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PRELIMINARY RESULTS ON COMPARISON OF
ADSORPTION-DESORPTION METHODS AND STATISTICAL
TECHNIQUES TO GENERATE K_d PREDICTOR EQUATIONS

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The radioactive waste isolation safety assessment program (WISAP) is being performed for the United State Department of Energy. A large bank of data have been collected under this program. A part of the program is devoted to the evaluation of radionuclide-geomedia interactions in order to determine the behavior of different elements in the environment. This paper introduces and briefly summarizes data collected thus far on methods of determining adsorption coefficients, thermodynamic predictions of stable solid and solution species, K_d data, and studies for determining adsorption mechanisms.

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INTRODUCTION

Preliminary analysis has shown that by using geologic selection criteria [1] for selecting a repository site, the probability of a repository breach and resulting hazard to man is very low. In the event that the repository is breached by intruding groundwater, radioactive wastes will be leached and radionuclides brought into solution. The most important barrier to radionuclide movement, aside from engineered barriers, is retardation due to interaction between radionuclides and geologic media (Figure 1). Because of higher than normal temperatures and the radiation field in the repository, groundwater leaving the disposal site is expected to contain radionuclides. The final radionuclide concentrations in any groundwater that may come in contact with the biosphere are of major concern.

For full comprehension of radionuclide behavior, one must understand the radionuclide chemistry as it affects various retardation mechanisms. Figure 1 lists the types of data required: 1) accurate thermodynamic data on solid phases and solution species that may be present or may form in the geomeadia, 2) adsorption-desorption isotherms, 3) equations that quantify effects of different factors as they influence exchange, adsorption, precipitation and dissolution, and solution species, and 4) mineralogical and physico-chemical properties of the geologic media. All such data are not presently available. Because of time and money constraints, thorough investigation of the different radionuclide interaction mechanisms is not possible. Therefore, an empirical approach in combination with a limited mechanistic approach was chosen by the Waste Isolation Safety Assessment Program (WISAP) to evaluate the radionuclide geologic media interactions. In the empirical approach, the influence of exchange and surface adsorption and of precipitation and dissolution are evaluated by determining adsorption distributions (K_d or more appropriately retardation factor) in the laboratory for a large number of well characterized geomeadia and solution types. The objectives of this paper are to discuss different methods of determining K_d and the progress on accumulating a data bank for geomeadia-radionuclide interactions.

METHODS OF DETERMINING K_d

The methods of determining K_d can be grouped into two categories, the static or "batch" technique and the dynamic or column methods. In the static method, solution traced with radionuclides is shaken with samples of geomeadia for a period before sampling and analysis. Investigation of dynamic systems entails the study of a tracer solution as it flows through geologic media. The dynamic methods (low pressure flow, axial filtration, high pressure intact core) differ in the type of pressure required to force liquid through the geomeadia. The advantages and disadvantages of different methods of K_d determination are discussed by Relyea, et al. [2]. The two methods (static and dynamic) for radionuclide-geologic media interaction studies are complementary, with the static method being most useful for screening investigations of radionuclide behavior in a variety of systems and for estimating the time needed to attain equilibrium. Static radionuclide adsorption distributions may then be compared to retardation factors obtained from dynamic systems under similar conditions to verify results. Crushed or uncrushed material may be used in either method. Solutions similar in composition to the final solutions in static tests may also be used in dynamic experiments. The most pressing current need is for a relationship to relate K_d values obtained on crushed material or uncrushed pieces to the natural geomeadia that may contain variable amounts of tortuous fissures and cracks.

Since a large number of factors inherent in the geomeadia and solution (Figure 1) can affect the K_d , a small change in procedures may give different results. Therefore, thorough characterization of solution and geomeadia should be done for all K_d determinations. A study is currently under way to evaluate the K_d determination methods.

The K_d values for Cs and Sr determined by the batch, flow through column (crushed material), and axial filtration methods for simple mineral-solution systems show favorable agreement [3]. Channel chromatographic and batch K_d

Figure 1 Factors that determine the concentration of radionuclides in solutions leached through the waste.

techniques used to determine the adsorption capacities of shale for Sr and Ni from dilute calcium nitrate solutions also compare favorably [4]. Although it is too premature to make definite conclusions, the different experimental methods give comparable results on crushed media for simple systems. We plan to relate sorption onto fissures versus crushed material via normalization of surface area. At present we have no conclusive data to verify this approach. More complex systems (natural rocks as opposed to pure minerals, natural groundwater as opposed to synthetic salt solutions, and multivalent nuclides such as the Pu) should and will also be studied by various experimental techniques.

