

## SORPTION OF TRACE CONSTITUENTS FROM AQUEOUS SOLUTIONS ONTO SECONDARY MINERALS.

### I. URANIUM

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**Abstract**—Well-characterized American Petroleum Institute clay standards, source clays from The Clay Minerals Society, and other secondary minerals were used to determine the effects of U concentration, temperature, and solution composition on U-sorption properties. Uranium concentrations ranged from about  $1.00 \times 10^{-4}$  M to  $4.00 \times 10^{-7}$  M, temperatures from 5° to 65°C and solution compositions containing 0.01 M NaCl and 0.01 M NaHCO<sub>3</sub>. Silica gel efficiently sorbed uranyl carbonate anion complexes. The higher cation-exchange capacity materials most readily sorbed uranyl ions from the 0.01 M NaCl solution. Temperature increases tended to affect uranyl ion sorption adversely except when the U was present as carbonate complexes. Noncrystalline ferric oxyhydroxides sorbed uranyl ions much more efficiently than any of the secondary crystalline minerals studied. A method for accurately extrapolating U-sorption efficiencies between experimental points based on the Freundlich equation is presented.

**Key Words**—Cation exchange, Clinoptilolite, Freundlich isotherm, Glauconite, Illite, Montmorillonite, Opal, Sorption, Uranium.

#### INTRODUCTION

Uranium is a relatively mobile element in temperate surface environments; its mobility as controlled by U-mineral solubility equilibria in low temperature waters is well documented (Langmuir, 1978a, 1978b). An additional, relatively unknown factor in U mobility is, however, that of sorption on secondary minerals commonly found on joint surfaces of rocks and in sediments normally encountered during aqueous transport. Quantitative sorption data are scarce. Goldsztaub and Wey (1955) reported that 7.5 g of U was sorbed from a 1% uranyl nitrate solution onto 100 g of calcined kaolinite. Starik *et al.* (1958) found that the sorption of trace concentration of U on iron hydroxide was optimum at about pH 5, and declined above and below this value. Uranium was desorbed with a carbonate solution.

Rancon (1973) studied the sorption of U using four soils described as: (1) a river sediment containing a mixture of quartz, clay, calcite, and organic matter, (2) a river peat, (3) a sediment from Cadarache containing a mixture of quartz, clay, and calcite with no organic matter, and (4) a soil developed on an altered schist from near LaHague containing a mixture of quartz and clay but no calcite or organic matter. The first two soils were equilibrated with their river waters containing 10 ppm U and the last two soils were equilibrated with their respective groundwaters also containing 10 ppm U. The resulting U distribution coefficients are shown in Table 1, which also includes the K<sub>d</sub> values on pure quartz, calcite, and illite. The clay minerals in Soils 1, 3, and 4 were not identified, nor were the soils further characterized. Rancon also examined the effects of ini-

tial U concentration on K<sub>d</sub> values. Both the U concentration and solution pH changed as U was added to the solution. At 0.1 mg U/liter, the pH was 7.6, for example, and at 1.0 g U/liter, the pH was 3.5. Because the pH changes were a function of U concentration changes, the results are not easily interpreted. In addition, the K<sub>d</sub> concept is invalid above the trace U concentration (~1.0 mg U/liter). Uranium adsorption data at 1 ppm vs. K<sub>d</sub> also were presented. For Soil 4, three peaks were observed: K<sub>d</sub> 300 ml/g at about pH 5.5, K<sub>d</sub> 2000 ml/g at pH 10, and K<sub>d</sub> 270 ml/g at pH 12. Rancon suggested that the adsorption maxima represented by the three peaks also represent electrokinetic potential maxima. Quartz was characterized as inert, calcite as a poor U adsorber, and clays as the best adsorbers of U from solution. Acid, organic-rich soils show much higher U K<sub>d</sub> values than the alkaline peat (Soil 2) of Rancon's (1973) study.

Langmuir (1978b) reported several U-enrichment materials based on the work of Schmidt-Collerus (1967) including noncrystalline titanium oxide ( $8 \times 10^4$  to  $1 \times 10^6$ ), noncrystalline Fe(III) oxyhydroxides ( $1.1 \times 10^6$  to  $2.7 \times 10^6$ ), peat ( $10^4$  to  $10^6$ ), fine-grained goethite ( $4 \times 10^3$ ), phosphorites (15), montmorillonite (6), and kaolinite (2). Giblin (1980) studied U sorption from a simulated groundwater containing 100 µg U/liter ( $4.202 \times 10^{-7}$  M) onto kaolinite over a pH range of 3.5 to 10. A maximum U distribution of 35,000 ml/g was attained at a pH of 6.5.

Hsi (1981) examined the sorption of U on hematite, goethite, and noncrystalline ferric oxyhydroxide as affected by pH, U concentration, and carbonate complexing. Tsunaskima *et al.* (1981) examined the sorp-

Table 1. Uranium Kd Values.<sup>1</sup>

Soil	Kd (ml/g)
1—River sediment (clay, CaCO <sub>3</sub> , organic matter)	39
2—River peat	33
3—Sediment (clay, CaCO <sub>3</sub> )	16
4—Altered schist (clay)	270
Quartz	0
Calcite	7
Illite	139

<sup>1</sup> From Rancon (1973).

tion of U by Volclay over the concentration range of 1–300 ppm U. The sorption isotherms were reported to follow Langmuir-type curves at higher U-solution concentrations. Giblin *et al.* (1981) examined the mobility of U as affected by Eh and pH at 25°C. Hydrrous ferric oxide and kaolinite were used as the solid phases. High mobility in a pH-Eh range where U was thermodynamically insoluble suggested that U was present in this region as a colloid.

Walton *et al.* (1981) examined the release of U from two volcanic glass sedimentary sequences in Texas during diagenesis. Uranium was not significantly mobilized during the solution of the glass. They reported that once U was effectively trapped by secondary phases, it did not move for about 30 million years. Nash *et al.* (1981) recently reviewed the few reported field occurrences of U deposition by sorption and concluded that sorption could be an important concentrating step prior to the formation of uranyl or uranous minerals. The lack of rigorous and comparable U-sorption data on characterized geological materials, however, made the role of sorption in U migration difficult to assess.

In addition to the migration and sorption of U and Ra in natural deposits, the subject also is pertinent to high-level radioactive waste disposal where certain clays are under consideration as a portion of the backfill component of the multiple barrier waste package (Wood and Aden, 1982). The primary function of the waste package backfill is to assist in meeting the Nuclear Regulatory Commission criteria that requires a radionuclide release rate of no more than one part in 10<sup>5</sup> of

the inventory from the engineered barrier system (waste package plus repository) after 1000 years. All other things being equal, radionuclide breakthrough time is a function of the backfill material equilibrium radionuclide distribution coefficient. The present investigation was conducted to determine the sorption of uranium on various clays and other secondary minerals as a function of U concentration, temperature, and solution composition.

## MATERIALS AND METHODS

### *Characterization of the secondary minerals*

The identification and location of the secondary minerals used in the sorption studies are given in Table 2. The clay minerals were either American Petroleum Institute clay standards (Kerr, 1950) or source clays from The Clay Minerals Society (van Olphen and Fripiat, 1979). The various size ranges selected for use were obtained by grinding or elutriation. Chemical analyses of these materials for major components were made by Teflon-bomb digestion and inductively coupled argon-plasma before sodium solution contact (Table 3). Thorium analysis was by neutron activation and U, by atomic fluorescence. X-ray powder diffraction results showed that most of the minerals were free of detectable impurities with the exception of the illite and opal samples. The major constituent of the opal was  $\alpha$ -cristobalite. Minor quartz contamination was carried over during recovery of the <2- $\mu$ m illite fraction.

Cation-exchange capacities (CEC), measured with Cs and a Cs radionuclide (Cs<sup>137</sup>) as chlorides at pH 7.0 and 25°C, are given in Table 4. The procedure used was similar to that given by Routson *et al.* (1973). An ethylene glycol-monoethyl ether sorption method (Heilman *et al.*, 1965) was utilized to measure the surface area of the secondary minerals (Table 4). The first number given represents a mean of three values; the following number is a standard deviation.

Following separations, the secondary minerals were contacted three times with 3 M NaCl solutions, washed with methanol, and centrifugation to remove excess NaCl. Some care had to be taken with the kaolinite to avoid pH values below 5 in the NaCl solutions.

Table 2. Identification and origin of secondary minerals.

Mineral	Location	Origin
Illite, <2 $\mu$ m	Fithian, Illinois	A.P.I. Clay Standard 35
Kaolinite, <2 $\mu$ m	Macon County, Georgia	A.P.I. Clay Standard 4
Montmorillonite, <2 $\mu$ m	Apache County, Arizona	The Clay Minerals Society Source Clay SAz-1
Nontronite, <2 $\mu$ m	Garfield, Washington	A.P.I. Clay standard 33A
Glaucanite, 20–50 mesh	New Jersey coastal plain	Ward's Natural Science Establishment
Clinoptilolite, 50–100 mesh	Death Valley Junction, California	Anaconda Minerals Company, 1010 A
Opal, 20–40 mesh	Virgin Valley, Nevada	Ward's Natural Science Establishment
Silica gel, 100–200 mesh, reagent grade	Synthetic	Fisher Scientific Company

Table 3. Chemical analyses of the secondary minerals used in the uranium sorption work.

Constituent	Illite	Kaolinite	Montmorillonite	Nontronite	Glauconite	Clinoptilolite	Opal	Silica gel	Detection limit
Main constituents (wt. %)									
SiO <sub>2</sub>	57.10	45.10	58.90	45.00	49.20	65.20	88.90	90.7	0.5
Al <sub>2</sub> O <sub>3</sub>	18.40	37.80	17.10	6.31	7.46	11.10	0.79	0.14	0.4
Fe <sub>2</sub> O <sub>3</sub>	5.97	0.38	1.58	35.00	20.70	0.79	0.09	—	0.04
CaO	0.53	0.03	1.08	1.00	1.08	1.55	0.15	0.03	0.01
MgO	1.87	0.27	6.08	0.41	3.55	0.58	0.11	0.03	0.01
Na <sub>2</sub> O	1.40	0.35	3.72	2.50	0.27	2.52	0.10	—	0.1
K <sub>2</sub> O	5.00	0.25	0.19	0.02	9.40	4.04	0.04	—	0.01
Loss on ignition	9.05	14.50	11.10	9.60	7.75	14.20	9.80	9.10	0.01
Total	99.84	98.68	99.90	99.84	99.90	99.98	99.98	100.00	
Major trace components (ppm)									
Barium	45	60	267	152	32	340	—	—	10
Manganese	279	30	720	380	4900	208	—	—	30
Strontium	101	35	131	44	37	789	—	—	10
Titanium	5210	9050	1510	512	436	640	—	172	50
Uranium	1.0	0.5	11.5	—	1.0	1.5	26.0	—	0.5
Thorium	16.0	20.0	32.0	3.0	3.0	19.0	—	—	2.0

— present below detection limits.

