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U.S. Nuclear Regulatory Commission  
Room 623-SS  
Washington, D.C. 20555

Dear Dave:

Please find enclosed the letter reports referenced in the progress report for the month of July. If you have any questions on the letter reports, please call the authors directly.

Sincerely,



Gary K. Jacobs  
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Enclosures: Letter Reports: LR-287-51,-52,-53

cc w/o encl:

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WM Project 10, 11, 16  
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LR-287-51  
8/5/86

TITLE: Review of "Solubility Effects on the Corrosion of Nuclear Defense Waste Glasses," by C. Maurer, D. E. Clark, L. L. Hench, and B. Grambow (1985). Nuclear and Chemical Waste Management 5, 193-201.

AUTHOR: G. D. O'Kelley

SUMMARY: Corrosion experiments were carried out on three simulated nuclear waste glasses at 70° and 90°C in deionized water. The glasses ranged from high Al and low Fe to low Al and high Fe. It was found that the results obtained generally supported the earlier work of Grambow on borosilicate glass and his prediction that the concentration of ions in solution is controlled by solubility. However, the relationship between bulk solubility and the formation of protective films on glass surfaces remains unclear.

LETTER REPORT

TITLE: Review of "Solubility Effects on the Corrosion of Nuclear Defense Waste Glasses," by C. Maurer, D. E. Clark, L. L. Hench, and B. Grambow (1985). Nuclear and Chemical Waste Management 5, 193-201.

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PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: G. K. Jacobs

ACTIVITY NUMBER: ORNL #41 88 54 92 4 (FIN No. B0287)  
NRC #50 19 03 01

REVIEW

Early in the consideration of glass as a nuclear repository waste form, it was recognized that the development of a surface film might be an important factor in controlling the release of radionuclides from the glass during corrosion. It has been noted that an assumption of congruent leaching tends to overpredict release rates from glass under repository conditions, but if a layer of alteration products builds up on the glass surface at low flow rates, then release rates may be considerably less than expected.

The literature concerning the occurrence of surface films on glasses has identified five principal surface conditions associated with glass corrosion. These conditions are briefly described as: a nearly undetectable surface film (Type I), a protective film (Type II), multiple protective surface films (Type III), a nonprotective surface film (Type IV), and no surface film due to high corrosion rates (Type V). It has been suggested that the composition and growth of these films is related to the solubility limits of the metal ion complexes concerned. The present concept of film formation suggests that glass corrosion involves diffusion of alkali metal and alkaline earth ions into solution and replacement by hydrogen ions. The hydrogen-infiltrated surface layer of the glass dissolves, resulting in saturation of metal ions in solution. When the solubility limit of the dominant metal ion complex is exceeded, precipitation of the complex occurs.

Grambow (1982) has proposed that precipitation accounts for the development of multiple protective surface films (Type III) and for the apparent incongruent dissolution observed for Type IV surfaces. In this latter case, the glass undergoes congruent dissolution, but simultaneous precipitation of metal ion complexes gives the appearance of incongruent

dissolution. Grambow was able to demonstrate these effects for a specific nuclear waste glass (PNL 76-68). The present work was undertaken to see if similar results were obtained with other types of nuclear waste glasses.

Three simulated nuclear waste glass compositions were prepared by adding to a borosilicate base glass about 30% of three different synthetic wastes, ranging from high  $\text{Al}_2\text{O}_3$  (49.3 wt %) and low  $\text{Fe}_2\text{O}_3$  (13.8 wt %) to low  $\text{Al}_2\text{O}_3$  (1.4 wt %) and high  $\text{Fe}_2\text{O}_3$  (59.1 wt %). Corrosion experiments were carried out at 70°C and 90°C in deionized water according to a modified MCC-1 static corrosion procedure. At the end of each corrosion period, analyses for Al, B, Ca, Fe, Li, Mg, Mn, Na, Si, and Ti were carried out, and the corroded surfaces were examined by several methods of surface analysis.

The normalized metal ion loss for each corrosion period (up to four weeks), temperature, and waste glass composition was divided by the appropriate mean mass loss for silicon and plotted against the final pH of each corrosion solution. For the hydroxides and for some carbonates, theoretical solubility curves were calculated for each set of conditions and normalized to the same scales as the plots of normalized mass loss ratio vs. pH. These theoretical solubility curves used values of thermodynamic constants from the literature.

Mass loss ratios for Na, Li, and B were near unity, although some systems high in Al were slightly greater than one, suggesting that some of the dissolved silica had precipitated out of solution onto the surface of the sample, reducing the amount remaining in solution. The results for calcium were near unity and also were close to the  $\text{Ca}^{2+}$  curve calculated from the reaction of  $\text{CaCO}_3$  and water. However, in most cases not enough  $\text{Ca}^{2+}$  went into solution to exceed the solubility limit of the silicate solid involved.

