

## EFFECT OF IONIC STRENGTH AND ION PAIR FORMATION ON THE ADSORPTION OF NICKEL BY KAOLINITE

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**Abstract**—Adsorption of Ni(II) by Ca- and Na-saturated kaolinites was studied in equilibrating solutions with total Ni concentrations ranging from 118 to 946  $\mu\text{g}/\text{liter}$ . Background electrolytes used in these experiments were 0.005, 0.01, 0.025, and 0.5 M  $\text{Ca}(\text{NO}_3)_2$ , 0.002 and 0.005 M  $\text{CaSO}_4$ , 0.01 and 0.1 M  $\text{NaNO}_3$ , and 0.005 and 0.05 M  $\text{Na}_2\text{SO}_4$ . Ion speciation in equilibrium solutions was calculated by the computer program GEOCHEM. Computed  $\text{Ni}^{2+}$  concentrations and activities at equilibrium were correlated with total Ni adsorbed by kaolinite. Increasing ionic strength resulted in decreasing Ni adsorption. Adsorption of Ni was greater from solutions when  $\text{NO}_3^-$  was the dominant anion. Based on adsorption data in  $\text{SO}_4$  medium, the standard free energy of adsorption of  $\text{Ni}^{2+}$  ion on kaolinite was computed to be  $-27 \text{ kJ}/\text{mole}$ .

**Key Words**—Ion speciation, Ionic strength, Ion pair, Kaolinite, Nickel adsorption.

### INTRODUCTION

Accumulation of excessive amounts of trace metals such as nickel in soils amended with municipal and industrial wastes can have a toxic effect on soil organisms and plants (Page, 1974; Dowdy *et al.*, 1976; Walsh *et al.*, 1976). Similar problems can be induced by accidental spills of geothermal brines on agricultural lands (Phelps and Anspaugh, 1976). Such concern has prompted many studies of trace metal chemistry in soils in order to understand, assess, and attenuate the risks involved in sludge applications to agricultural lands.

In soil, Ni exists in various solid and solution forms. In solution, Ni exists not only as the free aquo ion ( $\text{Ni}^{2+}$ ) but also as ion pairs and complexes with various inorganic and organic ligands. Reported concentrations of nickel in the saturation extracts of some California soils range from  $<0.01$  to 0.09 ppm (Bradford *et al.*, 1971). However, in some soils treated with sewage sludge, nickel concentrations in soil solutions may be as high as 53 ppm (L. Lund, Department of Soil and Environmental Sciences, University of California, Riverside, California 92521; personal communication). Ni in the solid phase exists not only in various mineral forms but also in exchangeable and specifically adsorbed forms. Therefore, a thorough understanding of Ni chemistry in soils should encompass a study of all possible phases of this metal.

One of the important aspects of Ni interaction in soils is its adsorption on mineral surfaces. Adsorption of Ni on clay minerals has been studied by McLean (1966), Kabata-Pendias (1968), Counts (1975), and Koppelman and Dillard (1977); however, these studies were not directed towards elucidating the effects of various factors such as ion-pair formation and ionic strength on the adsorption of Ni. Therefore, the purpose of the present study was to clarify the adsorption behavior of Ni on

kaolinite at solution concentrations encountered generally in uncontaminated soil solutions. Ni adsorption by kaolinite with respect to changing ionic strength in the presence of cations such as  $\text{Ca}^{2+}$  and  $\text{Na}^+$  and as influenced by ion-pair formation with ligands  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were also part of this study.

