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Letter Report

Calculations of Radioelement Solubilities in Basalt Ground Waters

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CALCULATIONS OF RADIOELEMENT SOLUBILITIES IN BASALT GROUND WATERS

1. Introduction

Estimates of radioelement solubilities are very important to performance assessment studies. The solubilities of elements contained in the waste form will control the release of radionuclides into the near field of the repository. In the far field, the solubilities of radioelements in ground waters along potential flow paths will strongly influence the migration rates of radionuclides. Development of the capability to estimate radioelement solubilities under a wide range of natural conditions is an important part of the performance assessment methodology at Sandia National Laboratories.

Duda, et al. (1982) presented preliminary estimates of radioelement solubilities in a basalt ground water at 40°C for several combinations of Eh and pH. The geochemical speciation code, PHREEQE was used in these calculations. The purpose of the above calculations was to estimate the ranges of radioelement solubilities that were possible over the potential physicochemical conditions for a basalt repository site. The lower limit for ground-water redox potential was set at -0.40 V. This value was estimated by Jacobs and Apted (1981) from mineralogical and aqueous speciation data. Measured values of Eh for water from the Grande Ronde basalt formation, however, range from +0.35 to -0.2 V. The purpose of the calculations described in Section 2 of this report is to estimate solubilities at the lower limit (-0.2 V) of <u>observed</u> Eh values. A temperature of 55°C and pH = 9.5 have been estimated for the reference repository horizon (Jacobs and Apted, 1981) and have been used in the present calculations.

Early, et al. (1982) have graphically presented calculations of radioelement solubilities in Grande Ronde waters at 25°C over an Eh range of -0.6 to 0 volts. Numerical results are listed for a "reference" Grande Ronde ground water at Eh = -0.3 V. We have calculated radioelement solubilities in the same ground-water composition using PHREEQE and the thermodynamic data base described in Duda, et al. (1982). This preliminary data base was compiled at SNLA and was intended to be a starting point for development of a more comprehensive compilation. The more extensive data base listed in Early, et al. (1982) is based primarily on the compilations of Benson and Teague (1980), Philips (1982) and Rai, et al. (1978, 1982). The verification exercise described in Section 3 of this report

will allow us to assess the adequacy of our calculational procedure and to identify important gaps in our data base (see Section 4).

A closed geochemical system was assumed in our calculations. This means that the mass of each element was fixed throughout the calculation; chemical constituents could not be added to the reaction system from external sources such as ground water or wall rock. Under certain conditions, this assumption could affect the calculated solubility. In Attachment A, the importance of this assumption to the calculated results is discussed. The calculational method used in this report is also reviewed in Attachment A.

2. Calculations of Radioelement Solubilities in Basaltic Ground Water at Eh = -0.2 V

Solubilities of radioelements have been calculated at 40°C in a basaltic ground water at Eh = +0.55 V and -0.40 V and pH = 9 and 10 previously (Duda, et al., 1982). The calculations described below estimate radioelement solubilities in a basaltic ground water at 55°C, Eh = -0.2 V and pH = 9.5. The concentration of all other ground-water constituents (cf. column 1, Table 1) assumed in this calculation are the same as those of Duda, et al. (1982). The pH and Eh of the solution were fixed during the calculation and the chemical activities of all other chemical components were calculated for the state of chemical equilibrium. The method of calculation is the same as that described in Duda, et al. (1982) and is reviewed in Attachment A. The mass of each element in the reaction system was fixed; addition of complexing ligands from an external source (such as ground water or wall rock) was not allowed.

The results of these calculations are shown in Table 2. The solubilities calculated in Duda, et al. (1982) are listed in Table 3 for comparison. The differences among the five sets of calculations are due to the effect of temperature, pH and redox potential.

A major objective of these calculations was to compare the solubilities estimated for Eh = -0.40 V and Eh = -0.2 V. The solubilities of Se, Pb, and Np are more than two orders of

magnitude higher at Eh = -0.2 V than at Eh = -0.4 V. The solubility of U is slightly higher (<1 order of magnitude) at the higher Eh whereas the solubilities of Ra, Sr, Sb and Sm are lower. The solubilities of other elements considered in these calculations were essentially the same as those calculated at Eh = -0.4 V. It is important to note that, with the exception of Th, all the radioelement solubilities calculated at pH = 9.5 and Eh = -0.2 V fall within the ranges calculated by Duda, et al. (1982).

