

NOTES

THE SORPTION OF THE RARE EARTH ELEMENT, Nd, ONTO KAOLINITE AT 25 °C

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INTRODUCTION

The question of the fractionation of rare earth metals (REE) between clay minerals and coexisting aqueous solutions is one of interest to the geochemical community. Research interest in the marine geochemistry of the REE, for instance, is partly driven by the need to better understand REE metal budgets in seawater and/or the geochemical cycle of REE. This, in turn, is linked to the proposition that models of hydrothermal fluxes associated with spreading ridges must consider the roles of secondary minerals as sinks for the REE, especially in view of the fact that smectite and chlorites are important products of low-temperature alteration of mid-oceanic ridge basalts (Chamley 1989). Clay minerals are also common products of hydrothermal alteration, weathering and diagenesis, and petrographic evidence indicates that some REE redistribution occurs under these low-temperature conditions (McLennan 1989 and references therein). Indeed, some petrographic evidence shows that REE remobilization may occur during diagenesis and that adsorption by clay minerals plays important roles in such fractionation processes (Awwiller and Mack 1991; Zhao et al. 1992).

A limited number of experimental studies have reported coefficients for the partition of REE between various minerals and coexisting aqueous solutions. Koeppenkastrop and De Carlo (1992) studied the sorption of REE, in the presence of seawater (pH = 7.8), onto the following synthetic phases: vernadite (δMnO_2), hydroxylapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$], amorphous goethite and crystalline goethite. The fractionation trends observed by them included the preferential uptake of light rare earth element (LREE) relative to heavy rare earth element (HREE), the existence of a positive Ce anomaly for sorption onto vernadite and a relatively enhanced uptake of Nd by hydroxylapatite.

According to Koeppenkastrop and De Carlo (1992), this enhanced uptake of Nd by hydroxylapatite and the positive anomaly for Ce sorption on vernadite suggest that the mechanism of sorption in the former was due to substitution for Ca^{2+} and to oxidative scavenging of Ce^{3+} in the latter. Nonetheless, mechanistic models of REE sorption have not yet evolved and the question of the relevant adsorption model (isotherm) on these phases is not resolved. Beall et al. (1979) measured distribution coefficients for the sorption of La, Sm, Yb, Am, Cm and Cf on kaolinite, montmorillonite and attapulgite at (room temperature); the experiments were conducted in NaCl solutions (0.25–4 M) buffered to a pH of 5 with acetate solutions. Their study suggested that metal uptake decreased with ionic strength, although the extent to which this might be due to the effects of competing metal complexation reactions was not addressed. At each ionic strength and for a given clay mineral, the values of the distribution ratios measured for both the lanthanides and actinides were only marginally different. Amongst the minerals, however, the actinides demonstrated a strong preference for attapulgite. Preliminary experimental investigations (Mecherri et al. 1990) into the sorption of Nd onto orthoclase and calcite at 50 °C have also been reported. According to them, Nd sorption onto orthoclase is best modeled by a Langmuir-type isotherm whereas a Freundlich-type isotherm characterized the sorption onto calcite. In addition, Mecherri et al. (1990) observed that only a small fraction of the sorbed metals could be desorbed and that increasing pH tends to decrease the partition of Nd onto the solid phases.

The focus of the studies discussed above has understandably been the determination of the distribution coefficients for various lanthanides. Besides the obvious petrologic utility of partition coefficients, they also have important practical applications. Such data are

needed, for instance, in the construction of reliable risk assessment models of geologic repositories of high-level nuclear wastes inasmuch as models of reactive transport through such clay layers require a thorough knowledge of the sorptive capacities of the potential backfill materials under a wide range of P-T-A (pressure, temperature and ion activities) conditions. Within this context, however, the available sorption data are quite limited and most of the available data apply to 25 °C. Though an important reference temperature, it is not representative of the thermal conditions anticipated in a geologic repository. In this article, we will present the results of our initial studies of the sorption of Nd onto kaolinite; this is the first in a series of contributions that will discuss the results of our ongoing experimental and theoretical investigations into the sorption of a variety of lanthanides (Nd, Eu, Ce, Gd, Yb) onto some clay minerals (kaolinite, Marblehead illite, Wyoming and Otay bentonites).

