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COMPUTER MODELING OF NUCLIDE ADSORPTION
ON GEOLOGIC MATERIALS

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During the aqueous transport of radionuclides through geologic media, physical and chemical processes can lead to the exchange of radionuclide mass between the aqueous and solid phases, e.g. sorption by the geologic materials, precipitation or dissolution, and complexation. Our program covers a theoretical and experimental study aimed at determining the important parameters that govern the sorption phenomena with the goal of developing methods by which the distribution of a given radionuclide between the solid and aqueous phases might be predicted for geologic materials and ground water types anticipated for terminal radioactive waste storage facilities.

A computer program, called MINEQL, has been developed¹ and is being tested for use in predicting the distribution of radionuclides between solid and aqueous species for a variety of geologic materials and solution conditions. MINEQL is designed to accept a list of components of a system (electrolytes, solid substrates and radionuclides) and their total analytical concentrations, solve the appropriate set of mass balance and equilibrium expressions, and produce a list of the identities and concentrations of all species formed by interactions among the components and between them and/or water. The mathematical methods have been described in detail elsewhere².

MINEQL uses the electrolyte binding electrical double layer model¹ formalism to describe the adsorption reactions. In this model, the acidic, basic and amphoteric hydroxyl groups present on oxides, hydroxides and silicates are assumed to be ionizable surface groups that can form positively and negatively charged adsorption sites. Equilibrium reactions and intrinsic

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(thermodynamic) constants can be written for the surface ionization reactions and for the adsorption of electrolyte ions by exchange with the hydroxyl protons. Estimates of the intrinsic constants can be made using surface charge data derived from acid/base titrations of aqueous suspensions of the solid materials¹. The model includes the effect of the development of surface charge on the solid surface equilibria.

Cesium and uranium adsorption isotherms have been measured at 26°C for the solid substrates quartz and Belle Fourche clay (montmorillonite) as a function of Cs and U concentration (10^{-4} M to 10^{-9} M), pH (5 to 10), and NaCl supporting electrolyte concentration (10^{-3} M to 1 M) in batch-type experiments using finely crushed material. In addition, U measurements were also made with solutions containing 10^{-4} M carbonate. As an example, the distribution coefficients, K_d , defined as the amount of nuclide adsorbed per gram of clay divided by the amount of nuclide per milliliter of solution, for Cs adsorption on the Belle Fourche clay are plotted as solid points in Figure 1 as a function of pH for several NaCl concentrations and an initial Cs solution concentration of 1.01×10^{-7} M.

The ability of MINEQL to simulate the measured adsorption data is presently being tested and only the Cs adsorption on the clay has been completed. Our titration data suggest that the Belle Fourche clay behaves like a mixture of at least two distinct, energetically different, uniform sets of exchange sites with different intrinsic constants, referred to here as S-OH and T-OH sites. Therefore, a two-site model was used in analysis of the clay data. The reactions, intrinsic constants and other parameters used in the Cs/clay modeling studies are presented in Table I. The results of the calculations using MINEQL are shown in Figure 1. The dashed curves result when the effect of surface charging is included while the solid curves result when it is omitted.

Comparisons of the calculations with the experimental data indicate that MINEQL is able to simulate the Cs adsorption data rather well.

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References

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TABLE I
REACTIONS, INTRINSIC CONSTANTS AND OTHER PARAMETERS USED
IN MINEQL MODELING OF Cs ADSORPTION ON BELLE FOURCHE CLAY.

Reactions	Constants
$\text{SOH} \rightleftharpoons \text{SO}^- + \text{H}^+$	$10^{-4.0}$
$\text{TOH} \rightleftharpoons \text{TO}^- + \text{H}^+$	$10^{-7.1}$
$\text{SOH} + \text{Na}^+ \rightleftharpoons \text{SO}^- \text{Na}^+ + \text{H}^+$	$10^{-0.24}$
$\text{TOH} + \text{Na}^+ \rightleftharpoons \text{TO}^- \text{Na}^+ + \text{H}^+$	$10^{-2.9}$
$\text{SOH} + \text{Cs}^+ \rightleftharpoons \text{SO}^- \text{Cs}^+ + \text{H}^+$	$10^{0.84}$
$\text{TOH} + \text{Cs}^+ \rightleftharpoons \text{TO}^- \text{Cs}^+ + \text{H}^+$	$10^{-1.8}$
$\text{Cs}^+ + \text{Cl}^- \rightleftharpoons \text{CsCl}^0$	$10^{-0.59}$

Adsorption site concentrations (meq/gm), SOH = 0.36, TOH = 0.84.