Early, et al. (1983) discuss the importance of sulfur speciation to radioelement solubilities. In our calculations, we assumed that all sulfur species were in chemical equilibrium. The differences in sulfur speciation at Eh = -0.2 V and Eh = -0.4 V may account for the differences in calculated solubilities of Sb, Pb and Ra at the two redox potentials. At Eh = -0.2 V nearly all of the sulfur present in the system exists as sulfate (SO_4^{-2}). At Eh = -0.4 V nearly all of the sulfur is present as bisulfide (HS^-). Uncertainties in the speciation of ground-water ligands may be as important to these solubility calculations as uncertainties in the properties of radionuclides themselves.

3. Comparisons of Calculations of Radioelement Solubilities in a Reference Grande Ronde Ground Water

Researchers at Rockwell Hanford Operations (RHO) (Early, et al. 1982) have presented calculated radioelement solubilities in Grande Ronde ground water at Eh = -0.3 V at 25°C. The computer code, reactions and associated equilibrium constants used in these solubility calculations have been listed in the above report. The results reported by Early, et al. (1982) were used to verify the method and data base used in the SNLA solubility calculations. We have calculated solubilities at 25°C in the reference Grande Ronde ground-water composition listed in Table 1 (column 2). The calculated solubilities, stable solid and dominant aqueous species are listed in Table 4. The results of calculations as described in Early, et al. (1982) are also shown for comparison. There is good agreement (about one order of magnitude) between the SNLA and RHO calculations only for Th, Sm, Np and Ra. There is fair agreement (within three orders of magnitude) for Tc, Zr, and Pb. Solubilities calculated by SNLA and RHO for Se, Pd, Sb, Sn, U, Pu, and Am differ by more than three orders of magnitude. The solubilities calculated by SNLA for Se, Tc, U, and Pu are much lower than those calculated by

RHO; SNLA calculations for the other elements (except Th) are higher. As will be discussed in the next section, differences between the thermodynamic data bases used in the RHO and SNLA calculations probably account for many of the differences between the calculated sets of solubilities for several elements. Table 4 shows that the SNLA data base did not contain the dominant aqueous species or stable solid identified in the RHO calculations for Se, Pd, Sb, Sm, Pb, U, Pu or Am. The dominant aqueous species identified by the SNLA calculations for Sn and Sm were not contained in the RHO data base. The differences between the solubilities of Zr, Tc, Ra, and Np as calculated by RHO and SNLA cannot be easily related to the thermodynamic data bases and need further investigation. Table 4 shows that different solubilities for Zr were estimated by the SNLA and RHO calculations even though the same stable solid and dominant aqueous species were identified in both studies. Both the SNLA and RHO data bases contain the species $NpO_2HCO_3^-$ and $Np(OH)_5^-$, yet the former species was chosen as dominant by SNLA while the latter was identified as dominant by RHO. Stable solids and dominant aqueous species for Tc and Ra were not identified in the RHO study.

4. Thermodynamic Data Bases

As discussed previously, the thermodynamic data base used in the SNLA calculation was the result of a preliminary compilation of thermochemical data. As part of this Technical Assistance, we have examined the data bases of Early, et al. (1982), Philips (1982) and Benson and Teague (1980) in order to identify gaps in the current SNLA data base. We found a total of 290 species that had been identified in these other bases but had not been included in the SNLA data base. Two hundred forty-five of these species were actinide complexes. The SNLA data base contained 47 species that were not included in the other data bases. We do not feel that all of the species are needed to perform accurate solubility calculations. One to four solid phases and 1 to 6 aqueous species are usually sufficient to describe the behavior of any element. The calculations described in Section 3 of this report identified 10 species and solids that were not included in the SNLA data base that may control radioelement solubilities (cf. Table 4). We plan to include these species and solids in the SNLA data base and repeat the verification calculations described in the previous section. The relative importance of other species can be estimated by simple calculations. The most important complexes and solids under relevant physicochemical conditions will be identified and included in the data base.

ATTACHMENT A

1. Method of Calculation

The use of PHREEQE to calculate radioelement solubilities has been described in Duda, et al. (1982); Guzowski et al. (1983) and Tien, et al. (1983). The following discussion is adapted from these references.

The solubility of a substance is defined as the amount of the substance in solution at equilibrium with some limiting solid phase. Without knowledge of this limiting solid, two schemes can be used with a program such as PHREEQE to estimate the solubility of a given element. Both of these methods require the inclusion of solid phases in the data base of PHREEQE. Normally, the data base includes only aqueous species. Solids are treated as a separate input (as "MINERALS" input). In the first scheme, a large excess of the element is "added" to the solution so that the limiting solid may precipitate. The sum of the concentrations of the various aqueous species containing the element equals the solubility. However, this technique causes numerical convergence problems in PHREEQE and is not an effective means of estimating the solubility.