MATERIALS AND METHODS

Kaolinite samples from the CMS Source Clays from Georgia, KGa-1, were employed in this study. The samples were pretreated using standard chemical purification and size fractionation techniques (Aja et al. 1991). The surface areas of the kaolinite samples were determined by $N_{2(g)}$ adsorption, multiple-point BET method (Micromeritics Inc., Norcross, Georgia). As to be expected, the measured surface areas varied with the particular size fraction of the samples; that is, surface areas were determined to be $13.02 \text{ m}^2 \text{ g}^{-1}$ and $7.81 \text{ m}^2 \text{ g}^{-1}$ for kaolin particles of size fractions 2–5 μm and $\geq 5 \mu\text{m}$, respectively. Only the fractions whose sizes were $\geq 5 \mu\text{m}$ were used in the study reported herein.

The sorption experiments were conducted using batch-type equilibration techniques by agitating, with a wrist-action shaker, 0.10 g of kaolinite with 15 mL of the reacting solutions. Reagent grade neodymium nitrate was used as the source of Nd. Two sets of experiments were conducted; in Milli-Q water ($\geq 18 \Omega\text{-ohm}$) and in 0.7 M NaCl solutions with the latter including both “free-drift” (or uncontrolled pH) and pH-buffered experiments. The pH, however, was not controlled by the manual addition of either acid or base. This is typically the case in mechanistic studies inasmuch as this facilitates application of surface complexation models to the data. However, such a precise control of pH is unlikely in geologic settings; rather, the pH of the system of interest will evolve as part of the equilibrium process. Thus, whereas sorption experiments in which the pH is allowed to evolve with the sorption reactions (Mecherri et al. 1990; Koeppen-kastrop and De Carlo 1992; this study) may not be ideally suited for mechanistic interpretations, the resulting variations in pH are attributable to self-titration

by the system and thus have important instructional values.

Each set of experiments was performed in duplicates. The concentration of Nd in the starting solutions varied from about 1 to 100 μmol . The experiments lasted, in general, from 15 min to nearly 2 weeks; selected long-term experiments (up to 482 d) were also executed. At the end of the experiments, the clays were separated by centrifugation and/or filtration. Centrifugation was carried out in a refrigerated centrifuge (Sorvall RT 6000 D) at 5200 rpm for 10 min. The supernatant was subsequently filtered to pass 0.22 μm pore size using a syringe filter assembly and then analyzed for Nd by ICP-MS (GeoAnalytical Laboratory, Washington State University); Si and Al were also analyzed using optical spectrophotometry. The latter analyses provide mass-balance constraints inasmuch as these elements would be contributed solely by the dissolution of kaolinite during the course of the experiments. Neither Al nor Si was detected in the reacted solutions.

Difficulties inherent in the design of experiments to study sorption reactions on mineral surfaces have been discussed by various workers (Mecherri et al. 1990; Beněš et al. 1994; Ticknor 1994). Mecherri et al. (1990) emphasized the importance of the use of double blanks. This is particularly important where the chemical composition of the reacted aqueous solution served as an index to the amount of adsorbed metal as was the case in this study. It is necessary therefore to determine whether metal adsorption occurs on the walls of the vessels. Control experiments were thus conducted with low density polyethylene (LDPE) and Teflon (TFE) bottles; Nd sorption levels measured in a series of replicate experiments, in which aqueous suspensions were equilibrated (30–240 min) in both types of bottle, were identical. Furthermore, desorption experiments did not reveal retention of any Nd on either type of bottle in the control experiments. Hence, not only were the metals not adsorbed on the walls of the containers to any significant extent, but accurate results may apparently be derived with equal facility from experiments conducted in either of these bottles.