The results for Mg and Mn were less clear than for the elements just discussed. For the glasses high in Al, which are known to exhibit low leach rates, the normalized mass loss ratios were near unity. However, for the glass low in Al and high in Fe, known to have a high leach rate, the observed mass loss ratios were less than unity, indicating that enough glass had leached so that the solubility limit of the controlling solid was exceeded. Although the observed ratios agreed with a solubility curve based on  $\text{Mg}(\text{OH})_2$ , the  $\text{Mg}^{2+}$  solubility curve calculated for  $\text{MgCO}_3$  is very similar. Because of uncertainties in the equilibrium constants used, it was not possible to distinguish between the two. It is probable that both solids play a role in controlling  $\text{Mg}^{2+}$  concentration.

The authors had expected that the mass loss ratio for manganese would remain at unity until a value of pH 9 was reached and then follow the curve for  $\text{Mn}(\text{OH})_2/\text{Mn}^{2+}$  at higher values of pH. For the high Al waste glass, the observed mass loss ratio was near unity, suggesting that no solubility-controlling reaction could be identified. For the glasses

of intermediate composition the observed data were near, but below the curve for  $\text{Mn}(\text{OH})_2\text{-MnOH}^+$ . Such a result implies that the solubility-limiting reaction involves a positive, singly-charged ion. Finally, for the high-Fe composition, no manganese was detected in the corrosion solutions. The pH was higher in solutions contacting this glass, possibly driving the solubility limit below that for the other two glasses.

Four of the elements (Fe, Al, Ni, and Ti) were below detection limits for the analytical methods used.

The authors found that the results obtained generally supported the work of Grambow (1982) and his prediction that the concentration of ions in solution is controlled by solubility limits of the metal ion complexes involved. However, it is not clear that the solubility relationships in the bulk corrosion solution relate to the formation of films on the glass surface. Instead, the significant concentrations which govern the composition of a surface layer would appear to be those in the solution boundary layer and in the porous gel layer on the glass.

The authors speculate that the corrosion and film production processes follow a sequence in which alkali and other mobile ions migrate into the solution boundary layer adjacent to the glass, which are replaced by hydrogen ions. This process creates an excess of hydroxyl ions in the boundary layer, which proceed to attack the glass network, producing high concentrations of Si and Al complexes in the boundary layer. These hydroxyl complexes combine with each other and precipitate onto the glass surface. Such precipitation would be controlled by the pH and by the hydroxyl ion concentration in the boundary layer. As a result of the breakdown of the silica network, the unconsumed silicic acid and other unconsumed species diffuse into the bulk solution, so that the bulk silicon concentration is lower than that in the boundary layer, and other solubility relationships control the solubility of metal ions.

If the above sequence is correct, then the hydroxide and carbonate reactions which may control solubility in the bulk solution may not be the significant reactions in determining film formation. The authors caution that a great deal of thermodynamic data is needed in order to carry out more detailed analyses of experiments such as those described in this paper.

### EVALUATION

This paper presents important observations and speculations on the interplay between solubility and corrosion of glasses. The presence of protective films on nuclear waste glasses may turn out to be an important factor in repository performance assessments, yet there is little detailed understanding of the chemistry of film formation. The work

described in this paper is an important first step toward an understanding of the corrosion of nuclear waste glasses.

In their attempts to interpret the results, the authors were impeded by a lack of thermodynamic data for some of the possible reactions. An important task for future work should be the measurement of equilibrium constant data for the needed reactions with iron, aluminum, and silicate species at elevated temperatures and values of pH typical of nuclear waste repository environments.

The authors quite properly pointed out that their conclusions were based on theoretical interpretations which assumed equilibrium conditions and that kinetic effects might in some cases act to conceal the true nature of the reactions studied. Thus, it may be that the behavior of Mn in these experiments was actually controlled by the same solubility reaction in a high Al or a high Fe glass, even though the role of Mn was observed to be quite different in the two cases. The observed differences could be due to kinetic behavior influenced by variations in pH or by concentration changes of some other species in solution. An investigation of the kinetics of some of the more important reactions would be useful in removing such ambiguities.

The sequence of events proposed by the authors as a mechanism for glass corrosion seems quite reasonable in view of the data available. Future experiments which would focus on microscopic features of the chemical alterations at glass surfaces would be very helpful. As the authors have suggested, hydroxide and carbonate reactions may well control the bulk solubility; however, the relationship between bulk solubility and formation of protective films remains unclear. Further work in this area is needed urgently. In future experiments it would seem advisable to carry out measurements in controlled atmospheres, varying the temperature and pH more widely. Finally, when processes in deionized water are understood, future needs should include corrosion experiments in actual or simulated groundwaters typical of nuclear waste repository sites.

#### REFERENCE

Grambow, B. (1982). "The Role of Metal Ion Solubility in Leaching of Nuclear Waste Glasses," in Scientific Basis for Nuclear Waste Management V, Vol. 11, W. Lutze, ed., pp. 93-102, Elsevier Science Publishing Co.

Letter Report

**TITLE:** Review of: "Sub-sea-floor alteration in the Galapagos Spreading Center," Chemical Geology, 49, 1985, 259-274, by H. Kawahata and T. Kuruta.

