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AN APPROACH TO THE PREDICTION OF WASTE-FORM STABILITY

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AN APPROACH TO THE PREDICTION OF WASTE-FORM STABILITY

ABSTRACT

Calculated activity diagrams, commonly used to interpret natural groundwater systems, are suggested as an aid in predicting the long-term stability of aluminosilicate types of nuclear waste forms. Possible storage sites can be characterized in terms mineral-fluid equilibria. Weathering reactions of given waste forms can then be estimated for a particular site. Chemical thermodynamic calculations of hypothetical solubility reactions of crystalline feldspars and glass of the same composition suggest that glass forms are about seven orders of magnitude less stable than crystalline forms in a groundwater environment.

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INTRODUCTION

A future nuclear-waste management concern at Hanford is the ultimate disposition of high-level alkaline waste liquors. The liquors consist of sodium nitrates, nitrites, carbonates, phosphates, and in some cases aluminates, in a high caustic (~4 to 5 molar NaOH) solution⁽¹⁾. Radionuclides of primary importance are ^{137}Cs , ^{90}Sr , and actinides. The high salt liquids with coexisting salt cakes are contained in underground storage tanks. The waste liquors are being converted to salt cake by an evaporation-crystallization process, but the salt cake contains interstitial liquor as well as deliquescent solids⁽²⁾. Even though most of the ^{137}Cs and ^{90}Sr is separated, the salt cake product is an interim storage form and as yet no ultimate disposal alternative has been selected. A number of possibilities for ultimate disposal have been conceived and are discussed elsewhere^(3,4,5).

Some of the longer-term waste management alternatives involve the use of a solidified, radionuclide-containing waste product in the form of an aluminosilicate glass or crystalline phase⁽³⁾. The aluminosilicate material may be made with either salt liquor or cakes containing radionuclides⁽¹⁾. If technical and economic problems involved with separation of radionuclides, including possible actinides, from large volumes (millions of gallons) of high salt-high caustic wastes are achieved, the aluminosilicate form will incorporate the separated radionuclides with a consequent reduction in bulk volume.

The radionuclide-containing product, whether aluminosilicate or other form, must be compatible (i.e., in equilibrium with) the environment of its final disposition site, or be capable of achieving equilibrium without mobilizing long-lived radionuclides. Thus, decisions regarding the optimum waste forms will be more logically developed if methods are available to predict their long-term stability with a reasonable degree of confidence. This report outlines a procedure, using both thermodynamic and geological arguments, which could be applied to such predictions. The thermodynamic data used in subsequent calculations are listed in Table I. Although the selection of subsurface sites is implied, it is recognized that they are not the only choice. The arguments presented here are equally applicable to surface sites.

TABLE I
STANDARD FREE ENERGIES OF FORMATION USED IN THIS REPORT

<u>Species</u>	<u>ΔG°_f, Kcal/mole @ 25°C</u>	<u>Ref.</u>
Al^{3+} (aq)	-116.000	14
$Al(OH)^{2+}$ (aq)	-165.930	14
$Al(OH)_2^+$ (aq)	-216.604	15
$Al(OH)_4^-$ (aq)	-310.200	14
AlO_2^- (aq)	-200.7	16
$Al(OH)_3$ (amorphous)	-271.9	16
$Al(OH)_3$ (cryptoxline)	-273.474	17
$Al(OH)_3$ (Gibbsite)	-274.160	14
$Al(OH)_3$ (Bayerite)	-273.670	14
$AlO(OH)_2$ (Diaspore)	-219.050	14
$AlO(OH)_2$ (Boehmite)	-216.850	14
$Al_2Si_2O_5(OH)_4$ (Kaolinite)	-903.430	14
$Al_2Si_2O_5(OH)_4$ (Halloysite)	-898.419	18
H^+ (aq, m = 1)	0	--
OH^- (aq, m = 1)	- 37.594	18
H_2O (e)	- 56.688	18
H_4SiO_4 (aq, m = 1)	-312.560	14
SiO_2 (Quartz)	-204.646	14
SiO_2 (amorphous)	-202.800	14
Na^+ (m = 1)	- 62.539	18
K^+ (m = 1)	- 67.700	18
Ca^{++}	-132.180	18
$NaAlSi_2O_6 \cdot H_2O$ (Analcite)	-737.055	27
$NaAlSi_3O_8$ (Albite)	-883.988	18
$NaAlSi_3O_8$ (Glass)	-873.252	18
$KAlSi_3O_8$ (Microcline)	-892.817	18
$KAlSi_3O_8$ (Glass)	-883.051	18
$CaAl_2Si_2O_8$ (Anorthite)	-955.626	18
$Na_{33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$ (NaMontmorillonite)	-1,277.732	17

Site Characterization as a Natural System

An initial step in determining a suitable waste form for a specific disposal site is to understand the geological, hydrological, and chemical (including mineralogical) properties of the site. This has been recognized at Hanford where several ongoing programs are aimed at evaluating the first two properties. Additional, but limited, work has also been done on groundwater chemistry and mineralogical properties, but these have not yet been applied in detail to the waste form stability question. It seems appropriate, therefore, to outline some of the pertinent relationships.