### Solutions

Two solutions containing four U concentrations were used with the above minerals. The uranyl concentrations are given in Tables 5–7 with the uranium in 0.01 M NaCl or 0.01 M NaHCO<sub>3</sub>. The two types of solutions allowed examination of the effects of U-carbonate complexing on U sorption and its interactions with temperature and U concentration.

Radiochemically pure and carrier-free U<sup>233</sup> as uranyl nitrate was used to trace U sorption on the minerals. The use of U<sup>233</sup> allowed accurate scintillation counting of U into the part per billion concentration range. Depleted uranyl nitrate (U<sup>238</sup>) was used along with the U<sup>233</sup> to make up the solutions. The specific activity of U<sup>233</sup> was too high ( $9.48 \times 10^{-3}$  Ci/g) to allow its practical use much above a solution concentration of  $1.0 \times 10^{-6}$  M.

### Methods

Three aliquots of each original solution before they were contacted with the minerals were set aside for later counting with the equilibrium solution aliquots. All solution aliquots were filtered through 15-Å membranes. Ten milliliters of each original solution was added for each gram of mineral. Each solution-solid equilibrium experiment was conducted in triplicate in sealed, polypropylene tubes. The tubes containing the radioactive solutions were later rapidly rinsed with a few milliliters of methanol to remove all solids and recounted to verify that tube sorption was less than 2% of the total activity, or to allow corrections for tube-wall sorption.

The slurries were gently rotated to assure uniformity for a 30-day equilibrium period. A minimum of 30

days of mineral-solution contact was required for the system to approach chemical equilibrium. Experiments were conducted at 5°, 25°, and 65°C in environmental chambers which contained facilities for agitating the samples and controlled temperatures to within  $\pm 2^\circ\text{C}$ .

After a 30-day solution-solid contact period, a 15-Å filtered aliquot of each solution was counted along with initial solution samples at their respective temperatures. From the scintillation counting efficiency, the initial and equilibrium solution counts, and the specific activities of the radionuclides, the concentrations of U in the equilibrium solution and on the mineral were calculated. Dissolved oxygen measurements on final solutions yielded an average of 8.3 mg O<sub>2</sub>/liter, or a computed Eh of +650 mV. Whereas, such solutions were not saturated in atmospheric O<sub>2</sub>, the environments were not sufficiently anoxic to reduce U(VI)

Table 4. Surface areas, ignition losses, and cation-exchange capacities of the based, freeze-dried minerals.

Mineral	Surface area (m <sup>2</sup> /g $\pm$ 1 s)	900°C ignition (% wt. loss)	Cesium cation-exchange capacity (meq/100 g, pH 7.0, 25°C)
Illite	116.1 $\pm$ 10.1	3.5	25.0
Kaolinite	68.3 $\pm$ 5.4	14.4	12.2
Montmorillonite	747.0 $\pm$ 52.8	20.1	120.0
Nontronite	861.0 $\pm$ 36.0	16.5	95.0
Glauconite	137.3 $\pm$ 7.9	0.8	16.03
Clinoptilolite	20.0 $\pm$ 2.2	10.1	140.2
Opal	46.8 $\pm$ 6.4	3.7	3.18
Silica gel	626.3 $\pm$ 25.0	10.2	2.79

Table 5. Experimental mean values for sorption of uranium by secondary minerals at 65°C from 0.01 M NaCl and 0.01 M NaHCO<sub>3</sub> solutions.

Solid	0.01 M NaCl			0.01 M NaHCO <sub>3</sub>		
	Initial U (mole/liter)	Equilibrium U (mole/liter)	U on solid (mole/g)	Initial U (mole/liter)	Equilibrium U (mole/liter)	U on solid (mole/g)
Illite	$1.005 \times 10^{-4}$	$1.585 \times 10^{-5}$	$9.307 \times 10^{-7}$	$1.004 \times 10^{-4}$	$4.047 \times 10^{-6}$	$1.059 \times 10^{-6}$
	$1.039 \times 10^{-5}$	$1.815 \times 10^{-8}$	$9.428 \times 10^{-8}$	$1.041 \times 10^{-5}$	$3.748 \times 10^{-7}$	$1.104 \times 10^{-7}$
	$1.393 \times 10^{-6}$	$1.754 \times 10^{-7}$	$1.339 \times 10^{-8}$	$1.353 \times 10^{-6}$	$6.282 \times 10^{-8}$	$1.418 \times 10^{-8}$
	$3.458 \times 10^{-7}$	$4.309 \times 10^{-8}$	$3.328 \times 10^{-9}$	$3.508 \times 10^{-7}$	$1.683 \times 10^{-8}$	$3.672 \times 10^{-9}$
Kaolinite	$1.005 \times 10^{-4}$	$3.545 \times 10^{-6}$	$1.083 \times 10^{-6}$	$1.004 \times 10^{-4}$	$7.130 \times 10^{-5}$	$2.447 \times 10^{-7}$
	$1.039 \times 10^{-5}$	$3.775 \times 10^{-7}$	$1.118 \times 10^{-7}$	$1.041 \times 10^{-5}$	$4.478 \times 10^{-6}$	$6.629 \times 10^{-8}$
	$1.393 \times 10^{-6}$	$5.069 \times 10^{-8}$	$1.499 \times 10^{-8}$	$1.353 \times 10^{-6}$	$2.433 \times 10^{-7}$	$1.240 \times 10^{-8}$
	$3.458 \times 10^{-7}$	$1.288 \times 10^{-8}$	$3.720 \times 10^{-9}$	$3.508 \times 10^{-7}$	$4.143 \times 10^{-9}$	$3.874 \times 10^{-9}$
Montmorillonite	$1.005 \times 10^{-4}$	$5.845 \times 10^{-6}$	$2.129 \times 10^{-6}$	$1.004 \times 10^{-4}$	$2.085 \times 10^{-5}$	$1.790 \times 10^{-6}$
	$1.039 \times 10^{-5}$	$3.540 \times 10^{-7}$	$2.258 \times 10^{-7}$	$1.041 \times 10^{-5}$	$1.568 \times 10^{-6}$	$9.946 \times 10^{-8}$
	$1.393 \times 10^{-6}$	$4.787 \times 10^{-8}$	$3.026 \times 10^{-8}$	$1.353 \times 10^{-6}$	$2.955 \times 10^{-7}$	$2.380 \times 10^{-8}$
	$3.458 \times 10^{-7}$	$1.399 \times 10^{-8}$	$7.465 \times 10^{-9}$	$3.508 \times 10^{-7}$	$8.764 \times 10^{-8}$	$5.918 \times 10^{-9}$
Nontronite	$1.005 \times 10^{-4}$	$3.918 \times 10^{-6}$	$2.137 \times 10^{-6}$	$1.004 \times 10^{-4}$	$9.064 \times 10^{-5}$	$2.159 \times 10^{-7}$
	$1.039 \times 10^{-5}$	$4.031 \times 10^{-7}$	$2.209 \times 10^{-7}$	$1.041 \times 10^{-5}$	$7.752 \times 10^{-6}$	$5.881 \times 10^{-8}$
	$1.393 \times 10^{-6}$	$4.843 \times 10^{-8}$	$2.975 \times 10^{-8}$	$1.353 \times 10^{-6}$	$5.330 \times 10^{-7}$	$1.770 \times 10^{-8}$
	$3.458 \times 10^{-7}$	$1.415 \times 10^{-8}$	$7.336 \times 10^{-9}$	$3.508 \times 10^{-7}$	$6.495 \times 10^{-8}$	$6.325 \times 10^{-9}$
Glauconite	$1.005 \times 10^{-4}$	$2.982 \times 10^{-6}$	$1.057 \times 10^{-6}$	$1.004 \times 10^{-4}$	$4.355 \times 10^{-6}$	$1.041 \times 10^{-6}$
	$1.039 \times 10^{-5}$	$4.783 \times 10^{-7}$	$1.074 \times 10^{-7}$	$1.041 \times 10^{-5}$	$6.887 \times 10^{-7}$	$1.054 \times 10^{-7}$
	$1.393 \times 10^{-6}$	$6.251 \times 10^{-8}$	$1.442 \times 10^{-8}$	$1.353 \times 10^{-6}$	$1.003 \times 10^{-7}$	$1.358 \times 10^{-8}$
	$3.458 \times 10^{-7}$	$1.956 \times 10^{-8}$	$3.536 \times 10^{-9}$	$3.508 \times 10^{-7}$	$2.917 \times 10^{-8}$	$3.432 \times 10^{-9}$
Clinoptilolite	$1.005 \times 10^{-4}$	$4.190 \times 10^{-6}$	$6.831 \times 10^{-7}$	$1.004 \times 10^{-4}$	$7.120 \times 10^{-5}$	$3.404 \times 10^{-7}$
	$1.039 \times 10^{-5}$	$6.440 \times 10^{-7}$	$1.136 \times 10^{-7}$	$1.041 \times 10^{-5}$	$7.027 \times 10^{-6}$	$3.944 \times 10^{-8}$
	$1.393 \times 10^{-6}$	$6.645 \times 10^{-8}$	$1.547 \times 10^{-8}$	$1.353 \times 10^{-6}$	$8.489 \times 10^{-7}$	$5.877 \times 10^{-9}$
	$3.458 \times 10^{-7}$	$1.765 \times 10^{-8}$	$3.826 \times 10^{-9}$	$3.508 \times 10^{-7}$	$3.304 \times 10^{-7}$	$2.379 \times 10^{-9}$
Opal	$1.005 \times 10^{-4}$	$4.199 \times 10^{-6}$	$1.068 \times 10^{-6}$	$1.004 \times 10^{-4}$	$5.724 \times 10^{-5}$	$4.786 \times 10^{-7}$
	$1.039 \times 10^{-5}$	$3.903 \times 10^{-7}$	$1.109 \times 10^{-7}$	$1.041 \times 10^{-5}$	$4.531 \times 10^{-6}$	$6.519 \times 10^{-8}$
	$1.393 \times 10^{-6}$	$6.195 \times 10^{-8}$	$1.476 \times 10^{-8}$	$1.353 \times 10^{-6}$	$4.797 \times 10^{-7}$	$9.684 \times 10^{-9}$
	$3.458 \times 10^{-7}$	$1.789 \times 10^{-8}$	$3.636 \times 10^{-9}$	$3.508 \times 10^{-7}$	$9.214 \times 10^{-8}$	$2.869 \times 10^{-9}$
Silica gel	$1.005 \times 10^{-4}$	$2.754 \times 10^{-6}$	$1.075 \times 10^{-6}$	$1.004 \times 10^{-4}$	$4.335 \times 10^{-6}$	$1.057 \times 10^{-6}$
	$1.039 \times 10^{-5}$	$4.414 \times 10^{-7}$	$1.095 \times 10^{-7}$	$1.041 \times 10^{-5}$	$4.862 \times 10^{-7}$	$1.092 \times 10^{-7}$
	$1.393 \times 10^{-6}$	$5.237 \times 10^{-8}$	$1.475 \times 10^{-8}$	$1.353 \times 10^{-6}$	$6.861 \times 10^{-8}$	$1.413 \times 10^{-8}$
	$3.458 \times 10^{-7}$	$1.407 \times 10^{-8}$	$3.649 \times 10^{-9}$	$3.508 \times 10^{-7}$	$2.272 \times 10^{-8}$	$3.610 \times 10^{-9}$