In addition, an interlaboratory comparison [5] of batch Kd values of oolitic limestone (Bedford, Indiana) and basalt (Sentinel Gap, Washington) for Cs, Sr, and Pu was also performed in order to find the precision of determining Kd by the batch method. The participating laboratories (Table 1) were provided with homogeneous samples of limestone and basalt and were given recipes for groundwater preparation. The solution used to determine the Kd of limestone was between 8.0 and 8.4 pH with the total concentration of various ions in ppm as $\text{Ca}^{2+} = 50$, $\text{Mg}^{2+} = 3.6$, $\text{Na}^+ = 2.3$, $\text{K}^+ = 0.4$, $\text{HCO}_3^- = 153$, $\text{SO}_4^{2-} = 14.4$, and $\text{Cl}^- = 3.5$. The solution used to determine the Kd of basalt was between 7.7 and 8.2 pH with the total concentration of various ions in ppm as $\text{Ca}^{2+} = 6.5$, $\text{Mg}^{2+} = 1.0$, $\text{Na}^+ = 30$, $\text{K}^+ = 9$, $\text{HCO}_3^- = 58$, $\text{SO}_4^{2-} = 23$, $\text{Cl}^- = 16$, and $\text{F}^- = 0.7$. The Kd was calculated using the following formula:

$$K_d = \left[\frac{C_o - C}{C} \right] \left[\frac{V}{W} \right]$$

in which C_o = activity of radionuclide in the original solution corrected for loss of activity from solution with no geomeedia, C = activity of radionuclide in the solution equilibrated with geomeedia, V = total volume of the solution, and W = weight of the soil. When the volume is in ml and weight in g the dimensions of Kd are ml/g.

The results reported [5] in Table I indicate that in general for all the isotopes compared (Cs, Sr, Pu), there was considerably more disagreement in Kd values for limestone than for basalt. The observed Kd values of Cs for limestone ranged over three orders of magnitude. For basalt, however, the Kd values of Cs varied by a factor of approximately two. The Kd values of Sr for limestone varied by an order of magnitude and for basalt by approximately a factor of two. A quick glance at the Kd values of Pu for both limestone and basalt shows that the values are generally high and that these vary by two to three orders of magnitude. The reasons for poor precision in Kd values (Table 1) determined by the batch method are not readily apparent. Since the data in Table 1 was obtained using the same geomeedia and solutions, the poor precision may be due to some of the uncontrolled variables (such as tracer concentrations, Eh, preparation of tracer solution, shaking method and speed, temperature, variation of pH of the equilibrium solution, phase separation technique). This study reemphasized the need for mechanistic studies, strict control and understanding of factors and procedures that affect Kd, and realization that Kd is an empirical parameter most useful for site specific geomeedia and solutions.

DATA BANK FOR GEOMEDIA-RADIONUCLIDE INTERACTIONS

Thermodynamic Data

Although, at the present, meaningful data for interaction of radionuclides with all geomeedia are not available [6], such data are accumulating rapidly [7,8]. In order to best utilize the data generated by many researchers from the United States and abroad, we are using chemical computer models and computerized data files. The data files of existing thermodynamic equilibrium computer models [9,10,11,12] are being updated to include actinide and long lived fission products. The data files consist of standard Gibbs free energies and entropies of formation for a wide variety of minerals, aqueous species and gases [13]. From these data the distribution of an element between solid, liquid and gaseous species may be predicted assuming equilibrium conditions. Based upon the

Table I. Interlaboratory Comparison of Kd (ml/g) Values for Limestone and Basalt for Cs, Sr and Pu* [5]