RESULTS

The number of moles of Nd adsorbed onto the kaolinite may be calculated using the expression (Sposito 1989):

$$q_{\text{Nd}} = \Delta m_{\text{Nd}} M_{\text{Tw}} \quad [1]$$

where q_{Nd} is the surface excess of Nd on kaolinite, Δm_{Nd} is the change of Nd concentration in solution attributed to sorption by the kaolinite and M_{Tw} is the total mass of water in the reactant solution mixed with 1 kg of clay. Figure 1 depicts the dependence of surface excess on concentration of aqueous Nd. Of the 4 general categories of adsorption isotherms (Sposito

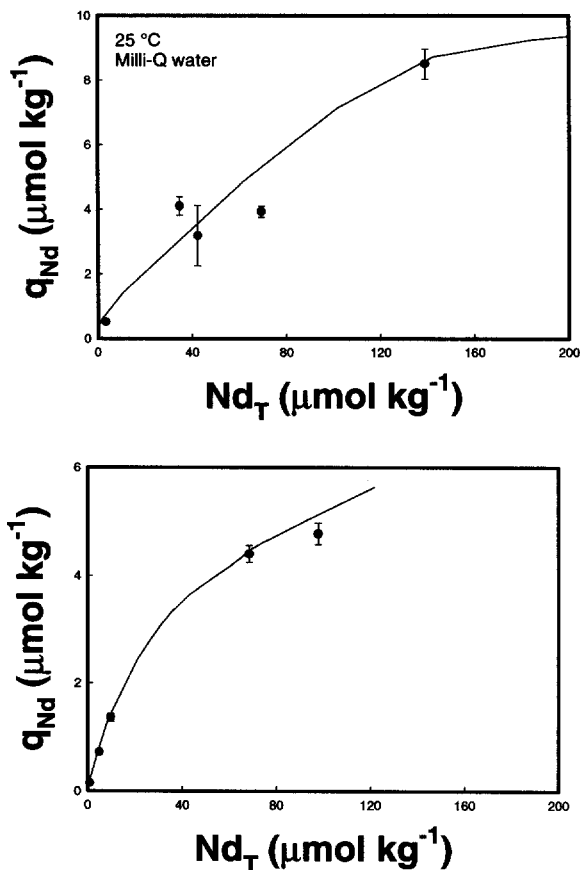


Figure 1. The dependence of surface excess on total Nd concentration in experiments conducted in (a) Milli-Q water and (b) 0.7 M NaCl. Error bars indicate variations in experiments conducted in quadruplets.

1989), the trend depicted in Figure 1 most closely approaches that of an L-curve. Typically, the functional forms of adsorption isotherms are described by the van Bemmelen–Freundlich or Langmuir isotherm equations (Sposito 1984, 1989). Attempts to fit the data to either a single or 2-surface Langmuir isotherm were largely unsuccessful. Hence, the choice of Freundlich isotherms considering especially that the Freundlich isotherm has been used to model the sorption of actinides and lanthanides (Beall et al. 1979; Ames et al. 1983a, 1983b; Mecherri et al. 1990). The general form of the Freundlich isotherm equation may be given as:

$$q_i = A c_i^\beta \quad [2]$$

where A and β are empirical constants. The value of β is constrained to lie between 0 and 1 inasmuch as the Freundlich isotherm converges to a 2-surface Langmuir isotherm as β approaches unity (Sposito 1984). To facilitate data interpretation, Equation [2] may be rewritten as:

