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Studies of Radionuclide Sorption by Clays in the Culebra Dolomite at the Waste Isolation Pilot Plant Site, Southeastern New Mexico

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STUDIES OF RADIONUCLIDE SORPTION BY CLAYS IN THE CULEBRA DOLOMITE
AT THE WASTE ISOLATION PILOT PLANT SITE, SOUTHEASTERN NEW MEXICO*

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ABSTRACT

The ability of radionuclide-rock interactions to retard the migration of plutonium and uranium within clay-lined fractures in the Culebra Dolomite Member of the Rustler Formation is being estimated in support of the performance assessment of the Waste Isolation Pilot Plant. This paper describes progress in three coordinated studies: characterization of the properties of the groundwater and minerals in the Culebra that will control radionuclide retardation; development of a thermodynamic model for the adsorption of uranium onto corrensite, the mixed chlorite-smectite clay mineral found in Culebra fractures; and development of a data base of equilibrium constants and interaction parameters for calculations of the aqueous speciation of uranium and plutonium in $\text{Na}-\text{Cl}-\text{Ca}-\text{SO}_4-\text{CO}_3$ solutions which contain organic ligands such as EDTA and range in ionic strength from approximately 0.8 to 6.0 molal.

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INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) in southeastern New Mexico is being designed for the safe geologic disposal of defense-generated transuranic (TRU) wastes. The Culebra Dolomite Member of the Rustler Formation lies approximately 450 m above the repository. This unit is the most likely pathway for long-term migration of radionuclides to the accessible environment. The ability of solute-rock interactions to retard the migration of radionuclides within the Culebra Dolomite is being estimated in support of performance assessment calculations for the WIPP.

Initial performance assessment calculations (1,2) indicate that releases of plutonium and uranium dominate the radiological and chemical discharges to the environment. Radionuclide/clay interactions may be the dominant mechanism for radionuclide retardation. For this reason, the focus of this study is to examine the extent of the sorption of uranium and plutonium onto clays within the Culebra matrix and fractures.

For the past two decades there has been an active debate concerning the proper way to represent radionuclide sorption in transport calculations. Part of the debate has been focused on the use of K_d 's or linear isotherms to represent solute/rock/water interactions in performance assessment calculations (3,4). It is recognized that these approximations ignore many potentially important geochemical phenomena.

The use of a K_d or linear isotherm implies that sorption is the only solute/rock reaction that occurs during transport. However, in real systems many other reactions may compete for the solute. These include processes that will decrease the extent of sorption, such as complexation with inorganic or organic ligands and formation of colloids. In batch sorption experiments, other processes such as precipitation will remove radionuclides from solutions and may lead to calculations of erroneously-high K_d 's (3,4).

Current limitations of computer hardware and codes suggest that for the foreseeable future, K_d 's or linear isotherms will be used in performance assessment calculations (1,3,5,6). An important task facing experimentalists and modelers is to estimate the strength of the interaction between the solute and rocks that is truly due to sorption. This interaction can be included in a K_d in performance assessment calculations and used to calculate a defensible lower limit for radionuclide retardation.

Evaluation of the potential retardation of radionuclide migration by sorption onto clays within the Culebra involves several coordinated activities. These include the following: characterization of the compositions of clays and groundwaters along potential radionuclide flow paths, measurement of surface complexation constants for uranium and plutonium in simple and mixed electrolyte solutions containing clays, and development of a data base of equilibrium constants and interaction parameters for calculations of the aqueous speciation of radionuclides.

CHARACTERISTICS OF MINERALOGY AND GROUNDWATER ALONG POTENTIAL FLOW PATHS

Radionuclide Release Scenario

Figure 1 describes the scenario used to guide the studies of rocks and waters along potential flow paths. Performance assessment calculations indicate that significant discharges of radionuclides may occur if the repository and a pressurized brine pocket in the underlying Castile Formation are intruded by a borehole after final emplacement of the waste (1, 2). Even if the borehole is plugged after the intrusion of the repository, it is possible that the plugs will degrade and allow flow of brine from the Castile into the repository, through the Salado via the borehole, and into the Culebra Dolomite.