to U(IV). Final pH measurements showed little change from the starting solution pH of approximately 7 for the NaCl and 8 to 9 for the NaHCO<sub>3</sub> solution.

## RESULTS

Tables 5, 6, and 7 give the U sorption results at 65°, 25° and 5°C, respectively. The equilibrium concentrations of U in the solution and on the solid (mineral) represent experimental means of three replicates. The initial U (that present in the solution before the experiment began) ranged from  $1.0 \times 10^{-4}$  M to  $3.5 \times 10^{-7}$  M in concentration; however, equilibrium concentrations covered a broader range due to varied sorption on the minerals.

The sorption data of Tables 5–7 fit the linearized Freundlich equation widely used in the study of organics sorption on solids (Reinbold *et al.*, 1979). The Freundlich equation (Freundlich, 1922) is  $(x/m) = KC^n$ , where  $(x/m)$  is the equilibrium U load on the mineral in mole/g, C is the equilibrium solution concentration, and K and n are constants. The Freundlich sorption isotherm is generally useful up to about 5% of the

capacity of the solid. A plot of  $\ln(x/m)$  vs.  $\ln C$  should result in a straight line with a slope of n and a Y axis intercept of K. Illite sorption of uranium from both solutions is shown in Figure 1 as an example of the Freundlich sorption isotherm. The Freundlich constants given in Table 8 for the various experimental conditions can be used to generate an equilibrium regression line for the respective experiments. The r is a regression coefficient that measures how well the experimental data fit the regression line. A perfect correlation would be  $\pm 1.0000$ .  $Sy \cdot x$  is the standard deviation from regression and is a measure of dispersion, similar to a standard deviation, applied to differences between estimated and observed values of  $\ln(x/m)$ . Using the Freundlich constants, an equilibrium solution concentration can be generated for a given U  $(x/m)$  value. From these data, a distribution coefficient (D) can be generated by  $(x/m)/(C)(0.001)$  which has the dimensions of ml/g. The distribution coefficients can be compared for minerals in the same experimental environment.

In addition to the straight line relationship generated

Table 6. Experimental mean values for sorption of uranium by secondary minerals at 25°C from 0.01 M NaCl and 0.01 M NaHCO<sub>3</sub> solutions.

Solid	0.01 M NaCl			0.01 M NaHCO <sub>3</sub>		
	Initial U (mole/liter)	Equilibrium U (mole/liter)	U on solid (mole/g)	Initial U (mole/g)	Equilibrium U (mole/liter)	U on solid (mole/g)
Illite	$1.004 \times 10^{-4}$	$2.341 \times 10^{-6}$	$1.078 \times 10^{-6}$	$1.004 \times 10^{-4}$	$1.792 \times 10^{-5}$	$9.069 \times 10^{-7}$
	$1.044 \times 10^{-5}$	$2.601 \times 10^{-7}$	$1.119 \times 10^{-7}$	$1.044 \times 10^{-5}$	$1.214 \times 10^{-6}$	$1.014 \times 10^{-7}$
	$1.438 \times 10^{-6}$	$2.954 \times 10^{-8}$	$1.548 \times 10^{-8}$	$1.437 \times 10^{-6}$	$1.400 \times 10^{-7}$	$1.426 \times 10^{-8}$
	$4.379 \times 10^{-7}$	$8.666 \times 10^{-9}$	$4.719 \times 10^{-9}$	$4.374 \times 10^{-7}$	$4.738 \times 10^{-8}$	$4.288 \times 10^{-9}$
Kaolinite	$1.004 \times 10^{-4}$	$2.445 \times 10^{-6}$	$1.095 \times 10^{-6}$	$1.004 \times 10^{-4}$	$8.362 \times 10^{-5}$	$1.875 \times 10^{-7}$
	$1.044 \times 10^{-5}$	$2.522 \times 10^{-7}$	$1.139 \times 10^{-7}$	$1.044 \times 10^{-5}$	$5.086 \times 10^{-6}$	$5.982 \times 10^{-8}$
	$1.438 \times 10^{-6}$	$3.034 \times 10^{-8}$	$1.573 \times 10^{-8}$	$1.437 \times 10^{-6}$	$1.833 \times 10^{-7}$	$1.401 \times 10^{-8}$
	$4.379 \times 10^{-7}$	$7.314 \times 10^{-9}$	$4.811 \times 10^{-9}$	$4.374 \times 10^{-7}$	$1.186 \times 10^{-8}$	$4.754 \times 10^{-9}$
Montmorillonite	$1.004 \times 10^{-4}$	$2.878 \times 10^{-6}$	$1.097 \times 10^{-6}$	$1.004 \times 10^{-4}$	$9.300 \times 10^{-5}$	$8.329 \times 10^{-8}$
	$1.044 \times 10^{-5}$	$1.852 \times 10^{-7}$	$1.153 \times 10^{-7}$	$1.044 \times 10^{-5}$	$9.580 \times 10^{-6}$	$9.670 \times 10^{-9}$
	$1.438 \times 10^{-6}$	$2.981 \times 10^{-8}$	$1.584 \times 10^{-8}$	$1.437 \times 10^{-6}$	$1.273 \times 10^{-6}$	$1.845 \times 10^{-9}$
	$4.379 \times 10^{-7}$	$8.904 \times 10^{-9}$	$4.826 \times 10^{-9}$	$4.374 \times 10^{-7}$	$3.780 \times 10^{-7}$	$6.681 \times 10^{-10}$
Nontronite	$1.004 \times 10^{-4}$	$2.754 \times 10^{-5}$	$8.060 \times 10^{-7}$	$1.004 \times 10^{-4}$	$8.693 \times 10^{-5}$	$1.490 \times 10^{-7}$
	$1.044 \times 10^{-5}$	$1.255 \times 10^{-6}$	$1.016 \times 10^{-7}$	$1.044 \times 10^{-5}$	$8.698 \times 10^{-6}$	$1.927 \times 10^{-8}$
	$1.438 \times 10^{-6}$	$4.734 \times 10^{-8}$	$1.538 \times 10^{-8}$	$1.437 \times 10^{-6}$	$1.121 \times 10^{-6}$	$3.496 \times 10^{-9}$
	$4.379 \times 10^{-7}$	$1.558 \times 10^{-8}$	$4.672 \times 10^{-9}$	$4.374 \times 10^{-7}$	$3.182 \times 10^{-7}$	$1.319 \times 10^{-9}$
Glauconite	$1.004 \times 10^{-4}$	$2.878 \times 10^{-6}$	$1.057 \times 10^{-6}$	$1.004 \times 10^{-4}$	$4.088 \times 10^{-5}$	$6.452 \times 10^{-7}$
	$1.044 \times 10^{-5}$	$3.311 \times 10^{-7}$	$1.096 \times 10^{-7}$	$1.044 \times 10^{-5}$	$2.428 \times 10^{-7}$	$8.685 \times 10^{-8}$
	$1.438 \times 10^{-6}$	$9.528 \times 10^{-8}$	$1.456 \times 10^{-8}$	$1.437 \times 10^{-6}$	$1.911 \times 10^{-7}$	$1.351 \times 10^{-8}$
	$4.379 \times 10^{-7}$	$3.188 \times 10^{-8}$	$4.401 \times 10^{-9}$	$4.374 \times 10^{-7}$	$3.792 \times 10^{-8}$	$4.331 \times 10^{-9}$
Clinoptilolite	$1.004 \times 10^{-4}$	$3.564 \times 10^{-6}$	$7.550 \times 10^{-7}$	$1.004 \times 10^{-4}$	$9.417 \times 10^{-5}$	$7.264 \times 10^{-8}$
	$1.044 \times 10^{-5}$	$7.143 \times 10^{-7}$	$1.159 \times 10^{-7}$	$1.044 \times 10^{-5}$	$9.936 \times 10^{-6}$	$5.870 \times 10^{-9}$
	$1.438 \times 10^{-6}$	$1.839 \times 10^{-7}$	$1.462 \times 10^{-8}$	$1.437 \times 10^{-6}$	$1.374 \times 10^{-6}$	$7.356 \times 10^{-10}$
	$4.379 \times 10^{-7}$	$6.535 \times 10^{-8}$	$4.343 \times 10^{-9}$	$4.374 \times 10^{-7}$	$4.172 \times 10^{-7}$	$2.354 \times 10^{-10}$
Opal	$1.004 \times 10^{-4}$	$3.451 \times 10^{-6}$	$1.075 \times 10^{-6}$	$1.004 \times 10^{-4}$	$9.209 \times 10^{-5}$	$9.213 \times 10^{-8}$
	$1.044 \times 10^{-5}$	$4.178 \times 10^{-7}$	$1.111 \times 10^{-7}$	$1.044 \times 10^{-5}$	$9.498 \times 10^{-6}$	$1.044 \times 10^{-8}$
	$1.438 \times 10^{-6}$	$5.270 \times 10^{-8}$	$1.536 \times 10^{-8}$	$1.437 \times 10^{-6}$	$1.295 \times 10^{-6}$	$1.579 \times 10^{-9}$
	$4.379 \times 10^{-7}$	$2.051 \times 10^{-8}$	$4.629 \times 10^{-9}$	$4.374 \times 10^{-7}$	$3.806 \times 10^{-7}$	$6.303 \times 10^{-10}$
Silica gel	$1.004 \times 10^{-4}$	$1.959 \times 10^{-6}$	$1.083 \times 10^{-6}$	$1.004 \times 10^{-4}$	$1.876 \times 10^{-6}$	$1.084 \times 10^{-6}$
	$1.044 \times 10^{-5}$	$2.345 \times 10^{-7}$	$1.123 \times 10^{-7}$	$1.044 \times 10^{-5}$	$1.809 \times 10^{-7}$	$1.129 \times 10^{-7}$
	$1.438 \times 10^{-6}$	$2.981 \times 10^{-8}$	$1.549 \times 10^{-8}$	$1.437 \times 10^{-6}$	$2.972 \times 10^{-8}$	$1.548 \times 10^{-8}$
	$4.379 \times 10^{-7}$	$1.550 \times 10^{-8}$	$4.657 \times 10^{-9}$	$4.374 \times 10^{-7}$	$7.393 \times 10^{-9}$	$4.731 \times 10^{-9}$