Chemical Equilibrium in Aquifers

In general, a given aquifer system with a relatively low flow rate can be assumed to approach a state of dynamic chemical equilibrium where the solute species are approximately in solution equilibrium with the mineral assemblage in the aquifer. An aquifer can be thought of as a natural water-bearing geologic formation. This assumption has proven feasible by several workers^(6,7,8) for both argillaceous and carbonate aquifers. Even if departures from equilibrium (ΔG_R) exist, a base for predicting reactions is available by observation of reactions involving primary and secondary aquifer minerals as pointed out by Barnes⁽⁹⁾.

Assessment of the state of an aquifer system requires reliable analytical data for the major cations and anions plus pH (field), temperature, and alkalinity. Total dissolved solids (TDS) determinations are useful as a check on the cation-anion balance. The oxidation potential (e_h) can be determined directly, or a close estimate can be calculated, from a determination of Fe^{+2}/Fe^{+3} ratios. In addition, a sample of the aquifer mineral assemblage should be taken and examined for primary, secondary, and opaque minerals. Several computer programs are available for calculating activities of the dissolved chemical species including many of the known chemical complexes^(17,18,19). These activities can be used to estimate the degree of saturation of the system on a thermodynamic foundation by calculating a function such as

$$\Delta G_R = RT \ln IAP/K$$

for specific minerals (where IAP refers to ion activity product and K to the usual equilibrium constant). Enough thermochemical data now exist in the literature so that reasonable estimates of saturation with respect to a wide variety of minerals can be made; ΔG_R values yield possible reactions, but the reaction processes, such as precipitation, must be demonstrated by experiment or observations (e.g., joint or vesicle fillings). A further consideration in the overall assessment is the influence of intensive variables to the system. These may include seasonal temperature fluctuation, bacterial sulfate reduction, CO_2 fluctuations, and osmotic effects across aquitards^(10,11). In deep aquifers, differences between lithostatic and hydrostatic pressure could conceivably affect

mineral-fluid reactions. Fortunately, for practical purposes, or as a first approximation in many aquifers, the pressure and membrane effects can be ignored because they are relatively small. It is commonly observed that calcium carbonates and sulfate are likely to precipitate in many aquifers partly because calcium, carbon dioxide, and sulfur are widespread components in nature. In alkaline waters in contact with volcanic glass, a good precipitation possibility may be zeolites. Even gel formation can sometimes be predicted by appropriate selection of super-saturation parameters⁽⁹⁾.

Disequilibrium in Natural Systems

The preceding discussion assumes near-equilibrium conditions in relatively undisturbed natural groundwater systems. In general, the dominant chemical control on the fluid phase is exerted by the major minerals in the aquifer and may resemble a buffer system.

In some instances, the natural system may deviate from equilibrium, then mass transfer models are required to make a reasonable evaluation. The driving force for mass transfer is, of course, the chemical potential gradient of the species involved and the magnitude of the gradient depends on how far the system is out of equilibrium. Some possible situations leading to such a deviation include introduction of foreign fluids or solids, changes in CO₂ concentration, biological activity, or exposure of new mineral phases. Adjustments of the system toward equilibrium could occur in a number of ways, including precipitation of either new or existing mineral phases, or the solution of one or more existing phases. This adjustment would almost certainly affect bulk ion exchange properties and hydrologic properties such as permeability.

Mass action models such as those developed by Helgeson, et al.,⁽²⁰⁾ and applied by Norton⁽²¹⁾, or mass transfer and deposition calculations such as those developed by Anderson⁽²²⁾ can be used to estimate the magnitude of these adjustments. Because of the buffering effect mentioned above, and the fact that usually the total volume of the aquifer system is large compared to foreign inputs, solution of solid foreign material would probably be undetectable except locally. Because of the potentially hazardous nature of even slight solution or leaching of nuclear waste solids, generation of disequilibrium condition resulting from input of these materials would assume considerable importance. Even though laboratory leaching and solution studies are carried out on nuclear waste forms, an assessment of aquifer conditions is required to predict their stability. After the aquifer conditions are known, the following outline can be used as a guide for selecting the waste form that is most compatible with the existing mineral assemblages and fluid compositions.