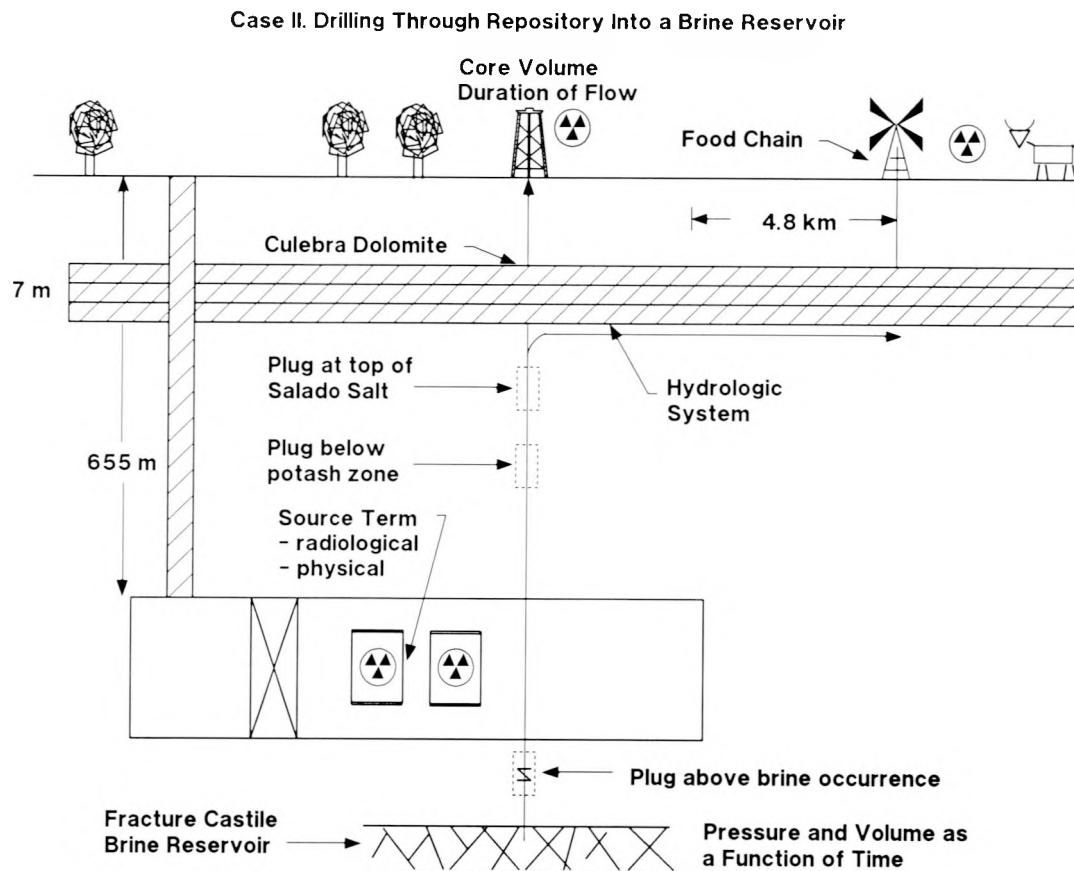


Figure 1. Radionuclide Release Scenario for WIPP Performance Assessment and Sorption Studies. The intrusion of the repository and underlying brine pocket is followed by leaching of waste from the repository by Castile brine and migration of radionuclide-rich brine through the Culebra Dolomite.

Figure 1 shows that mixing of fluids from the Castile Formation, Salado Formation, emplaced waste, and the Culebra Member will control the chemistry of the radionuclide-bearing brine as it enters the Culebra. Interaction of this water with rocks along the flow path may further alter the solution chemistry. The amount of radionuclide sorption is strongly dependent upon solution chemistry and the nature of the minerals that are exposed to the solutions. Identification of the minerals and prediction of the changes in solution chemistry along the flow path is a prerequisite to estimation of the K_d 's that should be used in performance assessment calculations.

Description of Mineralogy along the Radionuclide Transport Path

The dominant mineral in the Culebra Member is a fairly pure dolomite which comprises about 85% by weight of the bulk rock (7). In the most transmissive parts of the Culebra Dolomite, fluid flow is controlled by fractures (2). Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and corrensite (a mixed chlorite/smectite clay mineral) are the most abundant fracture-fill minerals (7,8). The concentration of clay in samples from the surface coatings of fractures in cores from several boreholes within the WIPP Four-mile Zone ranged from 5 to 25% by weight (8).

Only small amounts of clay can be sampled from the Culebra fracture coatings; therefore, initial technique and model development for the sorption studies are being carried out with reference corrensites from richer deposits. These include corrensite from a mudstone layer immediately below the Culebra Dolomite (AISCor) and a reference corrensite (CorWa) from the Source Clays Repository of the University of Missouri. X-ray patterns from the CorWa, AISCor, and Culebra corrensite are very similar (8,9). The specific surface area of the CorWa is $36 \text{ m}^2/\text{gm}$ as measured by the BET (Brunauer, Emmett, and Teller) method (10).

Electrophoretic studies of the CorWa reference corrensite indicate the presence of three sorption sites: a SiOH site, an AlOH site, and a fixed-charge (isomorphic substitution) site (10). As a first approximation, however, the CorWa is being modeled as a homogeneous surface with a single site and a site density of one site/ nm^2 . This is equivalent to an exchange capacity of approximately 6 meq/100 g. For comparison, a cation exchange capacity (CEC) of 31 meq/100 g was measured by Mg-Ca exchange for the AISCor sample (9).