$$\log q_i = \log A + \beta \log c_i \quad [3]$$

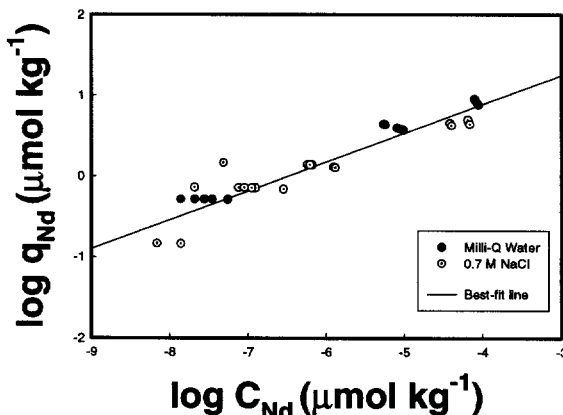


Figure 2. A plot of surface excess ($\log q_{Nd}$) as a function of equilibrium Nd concentration ($\log C_{Nd}$). Dotted circles represent experiments conducted in 0.7 M NaCl whereas solid circles show experiments conducted in water.

Thus, a linear dependence of $\log q_{Nd}$ on $\log C_{Nd}$ is predicted if a Freundlich isotherm is applicable. Figure 2 shows the results of least-squares regression analyses on available data; the equation of the best-fit line is:

$$\log q_{Nd} = 2.301 \pm 0.099 + 0.353 \pm 0.005 \log C_{Nd} \quad [4]$$

Clearly, Equation [4] is a first-order equation ($r^2 = 0.94$) and the measured slope of 0.353 is consistent with the fractional value expected for a Freundlich isotherm.

The fractionation of Nd between the solid (kaolinite) and the coexisting aqueous solutions were calculated using the relation:

$$K_d = \frac{\text{(Amount of Nd adsorbed by the solid phase)} \div \text{(Concentration of coexisting aqueous phase)}}{\text{[mmol/kg]}} \div \text{[mmol/kg]} \quad [5]$$

The distribution coefficients calculated in this manner have been plotted in Figure 3 as a function of Nd concentration in solution. Over the range of Nd solution concentrations investigated (0.98 – 139.07 $\mu\text{mol kg}^{-1}$), the distribution coefficients vary by nearly 3 orders of magnitude ($\log K_d \approx 3.6$ to 6.2). The inverse correlation between Nd concentration and distribution coefficient (Figure 3) reflects the greater partitioning of Nd into the solid phase at lower concentrations of Nd in solution. With increasing Nd concentration, the distribution coefficient stabilizes, owing ostensibly to saturation of the solid surfaces. It is also apparent from the data in Figures 2 and 3 that no distinction exists between the results obtained in water relative to experiments conducted in 0.7 M NaCl solutions.

The attainment of adsorption equilibrium was evaluated using Figure 4, which measures variations in surface excess of Nd on kaolinite as a function of reaction time. Evidently, the surface excess established

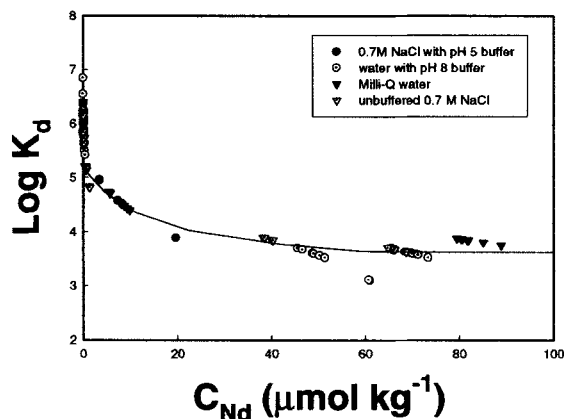


Figure 3. Variation of the logarithm of the distribution coefficient ($\log K_d$) as a function of neodymium concentration in solution (C_{Nd} in $\mu\text{mol/kg}$). The various sets of experiments are shown by the following symbols: solid circles, dotted circle, solid triangle and dotted triangle represent experiments conducted in 0.7 M NaCl solutions containing acetate pH buffer, Milli-Q water with pH controlled using carbonate buffer, Milli-Q water with no pH buffer and 0.7 M NaCl solution without any pH buffer, respectively.