**AUTHOR:** K. L. Von Damm

**PROJECT TITLE:** Technical Assistance in Geochemistry

**PROGRAM MANAGER:** G. K. Jacobs

**ACTIVITY NUMBER:** ORNL #41 88 54 92 4 (FIN No. B0287)  
NRC #50 19 03 01

The subject report documents the occurrence of alteration minerals in a Deep Sea Drilling Program (DSDP) core from Hole 504B located near the Galapagos Spreading Center in the eastern equatorial Pacific. The coring penetrated 1350m sub-seafloor, including 274m of sediment and the remainder basalt. The basaltic portion of the core has been divided into three zones which display different lithologies as well as varying degrees and temperatures of hydrothermal alteration. This letter report focuses on the alteration mineralogy reported in the subject document and compares it to the alteration mineralogy reported by Moore et al. (1985) for experimental interaction of Umtanum basalt and groundwater under hydrothermal conditions. Moore et al. (1985) is the subject of letter report 52.

Before a comparison of the alteration mineralogies is made the important differences between the two studies must be noted. The Moore et al. (1985) study is an experimental study and hence has a well defined water/rock ratio (10:1), temperature (100, 200 and 300° C), pressure (300 bars) and a finite and relatively short (6 months) period of reaction. It is also a true "closed system." The subject report is a field study with inferred water/rock ratios, temperatures, pressures, an unknown, but presumably long, period of reaction, and more closely approximates an "open system." The fluid in the subject report is seawater which becomes quite acidic during hydrothermal reactions, while the fluid in the Moore et al. (1985) study is groundwater which remains neutral to basic during the reactions. Such a large difference in pH is potentially important in defining the stability fields of various minerals. The continental basalt used by Moore et al. (1985) is more glass-rich than that sampled from the DSDP core which should infer faster reaction, but may imply a different final mineralogy from that observed in the more crystalline seafloor rocks. It is also more potassium-rich than the seafloor basalt. All of these

factors may lead to differences in the observed alteration mineralogies in the two studies.

Zone 1 of the core described in the subject report is the lower temperature zone as well as the most glass-rich zone and is most comparable to the 100° C experiment. Zones 2 and 3 have temperatures >200° C and are most comparable to the 200 and 300° experiments. While zone 2 contains a small amount of glass, zone 3 does not. Zone 1 is also interpreted to have been emplaced after the major period of hydrothermal alteration in zones 2 and 3 and hence has undergone less intense alteration. The major differences in the alteration mineralogies are the presence of illite and potassium feldspar in the experiments and not in the core and the presence of epidote and actinolite in the core and not in the experiments. The presence of illite and K-feldspar in the experiments and not in the core is presumably due to the larger amount of K available from the continental basalt in comparison to the seafloor basalt. Non-potassium clays and feldspars are present in the seafloor samples. This appears to be a readily explainable and expectable difference. The absence of epidote and actinolite is common in basalt-fluid experiments and is probably a function of slow kinetics and insufficient time for them to form. Hence they would be expected in the natural environment and their absence in the experiments is not a serious problem. Zeolites are observed in all three zones of the core but were only observed in the 300° C experiments. The zeolitic phases observed in the experiment and in the cores differ in chemistry, which is not unexpected, however one would expect to find zeolites in the experiments at the other temperatures. The absence of sulfide minerals in the experiments is surprising, since sulfide was detected in the fluid at 300° C. Some sulfide minerals would be expected although probably not as many as in the seafloor system since seawater contains much more sulfur than the groundwater.

In conclusion the agreement between the two reports is good. One might expect the mineralogy in a repository in basalt to approach that seen in the seafloor system with increasing time, with perhaps a smaller abundance of sulfide minerals and a different chemistry for any zeolites present. A true difference would be the additional presence of some potassium minerals such as illite and/or K-feldspar due to the higher potassium content of the continental rocks.

Reference:

Moore, E. L., G. C. Ulmer, and D. E. Grandstaff, Hydrothermal interaction of Columbia Plateau basalt from the Umtanum flow (Washington, U.S.A.) with its coexisting groundwater, Chemical Geology, 49 (1985) 53-71.

08/06/86

## LETTER REPORT

Title: A Summary of DOE/Hanford Data on the Solubilities/  
Concentrations of Radionuclide-Analog Elements in  
Barrier Materials + Groundwater Systems

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PROJECT TITLE: Technical Assistance in Geochemistry

PROJECT MANAGER: G. K. Jacobs

ACTIVITY NUMBER: ORNL #41 88 54 92 4 (FIN No. B0287)  
NRC #50 19 03 01

## SUMMARY

This letter report describes a new section that has been added to the topical review report Review and Assessment of DOE/Hanford Information on the Solubilities/Concentrations of Radionuclide-Analog Elements in the Systems: Simulated Waste Form ± Umtanum Basalt + Umtanum Groundwater. This new section - Section 5 of the topical review - is entitled: "A Summary of DOE/Hanford Data on the Solubilities/Concentrations of Radionuclide-Analog Elements in Barrier Materials + Groundwater Systems." The principal purpose of Sect. 5 is to summarize the numerous difficulties and uncertainties that are associated with measuring and calculating the solubilities/concentrations of radionuclides and radionuclide-analog elements. The various discussions serve to put DOE/Hanford solubility/concentration data into proper perspective.