Composition of Waters in the Culebra Prior to Waste Emplacement

An understanding of the chemical evolution of Rustler waters (11) provides a framework for predictions of the responses of the Culebra Member to the influx of brines from the Castile and repository. Within the WIPP site, the salinities of water in the Culebra range from <10,000 to >200,000 mg/L. Figure 2 shows that

the concentration of sodium varies by an order of magnitude over the WIPP-controlled area (Four-Mile Zone). The concentrations of the other major solutes (Cl, SO_4 , Mg, Ca, K), as well as the Mg/Ca ratio are correlated with the Na concentration. The variations in salinity can in turn be correlated with the occurrence of halite (NaCl) in the mudstone/anhydrite (CaSO_4) layers that stratigraphically bound the Culebra (12).

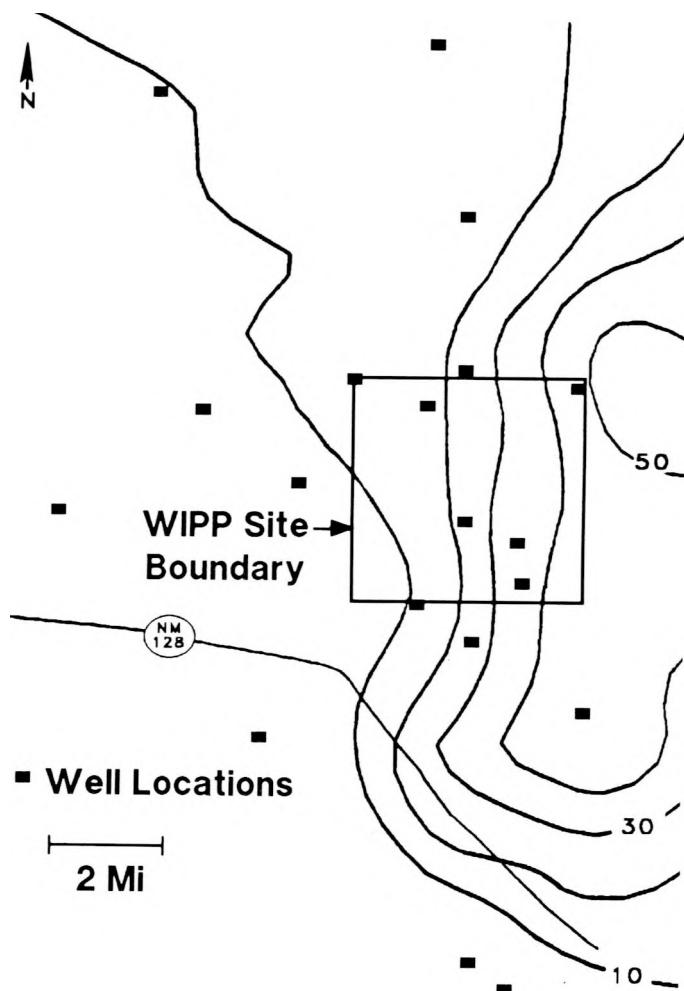


Figure 2. Contours of Sodium Concentration (g/L) in Culebra Dolomite Waters in the Vicinity of the Waste Isolation Pilot Plant.

Chemical reactions that control the concentrations of major solutes in Culebra waters were identified by calculation of mineral saturation indices using the PHRQPITZ code (11, 13). All of the water samples are saturated with respect to gypsum and calcite (CaCO_3); most of the samples are supersaturated with respect to dolomite ($\text{CaMg}(\text{CO}_3)_2$).

The relationships among the concentrations of major solutes, mineral saturation indices, and ionic strength suggest that the Culebra Member is a partial equilibrium system (11). In a partial equilibrium system, water/mineral equilibria shift along a reaction path driven by an irreversible physical or chemical process (14). Waters in the Culebra are undersaturated with respect to halite and other evaporite salts. As the fluids encounter these minerals along the flow path, the dissolution of the salts raises the ionic strength and changes the solubilities of dolomite, gypsum and calcite. The rock/water system is partially buffered; precipitation or dissolution of calcite and gypsum maintain equilibria between these minerals and the water; however, the solution becomes supersaturated with respect to dolomite because of kinetic barriers to dolomite precipitation (15).

The PHRQPITZ code was used to test this partial equilibrium model. Figure 3 summarizes the results of several alternative reaction paths for the chemical evolution of water in the Culebra. The paths differ in the identity of the accessory salts that are assumed to supply solutes to the Culebra and in the degree of dolomite saturation. The progress of the reactions is marked by the ionic strength; the changes in water composition are indicated by the Mg/Ca ratio.