Total surface area = $800 \text{ m}^2/\text{gm}$.

S denotes surface.

Figure 1. Variation of distribution coefficients for cesium with Ph for an initial Cs solution concentration of 1.01×10^{-7} M for several NaCl electrolyte concentrations. Solid points represent the experimental data. The solid and dashed curves result from calculations using MINEQL without and with the inclusion of the effects of surface charging. Where the curves coincide, only the solid curve is shown.

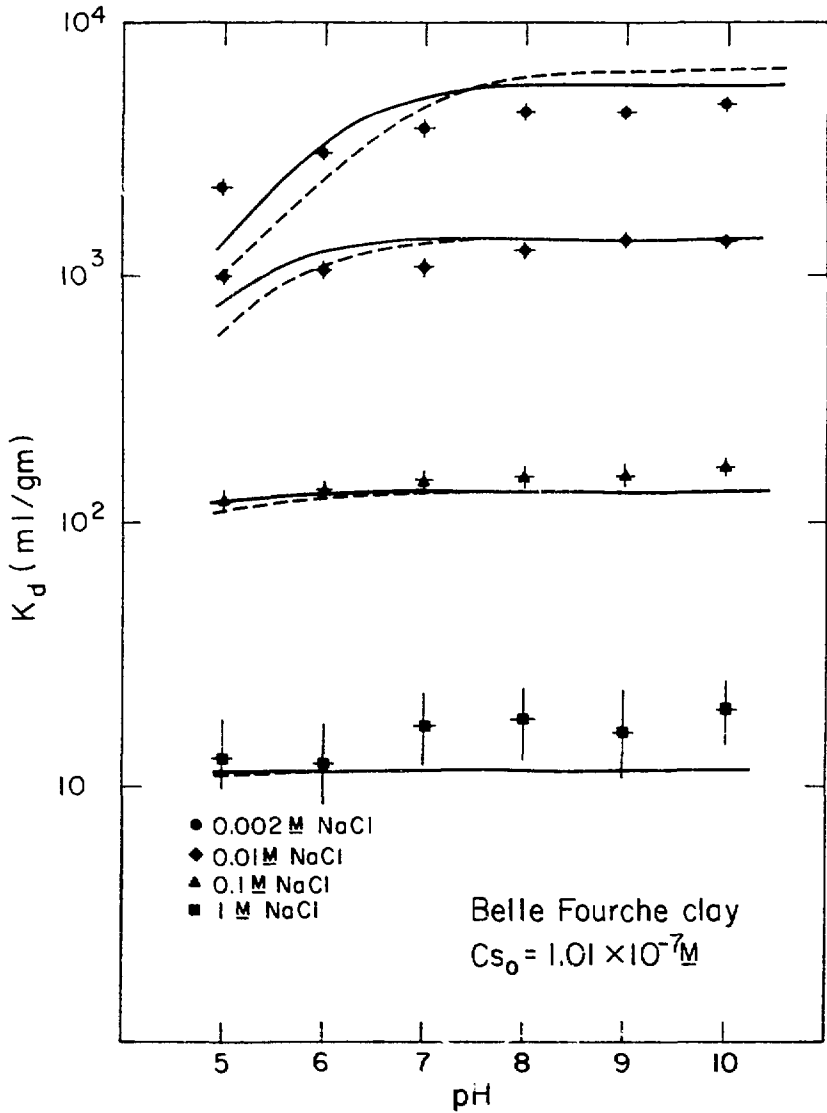


Figure 1

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