### MATERIALS AND METHODS

#### *Preparation of kaolinite suspension*

A sample of kaolinite from Birch Pit, Macon, Georgia was obtained from Ward's Natural Science Establishment. The  $<2\text{-}\mu\text{m}$  fraction of this material was collected by centrifugation. Part of this  $<2\text{-}\mu\text{m}$  material in suspension was saturated with Ca by washing it three times with 0.5 N  $\text{Ca}(\text{NO}_3)_2$ . Excess Ca was removed by successive washing with deionized water. Another part of the  $<2\text{-}\mu\text{m}$  fraction was saturated with Na by three washes with 1.0 N  $\text{NaNO}_3$  solution. Successive washing with 0.005 N  $\text{NaNO}_3$  was used to remove excess Na. These ion-saturated kaolinite suspensions were stored in plastic bottles and were used in all the adsorption experiments. The weight of clay per unit volume of suspension in each case was determined after drying four samples of suspension, each 10 ml in volume, for 48 hr at  $100^\circ\text{C}$ . The oven-dry weights of Ca-kaolinite and Na-kaolinite suspensions were determined to be 6.35 and 2.99 mg/ml, respectively. The cation-exchange capacity of the Ca-kaolinite was determined to be  $11.7 \pm 0.8 \text{ meq}/100 \text{ g}$  by displacement with ammonium acetate buffered at  $\text{pH} = 5.3$ .

#### *Adsorption experiments*

To study the adsorption of Ni by Ca-kaolinite, 1-ml suspensions were placed in 50-ml plastic centrifuge tubes. Solutions of  $\text{Ni}(\text{NO}_3)_2$  from 118 to 946  $\mu\text{g}/\text{liter}$  of Ni were prepared in a series of 0.005, 0.01, 0.025, and 0.5 M  $\text{Ca}(\text{NO}_3)_2$  solutions. Similar  $\text{Ni}(\text{NO}_3)_2$  solutions were prepared in 0.002 and 0.005 M  $\text{CaSO}_4$  solutions.

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Table 1. Stability constants for aqueous species at 25°C under 1 atmosphere pressure.

Reaction	log K	Reference
$\text{CO}_2(\text{g}) + \text{H}_2\text{O} = \text{H}_2\text{CO}_3^0$	$-1.46 \pm 0.003$	Harned and Davis (1943)
$\text{H}^+ + \text{HCO}_3^- = \text{H}_2\text{CO}_3^0$	$6.36 \pm 0.004$	Nakayama (1970)
$\text{H}^+ + \text{CO}_3^{2-} = \text{HCO}_3^-$	$10.33 \pm 0.04$	Nakayama (1970)
$\text{H}^+ + \text{SO}_4^{2-} = \text{HSO}_4^-$	$1.99 \pm 0.004$	Dunsmore and Nancollas (1964)
$\text{H}^+ + \text{NO}_3^- = \text{HNO}_3^0$	$-1.43$	Helgeson (1967)
$\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$	$14.00 \pm 0.001$	Olofsson and Hepler (1975)
$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3^0$	$3.15 \pm 0.08$	Reardon and Langmuir (1974)
$\text{Ca}^{2+} + \text{HCO}_3^- = \text{CaHCO}_3^+$	$1.02 \pm 0.10$	Jacobsen and Langmuir (1974)
$\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4^0$	$2.31 \pm 0.04$	Nakayama and Rasnick (1967)
$\text{Ca}^{2+} + \text{OH}^- = \text{CaOH}^+$	$1.39 \pm 0.04$	Bell and George (1953)
$\text{Ca}^{2+} + \text{NO}_3^- = \text{CaNO}_3^+$	$0.68$	Fedorov <i>et al.</i> (1974)
$\text{Ca}^{2+} + 2\text{NO}_3^- = \text{Ca}(\text{NO}_3)_2^0$	$0.65$	Fedorov <i>et al.</i> (1974)
$\text{Na}^+ + \text{CO}_3^{2-} = \text{NaCO}_3^-$	$0.55$	Nakayama (1970, 1971)
$\text{Na}^+ + \text{HCO}_3^- = \text{NaHCO}_3^0$	$0.16 \pm 0.06$	Nakayama (1970, 1971)
$\text{Na}^+ + \text{SO}_4^{2-} = \text{NaSO}_4^-$	$1.10 \pm 0.08$	Fisher and Fox (1975)
$2\text{Na}^+ + \text{SO}_4^{2-} = \text{Na}_2\text{SO}_4^0$	$1.51$	Lafon and Truesdell (1971)
$\text{Na}^+ + \text{NO}_3^- = \text{NaNO}_3^0$	$-0.60$	Davies (1927)
$\text{Na}^+ + \text{OH}^- = \text{NaOH}^0$	$-0.18$	Baes and Mesmer (1976)
$\text{Ni}^{2+} + \text{CO}_3^{2-} = \text{NiCO}_3^0$	$6.87^1$	Mattigod and Sposito (1977)
$\text{Ni}^{2+} + 2\text{CO}_3^{2-} = \text{Ni}(\text{CO}_3)_2^{2-}$	$10.11^1$	Mattigod and Sposito (1977)
$\text{Ni}^{2+} + \text{HCO}_3^- = \text{NiHCO}_3^+$	$2.14^1$	Mattigod and Sposito (1977)
$\text{Ni}^{2+} + \text{SO}_4^{2-} = \text{NiSO}_4^0$	$2.33$	Nair and Nancollas (1959)
$\text{Ni}^{2+} + 2\text{SO}_4^{2-} = \text{Ni}(\text{SO}_4)_2^{2-}$	$1.02^1$	Mattigod and Sposito (1977)
$\text{Ni}^{2+} + \text{HSO}_4^- = \text{NiHSO}_4^+$	$1.10^1$	Mattigod and Sposito (1977)
$\text{Ni}^{2+} + \text{NO}_3^- = \text{NiNO}_3^+$	$0.40$	Fedorov <i>et al.</i> (1973)
$\text{Ni}^{2+} + \text{OH}^- = \text{NiOH}^+$	$4.14$	Baes and Mesmer (1976)
$\text{Ni}^{2+} + 2\text{OH}^- = \text{Ni}(\text{OH})_2^0$	$9.00$	Baes and Mesmer (1976)
$\text{Ni}^{2+} + 3\text{OH}^- = \text{Ni}(\text{OH})_3^-$	$12.00$	Baes and Mesmer (1976)
$\text{Ni}^{2+} + 4\text{OH}^- = \text{Ni}(\text{OH})_4^{2-}$	$12.00$	Baes and Mesmer (1976)
$2\text{Ni}^{2+} + \text{OH}^- = \text{Ni}_2\text{OH}^{3+}$	$3.30$	Baes and Mesmer (1976)
$4\text{Ni}^{2+} + 4\text{OH}^- = \text{Ni}_4(\text{OH})_4^{4+}$	$28.26$	Baes and Mesmer (1976)