Cs				Sr				Pu				Participating Laboratories
Limestone		Basalt		Limestone		Basalt		Limestone		Basalt		
pH	Kd	pH	Kd	pH	Kd	pH	Kd	pH	Kd**	pH	Kd**	
7.9	880 $\pm$ 160	8.7	380 $\pm$ 70	7.9	14.9 $\pm$ 4.6	8.7	92 $\pm$ 3	7.9	1090 $\pm$ 120 ^a 690 $\pm$ 320 ^b	8.6	200 $\pm$ 170 ^a 15 $\pm$ 2 ^b	PNL
7.9	65 $\pm$ 2	7.8	401 $\pm$ 21	8.0	5.4 $\pm$ 0.3	8.1	68 $\pm$ 17	7.6	1027 $\pm$ 41 ^a 2134 $\pm$ 77 ^c	7.5	8.8 $\pm$ 3.4 ^a 67 $\pm$ 14 ^c	ANL
8.5	83 $\pm$ 1	8.4	265 $\pm$ 4	8.5	1.4 $\pm$ 0.2	8.4	81 $\pm$ 1	8.1	4745 $\pm$ 4931 ^a 3198 $\pm$ 512 ^c	8.0	1078 $\pm$ 716 ^a 843 $\pm$ 658 ^c	LASL
ND	60 $\pm$ 30	ND	290 $\pm$ 70	ND	2.7 $\pm$ 0.5	ND	45 $\pm$ 1	ND	770 $\pm$ 36 ^b	ND	580 $\pm$ 12 ^b	LLL
8.2	227 $\pm$ 14	8.3	380 $\pm$ 5	8.3	5.9 $\pm$ 0.2	8.4	89 $\pm$ 5	8.2	198 $\pm$ 50 ^a	8.2	592 $\pm$ 134 ^a	ORNL-I
ND	663 $\pm$ 61	ND	453 $\pm$ 12	ND	9.3 $\pm$ 2.4	ND	93 $\pm$ 6	ND	63000 $\pm$ 19000	ND	312 $\pm$ 66 ^a	ORNL-II
ND	6.8 $\pm$ 0.6	ND	255 $\pm$ 7	ND	13.4 $\pm$ 0.6	ND	73 $\pm$ 4	ND	2616 $\pm$ 1135 ^b		89 $\pm$ 17 ^b	RHO
7.8	1.3 $\pm$ 0.4	7.4	31 $\pm$ 2	7.6	1.8 $\pm$ 0.5	7.4	41 $\pm$ 6	7.5	547 $\pm$ 356 ^b	7.5	1000 $\pm$ 590 ^b	AEC (Canada)
ND	48.9 $\pm$ 5	ND	296 $\pm$ 10	ND	2.4 $\pm$ 0.1	ND	55 $\pm$ 2	ND	1009 $\pm$ 162 ^d	ND	221 $\pm$ 147 ^d	LBL

* The limestone and basalt samples were crushed to a 297 to 840 μ m size. All Kd's are for a 7 day equilibration period except ORNL-II which are for a 29 day equilibration period. The ND in the data means "not determined".

** Equilibration solution treatment, a = centrifuged at approx. 4000 g and filtered through 0.2 to 0.45 μ m filter, b = centrifuged at approx. 4000 g, c = absorbed activity was determined directly from the geomeia sample instead of calculating from the change in concentration of the radionuclide in solution, d = based on original influent which was not corrected for the loss of activity from the solution not containing geomeia.

thermodynamic data, a summary of stable solution species that may be present in relatively oxidizing and reducing environments is given in Table II.

Kd Data Bank

The second type of computerized data file, the Kd data bank, consists of a tabulation of nuclide distribution coefficients along with a complete information about the geomedium and solution [14]. To properly assess whether a nuclide distribution coefficient (Kd) or retardation factor previously determined is applicable to a scenario under study, it is necessary to have a complete description of the geologic media, contacting solution, nuclide properties and experimental details. Too often in available literature Kd values are presented without these necessary details. Without the supporting information it is difficult to assign confidence limits on the appropriateness of the data. The Kd data generated in the last two years for the WISAP program are currently being installed on a Pacific Northwest Laboratory (PNL) information-retrieval system. Data generated under the WISAP Program [7,8] and other literature data will also be incorporated into the data bank at a future date. This capability will allow to sort the data automatically and to search Kd data by computer using details regarding the author, experimental conditions, type of geologic material and its properties, solution properties, and information about species, concentration, and nature of radionuclide. For example, if a listing of all Kd data for basalt is needed, one can ask the computer to tabulate all basalt data. If one wants to compare Kd's from a salt brine across all rock types one can sort on brine, etc. The computer data bank sorting capability will also be linked to statistical programs such that selected data will automatically be transferred from the data bank to the statistical program and after manipulation the results will be displayed on a screen or produced as hard copies. In this fashion one can get means, standard deviations, and empirical predictor equations for Kd as a function of minerals, surface area, cation-exchange capacity, groundwater composition, etc.