The reaction path marked "Run 10" is consistent with the partial equilibrium model described above. It involves the addition of a Na-Mg-K-Cl component to the Culebra waters. In this simulation, the source of this solute assemblage was dissolution of halite, polyhalite ($\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$), and carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$).

This reaction path reproduces all of the relationships among the major solutes in the Culebra waters (11). Dissolution of these minerals in the layers adjacent to the Culebra is consistent with the observed mineralogy of the Rustler and Salado Formations (2,7,11). It has not yet been established that this particular reaction path is the only chemical process that can reproduce the observed solute concentrations; however, the simulations shown in Figure 3 provide strong support for the hypothesis that the Culebra Dolomite is a partial equilibrium system.

Implications of Partial Equilibrium Model for Radionuclide Release Scenarios

The reference compositions for the waters that will be mixed as a result of the release scenario described in Figure 1 are listed in Table I and are shown diagrammatically as a compositional pyramid in Figure 4. The PHRQPITZ code was used to model the chemical reactions and solution compositions that result from mixing of these brines in various proportions. Note that the

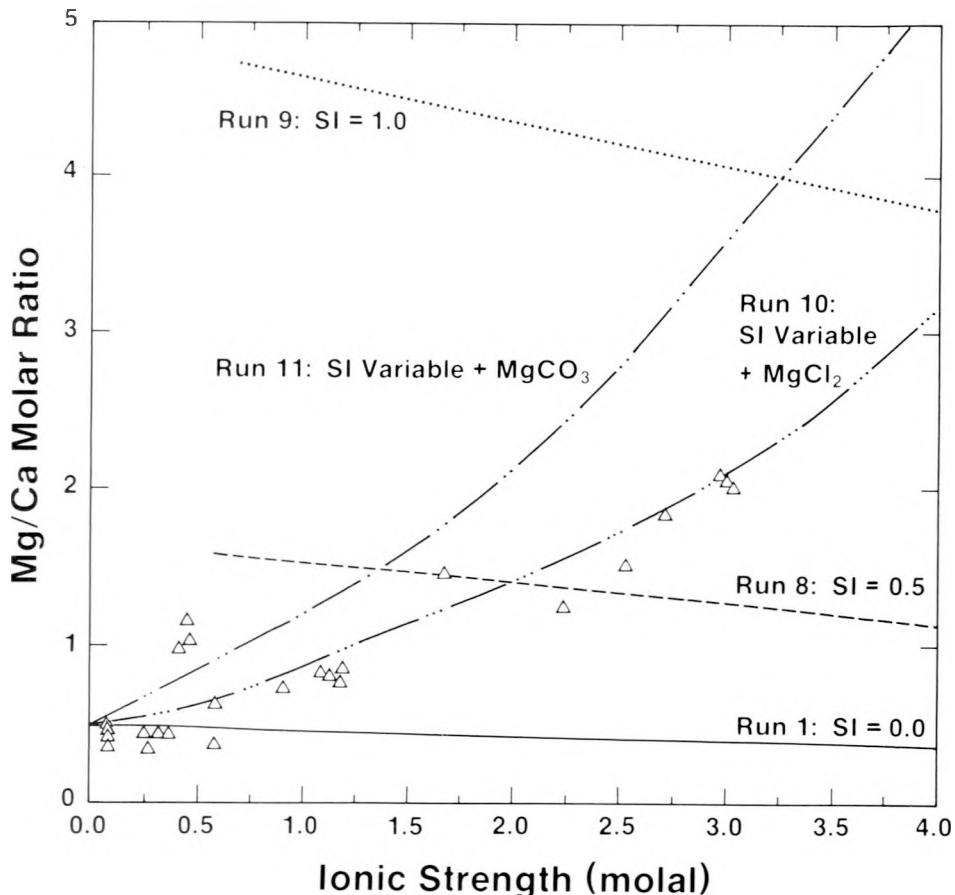


Figure 3. Change in Mg/Ca Molar Ratio as a Function of Reaction Progress (Ionic Strength) for Alternative Reaction Paths for Chemical Evolution of Culebra Water. SI = saturation index for dolomite. The accessory salt added with halite and polyhalite to the solution is identified for each run. Data points are Culebra water compositions.

Salado brine is a Na-Mg-Cl-rich fluid. As a first approximation, it was assumed that the Culebra water/rock system would respond to injection of this brine along the same partial equilibrium reaction path described in the previous section. This means that in the simulation, equilibrium would be maintained with respect to gypsum and calcite; dolomite would not precipitate or dissolve. Under these constraints, the simulations predict that calcite will precipitate and gypsum will dissolve in the Culebra as a result of the fluid mixing.