In addition to important new commentary, Sect. 5 contains five new tables - Tables 2-6 - which list selected "high-temperature" (90-300°C) experimental data on the solubilities/concentrations of radionuclide-analog elements in barrier materials + groundwater systems. These tables itemize not only solubilities/concentrations determined by DOE/Hanford (Myers et al., 1984), but also corresponding solubilities/concentrations that the author has generated from his own independent assessment of the DOE/Hanford data. Examination of these tables reveals that, in general, there is good numerical agreement between the DOE/Hanford solubilities/concentrations and corresponding figures developed by the author. However, it is also true that there are numerous instances in which DOE/Hanford and the author disagree that a particular solubility/concentration measured at or near the conclusion of an experiment in fact represents a steady-state concentration.

Finally, Sect. 5 also presents commentary concerning DOE/Hanford data on the solubilities/concentrations of radionuclide-analog elements at 25°C (Early et al., 1984). The most significant observation regarding these data is that, in general, calculated solubilities are much lower than corresponding experimentally measured solubilities/concentrations (Early et al., 1984, Table II). However, as explained in Sect. 5.4, it is to be expected that calculated solubilities of nuclides will generally be lower than corresponding experimentally measured solubilities/concentrations.

## REFERENCES

Early, T. O., G. K. Jacobs, and D. R. Drewes, "Geochemical Controls on Radionuclide Releases from a Nuclear Waste Repository in Basalt," Am. Chem. Soc. Symp. Ser. 246, 147-166, 1984.

Myers, J., M. J. Apted, and J. J. Mazer, Hydrothermal Reaction of Simulated Waste Forms with Basalt under Conditions Expected in a Nuclear Waste Repository in Basalt, RHO-BW-ST-59P, Rockwell Hanford Operations, Richland, Washington, 1984.

## 5. A SUMMARY OF DOE/HANFORD DATA ON THE SOLUBILITIES/CONCENTRATIONS OF RADIONUCLIDE-ANALOG ELEMENTS IN BARRIER MATERIALS + GROUNDWATER SYSTEMS

Published DOE/Hanford data on the solubilities/concentrations of radionuclide-analog elements in barrier materials + groundwater systems are here summarized in five separate tables - Tables 2-6 - one table for each of the five major types of systems that have been investigated experimentally. The data listed in Tables 2-5 are solubilities/concentrations derived from hydrothermal experiments performed at 100, 200, and 300°C. The data listed in Table 6 are solubilities/concentrations derived from experiments performed at 90 and 150°C. In each table, the data for individual radionuclide-analog elements are divided according to the temperature at which they were obtained. Individual columns of numbers compare two separate sets of data: (1) solubilities/concentrations listed by Myers et al. (1984), and (2) solubilities/concentrations generated by the author via his own independent assessment of the data presented by Myers et al. (1984).

### 5.1 THE RATIONALE FOR SEGREGATING THE SOLUBILITY/CONCENTRATION DATA BY SYSTEM AND TEMPERATURE

Before discussing the results presented in Tables 2-6, the author wishes to defend his decision to employ five separate tables to list DOE/Hanford hydrothermal data on the solubilities/concentrations of radionuclide-analog elements. First, it should be recognized that this approach is consistent with the format of discussions presented in Sect. 3 of the present report. The reader will recall that Sect. 3 dealt with DOE/Hanford experimental data on the solubilities/concentrations of radionuclide-analog elements at 10 to 30 MPa, 90 to 300°C, and in this section the discussions of experimental data were segregated according to system and temperature. The discussions were segregated by system because the solubilities/concentrations of radionuclide-analog elements are commonly strong functions of bulk composition, and the five barrier materials + groundwater systems that have been investigated by

DOE/Hanford to date are sufficiently different in bulk composition to warrant separate listings of data for each system. Subdividing the data by temperature is also justified, because the available solubility/concentration data have been obtained at temperatures that are sufficiently widely spaced to reveal the effects of temperature on solubility/concentration.

Classifying DOE/Hanford solubility/concentration data by system and temperature is satisfactory for the present time because only a small number of bulk compositions and temperatures have been investigated. However, should numerous additional simulated waste forms be investigated experimentally in the future, classification of solubilities/concentrations by system will become increasingly complicated and cumbersome. This is so because, instead of a single number for the solubility/concentration of a nuclide in a given system at a given temperature, there will be a range of solubilities/concentrations.\* Furthermore, it is distinctly possible that the solubilities/concentrations of some nuclides will vary extensively with relatively small changes in bulk composition. For these nuclides, categorization of solubility/concentration by system and temperature would no longer be satisfactory; instead, it would be necessary to specify solubility/concentration by bulk composition and temperature.