Construction of Activity Diagrams

The calculation of activity diagrams and their interpretation is discussed in detail elsewhere^(14,6,24) so only a brief outline will be presented here. The initial assumption is that mineral-fluid equilibrium has validity. In natural sedimentary formations, observation indicates that usually only about four or five mineral phases at most are present in major amounts and their reaction with water determines the fluid phase composition. As an example, consider the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. The activity diagram at 1 atmosphere, 25°C , for this system is shown in Figure 1 in terms of Na^+/H^+ activity ratio versus H_4SiO_4 . Figure 1 represents a recalculated version of previous diagrams for this system⁽¹⁴⁾ using more recent thermodynamic data for analcite⁽²⁵⁾ and assumes that alumina is a fixed component. The system was selected because albite ($\text{NaAlSi}_3\text{O}_8$) is similar to a strontium feldspar and analcite ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) is an end member of an apparent solid solution series with pollucite ($\text{CsAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$). Both pollucite and strontium feldspar are possible nuclear waste forms⁽³⁾. The initial step in calculating such a diagram is to use field observations of mineral assemblage compatibility⁽⁶⁾. For example, albite and gibbsite almost never occur together while kaolinite and montmorillonite are fairly common. A series of reactions involving mineral pairs then can be written in terms of solute concentrations. Application of the phase rule at fixed pressure and temperature indicates that such pairs are univariant under these conditions⁽⁶⁾ so that the reaction defines a stability boundary. As an illustration, consider the pair analcite-gibbsite. The reaction is:

The equilibrium constant for this reaction

$$K_1 = \frac{[\text{Na}^+] [\text{H}_4\text{SiO}_4]^2}{[\text{H}^+]} = 10^{-1.45}$$

where K_1 is calculated from $\Delta G_R^\circ = 2.303RT \log K_1$, with free energy data from Table I.

Taking logarithms of both sides and rearranging, the result is:

$$\log K_1 = -1.45 = \log [\text{Na}^+]/[\text{H}^+] + 2 \log [\text{H}_4\text{SiO}_4] \quad (1A)$$

Which can be plotted on Figure 1 by either substituting arbitrary values for the solutes as two points or using one point and the slope of (1A). The remaining equations used in Figure 1, calculated in a similar manner, are shown below:

FIGURE 1. ACTIVITY DIAGRAM OF THE SYSTEM $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ AT 25°C ASSUMING FIXED ALUMINUM. SMALL CIRCLES REPRESENT HANFORD DEEP-WELL WATER ANALYSES

Analcite-Kaolinite Analcite-NaMontmorillonite Gibbsite-Kaolinite NaMontmorillonite-Kaolinite Albite-NaMontmorillonite Analcite-Albite

As an interpretation of Figure 1, as well as partial support for the assumption of equilibrium, consider an aquifer system composed of clay minerals and quartz such as mudstone or siltstone. Figure 1 implies that waters in equilibrium with these rocks should have a composition along with the kaolinite-montmorillonite boundary. Hess(6) has plotted some data of this sort which are shown as the area labeled groundwater analyses.

Even if both phases were present, a linear distribution of solute species along the kaolinite-montmorillonite line would not be expected. Among the reasons are that pure mineral phases and unit activities were used in the calculations. Actual mineral composition must be known in order to correct the activities of solid phases.

The small open circles represent a similar plot of water analyses from deep wells (364 to 4283 feet) at Hanford. At this depth, the major minerals are plagioclase feldspar and volcanic glass in basalt with montmorillonite in joints and cavities along with either calcite or zeolites as vesicle fillings. As shown in Figure 1, the data lie near the albite-montmorillonite-analcite triple point and suggest near saturation with silica, in good agreement with the observed mineral assemblage.

A further long-term implication is apparent if we consider the siltstone aquifer system and add albite. Figure 1 implies that albite will eventually be converted to clay minerals. The extent of cation mobility during this process would probably be complicated by ion exchange properties of the clays.

An example of the change in stability field of a given solid as a result of the addition of another solute is shown in Figure 2. These diagrams were taken from Hess⁽⁶⁾ who included K_2O in the system. Note the decrease in kaolinite stability and the introduction of new phases such as analcite as the Na/H ratio increases. This suggests that if waters rich in potassium are mixed with sodium-bearing water, analcite is likely to precipitate.

