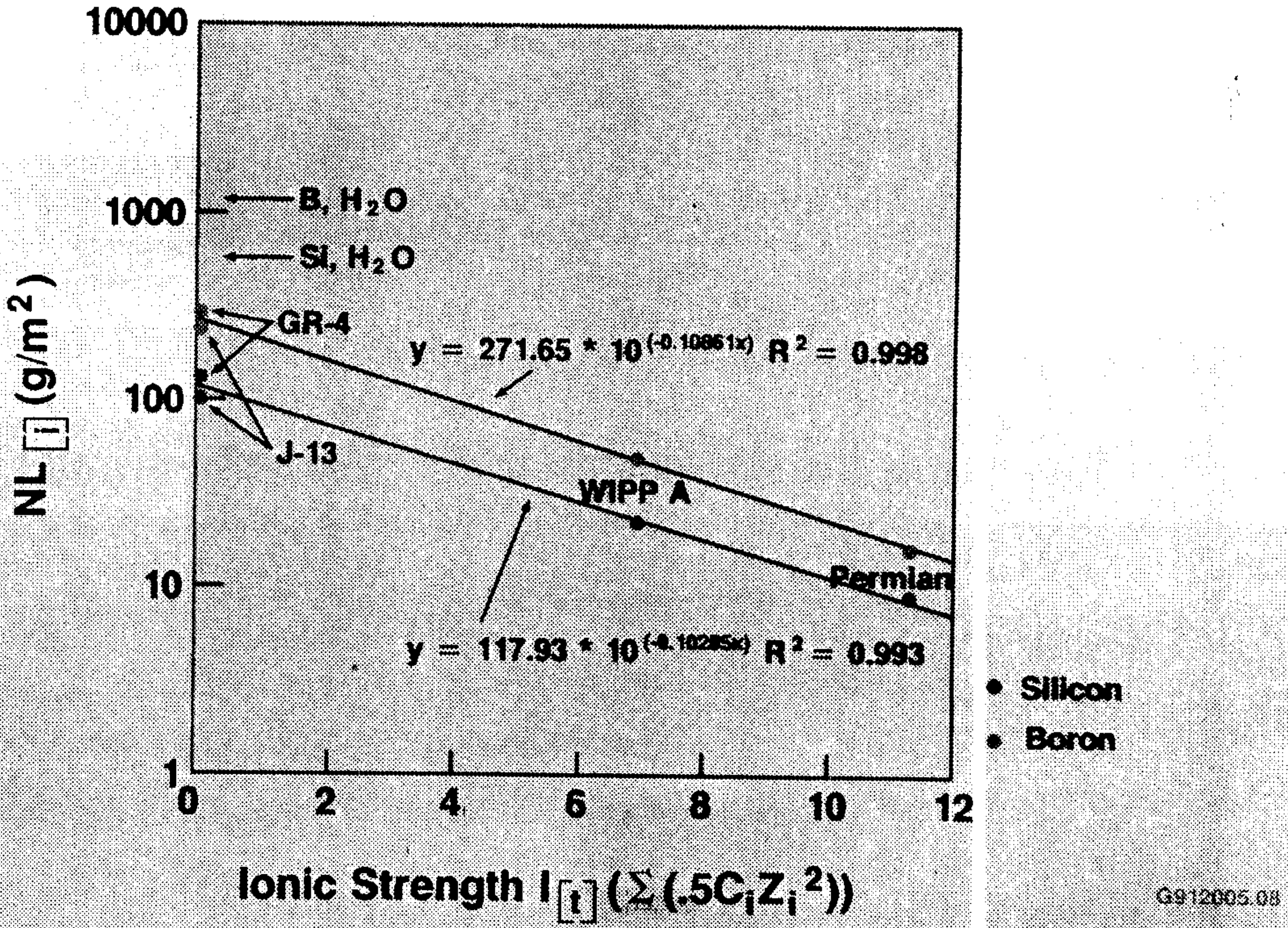