The flux of Culebra water to the mixing zone was assumed to be $6.3 \text{ m}^3/\text{yr}$ and was estimated from the hydraulic gradient and transmissivity in the Culebra above the repository (2). Estimates of ranges of discharges of Castile and Salado water to the Culebra in the release scenario were taken from Lappin et al. (2, pp. 7-12 to 7-16). Compositions of the resultant solutions

TABLE I. COMPOSITIONS OF REFERENCE BRINES AND MIXTURES

Solute	Solutions ¹				
	<u>SB-1ah</u>	<u>ERDA-6</u>	<u>AISc</u>	<u>A6E100S1</u>	<u>A6E10S1</u>
Ca ²⁺ (mmol)	10.5	13.2	22.8	15.0	22.3
Mg ²⁺ (mmol)	1171	20.8	21.5	34.9	109
Na ⁺ (mol)	3.92	5.35	0.61	5.05	3.53
K ⁺ (mmol)	586	107	8.2	107	108
Cl ⁻ (mol)	6.42	5.27	0.57	5.00	3.67
SO ₄ ²⁻ (mmol)	186	187	80	183	155
TIC ² (mmol)	0.4	17.5	1.6	15.3	9.4
log pCO ₂ (atm)	-2.4	-0.69	-2.83	-0.64	-1.10
pH	6.08	6.17	7.5	6.04	6.34
Ionic strength (molal)	8.20	5.82	0.84	5.56	4.24

¹The ERDA-6 brine is the average composition calculated for 10 samples from the ERDA-6 well (16). The SB-1ah brine is a composition calculated from a reference Salado brine composition (PAB1 in ref. 2) which has been brought to equilibrium with anhydrite and halite in a PHRQPITZ simulation. The AISc brine is a composition calculated from a reference composition for samples from the WIPP Air Intake Shaft (17) which has been brought to equilibrium with calcite in a PHRQPITZ simulation. The A6E100S1 brine is the composition of a solution resulting from the mixing of AISc, ERDA-6, and SB-1ah brines in the ratio 6.3:100:1.3. The A6E10S1 brine is the composition of a solution resulting from the mixing of the AISc, ERDA-6 and SB-1ah brines in the ratio 6.3:10:1.3. Both of these mixtures are in equilibrium with calcite and gypsum.

²Total inorganic carbon.

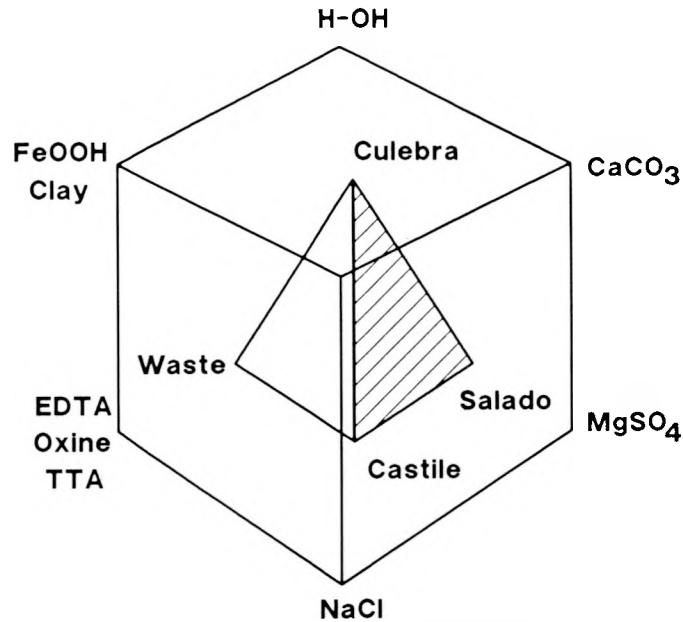


Figure 4. Compositions of Reference Brines and Simple Electrolytes Considered in Design of Sorption Experiments and K_d Measurements.

from two of the mixing calculations are shown in Table I. These solutions represent the estimated maximum and minimum rates of discharge of Castile brine to the Culebra (2). Future mixing calculations will include a higher salinity Culebra component to account for the wide range of composition in the Culebra waters (cf. Figure 2) and additional dilution of the fluid by Culebra waters along the flow path to the accessible environment. In this way, the full range of solution compositions resulting from mixing during the release scenario described in Figure 1 can be estimated.

STUDIES OF THE ADSORPTION OF URANIUM BY CORRENSITE

Experimental Design

Most of the K_d values obtained in previous studies of radionuclide sorption by geologic materials have been gathered without knowledge of the speciation of the radionuclides or the surface properties of the substrate (2,3,4). Such K_d values are at best valid for the conditions (e.g., solution composition, solid/solution ratio, substrate mineralogy) of a particular experiment. There is no reliable method to extrapolate the K_d values to different experimental conditions.

The mineralogical and hydrochemical studies summarized in the previous sections indicate that potential radionuclide flow paths in the Culebra Member are characterized by relatively simple mineralogy and complex solution chemistry. Measurements of K_d s for every possible solution composition are not feasible.