<sup>1</sup> Estimated.

Thirty-five milliliters of each of these solutions were equilibrated with the kaolinite suspensions at room temperature (~25°C) in an automatic wrist-action shaker for 5 hr. Preliminary studies had shown that the adsorption reached a steady state well within a span of 5 hr. After equilibration, the suspensions were centrifuged at ~20,000 g for 25 min, and the pH of the supernatant was measured. The Ni concentration in the supernatant was measured using a Perkin Elmer flameless atomic absorption spectrophotometer (FAAS), model 403, equipped with an HGA 2100 graphite furnace and a deuterium background corrector. To avoid electrolyte interferences and, where necessary, to concentrate Ni to levels greater than the limits of detection, Ni was extracted from equilibrium solutions using ammonium pyrrolidine dithiocarbamate–methyl isobutyl ketone (APDC-MIBK). This procedure, developed by Sprague and Slavin (1964), may be employed with a number of heavy metals and consists of adding a drop of 1.0 N HNO<sub>3</sub> and 1 ml of 5% solution of APDC to a 25 ml aliquot of the supernatant and shaking it vigorously for about half a minute. Next, the aliquot is agitated for another minute after adding 5 ml of MIBK. Ni in the organic phase was determined using an FAAS.

Similar series of Ni adsorption experiments were conducted with Na-saturated kaolinite. Solutions of Ni(NO<sub>3</sub>)<sub>2</sub> ranging from 118 to 946 μg Ni/liter were prepared with 0.01 and 0.10 M NaNO<sub>3</sub> as the background electrolyte for one series of experiments and with 0.005 and 0.05 M Na<sub>2</sub>SO<sub>4</sub> solutions for another series of experiments.

