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ESTIMATION OF THE EFFECTIVE DISTRIBUTION COEFFICIENT FROM THE SOLUBILITY CONSTANT

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I. INTRODUCTION

An updated version of RESRAD (version 5.0) has been developed by Argonne National Laboratory for the U.S. Department of Energy to derive site-specific soil guidelines for residual radioactive material.[1] In this updated version, many new features have been added to the RESRAD code. One of the options is that a user can input a solubility constant to limit the leaching of contaminants. The leaching model used in the code requires the input of an empirical distribution coefficient, K_d, which represents the ratio of the solute concentration in soil to that in solution under equilibrium conditions. This paper describes the methodology developed to estimate an effective distribution coefficient, K_d, from the user-input solubility constant and the use of the effective K_d for predicting the leaching of contaminants.

II. METHODOLOGY

Parameters that affect the measurement of a distribution coefficient include the physical and chemical characteristics of the soil and the properties of the chemical species in the contact solution. In soil, a specific chemical element may form several different compounds or may be associated with different geochemical species. In the early stages of the leaching process, chemical species with high solubilities are the first to be released into the solution phase. As leaching proceeds, chemical species with low solubilities start to dissolve. Investigating the presence of major chemical species in soil and the distribution of chemical elements among these species is useful for predicting the amount of chemical elements that will be released into the solution phase. Currently, little laboratory information is available on possible solids and solution species present in a soil-solution system. The information is mostly very site-specific and solution-specific, which makes extrapolation of data extremely difficult.

Available thermodynamic data have been reviewed by several research groups to develop a methodology for predicting possible solids present in a given soil solution system.[2-5] Currently the Eh-pH diagrams[2-3] and stability-pH diagrams[4-5] have been developed for several chemical elements that represent the existence of possible chemical compounds under given generic environmental conditions. As reported by Ames and Rai,[5] the Eh-pH diagrams predict the presence of different solids for elements that exist in more than one oxidation state, but these diagrams do not indicate the total amount of the element and the relative amount of various species in solution under specific conditions. Therefore, the stability-pH diagrams are used as the basis for this study. Equations developed for predicting the distribution coefficient are presented below.

A. Stability-pH Diagram

The methodology applied by Rai and Lindsay[4] and Rai and Serne[5] to develop a stability-pH diagram uses thermodynamic standard free energies of formation (ΔG_f^o) to calculate equilibrium constants for various minerals/solids under standard conditions, that is, 1 atm and 25°C. On the basis of the estimated equilibrium reaction constant, the equation for the concentration of related chemical species in a specific mineral or solid can be formulated. Concentrations of common cations (such as Ca^{+2}, Mg^{+2}, K^+, and Na^+) and anions (such as Cl^-, HCO_3^-, CO_3^{-2}, NO_3^-, F^-, SO_4^{-2}, and PO_4^{-3}) are generally used to represent environmental conditions for natural soil solution systems.[4,7] Equations for

concentrations of the investigated chemical elements can then be simplified as a function of the solution pH. For each chemical element investigated, the stability diagram can be constructed so as to provide information on the saturate solubility of the chemical element under given environmental conditions with different solution pHs. Details of the method for constructing stability diagrams have been described by Rai and Lindsay,[4] using aluminum minerals such as analcime ($NaAlSi_2O_6 \cdot H_2O$) as an example.

Stability diagrams for various chemical elements in an oxidizing soil environment are available.[6] For each chemical element reported, a stability diagram is constructed to provide information on the saturate solubility of the element under given environmental conditions with respect to different solution pHs. Any solid with its stability line below another solid's stability line is more stable than that other solid. For sites with specific soil solution properties, the stability diagram can be modified to correspond to the actual ionic concentration. This modification results in an upward or downward shift of the isotherms. A stability diagram for uranium species is shown in Figure 1 (adapted from reference 6) and is used as the basis for our sample calculation.