In the SNLA calculations, the following method and approximations were used to circumvent the convergence problems. Consider the dissolution of a solid AB as given by

$$AB_{(s)} \rightleftharpoons A^+ + B^- \qquad (1)$$

The equilibrium constant for the reaction is

$$K_{eq} = \frac{[A^+][B^-]}{[AB_{(s)}]} = \frac{[A^+][B^-]}{1} = K_{sp} \qquad (2)$$

where the bracketed quantities denote activities. For pure solids, the activity of AB is defined as unity and the equilibrium constant is called the solubility product constant, K_{sp}. If the product of $[A^+]$ and $[B^-]$ (commonly referred to as the ion activity product, IAP) exceeds the value of K_{sp}, precipitation occurs until IAP = K_{sp}.

In the SNLA calculations, a small amount of an element was "added" to an initial solution with a composition shown in Table 1, and the computer code was allowed to partition the mass into aqueous and solid "species". In these calculations,

the solid AB was treated as an aqueous complex AB* by PHREEQE, and its calculated activity was less than unity in unsaturated solutions. The ratio $[A^+]/[AB^*]$ calculated by PHREEQE for unsaturated solutions should be approximately the same as $[A^+]/[AB_{(s)}]$ for saturated solutions. This approximation was used in the following way. If A^+ is assumed to be the dominant aqueous species of A, then $[A^+]$ is equal to the solubility of A at saturation. In saturated solutions

$$\frac{[A^+]_{sat}}{1} = \frac{[A^+]_{sat}}{[AB_{(s)}]_{sat}} = \text{solubility of A} \qquad (3)$$

where "sat" refers to activities at equilibrium. In calculations for unsaturated solutions, the assumption was made that

$$[A^+]_e = \frac{[A]_{calc}}{[AB^*]_{calc}} \approx \frac{[A]_{sat}}{[AB_{(s)}]_{sat}} = \text{solubility of A} \qquad (4)$$

where "calc" refers to activities calculated by PHREEQE. It is important to emphasize that equation (4) has no physical or thermodynamic significance but is assumed to be mathematically approximate.

For the more general reaction

$$A_aB_{b(s)} \rightleftharpoons aA^+ + bB^{-(a/b)} \qquad (5)$$

with the equilibrium constant

$$K_{sp} = \frac{[A^+]^a [B^{-(a/b)}]^b}{[A_aB_{b(s)}]} \qquad (6)$$

The corresponding expression is

$$[A^+]_e = \frac{[A^+]_{calc}}{\left[A_aB_b^*\right]_{calc}^{1/a}} \quad \text{solubility of A} \qquad (7)$$

The above assumption was tested in the following manner: PHREEQE was run at a given input concentration of the element (e.g. 10^{-8} or 10^{-4} molal) and the dominant solid "species" was determined. The program was then rerun after deleting the limiting solid "species" from the data base, and assuming that equilibrium existed with the actual solid phase. This procedure was done for several elements, and calculated solubilities were compared. The assumption in equation (4) was found to be reasonable. Calculated solubilities from the two runs agreed

to within a factor of two. For example, the solubility of Zr was found to be 9.5×10^{-8} molal with $ZrSiO_4$* as the limiting solid "species". Under the same conditions, with $ZrSiO_4$ solid assumed in equilibrium with the solution, the solubility was calculated to be 9.0×10^{-8} molal, a difference of 6 percent. The solubility of Th was calculated to be 8.9×10^{-16} molal with ThO_2* as the limiting solid "species". Running the program defining equilibrium with solid ThO_2 gave the same value. Therefore, this technique is a reasonable computational scheme that can be used to estimate solubilities.

In some radioelement systems, several solid "species" with similar solubilities were identified. For such cases, the above mathematical assumption remained valid for the calculated solubilities within a factor of two. In some element systems, no limiting solid was found. For those cases, all the element added to the solution remained in solution. In the results, the solubility limit was specified as being "high". At very high input concentrations, a solid with a large K_{sp} will form and PHREEQE may have numerical problems converging to a solution. Physically, it is unlikely that either the concentration of ligands in the ground water or the radioelement concentration in the far field of a tuff repository will be high enough to reach saturation. The statement of "high" solubility, therefore, adequately describes the behavior of these radioelements.