for these sorption data by the linearized Freundlich equation, a Freundlich-like group of constants can also be generated by the linearized equation,  $\ln(x/m) = \ln L + p \ln C_1$ , where  $C_1$  is the initial U concentration in solution and  $L$  and  $m$  are constants. These constants are given in Table 9 along with their respective correlation coefficient ( $r$ ) and standard deviation from regression ( $Sy \cdot x$ ) values. They are potentially more useful than the actual Freundlich constants of Table 8 because they can be used to determine a U loading on a given secondary mineral when only the initial solution concentration ( $C_1$ ) is known.

#### DISCUSSION

The Freundlich sorption isotherm has been widely used to fit sorption of various substances onto soils (Hamaker and Thompson, 1972; Reinbold *et al.*, 1979), and its use here is not unique. Halsey (1952) and Adamson (1976) showed theoretically that the  $K$  and  $n$  constants in the Freundlich equation depend on the energy and entropy of sorption and on the energy of interaction between the sorption sites. The equation

describes a sorption isotherm from an ideal solution by an energetically heterogeneous set of sorption sites, with the sorption energy varying exponentially. The original Freundlich equation, however, for which the sorption isotherm was named, was purely empirical. The instance in which  $C_1$  is used in this work rather than  $C$  is merely a useful variation on Freundlich's original sorption isotherm.

One of the more practical measures of the efficiency of a solid in sorbing a dissolved substance from solution is the distribution coefficient,  $D$ . If  $D$  values are obtained at solution-mineral equilibrium and under comparable experimental conditions, they allow a comparison to be made of the efficiency of several minerals in sorbing a dissolved component from the same solution. A  $D$  value is defined as the equilibrium concentration of U on the mineral in mole/g divided by the equilibrium solution concentration in mole/ml and has the dimensions of ml/g.

Use of the same  $C$  value to compute U distribution coefficients also allows a sorption comparison between minerals. This use is somewhat artificial because dif-

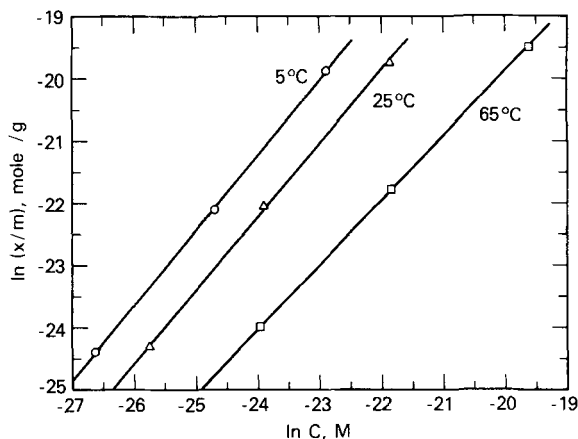


Figure 1. Freundlich equation plots of the natural logarithm of the equilibrium U concentration in solution (C) vs. the natural logarithm of equilibrium U loading on illite (x/m).

ferent  $C_1$  values for each mineral are required to produce the same C. A better comparison can be made by using the same  $C_1$  value for all minerals.

Fithian illite is used here to illustrate the sorption data. The experimental sorption values and the resulting regression lines (shown in Figure 1 for illite) are normal Freundlich sorption isotherms of  $\ln(x/m)$  plotted vs.  $\ln C$  at equilibrium.

Comparing D values between minerals exposed to the same initial U solution is possible by use of the data in Tables 8 and 9. The D value data were generated by assuming an initial U concentration, determining the (x/m) value with the Freundlich-like constants given in Table 9 and using the (x/m) value to compute a C value with the Freundlich constants given in Table 8. With illite as an example, D values decrease with increasing temperatures in NaCl solution, whereas they increase with increasing temperature from a  $\text{NaHCO}_3$  solution due to the heat sensitivity of the uranyl carbonate complex (Langmuir, 1978a). Further, D values

Table 7. Experimental mean values for sorption of uranium by secondary minerals at 5°C from 0.01 M NaCl and 0.01 M  $\text{NaHCO}_3$  solutions.

Solid	0.01 M NaCl			0.01 M $\text{NaHCO}_3$		
	Initial U (mole/liter)	Equilibrium U (mole/liter)	U on solid (mole/g)	Initial U (mole/g)	Equilibrium U (mole/liter)	U on solid (mole/g)
Illite	$1.005 \times 10^{-4}$	$7.668 \times 10^{-7}$	$1.097 \times 10^{-6}$	$1.005 \times 10^{-4}$	$6.184 \times 10^{-5}$	$4.251 \times 10^{-7}$
	$1.038 \times 10^{-5}$	$8.392 \times 10^{-8}$	$1.133 \times 10^{-7}$	$1.045 \times 10^{-5}$	$4.778 \times 10^{-6}$	$6.236 \times 10^{-8}$
	$1.403 \times 10^{-6}$	$4.987 \times 10^{-9}$	$1.537 \times 10^{-8}$	$1.434 \times 10^{-6}$	$4.475 \times 10^{-7}$	$1.085 \times 10^{-8}$
	$3.928 \times 10^{-7}$	$1.382 \times 10^{-9}$	$4.303 \times 10^{-9}$	$4.388 \times 10^{-7}$	$1.248 \times 10^{-7}$	$3.452 \times 10^{-9}$
Kaolinite	$1.005 \times 10^{-4}$	$7.958 \times 10^{-6}$	$1.401 \times 10^{-6}$	$1.005 \times 10^{-4}$	$8.081 \times 10^{-5}$	$2.200 \times 10^{-7}$
	$1.038 \times 10^{-5}$	$4.454 \times 10^{-7}$	$1.110 \times 10^{-7}$	$1.045 \times 10^{-5}$	$5.820 \times 10^{-6}$	$5.173 \times 10^{-8}$
	$1.403 \times 10^{-6}$	$1.745 \times 10^{-8}$	$1.549 \times 10^{-8}$	$1.434 \times 10^{-6}$	$1.882 \times 10^{-7}$	$1.392 \times 10^{-8}$
	$3.928 \times 10^{-7}$	$2.146 \times 10^{-9}$	$4.365 \times 10^{-9}$	$4.388 \times 10^{-7}$	$1.860 \times 10^{-8}$	$4.695 \times 10^{-9}$
Montmorillonite	$1.005 \times 10^{-4}$	$9.679 \times 10^{-6}$	$2.043 \times 10^{-6}$	$1.005 \times 10^{-4}$	$9.509 \times 10^{-5}$	$1.218 \times 10^{-7}$
	$1.038 \times 10^{-5}$	$8.585 \times 10^{-7}$	$2.142 \times 10^{-7}$	$1.045 \times 10^{-5}$	$9.972 \times 10^{-6}$	$1.075 \times 10^{-8}$
	$1.403 \times 10^{-6}$	$8.838 \times 10^{-8}$	$2.958 \times 10^{-8}$	$1.434 \times 10^{-6}$	$1.351 \times 10^{-7}$	$1.874 \times 10^{-9}$
	$3.928 \times 10^{-7}$	$1.987 \times 10^{-8}$	$8.389 \times 10^{-9}$	$4.388 \times 10^{-7}$	$4.054 \times 10^{-7}$	$7.512 \times 10^{-10}$
Nontronite	$1.005 \times 10^{-4}$	$6.185 \times 10^{-6}$	$2.086 \times 10^{-6}$	$1.005 \times 10^{-4}$	$9.123 \times 10^{-5}$	$2.051 \times 10^{-7}$
	$1.038 \times 10^{-5}$	$7.789 \times 10^{-7}$	$2.124 \times 10^{-7}$	$1.045 \times 10^{-5}$	$8.294 \times 10^{-6}$	$2.385 \times 10^{-8}$
	$1.403 \times 10^{-6}$	$5.292 \times 10^{-8}$	$2.987 \times 10^{-8}$	$1.434 \times 10^{-6}$	$1.217 \times 10^{-6}$	$4.808 \times 10^{-9}$
	$3.928 \times 10^{-7}$	$8.665 \times 10^{-9}$	$4.249 \times 10^{-9}$	$4.388 \times 10^{-7}$	$3.537 \times 10^{-7}$	$1.882 \times 10^{-9}$
Glauconite	$1.005 \times 10^{-4}$	$2.539 \times 10^{-6}$	$1.062 \times 10^{-6}$	$1.005 \times 10^{-4}$	$4.145 \times 10^{-5}$	$6.401 \times 10^{-7}$
	$1.038 \times 10^{-5}$	$3.519 \times 10^{-7}$	$1.092 \times 10^{-7}$	$1.045 \times 10^{-5}$	$3.439 \times 10^{-6}$	$7.600 \times 10^{-8}$
	$1.403 \times 10^{-6}$	$4.461 \times 10^{-8}$	$1.472 \times 10^{-8}$	$1.434 \times 10^{-6}$	$3.332 \times 10^{-7}$	$1.194 \times 10^{-9}$
	$3.928 \times 10^{-7}$	$2.568 \times 10^{-8}$	$3.979 \times 10^{-9}$	$4.388 \times 10^{-7}$	$6.916 \times 10^{-8}$	$4.007 \times 10^{-10}$
Clinoptilolite	$1.005 \times 10^{-4}$	$8.215 \times 10^{-5}$	$2.139 \times 10^{-7}$	$1.005 \times 10^{-4}$	$9.568 \times 10^{-5}$	$5.613 \times 10^{-8}$
	$1.038 \times 10^{-5}$	$8.108 \times 10^{-6}$	$2.649 \times 10^{-8}$	$1.045 \times 10^{-5}$	$1.004 \times 10^{-5}$	$4.749 \times 10^{-9}$
	$1.403 \times 10^{-6}$	$9.794 \times 10^{-7}$	$4.938 \times 10^{-9}$	$1.434 \times 10^{-6}$	$1.378 \times 10^{-6}$	$6.556 \times 10^{-10}$
	$3.928 \times 10^{-7}$	$2.631 \times 10^{-7}$	$1.512 \times 10^{-9}$	$4.388 \times 10^{-7}$	$4.185 \times 10^{-7}$	$2.363 \times 10^{-10}$
Opal	$1.005 \times 10^{-4}$	$7.480 \times 10^{-6}$	$1.031 \times 10^{-6}$	$1.005 \times 10^{-4}$	$9.125 \times 10^{-5}$	$1.026 \times 10^{-7}$
	$1.038 \times 10^{-5}$	$6.627 \times 10^{-7}$	$1.078 \times 10^{-7}$	$1.045 \times 10^{-5}$	$8.972 \times 10^{-6}$	$1.639 \times 10^{-8}$
	$1.403 \times 10^{-6}$	$7.065 \times 10^{-8}$	$1.477 \times 10^{-8}$	$1.434 \times 10^{-6}$	$1.208 \times 10^{-6}$	$2.506 \times 10^{-9}$
	$3.928 \times 10^{-7}$	$2.250 \times 10^{-8}$	$4.106 \times 10^{-9}$	$4.388 \times 10^{-7}$	$3.748 \times 10^{-7}$	$7.096 \times 10^{-10}$
Silica gel	$1.005 \times 10^{-4}$	$1.653 \times 10^{-6}$	$1.087 \times 10^{-6}$	$1.005 \times 10^{-4}$	$8.225 \times 10^{-7}$	$1.097 \times 10^{-6}$
	$1.038 \times 10^{-5}$	$1.205 \times 10^{-7}$	$1.129 \times 10^{-7}$	$1.045 \times 10^{-5}$	$9.259 \times 10^{-8}$	$1.140 \times 10^{-7}$
	$1.403 \times 10^{-6}$	$1.108 \times 10^{-8}$	$1.531 \times 10^{-8}$	$1.434 \times 10^{-6}$	$7.621 \times 10^{-9}$	$1.569 \times 10^{-8}$
	$3.928 \times 10^{-7}$	$3.365 \times 10^{-9}$	$4.284 \times 10^{-9}$	$4.388 \times 10^{-7}$	$3.180 \times 10^{-9}$	$4.792 \times 10^{-9}$