It is also possible that future DOE/Hanford experimental studies will further elucidate the effects of temperature on the solubilities/concentrations of radionuclide-analog elements. If so, then tables similar to Tables 2-6 would have to include many additional columns to properly document all of the variations in solubility/concentration with temperature. If these variations are found to be a sensitive function of bulk composition, then it is evident that a large number of tables would be required to list all of the available information.

Finally, eventually it may be necessary or desirable to develop mathematical functions to represent the solubility/concentration data. With small amounts of data, this task is readily accomplished by the usual methods of empirical mathematical fitting (e.g., least-squares regression analysis). However, as the quantity of solubility/concentration data increases, empirical mathematical fitting becomes increasingly cumbersome. This realization is one of the principal motivating factors behind the effort to develop geochemical computer codes that provide accurate calculated solubilities/concentrations of nuclides in barrier materials + groundwater systems.

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\*This statement is based on the assumption that DOE/Hanford staff members will continue to classify their experimentally-based solubility/concentration data as they have done in the past; viz., according to the "generic" barrier material(s) present in a given system (e.g., "spent fuel," "CHLW glass," "DHLW glass," "basalt," etc.). Of course, DOE/Hanford may eventually decide to further classify their solubility/concentration data in order to be more specific about the particular bulk compositions to which the data apply. For example, instead of classifying their experimentally-based solubility/concentration data on the basis of whether a system contains a particular general type of waste form (e.g., "spent fuel"), DOE/Hanford may decide to divide such systems into subsystems that would draw finer distinctions between the types of waste forms employed in experimentation (e.g., "H. B. Robinson spent fuel + .... + .... groundwater," "Turkey Point spent fuel + .... + .... groundwater," and so on). This method of classification would narrow the range of bulk compositions covered by a particular type of system, thereby making it more likely that a single number would be satisfactory for representing the solubility/concentration of a particular nuclide in a given system at a given temperature. However, a proliferation of systems is still no guarantee that this simplification can be achieved. This is so because a waste form of a given "origin" (e.g., spent fuel from a particular reactor) can still be physically or chemically heterogeneous and, furthermore, its particular physicochemical characteristics may depend on its "history" and "age" (e.g., for spent fuel, the degree of "burn-up," and the length of time it has been out of the reactor). Therefore, unless DOE/Hanford decides to segregate its solubility/concentration data into a very large number of systems (i.e., a different system for each barrier material of slightly different bulk composition and/or physicochemical make-up), it will probably be necessary to list a range of solubilities/concentrations for one or more nuclides in a particular system at a given temperature.

## 5.2 ADDITIONAL COMPLEXITIES IN EXPERIMENTAL MEASUREMENTS OF THE SOLUBILITIES/CONCENTRATIONS OF RADIONUCLIDE-ANALOG ELEMENTS

Unfortunately, complexities in experimental measurements of the solubilities/concentrations of radionuclide-analog elements are not limited to the complications that stem from the effects of bulk composition and temperature. In addition to these two factors, it is evident from the discussions presented in Sect. 3 that the solubilities/concentrations of many radionuclide-analog elements are also a function of time. Time is a significant parameter because barrier materials + groundwater systems are often highly unstable thermodynamically and, therefore, they frequently exhibit rapid initial solid/fluid interaction. (Accordingly, in these highly reactive systems, the solubilities/concentrations of nuclides tend to change rapidly at first.) However, after a few tens or hundreds of hours, it is typically observed that: (1) solid/fluid reaction rates diminish or become counterbalancing, and (2) nuclide solubilities/concentrations begin to stabilize. If the solubility/concentration of a given nuclide eventually becomes nearly constant with time, then the concentration is said to be at a "steady state." Significantly, one of the principal stated goals of DOE/Hanford hydrothermal experimentation is to delineate the steady-state concentrations of radionuclides and radionuclide-analog elements in barrier materials + groundwater systems.

However, there are several difficulties associated with measuring and interpreting steady-state concentrations of radionuclides and radionuclide-analog elements. First, as discussed more thoroughly below, it can be a matter of judgment whether or not a given set of solubility/concentration data truly establish that steady-state conditions have been achieved. Two factors are key in this regard: (1) the quantity and "distribution" of solubility/concentration data, and (2) the accuracy and precision of the solubility/concentration data. The first factor refers to the number of times that groundwater is sampled and analyzed during experimentation, and to the intervals of

time between sampling. To determine that a given nuclide has achieved a steady-state concentration, it is necessary to show that the concentration of the nuclide has remained nearly constant for a significant period of time. This determination is facilitated by sampling frequently at regularly spaced intervals of time. (Transient steady states may go undetected if samples are taken infrequently or at irregularly spaced intervals.) The accuracy and precision of solubility/concentration data is another key factor in detecting steady-state conditions, because excessive "scatter" in the data can make it difficult to establish that these conditions have, in fact, been achieved.

It is also evident from the discussions presented in Sect. 3 that there can be more than one steady state for a nuclide in a closed-system experiment at a constant pressure and temperature. One of the key factors in this regard is duration of experimentation. Given sufficient time, a typical barrier materials + groundwater system can be expected to react through a series of metastable states - each metastable state marked by the observation that one or more nuclides achieve steady-state concentrations. Therefore, both the number of steady states, and the concentrations of nuclides observed at the end of an experiment, are highly dependent on the duration of experimentation.