The data bank will be set up such that the operator is lead through the procedure step by step. It will be usable by nongeochemists. We want the data information-retrieval system to be usable by modelers without necessitating a lot of technical interpretation. If a modeler needs Kd's for a particular scenario the information-retrieval system will inquire about the type of scenario and after the operator inputs on the keyboard, the computer will select possible choices and display them along with any other basic details requested.

Statistical Technique to Synthesize Kd Data

The statistical analysis and synthesis of the experimental data is accomplished using the adaptive learning "self learning" networks developed by Adaptronics, Inc. [15,16,17,18]. The Adaptive Learning Network (ALN) is a mathematical method, made possible by high speed computers, which fits a multinomial (a polynomial in many variables) to the multidimensional surface describing a radionuclide Kd. Thus, the ALN methodology is a powerful tool for use in data modeling instances where little or no knowledge exists regarding the functional relationship of dependent to independent variables. In order to construct a self-learning network, a list of important variables along with data representative of variety of situations that can occur in the system is needed. The next step is to construct a generalized equation to link an output value to each possible pair of input variables. Variables are initially taken two at a time in quadratic form to describe the Kd. Special purpose computer programs are used to find the coefficients (the weights assigned to the variables in the quadratic equation for the Kd) for each equation that make it best fit the data. These equations and variables that produce the smallest prediction errors are determined and retained. In the next step, quadratic equations are taken as new variables and the above procedure is repeated to obtain polynomial equations (up to eighth order) which predict the Kd. This process is repeated as additional layers of equations are added to the network and retained if they can improve its predicting ability. The training procedure is terminated when the model would become so adept at fitting the data used to train it that it would be unable to generalize to data not previously seen. Special algorithms are used to detect and avoid this condition. To make certain that the model has indeed discovered

Table II. Predominant Solution Species of Elements in a pH 4 to 9, pO_2 0.68 to 80, pCO_2 1.52 to 3.52, $pCl^- = pNO_3^- = pSO_4^{2-} = 3.0$, $pF^- = 4.5$ and $pH_2PO_4 = 5.0$ Environment (Activities of Solution Ions in moles/l) Without Organic Ligands [6]

Elements	Predominant Solution Species of Elements		
	Little Affected by Oxidation-Reduction	In An Oxidizing Environment	In A Reducing Environment
Am	Am^{3+} , $AmSO_4^+$, $Am(OH)^{2+}$		
Sb		HsO_2^0 , $Sb(OH)_3^0$, $SbOFO$, $Sb(OH)_4^-$	SbO^+
Ce	Ce^{3+} , $CeSO_4^+$		
Cs	Cs^+		
Co	Co^{2+} , $Co(OH)_2^0$		
Cm	Cm^{3+} , $CmOH^{2+}$, $Cm(OH)_2^+$		
Eu	Eu^{3+} , $EuSO_4^+$, $Eu_2P_2O_7^{2+}$		
I	I^- , IO_3^-		
Np		NpO_2^+ , $NpO_2HPO_4^-$, $NpO_2HCO_3^-$	$NpOH^{3+}$, Np^{4+}
Pu		PuO_2^{2+} , $PuO_2(CO_3)(OH)_2^{2-}$, PuO_2^+	$PuOH^{2+}$, Pu^{3+}
Pm	Pm^{3+}		
Ra	Ra^{2+}		
Ru		$Ru(OH)_2^{2+}$, RuO_4^- , RuO_4^{2-}	RuO_4^-
Sr	Sr^{2+}		
Tc		TcO_4^-	Tc^{2+}
Th	ThF^{3+} , $Th(OH)_3^+$		
3H	H^+ , $^3H-O-H$		
U		UO_2^{2+} , UO_2F^+ , $UO_2(OH)_2^0$, $UO_2(CO_3)_3^{4-}$	UO_2^{2+} , UOH^{3+} , UO_2^+ , $UO_2(CO_3)_3^{4-}$
Zr	$Zr(OH)_4^0$, $Zr(OH)_5^-$, ZrF^{3+}		

for itself the pertinent physical laws, additional experimental data not used in the training phase are introduced to test the ability of the model to generalize on its prior experience in dealing with new situations.