#### Calculation of ion speciation in solution

In these experiments, total Ni adsorbed by Ca- or Na-kaolinite can be calculated from the difference between Ni added and that recovered in the equilibrium solutions. But, it should be noted that Ni in solution may exist not only as Ni<sup>2+</sup>, but also as ion pairs and complexes with various ligands. Therefore, it is useful to know the Ni<sup>2+</sup> concentration in solution in order to correlate with observed adsorption of Ni onto kaolinite. The solution speciation of metal ions in a multicomponent chemical system is a function of various parameters such as the total concentrations of various metals and ligands, pH, temperature, and partial pressure of various gases. Therefore, calculations were made of the distribution of various ion species using the computer program GEOCHEM (Sposito and Mattigod, 1977).

Table 2. Computed distribution of aqueous species in equilibrium solution at 25°C under 1 atmosphere pressure.

Ca(NO <sub>3</sub> ) <sub>2</sub> medium							
	Total conc. pC <sub>T</sub>	Free conc. pC <sub>M<sup>2+</sup></sub>	MNO <sub>3</sub> <sup>+</sup>	M(NO <sub>3</sub> ) <sub>2</sub> <sup>0</sup>	MOH <sup>+</sup>	MHCO <sub>3</sub> <sup>+</sup>	MCO <sub>3</sub> <sup>0</sup>
Ni	4.91	4.99	5.68	—	9.92	9.24	9.64
Ca	0.78	0.94	1.35	2.29	8.57	6.29	9.29
CaSO <sub>4</sub> medium							
			MSO <sub>4</sub> <sup>0</sup>	MNO <sub>3</sub> <sup>+</sup>	MOH <sup>+</sup>	MHCO <sub>3</sub> <sup>+</sup>	MCO <sub>3</sub> <sup>0</sup>
Ni	4.84	4.89	5.80	9.12	9.56	8.87	9.19
Ca	2.90	2.95	3.86	6.88	—	8.03	—

All concentrations are in M indicated as negative logarithms. Only those species which are present in concentrations greater than 10<sup>-10</sup> M are included in this table.

Critically evaluated experimental association constants of various aqueous species were used in these calculations (Table 1). Association constants were estimated for aqueous species for which the experimental values were not available (Mattigod and Sposito, 1977). In these calculations only those aqueous species whose existence has been experimentally confirmed were included. There is sufficient experimental evidence to confirm the existence of complexes such as NiNO<sub>3</sub><sup>+</sup>, NiHCO<sub>3</sub><sup>+</sup>, NiCO<sub>3</sub><sup>0</sup>, NiHSO<sub>4</sub><sup>+</sup>, NiSO<sub>4</sub><sup>0</sup>, NiOH<sup>+</sup>, Ni(OH)<sub>2</sub><sup>0</sup>, Ni(OH)<sub>3</sub><sup>-</sup>, Ni(OH)<sub>4</sub><sup>2-</sup>, Ni<sub>2</sub>OH<sup>3+</sup>, and Ni<sub>4</sub>(OH)<sub>4</sub><sup>4+</sup> (Fedorov *et al.*, 1973; Pitwell, 1967; Nair and Nancollas, 1959; Baes and Mesmer, 1976). All the above Ni species, as well as similar Ca and Na species, were included in the calculations. Such a procedure is an essential aspect of chemical equilibrium calculations for multicomponent systems (Mattigod and Sposito, 1977). The partial pressure of carbon dioxide in all these computations was fixed at 10<sup>-3.5</sup> atmospheres. The activity coefficients were calculated by Davies' equation (Davies, 1962). A typical result of a calculation of ion speciation is indicated in Table 2. The results of these calculations indicate that, under the experimental conditions, only soluble complexes of metal-nitrate and metal-sulfate were significant. The NiNO<sub>3</sub><sup>+</sup> species constituted from 1% to 17% of the total Ni concentration in various solutions, whereas the NiSO<sub>4</sub><sup>0</sup> species accounted for 6% to 38% of the total soluble Ni. The calculations also indicate that supersaturated conditions with respect to solids, such as nickel hydroxide and nickel carbonate, did not exist in any of the initial or the equilibrium solutions.