Aluminum and Weathering Processes

The previous discussion treated alumina as a fixed component, but several lines of reasoning suggest that some form of soluble alumina is involved with weathering processes^(23,26). Among these is that the conversion of feldspar, a framework silicate, to clay minerals, a sheet silicate weathering product, requires the breaking and reforming of silica and alumina tetrahedral groups. Consequently, some workers prefer to examine mineral stability in terms of mobile aluminum species⁽²⁷⁾. In an attempt to understand the initial weathering process, Wollast⁽²⁶⁾ investigated the kinetics of dissolution of potassium feldspar ($KAlSi_3O_8$). His data suggest that alkali ions are removed first, followed by the formation of a complex amorphous aluminum hydroxide coating through which silica must diffuse. At high flow rates, silica is removed leaving a hydrated alumina behind. At low flow rates, the hydrated alumina phase may conceivably react with silica to eventually form precursors of clay minerals.

A major problem in understanding the process concerns the form of aluminum in solution. This is still incompletely understood, but as a starting point, many workers consider the species Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$, and

$\log \text{Na}/\text{H} = 4$

$\log \text{Na}/\text{H} = 8.5$

FIGURE 2. ACTIVITY DIAGRAMS IN THE SYSTEM
 $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ AT $\log \text{Na}^+/\text{H} = 4$
 AND 8.5, AFTER HESS (8)

$\text{Al}(\text{OH})_4^-$. The stability of these forms in terms of hydrolysis reactions can be estimated from the data of Table I. The pH at which the ratios of pairs of these species is unity is shown below:

<u>Ratio</u>	<u>pH</u>
$\frac{\text{Al}(\text{OH})_2^+}{\text{Al}^{3+}}$	4.95
$\frac{\text{Al}(\text{OH})_2^+}{\text{Al}(\text{OH})_2^+}$	4.41
$\frac{\text{Al}(\text{OH})_2^+}{\text{Al}^{3+}}$	4.68
$\frac{\text{Al}(\text{OH})_4^-}{\text{Al}(\text{OH})_2^+}$	7.25

These data suggest that Al^{3+} is the dominant form of aluminum up to a pH of about 4.7; $\text{Al}(\text{OH})_2^+$ appears to be unstable because it tends to hydrolyze above pH 4.4.

Huang⁽²⁷⁾ has examined the stability of albite ($\text{NaAlSi}_3\text{O}_8$) in terms of these forms with respect to several clay minerals. His results giving the $\text{Al}/\text{H}_4\text{SiO}_4$ ratio needed to stabilize albite-clay pairs as a function of pH are shown in Figure 3. He used a value of $\log \text{Na}^+ = 3.58$ in his calculations which is a reasonable freshwater average. If clay minerals are presumed to be the stable phase at low-to-moderate flow rates, it would be desirable to investigate the stable sequence of phases at high flow rates. Figures 4 and 5 are an attempt to do this using a technique similar to Huang's⁽²⁷⁾.

As stated previously, a hydrated alumina phase, perhaps analogous to bauxite, would be formed at high flow rates. Thus, figures 4 and 5 were calculated using gibbsite, bayerite, and amorphous $\text{Al}(\text{OH})_3$, all forms of $\text{Al}(\text{OH})_3$, as possible weathering products of albite ($\text{NaAlSi}_3\text{O}_8$) and anarthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$).

The following reactions were used in constructing Figure 4, along with average freshwater values for $\log \text{Na}^+ = -3.58$ and $\log \text{Ca}^{++} = -4.30$. Up to pH 4.7

Log K for this reaction was calculated as described previously using the data of Table I.

FIGURE 3. STABILITY OF ALBITE ($\text{NaAlSi}_3\text{O}_8$) WITH RESPECT TO CLAY MINERALS
 AT $\log \text{Na}^+ = -3.58$ AT 25 °C, FROM HUANG (29)

FIGURE 4. STABILITY OF ALBITE ($\text{NaAlSi}_3\text{O}_8$) WITH RESPECT TO HYDRATED ALUMINA PHASES AT 25°C AND $\log \text{Na}^+ = -3.58$

FIGURE 5. STABILITY OF ANORTHITE ($CaAl_2Si_2O_8$) WITH RESPECT TO HYDRATED ALUMINA PHASES AT $\log Ca^{++} = -4.30$ AND $25^\circ C$

Log K values for the three forms of Al(OH) in Equation 2 are:

$$\log K_{\text{Gibb}} = -13.44$$

$$\log K_{\text{Amorph}} = -16.75$$

$$\log K_{\text{Bayerite}} = 14.16$$

Equation (2) can then be expressed in terms of log K as:

$$\log [1^{3+}]/[\text{H}_4\text{SiO}_4]^3 = \log K + \log [\text{Na}^+] - 2 \text{ pH} \quad (2A)$$