Instead, the approach taken here is to obtain surface complexation constants that can be used to calculate K_d s over the range of solution compositions. The conceptual basis of the surface complexation modeling approach is reviewed by Kent et al. (3). In this approach, the sorption sites of the clay are assumed to be ligands that complex with the radionuclides. The partitioning of the radionuclides between the solution and sorption sites is calculated from the concentrations of the radionuclides, surface sites, aqueous ligands, and other solution parameters and the equilibrium constants for the surface and aqueous complexation reactions.

The surface complexation constants are obtained in a series of experiments which start with simple electrolyte solutions and proceed to include more components and more complex interactions. Figure 4 illustrates the simple and complex systems that are considered in this study. As discussed in the next section, surface complexation constants have been obtained in dilute ($I = 0.01$ M) solutions containing uranium, corrensite and a non-complexing background electrolyte. The complexation constant obtained for this system is used to obtain complexation constants in more complex solutions containing sequestering ligands (e.g., CO_3^{2-} , EDTA) or cations that compete for the surface sites (e.g., Mg^{2+} , Ca^{2+}). The K_d s in groundwaters of interest (within the compositional pyramid in Figure 4) can be calculated from the surface complexation constants and solution compositions using the HYDRAQL code (18). Direct measurement of K_d s in the complex solutions provides a final validation of the data and model.

Measurement of Uranium Sorption

A stripping voltammetry technique for analysis of low-level (0.1 ppb) concentrations of uranium (19) is being used to obtain surface complexation constants in simple electrolyte solutions. Figure 5 shows the adsorption of uranium onto the CorWa reference corrensite in 0.01 molal NaClO_4 solutions containing different concentrations of CO_3^{2-} . The maxima in adsorption at intermediate pH values are consistent with the predominance of nonsorbing uranyl-carbonate complexes in alkaline solutions. Also shown are the adsorption curves calculated with the HYDRAQL code assuming equilibria between various uranyl-hydroxy-carbonato-complexes as well as an equilibrium constant $\log K = 1.68$ for the following surface (SOH) complexation reaction:

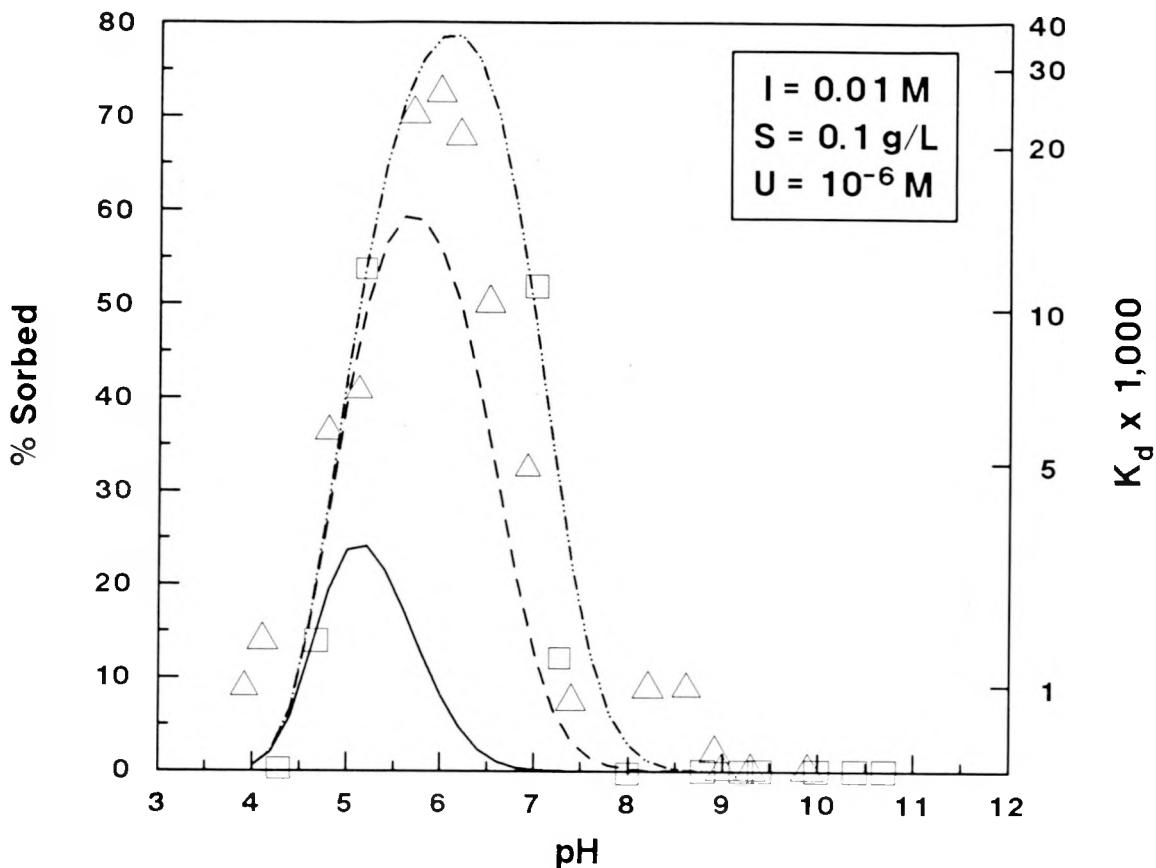
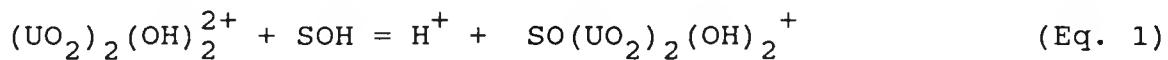