after 15 min reaction time changes very little with further reaction time. In other words, the adsorption of Nd onto kaolinite surface, at 25 °C, occurs fairly quickly. Being that these are the first set of experiments dealing with the sorption of Nd onto kaolinite, no comparison with existing data is possible. Nonetheless, it is instructive to discuss the results of this study within the context of studies of related systems. The fast kinetics of REE sorption processes on kaolinite is consistent with the rapid exchange kinetics characteristic of the sorption of REE on other solid substrates (Beall et al. 1979; Mecherri et al. 1990; Koepenkastrup and De Carlo 1992). Overall, the attainment of sorption equilibrium within the very first few minutes of contact implies a high affinity of the REE for a wide range of solid substrates.

Figure 5 shows the dependence of the distribution coefficient ($\log K_d$) on final pH in reacted solutions. The overall distribution coefficients (K_d) measured in Milli-Q water and in NaCl solutions are of the same order of magnitude and a positive correlation exists between pH and $\log K_d$ and in both instances the sorption is completed over a narrow pH range. These observations provide some useful insights into the sorption mechanisms. For instance, it is evident that the adsorption of Nd onto kaolinite is independent of ionic strength. Usually, this implies coordination of metal cations with surface hydroxyl groups (Davis and Kent 1990) and thus one may then speculate that the mechanism of adsorption of Nd onto kaolinite surfaces proceeds by inner-sphere surface complexation mechanism. Secondly, an obvious implication of the application of Freundlich isotherm to the data (this study)

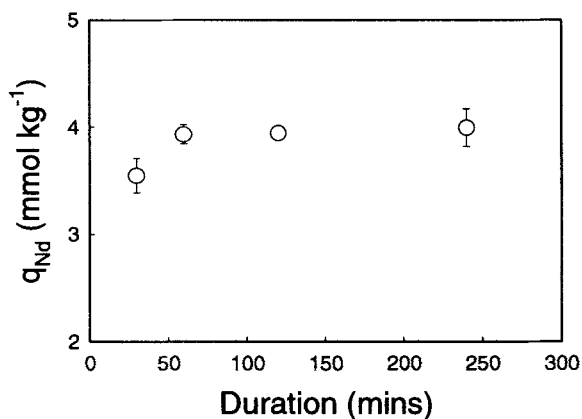


Figure 4. Variation of surface excess (q_{Nd}) as a function of reaction time. Starting solutions in this set of experiments contained 42.3 $\mu\text{mol Nd}$. The error bars represent standard deviation (1 δ) for 2 sets of separate experiments conducted in duplicates.

is the likely existence of heterogeneous sorption sites (Adamson 1990). Adsorption by kaolinite is generally attributed to the edge-surface hydroxyl groups—the aluminol and silanol surface functional groups (Sposito 1984). The former is a Lewis acid site and is expected to be reactive under acidic conditions whereas the latter is expected to be reactive under alkaline conditions. Though a Freundlich isotherm does not *prove* the heterogeneity of the surface of the adsorbent, such a model is entirely consistent with the distribution of functional groups on kaolinite surfaces. Apparently, both surface hydroxyl groups may then be reactive in acidic media, considering that these experiments were conducted under acidic conditions.

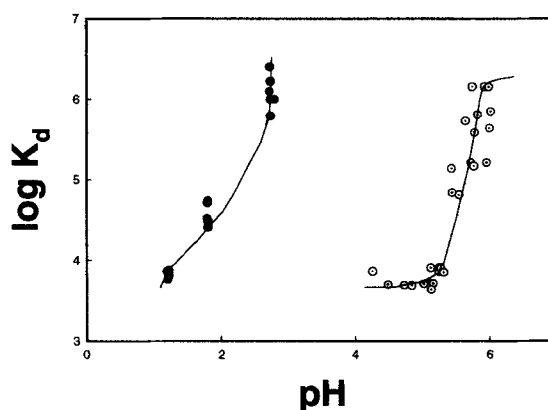


Figure 5. A plot of the variation of the logarithm of the distribution coefficient as a function of pH. Solid circles represent experiments conducted in water whereas dotted circles represent experiments conducted in 0.7 M NaCl solutions; the low pH of runs in water resulted from the acidic content of Nd stock solution used for the experiments.