A temperature of 55°C was assumed in these calculations. PHREEQE uses the van't Hoff expression to account for the effect of temperature. If the enthalpy of reaction is known, the equilibrium constant of the reaction is adjusted using the following equation.

$$\log K = \log K_{T_r} - \frac{\Delta H_{T_r}}{2.3R} \cdot \left(\frac{1}{T} - \frac{1}{T_r}\right) \qquad (8)$$

where T_r is the reference temperature (298.15K). For those cases where the enthalpy data are unavailable, the equilibrium constant at 25°C was used.

2. Assumption of a Closed Geochemical System

It was necessary to assume a closed geochemical system with the version of PHREEQE that was used in these calculations (i.e., transfer of mass out of the solution by precipitation or into solution by dissolution was not considered). The masses of complexing agents in the ground water (when summed over all species) were set equal to values for water compositions listed

in Table 1 for the entire calculation. Natural systems are not necessarily closed-geochemical systems for all elements. If precipitation or dissolution rates are high relative to the rate of radionuclide transport, then the ground water may be an open-geochemical system. Previous calculations of mineral saturation indices for ground waters in natural systems such as NTS (White, 1979) or the BWIP Site (Deutsch, et al., 1981) however, suggest that many mass transfer reactions are sluggish, resulting in apparent supersaturation. By analogy the assumption of a closed system may be correct for some radionuclides.

The computational method used in the SNLA calculations as described in the previous subsection reduced the uncertainties associated with the closed-system assumption. The amount of radioelement assumed in these calculations [10^{-5} to 10^{-8}m] was lower than the ligand concentrations. Consumption of ligands by complexation of all the available radioelement had a minor effect on the ground-water composition. This can be illustrated using solubilities calculated for Zr. Figure 1 shows calculated Zr solubilities, concentrations of aqueous silica species and fractions of the total Zr contained in various chemical forms for several different total Zr concentrations. As discussed in the previous section, the terms $Zr(OH)_4$* and $ZrSiO_4$* refer to solid "species" as calculated by PHREEQE. The terms [$Zr(OH)_4$*]/[Zr]i and [$ZrSiO_4$*]/[Zr]i are the fractions of total Zr of the system [Zr]i that are complexed with the solids $Zr(OH)_4$* and $ZrSiO_4$* respectively. Figure 1 shows that when the total Zr in the system [Zr]i is 10^{-4} molal or less, nearly all of the Zr is bound up in solid $ZrSiO_4$*. The dominant aqueous species is $Zr(OH)_5^-$; the solubility of Zr is calculated as 6.2×10^{-7} molal from [$Zr(OH)_5^-$]/[$ZrSiO_4$*] (cf equation 4). When [Zr]i is 10^{-2} molal, most of the Zr is bound up in $Zr(OH)_4$*. The dominant aqueous species is still $Zr(OH)_5^-$ but the solubility is calculated as 6.8×10^{-3} molal from [$Zr(OH)_5^-$]/[$Zr(OH)_4$*]. The reason for the difference in the calculated solubility can be understood by examination of the curves for [$Zr(OH)_5^-$]/[$Zr(OH)_4$*] and [SiO_2] in Figure 1. The value of the former term is independent of the total Zr. This indicates that the concentration of $Zr(OH)_5^-$ is controlled by the reactions

$$Zr^{+4} + 4(OH)^- \rightleftharpoons Zr(OH)_4^{\bullet} \qquad (9)$$

$$Zr(OH)_4^{\bullet} + OH^- \rightleftharpoons Zr(OH)_5^- \qquad (10)$$

$$Zr(OH)_4^{\bullet} \rightleftharpoons Zr(OH)_4* \qquad (11)$$

Because the pH is kept constant in these calculations, the ratios of the constituents of the reactions are constant.

$ZrSiO_4$* is more stable than $Zr(OH)_4$*. As long as there is sufficient silica in the system, $ZrSiO_4$* will form in greater amounts than $Zr(OH)_4$*. Figure 1 shows that when the total Zr concentration of the system is greater than the total Si concentration (1.8×10^{-3} molal, cf Table 1), nearly all of the silica is consumed by reaction to form $ZrSiO_4$*, and little remains in solution (cf [SiO_2] curve). The excess Zr forms $Zr(OH)_4$*. The higher amount of $Zr(OH)_4$* implies a higher amount of $Zr(OH)_5^-$ and hence a higher calculated Zr solubility.