The reactivities and evolutionary histories of barrier materials + groundwater systems are also influenced by the initial physical states of solid starting materials. The potential importance of the initial physical characteristics of solid starting materials is well exemplified by the different reactivities of real spent fuel and simulated spent fuel. Real spent fuel is dense (sintered) and, therefore, it is little altered during hydrothermal experimentation (Thomas et al., 1985). By contrast, simulated spent fuel is an unconsolidated admixture of several physically discrete chemical constituents and, therefore, compared to real spent fuel, it is highly reactive with groundwater (Myers et al., 1984; Grandstaff et al., 1984).

The particular results obtained in experiments can also be profoundly affected by fine-grinding of solid starting materials, as Myers et al. (1984) discovered in their experiments on the system simulated spent fuel + Umtanum basalt + Umtanum groundwater. In general, much more rapid reaction rates (and, hence, much more rapid approaches to steady-state conditions) are achieved when solid starting materials are comminuted to small grain sizes. However, along with more rapid rates of solid/fluid reaction, comminution of solid starting materials introduces yet another potential experimental complexity: namely, that the particular steady states achieved during experimentation may depend on the degree of comminution (e.g., see Myers et al., 1984, Figure 6-4). The only way to eliminate this uncertainty is to conduct experiments with different grain sizes of solid starting materials.

Reaction rates in a system of a given bulk composition are also influenced by the kinds of solid phases that are present. For example, it is generally observed that amorphous solid phases (glasses or gels) are more reactive than crystalline phases. Also, some crystalline phases are more reactive than others.

In summary, it is evident from foregoing discussion that the following factors influence the numbers and kinds of steady states that are achieved and detected in barrier materials + groundwater experiments: (1) sampling protocol, (2) the accuracy and precision of the solubility/concentration data, (3) duration of experimentation, (4) the physical characteristics of the solid starting materials, (5) the degree of crystallinity of the solids in the starting materials, and (6) the kinds of solid phases that are present in the solid starting materials.

Finally, it should be borne in mind that, regardless of the duration of a barrier materials + groundwater experiment, the solid reaction products invariably contain one or more metastable solid phases. Thus, at the conclusion of experimentation, it is usually observed that

radionuclides and/or radionuclide-analog elements are either sorbed onto - or incorporated into - a mixture of stable and metastable solid phases. Significantly, these assemblages of solid phases typically do not include many of the radionuclide-bearing and/or radionuclide-analog-element-bearing crystalline phases that geochemical computer codes predict to be stable. The usual explanation for this discrepancy is that stable crystalline phases that incorporate radionuclides and radionuclide-analog elements into their structures are slow to crystallize in hydrothermal experiments.

### 5.3 DIFFERENCES BETWEEN THE SOLUBILITIES/CONCENTRATIONS LISTED BY MYERS ET AL. (1984) AND CORRESPONDING VALUES DEVELOPED BY THE AUTHOR

Examining the experimentally-based solubility/concentration data listed in Tables 2-6, it is evident that - with a few minor exceptions - there is generally good numerical agreement between the data listed by Myers et al. (1984) and corresponding figures developed by the author. However, it is also evident that there are numerous instances in which Myers et al. and the author disagree that a particular solubility/concentration measured at or near the conclusion of an experiment in fact represents a steady-state concentration. Such determinations depend on individual judgments concerning: (1) changes in solubility/concentration with time, and (2) the accuracy and precision of the solubility/concentration data. These judgments can, of course, be highly subjective. But that is precisely the point. The author's principal purpose in reinterpreting some of the key experimental data listed by Myers et al. (1984) is to show that human judgment can play an important role in identifying steady-state conditions.

### 5.4 CALCULATED SOLUBILITIES FOR RADIONUCLIDE-ANALOG ELEMENTS AT 25°C

DOE/Hanford data on the solubilities/concentrations of radionuclide-analog elements at 25°C are described by Early et al. (1982) and Early et al. (1984). Significantly, the latter investigators present both calculated solubilities and a limited quantity of corresponding

experimental data (Early et al., 1984, Table II) (see Table 1). Examining these data, it is evident that most of the calculated solubilities are much lower than the experimentally measured solubilities/concentrations. (See also Table 8-2 in Myers et al., 1984.)

In attempting to understand why most of the calculated solubilities listed in Table 1 are significantly lower than corresponding experimentally measured solubilities/concentrations, it must be kept in mind that the calculated solubilities are really not directly comparable to the experimentally measured solubilities/concentrations. This is so principally because the calculated solubilities are based on the unrealistic assumption that it is possible to achieve essentially complete (stable) thermodynamic equilibrium between groundwater and coexisting solid phases. This assumption is unrealistic because it ignores the effects of: (1) sluggish solid/fluid reaction kinetics (i.e., the crystallization and/or persistence of metastable solid phases), and (2) the presence of suspended colloidal material.