Table 8. Freundlich constants for the uranium sorption isotherms of Tables 5-7.

Solid	Temperature (°C)	Solution	K	p	r	Sy·x (ln units)
Illite	5	NaCl	0.1515	0.8502	0.9969	±0.2323
	5	NaHCO <sub>3</sub>	7.409 × 10 <sup>-4</sup>	0.7673	0.9995	±0.0849
	25	NaCl	0.2748	0.9642	0.9996	±0.0799
	25	NaHCO <sub>3</sub>	0.01731	0.8938	0.9984	±0.1611
	65	NaCl	0.0274	0.9390	0.9989	±0.1432
	65	NaHCO <sub>3</sub>	0.4696	1.0413	0.9992	±0.1206
Kaolinite	5	NaCl	3.849 × 10 <sup>-3</sup>	0.6931	0.9954	±0.2947
	5	NaHCO <sub>3</sub>	1.359 × 10 <sup>-5</sup>	0.4483	0.9975	±0.1450
	25	NaCl	0.1867	0.9371	0.9994	±0.1007
	25	NaHCO <sub>3</sub>	9.478 × 10 <sup>-6</sup>	0.4175	0.9998	±0.0364
	65	NaCl	0.3405	1.0089	1.0000	±0.0090
	65	NaHCO <sub>3</sub>	5.460 × 10 <sup>-5</sup>	0.5558	0.9978	±0.1480
Montmorillonite	5	NaCl	0.05634	0.8890	0.9998	±0.0625
	5	NaHCO <sub>3</sub>	6.102 × 10 <sup>-4</sup>	0.9338	0.9974	±0.1964
	25	NaCl	0.2094	0.9443	0.9979	±0.1890
	25	NaHCO <sub>3</sub>	2.597 × 10 <sup>-4</sup>	0.8733	0.9994	±0.0921
	65	NaCl	0.1828	0.9313	0.9970	±0.2322
	65	NaHCO <sub>3</sub>	0.1114	1.0297	0.9987	±0.1525
Nontronite	5	NaCl	0.1054	0.9133	0.9967	±0.2642
	5	NaHCO <sub>3</sub>	5.191 × 10 <sup>-4</sup>	0.8478	0.9995	±0.0644
	25	NaCl	4.871 × 10 <sup>-4</sup>	0.6158	0.9995	±0.1042
	25	NaHCO <sub>3</sub>	3.823 × 10 <sup>-4</sup>	0.8442	0.9996	±0.0691
	65	NaCl	0.6858	1.0123	0.9996	±0.0858
	65	NaHCO <sub>3</sub>	1.681 × 10 <sup>-5</sup>	0.4830	0.9995	±0.0606
Glauconite	5	NaCl	3.1205	1.1539	0.9935	±0.3388
	5	NaHCO <sub>3</sub>	1.837 × 10 <sup>-3</sup>	0.7959	0.9992	±0.1118
	25	NaCl	8.7606	1.2397	0.9961	±0.2592
	25	NaHCO <sub>3</sub>	9.214 × 10 <sup>-4</sup>	0.7183	1.0000	±0.0187
	65	NaCl	1.4554	1.1175	0.9990	±0.1477
	65	NaHCO <sub>3</sub>	1.1591	1.1340	0.9994	±0.1059
Clinoptilolite	5	NaCl	6.441 × 10 <sup>-4</sup>	0.8549	0.9996	±0.0720
	5	NaHCO <sub>3</sub>	5.958 × 10 <sup>-4</sup>	1.0108	0.9990	±0.1343
	25	NaCl	11.4636	1.3127	0.9985	±0.1643
	25	NaHCO <sub>3</sub>	1.282 × 10 <sup>-3</sup>	1.0608	0.9996	±0.0904
	65	NaCl	0.07412	0.9365	0.9995	±0.0841
	65	NaHCO <sub>3</sub>	2.225 × 10 <sup>-3</sup>	0.9205	1.0000	±0.0233
Opal	5	NaCl	0.06827	0.9388	0.9993	±0.1066
	5	NaHCO <sub>3</sub>	4.921 × 10 <sup>-4</sup>	0.9002	0.9980	±0.1670
	25	NaCl	0.5441	1.0450	0.9992	±0.1168
	25	NaHCO <sub>3</sub>	4.417 × 10 <sup>-4</sup>	0.9173	0.9991	±0.1128
	65	NaCl	0.4060	1.0323	0.9994	±0.1037
	65	NaHCO <sub>3</sub>	1.214 × 10 <sup>-3</sup>	0.8020	0.9997	±0.0618
Silica gel	5	NaCl	0.1391	0.8812	0.9992	±0.1150
	5	NaHCO <sub>3</sub>	0.5784	0.9442	0.9973	±0.2131
	25	NaCl	1.1580	1.0556	0.9988	±0.1449
	25	NaHCO <sub>3</sub>	0.5415	0.9949	0.9993	±0.1125
	65	NaCl	0.7515	1.0611	0.9982	±0.1813
	65	NaHCO <sub>3</sub>	0.6236	1.0727	0.9995	±0.0978

increase as U concentrations decrease in NaCl solutions. In NaHCO<sub>3</sub> solutions, D values also increase with temperature at 5°C, but at 25° and 65°C, they decrease with increasing temperature. In general, NaHCO<sub>3</sub> solution D values are less than those from NaCl solutions for the cation-exchange materials (illite, kaolinite, smectites, zeolites, and opal) due to carbonate complexing of the U. The effects of temperature, solution composition, and initial solution concentration of U on U sorption on illite are more easily seen

graphically in Figures 2 and 3. The D values represent a response to complex interactions between carbonate complexing, the exothermic nature of the sorption, the type of sorption sites on the mineral and temperature effects on the aqueous species.

The comparison between opal and silica gel sorption of U is of interest because of the prior work by Zielinski (1980) on uranium in secondary silica. He found that dried silica gel contained from 400 to 1000 times the U concentration in solution. Zielinski utilized a some-

Table 9. Freundlich-like constants for the uranium sorption isotherms of Tables 5–7 for the equation  $\ln(x/m) = \ln K + p \cdot \ln C_1$ .