## RESULTS AND DISCUSSION

### Effects of ionic strength

The effect of ionic strength on the adsorption of Ni by Ca-kaolinite is shown in Figure 1. All adsorption isotherms appear to be linear and those isotherms for ionic strengths less than 0.37 M appear to be constant par-

titution type according to the classification system of Giles *et al.* (1960). This type of isotherm is characterized by a constant partition of ions between solution and the adsorbent up to the maximum possible adsorption, where an abrupt change to a horizontal plateau occurs. The linearity of the isotherms indicates that the number of sites for adsorption remains constant (Giles *et al.*, 1960). Apparently, adsorption maxima were not reached for the range of Ni concentrations used in these experiments.

Generally, these adsorption isotherms (Figure 1) show that there is a corresponding decrease in Ni adsorption with increasing ionic strength [Ca(NO<sub>3</sub>)<sub>2</sub> as the background electrolyte]. For instance, for the same equilibrium concentration of Ni<sup>2+</sup> in solution, Ni adsorption at an ionic strength of 0.37 M is roughly 40% of that observed at an ionic strength of 0.005 M. Similar decreases in Ni adsorption with increasing ionic strength were observed in experiments with CaSO<sub>4</sub>, NaNO<sub>3</sub>, and Na<sub>2</sub>SO<sub>4</sub> as background electrolytes. This phenomenon can be attributed to (1) increasing Ca<sup>2+</sup> concentration (or Na<sup>+</sup> concentration) with increasing ionic strength and therefore increasing competition for the adsorption sites on the clay mineral, and (2) decreasing activity of Ni<sup>2+</sup> ion in solution due to increasing non-ideality of solution with ionic strength. This non-ideality is due to increasing electrostatic interaction and resulting formation of NiNO<sub>3</sub><sup>+</sup> and NiSO<sub>4</sub><sup>0</sup> ion pairs. Since Ni adsorption is governed by its activity in solution, decreased activity in solution means decreased adsorption on kaolinite.

### Effect of exchangeable cations

To compare the Ni adsorption on kaolinite in competition with Ca and Na, free nickel (Ni<sup>2+</sup>) ion activities in the equilibrium solution were plotted against total Ni adsorbed in mg/mole of kaolinite (Figures 2, 3). In solution media with NO<sub>3</sub><sup>-</sup> as the dominant anion, substantially more Ni was adsorbed on Na-kaolinite than on Ca-kaolinite at comparable Ni<sup>2+</sup> activities in solu-

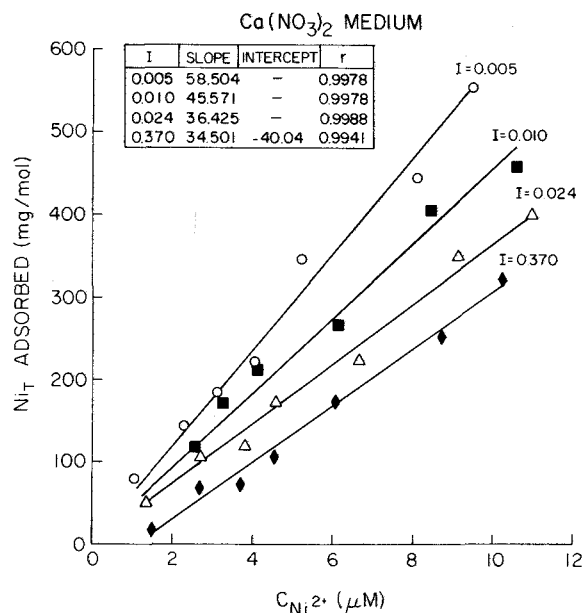


Figure 1. Effect of increasing ionic strength on the adsorption of Ni on kaolinite with  $\text{Ca}(\text{NO}_3)_2$  as the background electrolyte.

tion. Similar results were obtained in solution media in which  $\text{SO}_4^{2-}$  was the principal anion.