Figure 5. Effect of Carbonate Concentration on Uranium Sorption by Corrensite: Data and Model Fit for CorWa Reference Corrensite. Experimental data: $\Delta = 10^{-4} \text{ M } \text{CO}_3^{2-}$; $\square = 10^{-5} \text{ M } \text{CO}_3^{2-}$. Model calculations: $\text{---} = 10^{-3} \text{ M } \text{CO}_3^{2-}$; $\text{----} = 10^{-4} \text{ M } \text{CO}_3^{2-}$; $\text{--- ---} = 10^{-5} \text{ M } \text{CO}_3^{2-}$. $S = \text{concentration of solid in the suspension.}$



This constant and reaction stoichiometry were obtained from uranium sorption data in a CO_2 -free system.

Figure 5 illustrates how the collection and modeling of the sorption data are bound together in the surface complexation modeling approach. The model predicts a decrease in the degree of sorption as the carbonate concentration is increased. The experimental data plotted in Figure 5 are not adequate to show this effect unambiguously. Additional data must be obtained at higher carbonate concentrations (e.g., 10^{-3} M) to test the validity of the sorption reaction and constant described in Eq. 1. Used in this way, the surface complexation modeling approach provides a structured means of evaluating the quality and quantity of the sorption data.

The K_d corresponding to points along the model curves or the experimental data can be calculated from the following relation:

$$K_d(\text{ml/gm}) = \frac{1000 \cdot \%U}{(100 - \%U)S} \quad (\text{Eq. 2})$$

where $\%U$ is the percent of the total uranium sorbed and S is the concentration of the solid in the suspension in gm/L. K_d values obtained in this way can be used in transport calculations to estimate the amount of radionuclide retardation due to sorption if values of parameters such as the effective porosity and density of the transport medium are known.

CALCULATION OF THE SPECIATION OF RADIONUCLIDES IN BRINES

Values of the complexation constants for all important aqueous species in a solution of interest are required for estimation of the surface complexation constants and calculation of K_d 's as shown in the previous section. The HYDRAQL code uses the Davies equation to calculate the complexation constants (also called apparent equilibrium constants) at specified ionic strengths from thermodynamic data (18). This approach is not valid at ionic strengths greater than approximately 0.5 M and is not adequate for Culebra waters or solutions that are produced in the mixing scenarios described previously. Several methods for calculating apparent equilibrium constants for formation of inorganic and organic uranium and plutonium complexes in these waters have been evaluated (20). Extended Debye-Huckel equations appear satisfactory for pure electrolytes such as NaCl up to 4.0 molal ionic strength. Equations employing the Bronsted-Guggenheim interaction theory are required when SO_4^{2-} and Ca^{2+} are present in moderately high concentrations as observed in some Culebra waters. A correlation has been established between the specific interaction parameters compiled by the Nuclear Energy Agency for pure electrolytes (21) and interaction parameters B_W calculated for solutions with ionic proportions similar to that of seawater. The values of B_W for uranium and solutes in the Culebra were calculated using a fit to the following equation and the activity coefficients of trace metals in seawater as calculated by Whitfield (22).

$$\log \gamma_i + 0.511z^2 \frac{I^{1/2}}{1 + 1.5I^{1/2}} = B_W I \quad (\text{Eq. 3})$$

where γ_i are the ion activity coefficients in solution with ionic proportions equal to that of seawater, z is the charge of the ion, I is the ionic strength, and B_W is the interaction coefficient for the ion in the seawater solution. The correlation between the NEA specific interaction parameters (21) and the B_W values for the trace metals in seawater was then used to obtain values of B_W for other radionuclides. Through this correlation

approach, the quantity of data available for initial calculations of apparent equilibrium constants and solubilities of plutonium and uranium has been greatly enhanced. Results to date indicate that this approach will be useful for brines that range in ionic strength from 0 to 3 molal. Additional work is required to extend Eq. 3 to 6 molal ionic strength solutions.