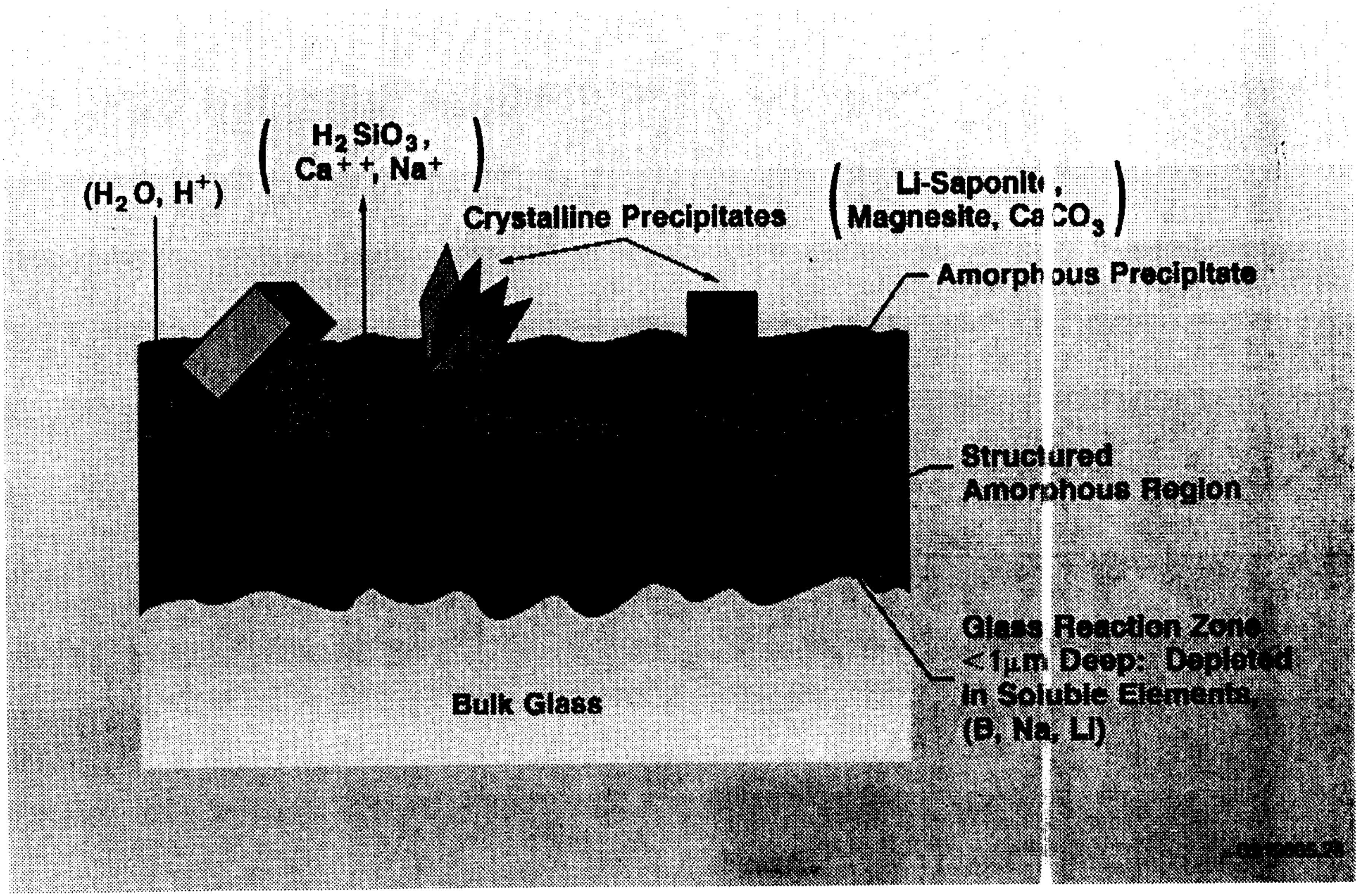