In summary, Figure 1 illustrates the following points:

1. In a closed geochemical system, the calculated solubility will depend on the relative amounts of radioelements and complexing ligands in the system.

2. At low radionuclide concentrations (10^{-4} molal), the calculated radioelement solubilities for a closed geochemical system will be the same as for an open geochemical system. This is because the radioelements are not present in amounts sufficient to consume appreciable portions of the complexing ground-water ligands.

TABLE 1

Initial Ground-Water Compositions Used in Solubility Calculations (molal)

SPECIES	1*	2**
Na^+	9.8×10^{-3}	1.6×10^{-2}
K^+	6.4×10^{-5}	8.8×10^{-5}
Ca^{+2}	2.6×10^{-5}	6.9×10^{-5}
Mg^{+2}	2.9×10^{-6}	1.6×10^{-7}
Cl^-	9.3×10^{-3}	8.8×10^{-3}
F^-	1.5×10^{-3}	1.8×10^{-3}
SO_4^{-2}	7.5×10^{-4}	1.8×10^{-3}
SiO_2	1.8×10^{-3}	1.3×10^{-3}
Total C	4.6×10^{-4}	9.0×10^{-4}
Alkalinity(eq)	2.2×10^{-3}	1.8×10^{-3}

* Ground-water composition used in Duda et al. (1982) and in calculations described in Section 2 of this report. T=55°C, Eh=-0.2, pH=9.5 in these calculations.

** Ground-water composition used in Early et al. (1982) and in Section 3 of this report. Eh=-0.3, pH=9.76.

TABLE 2

Solubilities of Radioelements in Hypothetical*
Basalt Ground Water at 55°C

ELEMENT	SOLUBILITY (Log Molality)	STABLE SOLID	DOMINANT AQUEOUS SPECIES
Se	-9.4	Se	SeO_3^{-2}
Zr	-6.2	$ZrSiO_4$	$Zr(OH)_5^-$
Tc	<-16.0	TcO_2	TcO_4^-
Pd	-5.4	$Pd(OH)_2$	$Pd(OH)_2^o$
Sn	-14.7	SnO_2	$SnO(OH)F^o$
Sb	-4.4	Sb_2O_4	$HSbO_2^o, Sb(OH)_3^o$
I	no limit	none	I^-
Cs	no limit	none	Cs^+
Sm	-8.5	$Sm_2(CO_3)_3$	$SmCl^+$
Pb	-4.5	$PbCO_3$	$PbOH^+, Pb(OH)_2^o, PbCO_3^o$
Sr	-4.7	$SrCO_3$	Sr^{+2}
Ra	-6.3	$RaSO_4$	Ra^{+2}
Th	-14.7	ThO_2	$Th(OH)_4^o$
Pa	no limit	none	$Pa(OH)_2^+$
U	-15.5	UO_2	$U(OH)_5^=$
Np	-8.7	NpO_2	$NpO_2HCO_3^o$
Pu	< -16.0	PuO_2	$Pu(OH)_4^o$
Am	no limit	AmO_2	$AmOH^{+2}$

* Ground-water composition listed in Column 1, Table 1. Eh=-0.2, pH=9.5.

TABLE 3

Solubilities of Radioelements in Hypothetical Basalt Ground Water Reported in Duda et al. (1982)*

NUCLIDE	pH=9 Eh=+.55	pH=9 Eh=-.40	pH=10 Eh=+.55	pH=10 Eh=-.40
Se	High	Low	High	Low
Sr	- 3.7	- .03	- 1.0	- 1.0
Zr	- 7.0	- 7.0	- 5.5	- 5.5
Tc	High	Low	High	Low
Pd	- 5.4	- 5.4	- 5.4	- 5.4
Sn	-14.1	-14.1	-15.1	-15.1
Sb	-16.3	>- 1	-18.9	>- 1
I	High	High	High	High
Cs	High	High	High	High
Sm	- 9.6	- 4.8	- 9.4	- 5.0
Pb	- 5.2	-16.8	- 4.0	-12.7
Ra	- 6.5	- 1.4	- 6.5	- 6.5
Th	-15.0	-15.0	-15.0	-15.0
Pa	High	High	High	High
U	- 4.1	-16.3	- 6.5	-15.3
Np	High	-11.5	High	-11.3
Pu	- 8.8	-17.3	- 7.9	-17.3
Am	High	High	High	High

* All solubilities are reported in units of log molality. Eh units are volts; temperature is 40°C. Ground-water composition is described in Column 1, Table 1.