Table 1. Distribution coefficients ($\log K_d$) reported for Nd sorption onto solid phases.

Mineral	Temp (°C)	Surface area (m ² /g)	$\log K_d$	pH	Background electrolyte	Sources
Kaolinite†	25	7.81	3.69–6.37	4.03–6.02	0.7 M NaCl	1
			3.75–6.22	1.20–2.74	none	1
			4.48 ± 0.44	8.14 ± 0.03	none	1
Vernadite	25	n.a.	6.0	7.8	seawater	2
Hydroxylapatite	25	n.a.	6.0	7.8	seawater	2
Goethite (cr)	25	n.a.	6.0	7.8	seawater	2
Goethite (am)	25	n.a.	5.7	7.8	seawater	2
Orthoclase	50	0.5	2.43	n.a.	none	3

References: 1) this study, 2) Koeppenkastrap and De Carlo (1992), 3) Mecherri et al. (1990). n.a. stands for not available. † Size-fractionated (> 5 µm) Clay Mineral Society Reference kaolinite, kGa-1.

DISCUSSION

Methodological problems associated with the batch method (Konishi et al. 1988; Benš et al. 1994; Ticknor 1994) include incomplete separation of phases, abrasion of particles by their mutual collisions in stirred reactors and low fluid/rock (V/m) ratios. The possible effects of phase separation techniques were examined using control experiments. In other words, results of test runs in which the only variable was the phase separation method (that is, centrifugation vs. filtration vs. centrifugation-filtration) were largely consistent. Other investigators (Ticknor 1994) have similarly concluded that significant differences in measured partition coefficients do not usually arise as a result of the particular phase separation adopted. Thus, one sees the inherent validity of the combination of low-speed centrifugation and syringe filtration techniques adopted, in this study, for phase separation.

Owing to the need to extrapolate experimentally derived partition coefficients to *in situ* geologic conditions, the practical application of partition coefficients determined in static batch-type experiments (as in the current study) relative to those extracted from dynamic flow-through studies is a question of fundamental importance (Miller et al. 1989; Seyfried et al. 1989). Adsorption affinities measured in batch experiments, for instance, tend to be greater than those measured in flow systems, although the amounts sorbed at equilibrium are of the same order of magnitude. Furthermore, there is also a tendency towards accumulation of reaction products in the batch method. Perhaps, it is important to note that the different experimental designs employed by various investigators render direct comparisons of the results of the different approaches somewhat semiquantitative. Clearly, the restricted range of solid/solution ratios and the use of solid phase at rest relative to the fluid phase imply that dynamic systems more closely approximate field conditions. The ability to vary flow rates and fluid rock ratios make the dynamic approach a rather attractive experimental option. Nonetheless, Miller et al. (1989) have reasoned that flow systems are thermodynamically

equivalent to batch systems having very wide solid/solution ratios. Moreover, realistic models of reactive transport through clay beds must consider the effect of local equilibrium and thus the relative importance of the static batch-type approach owing to its unique role in establishing the thermodynamic state functions of adsorption reactions.