NL [i] (g/m²)
10000
1000
100
10
1
0
2
4
6
8
10
12
Ionic Strength I [t] (Σ(.5CᵢZᵢ²))
B, H₂O
Si, H₂O
GR-4
J-13
y = 271.65 * 10^(-0.10861x) R² = 0.998
y = 117.93 * 10^(-0.10285x) R² = 0.993
WIPP A
Permian
● Silicon
● Boron
G912005.08

# Objectives

The Effects of the Following On Glass Durability:

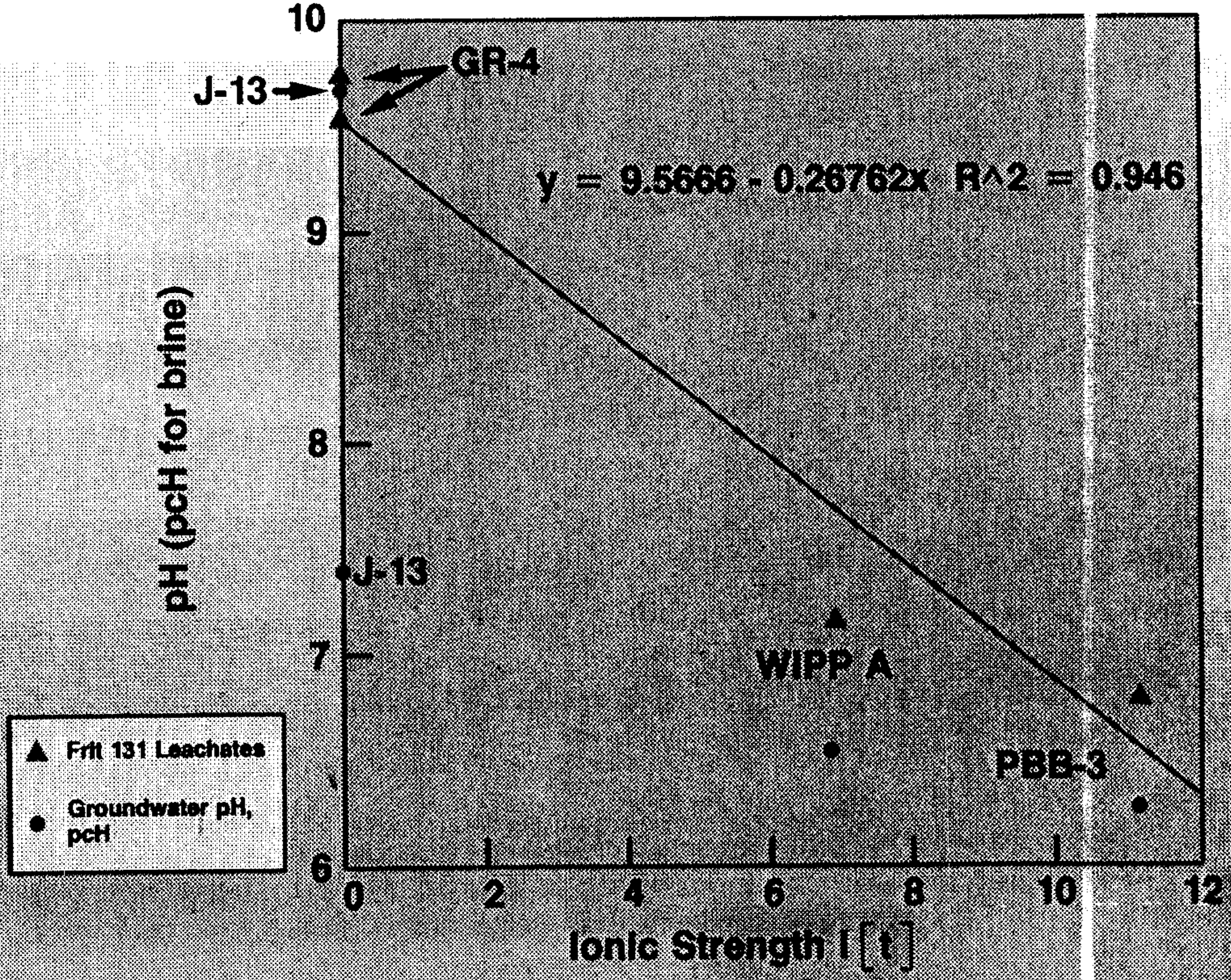
- Glass Composition and Solution pH
- Groundwater Composition and Ionic Strength
- "Back Reaction" Precipitation


($H_2O$, $H^+$)
($H_2SiO_3$, $Ca^{++}$, $Na^+$)
Crystalline Precipitates
(Li-Saponite, Magnesite, $CaCO_3$)
Amorphous Precipitate
Structured Amorphous Region
Glass Reaction Zone <1µm Deep: Depleted in Soluble Elements, (B, Na, Li)
Bulk Glass

| Glass | GR-4 Groundwater<br>XRD | <br>SEM | J-13 Groundwater<br>XRD | <br>SEM |
|---|---|---|---|---|
| ESF 151 | Alpha KOH<br>$CaCO_3$<br>$Na_3Ca_6(PO_4)_5$ | $CaCO_3$ with Mg | Alpha KOH<br>$CaCO_3$<br>$Na_3Ca_6(PO_4)_5$ | Ca O$_3$ with Mg<br>an Mn |
| ESF 149 | $CaCO_3$ | $CaCO_3$ with Mn | $CaCO_3$ | Ca O$_3$ with Mn<br>Mg Al, Si Clay |
| Frit 131 | Hectorite* | Enriched in Ca, Mg, and Ti | Hectorite* | En ched in Ca,<br>Mg and La |
| SRS 131 | Hectorite* | Enriched in Ca, Fe, and Al | Hectorite* | En ched in Ca,<br>an Mg |
| SRS 165 | Hectorite* | Enriched in Ca, Fe, and Al | Hectorite* | En ched in Ca,<br>Mg and Al |
| Basalt | Saponite (Ca Smectite) | | Saponite (Ca Smectite) | |
| Obsidian | Minor Spinel | Spinel<br>No Surface | Minor Spinel | Sp nel<br>No Surface |
| $SiO_2$ | Amorphous | No Surface | Amorphous | No Surface |

*Li Saponite of the Smectite Family
$LixMg_3$-$xSi_4 0_2 0$ $(OH)_4$ · $xNa+$

76 26


10
9
8
7
6
0
2
4
6
8
10
12
pH (pcH for brine)
Ionic Strength I [t]
J-13
GR-4
J-13
y = 9.5666 - 0.26762x R^2 = 0.946
WIPP A
PBB-3
▲ Frit 131 Leachates
● Groundwater pH, pcH

# Conclusions

- The Thermodynamic Approach Models the Suppression of Glass Dissolution In Repository Groundwaters
- Interactions Between the Ionic Strength of the Solution and Precipitation Reactions Buffer the pH
- Waste Glass Durability In Saturated Repository Environments can be Predicted from Glass Composition and Repository pH

G912005.09