B. Estimation of Saturate Solubility

Consider a soil-solution system in which the total mass of chemical element E in soil is $S_E(0)$ (g/g soil) and the volume of contact solution is $V_{solution} = \theta\ V$(mL), where θ is the volumetric water content and V is the volume of contaminated soil (mL). For the purpose of model development, we assume that there is no solubility limit for chemical dissolution and that all of chemical element E can be released into the solution phase under the worst leaching conditions. The total concentration of chemical element E, $C_{E,tot}$ (mole/L), in soil solution under this assumed 100% released condition is

$$C_{E,tot} = S_E(0) \times \frac{\rho_b}{\theta} \times \frac{1}{AW_E} \times 1{,}000 \qquad (1)$$

where ρ_b = bulk density of soil (g/cm^3) and AW_E = atomic weight of chemical element E (g/mole). A horizontal line $L_1 = \log C_{E,tot}$ in the stability diagram is drawn to represent the total concentration of chemical element E in the investigated system.

With uranium as the example contaminant, the stability diagram shown in Figure 1 indicates that several uranium species exist in a given soil solution system. To

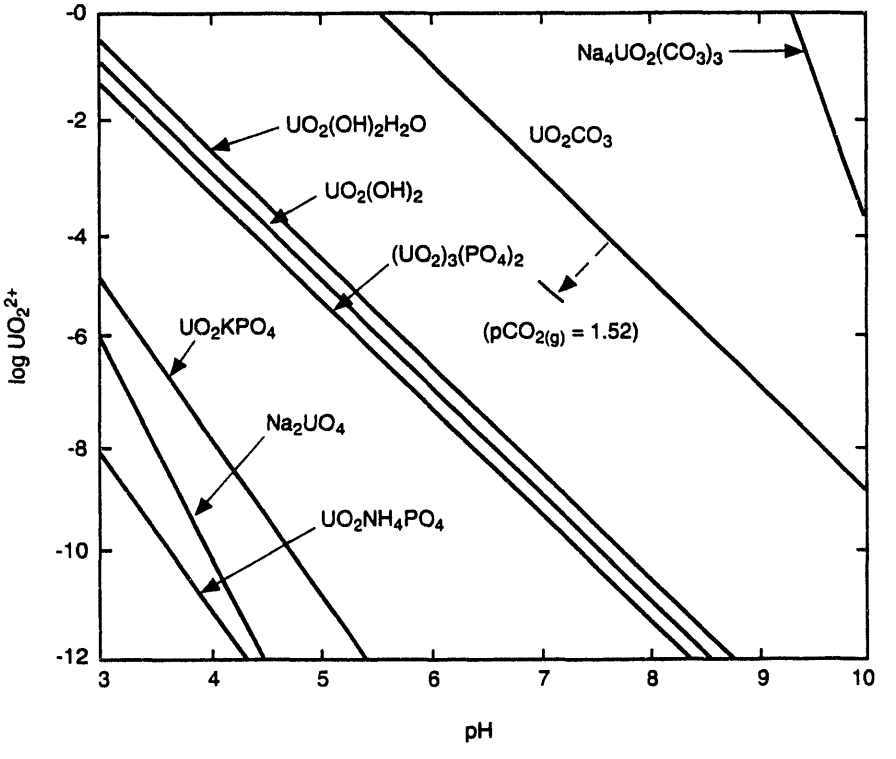

FIGURE 1 Relative Stability of Various Uranium Solids in an Oxidizing Soil Environment [$PO_{2(g)}$ = 0.68 atm, $PCO_{2(g)} = 10^{-3.52}$ atm, and $pNa^+ = pNH_4^+ = 3.0$] with Phosphate Levels in Equilibrium with Variscite and Gibbsite (Source: Adapted from reference 6)

predict the most soluble chemical species in the system, a vertical line L_2 is drawn to represent the solution pH. The intercept between L_2 and the solubility line right below L_1 represents the presence of the most soluble chemical species and its saturate solubility, $C_{E,max}$ (mole/L), at a specific solution pH.