In the pH range 4.7 to 7.3, a similar set of equations are:

$$\log K_{\text{Gibb}} = -4.07$$

$$\log K_{\text{Amorph}} = -7.39$$

$$\log K_{\text{Bayerite}} = -4.79$$

$$\log [\text{Al}(\text{OH})_2^+]/[\text{H}_4\text{SiO}_4]^3 = -\log K + \log \text{Na}^+ \quad (3A)$$

And in the pH range greater than 7.3, the equations are:

$$\log K_{\text{Gibb}} = 10.43$$

$$\log K_{\text{Amorph}} = 7.11$$

$$\log K_{\text{Bayerite}} = 9.71$$

$$\log [\text{Al}(\text{OH})_4^-]/[\text{H}_4\text{SiO}_4]^3 = -\log K + \log \text{Na}^+ + 2 \text{ pH} \quad (4A)$$

The set of equations for the Anorthite stability diagrams, Figure 5, are listed as follows:

Up to pH 4.7,

$$\log K_{\text{Gibb}} = -1.49$$

$$\log K_{\text{Amorph}} = -6.51$$

$$\log K_{\text{Bayerite}} = -2.57$$

$$\log [\text{Al}^{3+}]/[\text{H}_4\text{SiO}_4]^2 = -\log K + \log [\text{Ca}^{++}] - \text{pH} \quad (5A)$$

Between pH 4.7 and pH 7.3

$$\log K_{\text{Gibb}} = 7.87$$

$$\log K_{\text{Amorph}} = 2.90$$

$$\log K_{\text{Bayerite}} = 6.79$$

$$\log [\text{Al}(\text{OH})_2^+]/[\text{H}_4\text{SiO}_4]^2 = -\log K + \log [\text{Ca}^{++}] + \text{pH} \quad (6A)$$

Above pH 7.3

$$\log K_{\text{Gibb}} = 22.37$$

$$\log K_{\text{Amorph}} = 17.40$$

$$\log K_{\text{Bayerite}} = 21.29$$

$$\log [\text{Al}(\text{OH})_4^-]/[\text{H}_4\text{SiO}_4] = -\log K + \log [\text{Ca}^{++}] + 3 \text{pH}$$

In interpreting Figures 3, 4, and 5, it is apparent that the stablest form of clay with respect to albite is sodium montmorillonite, while the stablest form of aluminum hydroxide is gibbsite. The amorphous hydrated alumina, which may form initially during weathering, will convert to gibbsite through time.

Crystal-Glass Relative Stability

Aluminosilicate glasses containing radionuclides have also been considered as waste forms and it may be interesting to compare their stability relative to crystalline phases. Robie and Waldbaum⁽¹⁶⁾ list free energies of formation (shown in Table I) for albite glass and K-feldspar glass (KAlSi_3O_8).

These data can be used in a hypothetical solubility reaction such as, for albite

The equilibrium constants calculated from Table 1 data are:

$$\log K_{\text{crystal}} = 4.02$$

$$\log K_{\text{glass}} = 11.89$$

which can be expressed as:

$$4 \log [\text{H}^+] = -\log K + \log [\text{Na}^+] + \log [\text{Al}^{3+}] + 3 \log (\text{H}_4\text{SiO}_4)$$

or

$$4 \text{ pH} = \log K - \log [\text{Na}^+] - \log [\text{Al}^{3+}] - 3 \log [\text{H}_4\text{SiO}_4] \quad (8A)$$

Assuming reasonable freshwater values for aqueous silica and alumina of $\log \text{H}_4\text{SiO}_4 = -3.50$ and $\log \text{Al}^{3+} = -4.89$, equation 8A can be plotted in terms of $\log [\text{Na}^+]$ and pH as shown in Figure 6.

Similar equations for K-feldspar are

$$\log K_{\text{crystal}} = 1.33$$

$$\log K_{\text{glass}} = 8.49$$

$$4 \text{ pH} = \log K - \log [\text{K}^+] - \log (\text{Al}^{3+}) - 3 \log [\text{H}_4\text{SiO}_4] \quad (9A)$$

Equation (9A) is also shown in Figure 6 using the same values for silica and alumina.

Figure 6 suggests that potassium aluminosilicates are slightly more stable than sodium aluminosilicates, in general agreement with observation of weathering reactions. In addition, it suggests that glass forms are about seven orders of magnitude less stable than corresponding crystalline forms.

FIGURE 6. COMPARISON OF SOLUBILITY OF CRYSTALLINE AND GLASS
FELDSPAR FORMS AT $\log (\text{Al}^{3+}) = -4.89$ AND $\log (\text{SiO}_2) = -3.50$
At 25°C .

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