The performance of the ALN method was compared with the regression method [15] by using the Kd data generated by Relyea et al. [19]. In this evaluation, Kd as the dependent variable was related to different properties of the geomedial (cation exchange capacity, surface area), solution properties (Na^+ , Ca^{2+} , Cl^- , HCO_3^-), time (time dependent Kd experiments), and pH and Eh of the mineral-solution suspensions. A part of the results are shown in Table III. The results [15] presented in Table III show that there was a considerable improvement in predicting Kd when the ALN method was used than when the regression method was used. While performing clustering techniques on these data [19], it was discovered that the adsorption coefficients for silicate minerals were a function of the structural group (phyllosilicates, tektosilicates, and inosilicates). Although studies are under way, it is not known at present whether the rock Kd can be modeled from the information regarding its chemical, physical, and mineralogical properties. We plan to use all available data to generate equations that would relate Kd as a function of geologic media, groundwater and nuclide characteristics. Although the derived relationships will not prove "cause and effect" or confirm sorption mechanisms, they will allow prediction of trends. Thus from Kd data on a finite number of rock and water types, estimates of Kd for a nuclide for other rock-water environments not directly studied can be made if precautions, such as avoiding extrapolation beyond the ranges of variables used to construct the empirical mathematical relationship, are observed.

Adsorption Data Based Upon Mechanistic Studies

The Kd concept, computer data bank, and empirical Kd predictor equations do not rigorously lend themselves to an understanding of controlling mechanisms. A limited number of mechanistic studies are under way at present, with more emphasis to be placed upon this type of study in following years. Studies conducted thus far at PNL have revealed that:

- 1) in radioactive waste disposal cribs containing discrete PuO_2 particles, the concentration of soluble Pu is predictable from a solubility relationship [20],
- 2) the solubility of PuO_2 and Pu(IV) hydroxide actually observed under environmental conditions differ from theoretical predictions [20,21],
- 3) Pu(IV) polymer formation can be predicted from pH and total soluble Pu concentration [22],
- 4) Pu(V) rather than Pu(VI) may be the dominant species in environmental samples in relatively oxidizing conditions [23], and
- 5) a potentiostat can be used to control the Eh of geochemical suspensions to aid in the determination of adsorption coefficients of various oxidation states of multivalent elements such as Pu, Np and Tc [24].

Microautoradiography studies of rock thin sections performed at Lawrence Berkeley Lab (LBL) and Los Alamos Scientific Laboratory (LASL) have shown that the active sorption sites in bulk rocks (basalt, quartz monzonite, argillite, tuffaceous alluvium and tuff) for actinides are generally the secondary mineral alteration products such as clays, zeolites etc. [25,26].

Accelerated weathering studies on basalt and argillite increased the sorption tendencies for most isotopes studied (Cs, Sr, Pu, Am, Np). Weathering of granite showed no observable changes in sorption [27].

Systematic ion-exchange studies versus supporting electrolyte concentration at constant pH show the adsorption of Sr and Cs is approximately as expected from conventional idealized ion exchange equations. The trivalent ions Eu and Am however do not conform to idealized equations. Details on this work performed at Oak Ridge National Laboratory (ORNL) can be found in these [3,8] references.

Table III. Performance of ALN and Regression (Reg) Techniques On Data Not Used In Model Synthesis [15]

Method	Tc (0 to 22) ^{1/}		Sr (0 to 1680) ^{1/}		Cs (1.3 to 140000) ^{1/}		Np (0 to 7324) ^{1/}	
	Average Absolute Error	Correlation Coefficient	Average Absolute Error	Correlation Coefficient	Average Absolute Error	Correlation Coefficient	Average Absolute Error	Correlation Coefficient
<u>Time Independent</u>								
ALN	1.3	.88	75.4	.91	5481	.67	15.4	.87
Reg.	2.4	.62	91.0	.85	6330	.52	25.4	.31
<u>Time Dependent</u>								
ALN	1.3	.65	59.4	.96	4151	.41	18.4	.74
Reg.	1.5	.60	79.4	.90	4452	.18	23.3	.35

^{1/} Numbers in parentheses denote the range of values of K_d for the particular nuclide.

In other studies at ORNL [4] it was found that redox sensitive elements Np and Tc should not be stable in their mobile NpO_2^+ and TcO_4^- forms in contact with igneous rock-anoxic groundwater suspensions. Np and Tc added in their mobile oxidized states are reduced to much less mobile species by these environments. The current safety assessments which consider the oxidized forms (NpO_2^+ and TcO_4^-) only may be overestimating their potential hazard to the public.

At Argonne National Laboratory (ANL) kinetic and partitioning data for Am in fissures of unpermeable rock were used as input to a transport model which includes time dependent sorption (kinetic effects). Laboratory infiltration experiments into fissures were compared with model predicted behavior. The favorable comparison emphasizes the need to consider reaction kinetics in the prediction of nuclide migration [28].

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