Solid	Temperature (°C)	Solution	K	p	r	Sy·x (ln units)
Illite	5	NaCl	0.01097	1.0000	1.0000	±0.0016
	5	NaHCO <sub>3</sub>	0.001492	0.8826	0.9997	±0.0643
	25	NaCl	0.01065	0.9993	1.0000	±0.0020
	25	NaHCO <sub>3</sub>	0.009354	0.9923	0.9980	±0.1801
	65	NaCl	0.008432	0.9912	1.0000	±0.0229
	65	NaHCO <sub>3</sub>	0.01076	1.0018	1.0000	±0.0055
Kaolinite	5	NaCl	0.01845	1.0377	0.9995	±0.0989
	5	NaHCO <sub>3</sub>	$1.432 \times 10^{-4}$	0.6964	0.9974	±0.1470
	25	NaCl	0.01076	0.9987	1.0000	±0.0020
	25	NaHCO <sub>3</sub>	$1.141 \times 10^{-4}$	0.6740	0.9857	±0.3334
	65	NaCl	0.01080	1.0003	1.0000	±0.0004
	65	NaHCO <sub>3</sub>	$2.4836 \times 10^{-4}$	0.7364	0.9957	±0.2077
Montmorillonite	5	NaCl	0.01866	0.9909	1.0000	±0.0026
	5	NaHCO <sub>3</sub>	$6.093 \times 10^{-4}$	0.9381	0.9977	±0.1866
	25	NaCl	0.01081	0.9986	1.0000	±0.0900
	25	NaHCO <sub>3</sub>	$3.216 \times 10^{-4}$	0.8936	0.9996	±0.0690
	65	NaCl	0.02069	0.9967	1.0000	±0.0112
	65	NaHCO <sub>3</sub>	0.01199	0.9818	0.9925	±0.3650
Nontronite	5	NaCl	0.05374	1.0909	0.9958	±0.2983
	5	NaHCO <sub>3</sub>	$5.299 \times 10^{-4}$	0.8615	0.9990	±0.1148
	25	NaCl	$5.036 \times 10^{-3}$	0.9461	0.9998	±0.0494
	25	NaHCO <sub>3</sub>	$4.377 \times 10^{-4}$	0.8707	0.9998	±0.0492
	65	NaCl	0.02565	1.0136	1.0000	±0.0272
	65	NaHCO <sub>3</sub>	$6.608 \times 10^{-5}$	0.6162	0.9983	±0.1800
Glauconite	5	NaCl	0.01127	1.0063	1.0000	±0.0145
	5	NaHCO <sub>3</sub>	$3.463 \times 10^{-3}$	0.9342	1.0000	±0.0116
	25	NaCl	0.01155	1.0094	1.0000	±0.0107
	25	NaHCO <sub>3</sub>	$3.187 \times 10^{-3}$	0.9205	0.9999	±0.0465
	65	NaCl	0.01092	1.0043	1.0000	±0.0052
	65	NaHCO <sub>3</sub>	0.01131	1.0095	1.0000	±0.0067
Clinoptilolite	5	NaCl	$7.372 \times 10^{-4}$	0.8872	0.9998	±0.0512
	5	NaHCO <sub>3</sub>	$5.779 \times 10^{-4}$	1.0116	0.9991	±0.1273
	25	NaCl	$5.487 \times 10^{-3}$	0.9544	0.9984	±0.2619
	25	NaHCO <sub>3</sub>	$1.415 \times 10^{-3}$	1.0675	0.9991	±0.1309
	65	NaCl	$3.565 \times 10^{-3}$	0.9177	0.9983	±0.1627
	65	NaHCO <sub>3</sub>	$1.136 \times 10^{-3}$	0.8894	0.9982	±0.1637
Opal	5	NaCl	$9.907 \times 10^{-3}$	0.9960	1.0000	±0.0064
	5	NaHCO <sub>3</sub>	$3.305 \times 10^{-4}$	0.8723	0.9991	±0.2141
	25	NaCl	0.01088	1.0018	1.0000	±0.0048
	25	NaHCO <sub>3</sub>	$4.420 \times 10^{-4}$	0.9254	0.9993	±0.0997
	65	NaCl	0.01084	1.0018	1.0000	±0.0054
	65	NaHCO <sub>3</sub>	$2.075 \times 10^{-3}$	0.9073	0.9999	±0.0348
Silica gel	5	NaCl	0.01066	0.9983	1.0000	±0.0017
	5	NaHCO <sub>3</sub>	0.01096	1.0000	1.0000	±0.0039
	25	NaCl	0.01098	1.0018	1.0000	±0.0056
	25	NaHCO <sub>3</sub>	0.01079	0.9999	1.0000	±0.0025
	65	NaCl	0.01087	1.0021	1.0000	±0.0051
	65	NaHCO <sub>3</sub>	0.01092	1.0037	1.0000	±0.0057

what different methodology in that his silica gel was precipitated in the U-containing solution from a Na-stabilized silica sol. The silica gel used in the present study was added to the solution as a 100 to 200 mesh solid originally containing 9.1 wt. % water. It was also a high surface area ( $626.3 \pm 25.0$  m<sup>2</sup>/g), low cation-exchange capacity (1.28 meq/100 g) material. The D values plotted vs.  $\ln C_1$  for opal and silica gel are given in Figures 4–7. Note that opal behaves much like illite in its response to temperature during U sorption. Ura-

nium D values were not very large from sodium bicarbonate solutions, but the order of magnitude of D was reversed with temperature as compared to NaCl solutions. Silica gel, on the other hand, showed the same order and type of U sorption with changing temperature. Uranium sorption was somewhat greater when complexing bicarbonate was present with D values of about 1800 ml/g at the lower end of the concentration range studied. Illite, however, attained D values > 3000 ml/g in 0.01 M NaCl solutions. An important aspect



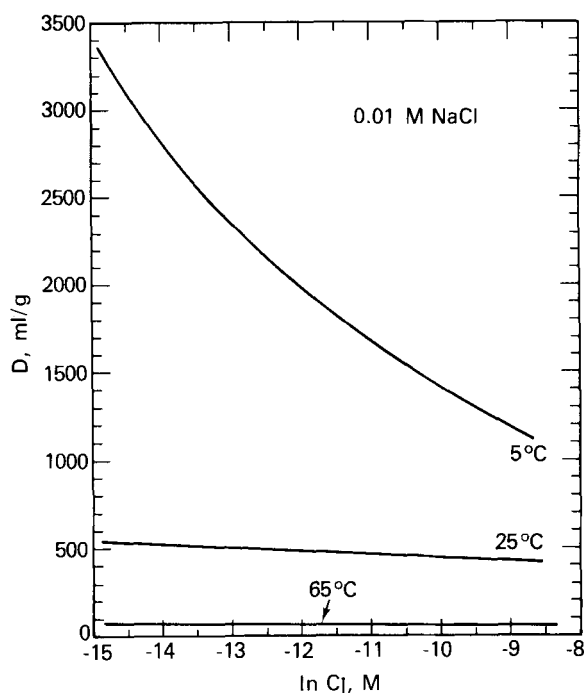


Figure 2. Natural logarithm of the initial U concentration in the solution ( $C_1$ ) vs. the U equilibrium distribution coefficient (D) for illite in 0.01 M NaCl.

of silica gel is that it is able to sorb both uranyl cations to some extent and anionic carbonate complexes from solution. This also is true for glauconite at the lower U concentrations, but to a lesser extent.

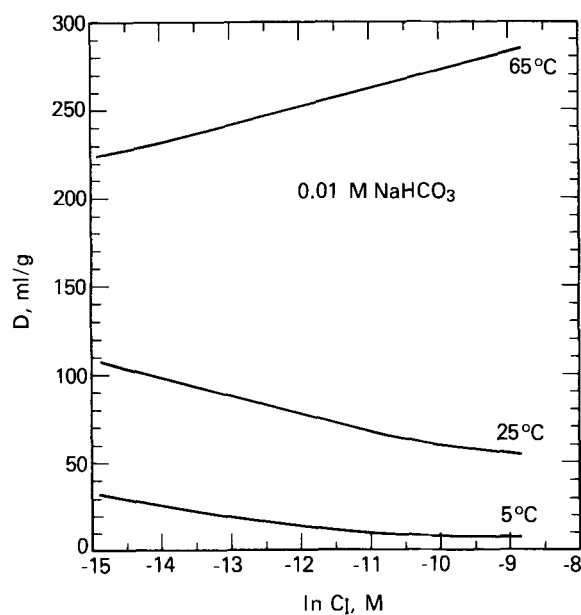


Figure 3. Natural logarithm of the initial U concentration in the solution ( $C_1$ ) vs. the U equilibrium distribution coefficient (D) for illite in 0.01 M  $\text{NaHCO}_3$ .

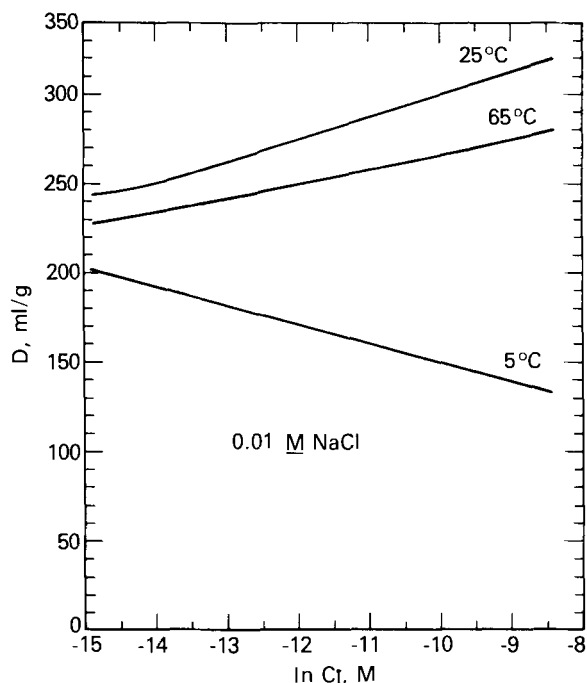


Figure 4. Natural logarithm of the initial U concentration in solution ( $C_1$ ) vs. the U equilibrium distribution coefficient (D) for opal in 0.01 M NaCl.

Galloway and Kaiser (1980) reported in a study of uranium deposits of the Catahoula Formation on the Texas coastal plain that groundwaters were more closely associated with the U mineralization plot on mont-

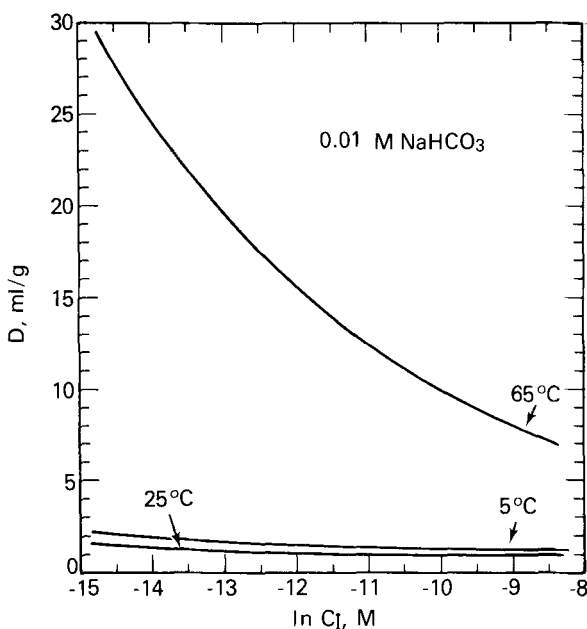


Figure 5. Natural logarithm of the initial U concentration ( $C_1$ ) vs. the U equilibrium distribution coefficient (D) for opal in 0.01 M  $\text{NaHCO}_3$ .