C. Estimation of Distribution Coefficient

For the soil solution system discussed above, assuming that X fraction in percent of chemical element E will be released into the solution phase under equilibrium conditions, the empirical distribution coefficient K_d (mL/g) for chemical element E is defined as

$$K_{d,E} = \frac{\text{Chemical element E remaining in soil phase (g/g soil)}}{\text{Chemical element E released into solution phase (g/mL solution)}}$$

Then

$$K_{d,E} = \frac{S_E(0) \times (1 - X) \times \rho_b V \times \frac{1}{\rho_b V}}{S_E(0) \times X \times \rho_b V \times \frac{1}{\theta V}}$$

$$= \frac{1 - X}{X} \times \frac{\theta}{\rho_b} \qquad (2)$$

The distribution coefficient can be calculated by the following procedure:

1. Calculate the maximum mass concentration of chemical element E, $S_{E,max}$ (g/mL solution), on the basis of the estimated saturate solubility:

$$S_{E,max} = C_{E,max} \left(\frac{\text{mole}}{\text{L}}\right) \times \frac{\text{L}}{1{,}000 \text{ mL}} \times AW_E \text{ (g/mole)} \qquad (3)$$

2. Calculate the fraction of the total chemical element E released into the solution phase, X_{max}:

$$X_{max} = \frac{S_{E,max}}{S_E(0)} \times \frac{\theta}{\rho_b} \qquad (4)$$

3. Calculate the distribution coefficient:

$$K_{d,E} = \frac{1 - X_{max}}{X_{max}} \times \frac{\theta}{\rho_b} \qquad (5)$$

III. SAMPLE CALCULATION

The following sample calculation assumes that uranium-238 is the principal contaminant. Input parameters representing the properties of a contaminated site are summarized in Table 1. The distribution coefficient is estimated as follows:

1. Calculate the total concentration of uranium-238 in the soil solution system investigated, $C_{E,tot}$.

2. Estimate the saturate solubility of the most soluble uranium-238 species in solution. Draw a horizontal line $L_1 = \log C_{E,tot}$ to represent the total activity of uranium-238. Draw a vertical line L_2 to represent the solution pH. The UO_2^{+2} solid with a stability line right below L_1 at each solution pH is considered to be the most soluble solid. The intercept between L_2 and the stability line of the most soluble solid indicates the saturate solubility of UO_2^{+2} in the soil solution system investigated, $C_{E,max}$.

3. Calculate the distribution coefficient for each soil solution system with a different solution pH by the following process:

   a. Calculate the maximum mass concentration of uranium-238 in the soil solution by equation 3.

   b. Calculate the maximum fraction of total uranium-238 released into the solution phase by equation 4.

   c. Calculate the distribution coefficient for uranium-238 by equation 5.

The results of the sample calculation for a soil solution system with a solution pH varying from 4 to 9 are summarized in Table 2, including the most soluble solids, their saturate solubility, and the estimated effective distribution coefficients (K_d) for uranium species. The major uranium solid for soil solution systems with solution pHs between 4 and 6 is $UO_2(OH)_2 \cdot H_2O$. The compound UO_2CO_3 represents the major solid in the same soil solution system with solution pHs between 7 and 9. For systems with the same most soluble chemical species, an increase in solution pH will decrease the saturate solubility and result in a higher distribution coefficient. A decrease in solution pH will enhance the solubilization of chemical species, resulting in a higher saturate solubility and lower distribution coefficient for the system investigated. The accuracy of the distribution coefficient estimated depends heavily on the selection of appropriate solids to construct the stability diagram.

TABLE 1 Properties of Contaminated Soil and Contaminant for Sample Calculation

	Parameter	Value
Contaminated soil	Area	1,000 m^2
	Depth	1 m
	Bulk density, ρ_b	1.6 g/cm^3
	Volumetric water content, θ	0.2
Contaminant (uranium-238)	Initial concentration	2.98×10^{-3} g U-238/g soil
	Specific activity, SA	3.36×10^5 pCi/g U-238

TABLE 2 Results of Sample Calculation

Solution pH	Major Solid	Saturate Solubility (mol/L)	Calculated K_d (mL/g)
4	$UO_2(OH)_2 \cdot H_2O$	4×10^{-3}	3
5	$UO_2(OH)_2 \cdot H_2O$	5×10^{-5}	2.50×10^2
6	$UO_2(OH)_2 \cdot H_2O$	3×10^{-7}	4.17×10^4
7	UO_2CO_3	1×10^{-3}	1.24×10^1
8	UO_2CO_3	1×10^{-5}	1.25×10^3
9	UO_2CO_3	1×10^{-7}	1.25×10^5

IV. DISCUSSION

The currently available stability diagram presented by Ames and Rai[6] is generally used for inorganic compounds present in our natural soil. When organic contamination is investigated, the solubility of nonionic organic chemicals can be estimated by a correlation equation modified by Lyman et al.[8] as

$$\log \frac{(1{,}000)\ MW}{S} = 1.339 \log K_{ow} - 0.978 \qquad (6)$$

where S = solubility (mg/L), MW = molecular weight (g/mole), and K_{ow} = octanol water distribution coefficient.