The WIPP Aqueous Solutions Data Base (WIPP-ASD) has been developed to store and process thermodynamic data and interaction parameters and associated uncertainties for the modeling of experimental data and sensitivity analyses (20). The calculation of apparent equilibrium constants with the WIPP-ASD is illustrated in Figure 6. The calculated apparent equilibrium constants can be used in the HYDRAQL code to interpret experimental data and to calculate K_d values in specific solutions.

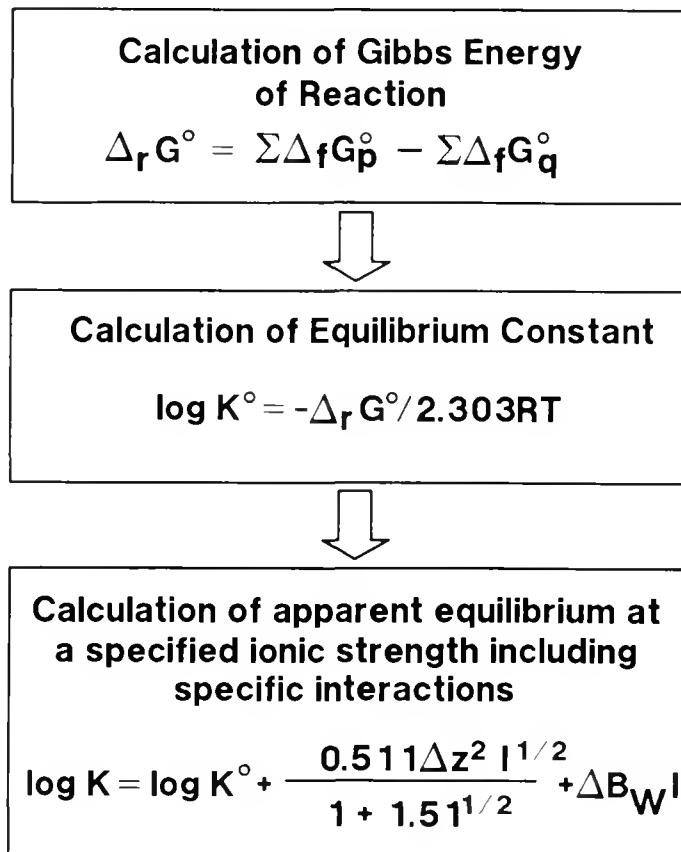


Figure 6. Use of the WIPP-ASD to Calculate Apparent Equilibrium Constants Including Specific Interactions at a Specified Ionic Strength.

SUMMARY

Performance assessment calculations indicate that significant discharges of radionuclides from the WIPP may occur if the repository and a pressurized brine pocket in the underlying Castile Formation are intruded by a borehole after final emplacement of the waste. Predictions of changes in the composition of water in the Culebra due to the influx of brine from the repository are based on a partial equilibrium model for the groundwater. This model suggests that equilibrium would be maintained with gypsum and calcite, but that dolomite would become supersaturated as the Mg content of the water increases. Calculations using the PHRQPITZ chemical equilibrium model show that in the Culebra above the repository the ionic strength and Mg would range from 4.2 to 5.6 molal and 35 to 109 mmolal respectively; the pH would range from 6 to 6.4.

Initial calculations of radionuclide release and site characterization studies of the WIPP indicate that adsorption of radionuclides by fracture-lining clays in the Culebra Dolomite would be an important barrier to radionuclide migration. Studies of rock samples from cores and shafts indicate that corrensite (a mixed chlorite/smectite) is an abundant fracture-fill mineral in the Culebra. Therefore, measurement of purely empirical K_d s for adsorption of radionuclides by corrensite in all possible solution compositions is not feasible; more robust surface complexation constants, which are valid over a wide range of solution compositions, are being measured. With this approach, K_d s for a variety of solution compositions can be calculated.

A stripping voltammetry technique has been used to measure the sorption of uranium onto corrensite in simple electrolyte solutions. The extent of sorption is a strong function of pH and the amount of available clay surface area; the effect of carbonate concentration on sorption cannot be evaluated from the available data. In a CO_2 -free solution containing 0.1 g/L clay, the K_d varies from 400 to 27,000 ml/g over a pH range of 6 to 8.

Surface complexation constants can be extracted from the experimental sorption data using the HYDRAQL code. These constants can in turn be used with apparent equilibrium constants to calculate K_d s in more complex brines. The WIPP-ASD has been developed to facilitate calculation of apparent equilibrium constants in high ionic strength solutions from thermodynamic data and interaction parameters obtained in solutions with ionic proportions similar to that of seawater. Sensitivity analyses are being carried out to identify the predominant aqueous species over a range of solution compositions and to identify crucial data needs. Measurement of K_d s in complex brines will provide validation of the surface complexation constants for the WIPP waters.

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