In view of the failure to account for the effects of solid/fluid reaction kinetics, it is not surprising that the calculations performed by Early et al. (1984) predict an assemblage of solids + groundwater that has never been observed to form in any barrier materials + groundwater experiment (including experiments performed at temperatures as high as 300°C). This fact underscores a point made previously: namely, that many of the solids which geochemical computer codes indicate should be stable are, in fact, absent in the reaction products of barrier materials + groundwater experiments. In this regard, it should be recognized that discord between predicted and observed reaction products does not automatically preclude the use of computer codes to analyze the data obtained from barrier materials + groundwater experiments. This is so because current geochemical computer codes are capable of modeling metastable equilibria. Unfortunately, however, the available thermodynamic data for numerous key solid phases (e.g., waste

glass, basalt glass, and many radionuclide-bearing crystalline phases) are frequently either inaccurate, incomplete, or totally lacking. Therefore, at present, it is very difficult to employ geochemical computer codes to properly model metastable equilibria in barrier materials + groundwater systems.

It is evident from the discussion above that many of the discrepancies between calculated solubilities and measured solubilities/concentrations can be attributed to sluggish solid/fluid reaction kinetics in barrier materials + groundwater experiments. However, there is yet another potential difficulty in employing computer codes to calculate the solubilities of radionuclides and/or radionuclide-analog elements. This difficulty is that the assemblage of solid phases that a geochemical code predicts to be stable may, in fact, not be the most stable assemblage of solid phases for the particular set of geochemical conditions (bulk composition, pressure, temperature) under consideration.\* It is a well established fact that the phase relations of multicomponent systems can be very sensitive to bulk composition and temperature. Therefore, multicomponent phase relations predicted by computer codes should be considered hypothetical until unambiguously validated by careful experimentation.

For the reasons cited above, there is little hope that, in the near future, geochemical computer codes will provide calculated solubilities that are accordant with experimentally measured solubilities/concentrations. Consequently, in the meantime, we are left to rely on the empirical rule of thumb that, due to the fact that the reaction products of barrier materials + groundwater experiments typically

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\* This problem is of potential consequence in predicting the solubilities/concentrations of nuclides in natural environments or laboratory experiments where it is at least possible to achieve complete thermodynamic equilibrium; for instance, in favorable local regions of natural rock/groundwater systems, and in hydrothermal experiments performed at elevated temperatures (> -250°C).

contain one or more metastable solid phases, measured solubilities/ concentrations of nuclides will generally be higher than corresponding solubilities predicted by geochemical computer codes.

Table 2. Solubilities/concentrations (mg/L) of radionuclide-analog elements in the system: simulated spent fuel + Umtanum groundwater<sup>a</sup>

Element	Temperature -->	100°C	200°C	300°C
	Run # ---->	D6-8	D6-1	D5-1
Ba		0.18 <sup>b</sup> (~0.3 <sup>b</sup> )	0.12 <sup>b</sup> (~0.12 <sup>b</sup> )	0.03 <sup>b</sup> (~0.05 <sup>b</sup> )
Mo		71 <sup>b</sup> (~80 <sup>b</sup> )	68 <sup>b</sup> (~68 <sup>b</sup> )	150 <sup>b</sup> (136)
Sr		0.04 <sup>b</sup> (~0.05)	0.01 <sup>b</sup> (0.01)	0.007 <sup>b</sup> (~0.008 <sup>b</sup> )

<sup>a</sup>The solubilities/concentrations listed in this table are based on experimental data presented by Myers et al. (1984, Figures A-2, A-3, and A-4). For a given radionuclide-analog element and temperature, the first number listed is the solubility/concentration given by Myers et al. (1984, Table B-2) (see Table B.1 in Appendix B). Immediately to the right of this number, there is a second number enclosed in parentheses. This number is a solubility/concentration generated by the author via his own independent assessment of the data presented by Myers et al. (1984, Figures A-2, A-3, and A-4).

<sup>b</sup>Judged to be a steady-state solubility/concentration.

Table 3. Solubilities/concentrations (mg/L) of radionuclide-analog elements in the system: simulated spent fuel + Umtanum basalt + Umtanum groundwater<sup>a</sup>

Element	Temperature -->	100°C	200°C	300°C
	Run # ----->	BSF-4	BSF-2	BSF-3
Ba		1.0 <sup>b</sup> (0.0-3.5)	<0.03 <sup>b</sup> (~0)	<0.03 <sup>b</sup> (0.0-1.3)
Cs		50.0 <sup>b</sup> (~50 <sup>b</sup> )	30.5 <sup>b</sup> (~30 <sup>b</sup> )	46.8 <sup>b</sup> (46.8)
I		11.0 <sup>c</sup> (~11.0 <sup>c</sup> )	0.04(?)	11.2 <sup>c</sup> (~11 <sup>c</sup> )
Mo		75 <sup>b</sup> (~75 <sup>b</sup> )	76 <sup>b</sup> (~49)	18.9 <sup>b</sup> (18.9)
Sr		2.1 <sup>b</sup> (~2.2 <sup>b</sup> )	0.36 <sup>b</sup> (~0.3 <sup>b</sup> )	0.21 <sup>b</sup> (0.2)
U		0.29 <sup>b</sup> (~0.3 <sup>b</sup> )	0.10 <sup>b</sup> (~0.1)	0.13 <sup>b</sup> (0.1 <sup>b</sup> )