When radionuclide contamination is investigated, this methodology can be applied by assuming that radionuclides for the same chemical element have the same chemical properties. Usually, measurement of radioactivity is reported as picocuries per gram (pCi/g) of contaminated soil. Conversion of activity unit to mass unit for specific radionuclide is required. The specific activity, SA_i, is used to calculate the mass concentration of each individual radionuclide as $S_E(0) = S_i(0)/SA_i$, where i represents an isotope of element E and $S_i(0)$ is the initial activity of radionuclide i per gram of soil. The total concentration of element E in the soil solution system, $C_{E,tot}$, can be calculated as $C_{E,tot} = \Sigma_i C_i$.

In our methodology, the calculated $C_{E,tot}$ is considered to be the upper limit of total chemical element E to be released into the solution phase. When the solution pH is specified, the possible chemicals compound in the soil solution system can be identified from the stability diagram. Because saturate solubilities for different chemical compounds are different, the chemical species with the highest saturate solubility is considered in our method. For chemical elements with a simple stability diagram, the contribution of chemical

concentration from less soluble chemical species is insignificant. For some specific chemical elements, the stability lines appearing in the stability diagram for chemical compounds with high solubilities are so close that competition for dissolution needs to be considered. In these cases, the saturate solubility can be estimated as the average value obtained from all soluble chemical compounds shown in the stability diagram. The saturate solubility for the most soluble compound can still be used for modeling purposes, which gives a higher value of saturate solubility and a lower value of estimated distribution coefficient.

In the natural system, dissolution of chemical species from soil to solution tends to be slow. It was assumed in this study that equilibrium conditions have been reached. The leaching process releases chemical elements from soil to solution and forces the dissolved chemical elements to move to the lower portion of the soil stratum. Loss of chemical elements in this process indicates a downward movement of the horizontal line $L_1 = \log C_{E,tot}$ in the stability diagram and possibly the presence of less soluble compounds in the system. A distribution coefficient with a higher value can then be expected when leaching proceeds under the same environmental conditions.

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REFERENCES

1. C. Yu et al., *Manual for Implementing Residual Radioactive Material Guidelines Using RESRAD, Version 5.0,* ANL/EAD/LD-2, Argonne National Laboratory, Argonne, Illinois (1993).

2. R.M. Garrels and C.L. Christ, *Solutions, Minerals, and Equilibria*, Harper and Row, New York, New York, pp. 213-216 (1965).

3. M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solution*, Pergamon Press, Oxford, United Kingdom (1966).

4. D. Rai and W.L. Lindsay, "A Thermodynamic Model for Predicting the Formation, Stability, and Weathering of Common Soil Minerals," *Soil Sci. Soc. Am. Proc.*, **39**, 991-996 (1975).

5. D. Rai and R.J. Serne, "Plutonium Activities in Soil Solutions and the Stability and Formation of Selected Plutonium Minerals," *J. Environ. Qual.*, **6**, 89-95 (1977).

6. L.L. Ames and D. Rai, *Radionuclide Interaction with Rock and Soil Media, Volume I: Processes Influencing Radionuclide Mobility and Retention, Element Chemistry and Geochemistry; Conclusion and Evaluation,* EPA520/6-78-007-a, U.S. Environmental Protection Agency, Office of Radiation Programs, Las Vegas, Nevada (1978).

7. K.F. Nieto and W.T. Frankenberger, Jr., "Single Column Ion Chromatography, I. Analysis of Inorganic Anions in Soils," *Soil Sci. Soc. Am. J.*, **49**, 587-592 (1985).

8. W.J. Lyman et al., *Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds*, McGraw-Hill, St. Louis, Missouri (1982).

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