Measured and literature values of coefficients for the partition of Nd between various solid substrates and coexisting aqueous solutions have been summarized in Table 1. Certainly, any comparison of the results of these disparate studies must take cognizance of inherent differences in the solid phases investigated, experimental techniques and conditions. For instance, the range of values measured from this study (Table 1) partially reflects differences in concentration of Nd in the starting solutions. That is, at low Nd concentrations (0.98 µmol kg⁻¹) high distribution coefficients results whereas the converse is the case at high starting Nd concentrations. In the latter case (68–139.08 µmol kg⁻¹), the values of the distribution coefficient stabilizes somewhat ($\log K_d \approx 3.6$) suggesting apparent saturation of available surface sites. In addition, the coefficients measured in this study at low values of initial Nd concentrations are identical to those determined by Koeppenkastrap and De Carlo (1997) at somewhat comparable initial Nd concentration (1.73 µM). By contrast, distribution coefficients obtained by Mecherri et al. (1990) upon reacting orthoclase and calcite with aqueous solutions containing Nd, though high, are generally lower than the values obtained for sorption onto kaolinite, vernadite, hydroxylapatite and goethite.

Application to Disposal of High-Level Nuclear Wastes

Over the last 50 years, high-level radioactive wastes have been accumulated from nuclear weapons programs and commercial nuclear reactors. The biologically significant radionuclides in high-level radioactive wastes include elements of the second row transition series (⁹⁰Y, ⁹¹Y, ⁹³Zr, ⁹⁵Zr, ⁹⁵Nb, ⁹⁹Tc, ¹⁰⁶Ru, ¹⁰⁶Rh), the lanthanides (such as ¹⁴⁴Ce, ¹⁴⁷Pm, ¹⁵²Eu, ¹⁵⁴Eu) and ac-

tinides (^{232}Th , ^{234}U , ^{235}U , ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu , ^{241}Am , ^{244}Cm). The actinides are clearly a major by-product of the nuclear industry and the disposal of nuclear wastes is a major environmental geochemical question. The toxicity of radioactive metals poses significant handling problems during experimental studies. Because the health hazards posed by their toxicity increases with increasing concentration (Ames et al. 1983a, 1983b), a severe limitation exists in the concentration range that may be used for experimentation. Moreover, the short half-lives of some of these metals restrict their utility in aqueous geochemical studies. Hence, the obvious advantages of using nonradiotoxic elements such as the lanthanides for constraining the mobility of radiotoxic elements under hydrothermal conditions. The lanthanides are not only valid geochemical analogs for trivalent actinides (Am^{3+} , Cm^{3+} , Pu^{3+} and Bk^{3+} ; Brookins 1984; Henrion et al. 1985; Nitsche et al. 1992) but are also important products of nuclear fission. Moreover, Beall et al. (1979) reported identical partition coefficients for some actinides and lanthanides onto some clay minerals; this emphasizes the essential utility of the concept of REE as geochemical analogs of the actinides despite apparent limitations (Haas et al. 1995).

Possible measures of the potential effectiveness of a backfill material to retard the migration of radionuclides include high sorption efficiency and fixation constant. The distribution coefficient may serve as a reliable index to the sorption efficiency of a particular adsorbent. In that case, the strong partitioning of Nd onto kaolinite indicated by the experimentally measured distribution coefficients (Table 1) implies a high sorption efficiency for Nd. The second parameter (the fixation constant) may be retrieved from the Freundlich isotherm equation (Equation [4]) by extrapolation to $\log C_{\text{Nd}} = 0$. This yields a surface excess of 200 μmol Nd per kg for an infinitely dilute solution. In other words, kaolinite can scavenge and hold significant amounts of Nd from aqueous solutions. Apparently, the presence of kaolinite in geologic materials being used as backfill materials is likely to be beneficial to the performance of geologic repositories and its role may be comparable to that of oxides and oxyhydroxides (vernadite, goethite) which are generally known to have high cation sorbing efficiencies. Nonetheless, the major clay minerals found in the sedimentary sequence include illite, mixed-layered illite-smectite and smectite and thus a proper evaluation of the performance of potential geologic repositories must entail studies of the sorption behavior of the latter minerals. The study with kaolinite, a relatively common and simple clay mineral, afforded us an opportunity both to develop and test our experimental protocols for application to the more complex 2:1 layer clay minerals.

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