<sup>a</sup>The solubilities/concentrations listed in this table are based on experimental data presented by Myers et al. (1984, Figures A-5, A-6, and A-8). For a given radionuclide-analog element and temperature, the first number listed is the solubility/concentration given by Myers et al. (1984, Table B-2) (see Table B.2 in Appendix B). Immediately to the right of this number, there is a second number enclosed in parentheses. This number is a solubility/concentration generated by the author via his own independent assessment of the data presented by Myers et al. (1984, Figures A-5, A-6, and A-8).

<sup>b</sup>Judged to be a steady-state solubility/concentration.

<sup>c</sup>Judged to be an inventory-limited concentration.

Table 4. Solubilities/concentrations (mg/L) of radionuclide-analog elements in the system: simulated CHLW borosilicate glass + Umtanum groundwater<sup>a</sup>

Element	Temperature -->	100°C	200°C	300°C
	Run # ---->	GLSN3-1	GLSW2-1	GLSW1-2
Ba		1.27 <sup>b</sup> (1.08)	0.03 <sup>b</sup> (~0.05)	0.18 <sup>b</sup> (~0.1)
Mo		188 <sup>b</sup> (412)	650 <sup>b</sup> (650 <sup>b</sup> )	1290 <sup>c</sup> (~1300 <sup>c</sup> )
Sr		0.89 <sup>b</sup> (0.73)	0.004 <sup>b</sup> (~0.1 <sup>b</sup> )	0.04 <sup>b</sup> (0.04)

<sup>a</sup>The solubilities/concentrations listed in this table are based on experimental data presented by Myers et al. (1984, Figures A-10, A-12, and A-14). For a given radionuclide-analog element and temperature, the first number listed is the solubility/concentration given by Myers et al. (1984, Table B-2) (see Table B.3 in Appendix B). Immediately to the right of this number, there is a second number enclosed in parentheses. This number is a solubility/concentration generated by the author via his own independent assessment of the data presented by Myers et al. (1984, Figures A-10, A-12, and A-14).

<sup>b</sup>Judged to be a steady-state solubility/concentration.

<sup>c</sup>Judged to be an inventory-limited concentration.

Table 5. Solubilities/concentrations (mg/L) of radionuclide-analog elements in the system: simulated CHLW borosilicate glass + Umtanum basalt + Umtanum groundwater<sup>a</sup>

Element	Temperature -->	100°C	200°C	300°C
	Run # ----->	BGLW3-1	BGLW2-1	BGLW1-1
Ba		0.47 <sup>b</sup> (0.47)	0.07 <sup>b</sup> (~0.06 <sup>b</sup> )	0.06 <sup>b</sup> (0.06)
Mo		69 <sup>b</sup> (69)	161 <sup>b</sup> (161)	620 <sup>c</sup> (~600 <sup>c</sup> )
Sr		0.28 <sup>b</sup> (0.28)	0.02 <sup>b</sup> (0.02 <sup>b</sup> )	0.02 <sup>b</sup> (~0.01)

<sup>a</sup>The solubilities/concentrations listed in this table are based on experimental data presented by Myers et al. (1984, Figures A-15, A-16, and A-17). For a given radionuclide-analog element and temperature, the first number listed is the solubility/concentration given by Myers et al. (1984, Table 8-2) (see Table B.4 in Appendix B). Immediately to the right of this number, there is a second number enclosed in parentheses. This number is a solubility/concentration generated by the author via his own independent assessment of the data presented by Myers et al. (1984, Figures A-15, A-16, and A-17).

<sup>b</sup>Judged to be a steady-state solubility/concentration.

<sup>c</sup>Judged to be an inventory-limited concentration.

Table 6. Solubilities/concentrations (mg/L) of radionuclide-analog elements in the system: simulated DHLW borosilicate glass + Umtanum basalt + Umtanum groundwater<sup>a</sup>

Element	Temperature ---->	90°C	150°C
	Run # ----->	D7-1	D8-1
Ba		0.037 <sup>b</sup> (0.037)	0.012 <sup>b</sup> (0.012 <sup>b</sup> )
Sr		0.006 <sup>b</sup> (~0.005 <sup>b</sup> )	0.018 <sup>b</sup> (0.018)

<sup>a</sup>The solubilities/concentrations listed in this table are based on experimental data presented by Myers et al. (1984, Figures A-21 and A-23). For a given radionuclide-analog element and temperature, the first number listed is the solubility/concentration given by Myers et al. (1984, Table B-2) (see Table B.5 in Appendix B). Immediately to the right of this number, there is a second number enclosed in parentheses. This number is a solubility/concentration generated by the author via his own independent assessment of the data presented by Myers et al. (1984, Figures A-21 and A-23).

<sup>b</sup>Judged to be a steady-state solubility/concentration.