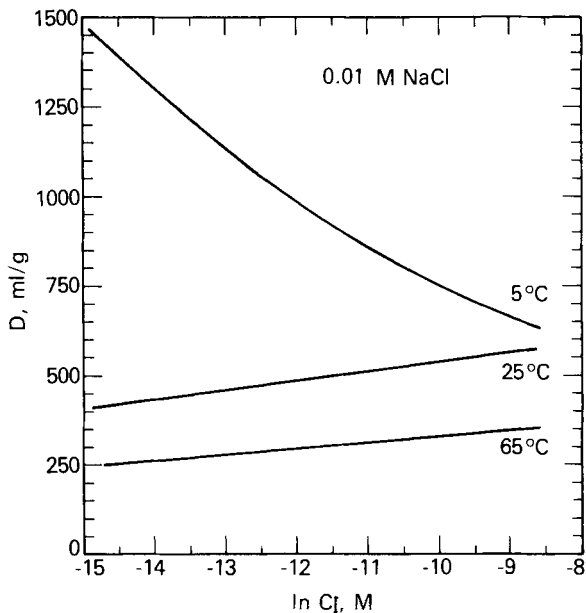


Figure 6. Natural logarithm of the initial U concentration in solution ( $C_i$ ) vs. the U equilibrium distribution coefficient (D) for silica gel in 0.01 M NaCl.

morillonite-clinoptilolite activity diagrams deepest into the montmorillonite field. Implied was an important role for montmorillonite in U concentration and an unimportant role for clinoptilolite. Assuming that ini-

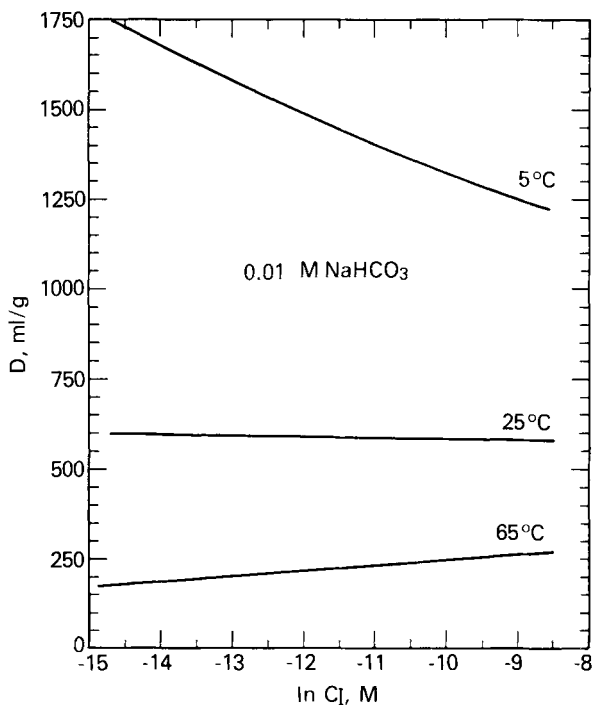


Figure 7. Natural logarithm of the initial U concentration in solution ( $C_i$ ) vs. the U equilibrium distribution coefficients (D) for silica gel in 0.01 M  $\text{NaHCO}_3$ .

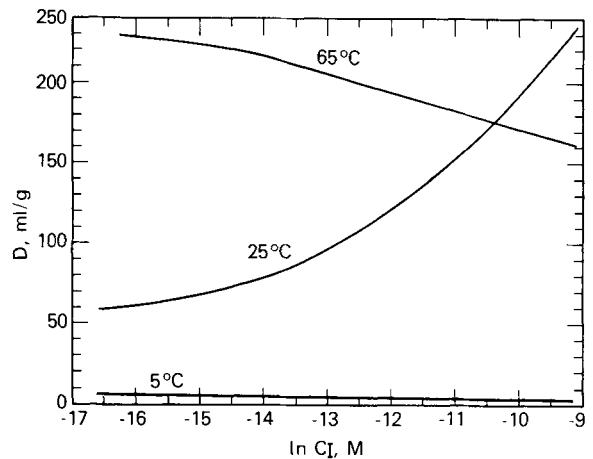


Figure 8. Natural logarithm of the initial U concentration in solution ( $C_i$ ) vs. the U equilibrium distribution coefficient (D) for clinoptilolite in 0.01 M NaCl.

tial U concentration was by sorption, an examination of the comparative U-sorption efficiencies of montmorillonite and clinoptilolite should confirm the above suggested U-montmorillonite association.

Comparable D curves for clinoptilolite are shown in Figures 8 and 9 for 0.01 M NaCl and 0.01 M  $\text{NHCO}_3$  solutions, respectively, and for montmorillonite in Figures 10 and 11 for the same solutions. As usual, the presence of anionic uranyl carbonate complexes in the 0.01 M  $\text{NaHCO}_3$  solution greatly diminished uranyl sorption by the clinoptilolite and montmorillonite, both of which are cation-exchange materials. At 65°C, U sorption was greatest due to uranyl carbonate complex heat sensitivity and a resulting higher uncomplexed uranyl ion concentration. Montmorillonite is obviously a much more efficient U sorbent than clinoptilolite over the initial U concentration shown in Figures 8–11. Hence, the laboratory results here tend to support

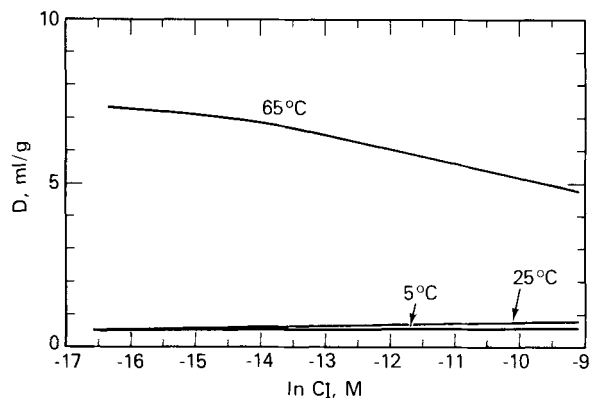


Figure 9. Natural logarithm of initial U concentration in solution ( $C_i$ ) vs. the U equilibrium distribution coefficient (D) for clinoptilolite in 0.01 M  $\text{NaHCO}_3$ .

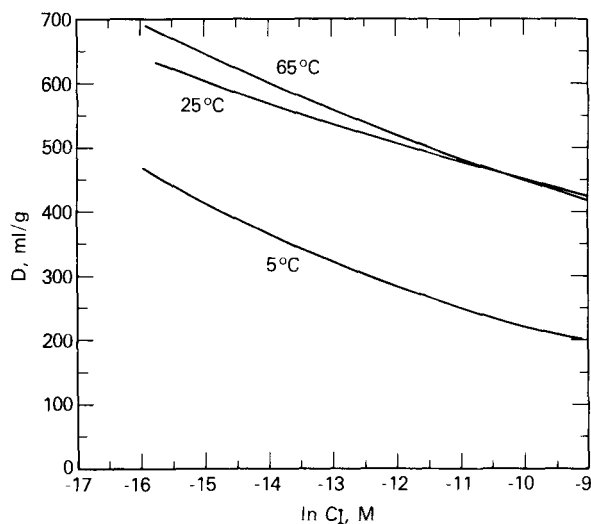


Figure 10. Natural logarithm of the initial U concentration in solution ( $C_i$ ) vs. the U equilibrium distribution coefficient ( $D$ ) for montmorillonite in 0.01 M NaCl.

the field observations of Galloway and Kaiser (1980) concerning the U montmorillonite association in Cahoula Formation U deposits.

Giblin (1980) reported some rather large (up to 35,000 ml/g at pH 6.5) U distribution coefficients on a kaolinite, whereas Langmuir (1978a, 1978b) reported some very low distribution coefficients (as low as 2 ml/g).  $D$  curves at 5°, 25°, and 65°C for 0.01 M NaCl and kaolinite are shown in Figure 12. The curve at 25°C and  $C_i$  of about  $4.2 \times 10^{-7}$  M U ( $-14.683$ ) and approximately pH 7 should be close to Giblin's 35,000 ml/g U distribution coefficient, but it is not. The reasons for the divergence between the above two reported distribution coefficients and those reported in Figure 12 are unknown, but may be due to any of several experimental factors, not all of which can be deduced

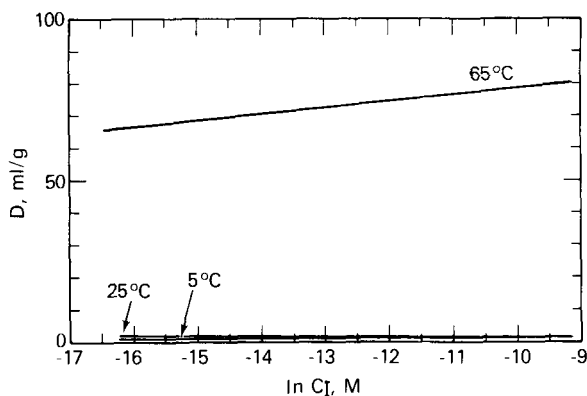


Figure 11. Natural logarithm of the initial U concentration in solution ( $C_i$ ) vs. the U equilibrium distribution coefficient ( $D$ ) for montmorillonite in 0.01 M  $\text{NaHCO}_3$ .

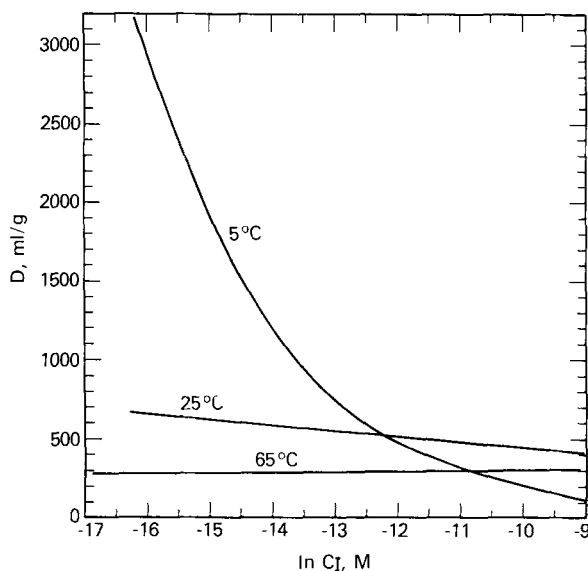


Figure 12. Natural logarithm of the initial U concentration in solution ( $C_i$ ) vs. the U equilibrium distribution coefficient ( $D$ ) for kaolinite in 0.01 M NaCl.

from the Giblin and Langmuir reports. For example, U tube-wall sorption corrections were found to be required in some cases. Failure to do so resulted in distribution coefficients that were too low when the tube-wall sorption occurred in the original solution samples and too high when it occurred on the equilibrating solution-solid sample tubes.

Nearly all secondary clay minerals show surficial coatings of noncrystalline Fe, Mn, Al, and Si oxyhydroxides that can potentially result in control of sorption of some dissolved substances, including U. Of the above noncrystalline surficial coatings, ferric oxyhydroxide probably has the most potential for increasing U sorption above that of the secondary clay mineral itself.

As mentioned above, no attempt was made to remove the small quantities of noncrystalline oxyhydroxides of Fe, Mn, Al, and Si that are usually present, even on reference or source clays. For example, Anderson and Jenne (1970) reported that the A.P.I. ka-

Table 10. Experimental mean values for sorption of uranium by ferric oxyhydroxide at 60°C from the solution composition given in Table 11.

Initial U (mole/liter)	Equilibrium U (mole/liter)	U on ferric oxyhydroxide (mole/g)
$1.005 \times 10^{-4}$	$4.113 \times 10^{-6}$	$3.452 \times 10^{-4}$
$1.051 \times 10^{-5}$	$1.724 \times 10^{-7}$	$3.702 \times 10^{-5}$
$1.513 \times 10^{-6}$	$1.805 \times 10^{-8}$	$5.353 \times 10^{-6}$
$5.041 \times 10^{-7}$	$6.756 \times 10^{-9}$	$1.781 \times 10^{-6}$

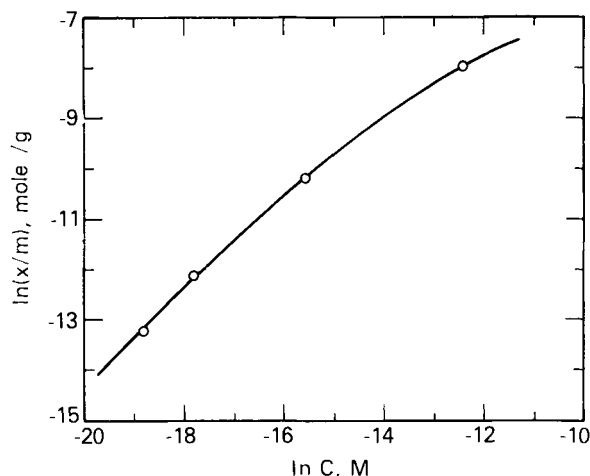


Figure 13. Natural logarithm of the equilibrium U concentration in the solution (C) vs. the natural logarithm of equilibrium U loading on ferric oxyhydroxide (x/m).

onilite 4 used in the present study contained 0.01 wt. %  $\text{Fe}_2\text{O}_3$  and 0.001 wt. %  $\text{MnO}_2$ . The most important noncrystalline sorbent of uranium was ferric oxyhydroxide with distribution coefficients in excess of  $2 \times 10^6$  ml/g. It always produced U isothermal sorption data that fit the Dubinin-Radushkevich sorption isotherm (Ames *et al.*, 1983). A ferric oxyhydroxide-coated dioctahedral smectite (0.68 wt. % Fe) produced Dubinin-Radushkevich sorption isotherms. Removal of the ferric oxyhydroxide coating and reoxidation of the dioctahedral smectite not only reduced U sorption by an order of magnitude, but the sorption data then fit a Freundlich sorption isotherm (Ames *et al.*, 1982). Hence, if ferric oxyhydroxide U sorption comprises a substantial portion of the total clay plus ferric oxyhydroxide U sorption, the data fit a Dubinin-Radushkevich sorption isotherm. If ferric oxyhydroxide made a minimal contribution to total U sorption, the data fit a Freundlich sorption isotherm. Because all of the U-sorption data for the minerals in the present study fit the Freundlich sorption isotherm, U-sorption on ferric oxyhydroxide was considered to be minimal.

Table 11. Solution composition used in the ferric oxyhydroxide experiments.<sup>1</sup>

Compound	Concentration (mg/liter)	Constituent	Concentration (mg/liter)
$\text{NaHCO}_3$	112.2	$\text{Na}^+$	30.7
$\text{K}_2\text{SO}_4$	20.1	$\text{K}^+$	9.0
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	23.8	$\text{Ca}^{2+}$	6.5
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	8.4	$\text{Mg}^{2+}$	1.0
$\text{SiO}_2$ (noncrystalline)	22.5	$\text{HCO}_3^-$	81.5
		$\text{SO}_4^{2-}$	11.1
		$\text{Cl}^-$	14.4

<sup>1</sup> pH = 8.0; ionic strength = 0.002132.

An example of the efficiency of ferric oxyhydroxide for sorption of U is given in Table 10. One milliliter of 0.1 M  $\text{FeCl}_3$  solution was added to 40 ml of distilled water and titrated to pH 7 in 50-ml polypropylene centrifuge tubes. The X-ray amorphous precipitate was washed three times with the solution composition given in Table 11. Uranium was added to the solution, and the ferric oxyhydroxide and solution were contacted with agitation for seven days. These sorption data yielded a straight line with the Dubinin-Radushkevich sorption isotherm (Dubinin and Radushkevich, 1974), but are presented as Freundlich sorption isotherms in Figure 13. The relationship between the Freundlich and Dubinin-Radushkevich sorption isotherms was given by Sokolowska and Szczypa (1980). The D values for ferric oxyhydroxide varied from 85,000 ml/g at a  $C_1$  value of  $1.005 \times 10^{-4}$  M U to 300,000 ml/g at a  $C_1$  of  $5.041 \times 10^{-7}$  M U, about two orders of magnitude above comparable D values for the most efficient U-sorbing secondary minerals in a similar environment. Uranium sorption on crystalline secondary minerals probably should not be considered as a process leading directly to the formation of U ore deposits. Although sorption may contribute to other U concentrating processes leading to ore deposits, instances of sorption on crystalline secondary minerals as the principal U concentration process would be rare.

#### ACKNOWLEDGMENT

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**Резюме**—Хорошо схарактеризованные образцы стандартных глин из Американского Нефтяного Института, образцовые глины из Общества по Глинистым минералам и другие вторичные минералы использовались для определения влияния концентрации урана, температуры и состава раствора на свойства сорбции урана. Концентрации урана находились в диапазоне от около  $1,00 \times 10^{-4}$  М до  $4,00 \times 10^{-7}$  М, температуры изменялись от 5° до 65°C и растворы содержали 0,01 М NaCl и 0,01 М NaHCO<sub>3</sub>. Кремнеземный гель эффективно сорбировал анионные комплексы уранилового карбоната. Минералы с повышенной катионо-обменной способностью наиболее охотно сорбировали ураниловые ионы их 0,01 М раствора NaCl. Увеличение температуры влияло обратнопропорционально на сорбцию ураниловых ионов, за исключением случая, когда U присутствовал в виде карбонатных комплексов. Некристаллические железные гидроксиды сорбировали ураниловые ионы более эффективно, чем все введенные вторичные кристаллические минералы. Представлен, разработанный на основе уравнения Фрейндлиха, метод для точной экстраполяции эффективности сорбции U между экспериментальными точками. [E.G.]

**Resümee**—Gut bestimmte Tonstandards des American Petroleum Institute und der Clay Minerals Society sowie andere sekundäre Minerale wurden verwendet, um die Auswirkungen der U-Konzentration, der Temperatur und der Lösungszusammensetzung auf die U-Adsorption zu bestimmen. Die U-Konzentrationen reichten von etwa  $1,00 \times 10^{-4}$  M bis  $4,00 \times 10^{-7}$  M, die Temperatur von 5° bis 65°C. Die Lösungszusammensetzung war 0,01 M NaCl und 0,01 M NaHCO<sub>3</sub>. Silikagel adsorbierte Uranylkarbonatanionenkomplexe sehr gut. Die Substanzen mit höherer Kationenaustauschkapazität adsorbierten sehr leicht Uranylionen aus der 0,01 M NaCl-Lösung. Ein Temperaturanstieg zeigte einen negativen Effekt auf die Uranyladsorption, außer das U war in Form eines Karbonatkomplexes vorhanden. Nichtkristalline Eisenoxyhydroxide adsorbierten Uranylionen viel wirksamer als alle andere untersuchte sekundäre kristalline Minerale. Es wird eine Methode zur genauen Extrapolation zwischen experimentell bestimmten Punkten der U-Adsorptionseffizienz angegeben, die auf der Freundlich-Gleichung beruht. [U.W.]

**Résumé**—Des standards d'argile bien caractérisés de l'American Petroleum Institute, des argiles de source du Clay Minerals Society, et d'autres minéraux secondaires ont été employés pour déterminer les effets de la concentration d'U, de la température, et de la composition de la solution sur les propriétés de la sorption d'U. Les concentrations d'uranium s'étagaient d'à peu près  $1,00 \times 10^{-4}$  à  $4,00 \times 10^{-7}$  M, les températures de 5°C à 65°C et les compositions des solutions contenant 0,01 M NaCl et 0,001 M NaHCO<sub>3</sub>. Le gel de silice a sorbé de manière efficace les complexes anion de carbonate uranyl. Les matériaux ayant la capacité d'échange de cations la plus élevée ont sorbé le plus facilement les ions uranyles de la solution 0,01 M NaCl. Des augmentations de température tendaient à affecter adversément la sorption de l'ion uranyl, sauf lorsque l'U était présent en tant que complexes carbonates. Des oxyhydrides ferriques non-cristallins ont sorbé les ions uranyles de manière beaucoup plus efficace qu'aucun des minéraux cristalline secondaires étudiés. Une méthode est présentée pour extrapoler précisément les efficacités de sorption d'U entre des points expérimentaux basée sur l'équation de Freundlich. [D.J.]