#### Effects of ion-pair formation

The principal effect of ion-pair formation is the reduced  $\text{Ni}^{2+}$  concentration in the equilibrating solution. Therefore, a ligand which forms ion pairs of greater stability with a given metal decreases the concentration of free divalent metal to a greater degree than a ligand which forms a weak ion pair. Reduction in metal adsorption can, therefore, be related to the nature of ion pairs involving the dominant anion in a system. The  $\text{SO}_4^{2-}$  ion forms neutral ion pairs with  $\text{Ni}^{2+}$ . Ion pairs involving  $\text{NO}_3^-$  and  $\text{Ni}^{2+}$  also exist. The association constants for  $\text{NiSO}_4^0$  and  $\text{NiNO}_3^+$  are  $10^{2.33}$  and  $10^{0.40}$ , respectively (Nair and Nancollas, 1959; Fedorov *et al.*, 1973). Therefore,  $\text{SO}_4^{2-}$  is considerably more effective in reducing  $\text{Ni}^{2+}$  concentrations in comparison with  $\text{NO}_3^-$  ion. This effect, in turn, should be reflected in a decreased  $\text{Ni}^{2+}$  concentration (and activity) in solution and hence a decreased Ni adsorption on kaolinite. The Ni adsorption isotherms for Ca-kaolinite (Figures 2, 4) show clearly that the adsorption of Ni is considerably less for the  $\text{SO}_4^{2-}$  system in comparison with the  $\text{NO}_3^-$  system. Similar comparisons also can be made for Ni adsorption on Na-kaolinite (Figure 3).

The difference in adsorption of Ni on kaolinite between the  $\text{NO}_3^-$  and the  $\text{SO}_4^{2-}$  system can also be examined in light of the ionic species of Ni present in equilibrium solutions. A number of studies indicated that specific adsorption of ion pairs of transition metals,

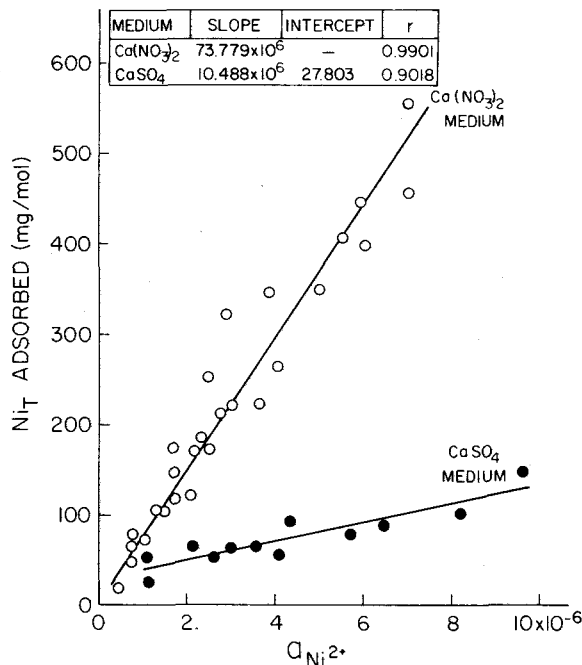


Figure 2. Ni adsorption on Ca-kaolinite as a function of  $\text{Ni}^{2+}$  activity in  $\text{Ca}(\text{NO}_3)_2$  and  $\text{CaSO}_4$  media.

such as  $\text{CuCl}^+$ ,  $\text{CuOH}^+$ , Cu-glycine<sup>+</sup>,  $\text{ZnOH}^+$ , and  $\text{ZnCl}^+$ , can occur on clay minerals (Elgabaly and Jenny, 1943; Farrah and Pickering, 1976; Koppelman and Dillard, 1977; Papanicolaou and Nobeli, 1977). It has also been established that neutral ion pairs and negatively charged complex species are not adsorbed to any measurable extent on kaolinite. These studies suggest that in the present experiments,  $\text{Ni}^{2+}$  as well as  $\text{NiNO}_3^+$  ion pair are the adsorbing species in the  $\text{NO}_3^-$  system, whereas only  $\text{Ni}^{2+}$  ion is the adsorbing species in the  $\text{SO}_4^{2-}$  system. Therefore, when the total Ni concentration is the same in the two systems, the concentration of adsorbing species in solution will be higher in the  $\text{NO}_3^-$  system than in the  $\text{SO}_4^{2-}$  system, leading to greater adsorption of Ni on kaolinite in the  $\text{NO}_3^-$  system.

#### Free energies of adsorption

Since  $\text{Ni}^{2+}$  ion is the only Ni species to be adsorbed on kaolinite in the  $\text{SO}_4^{2-}$  system, the free energy of adsorption of this ion can be calculated as follows:

A metal ion adsorbing onto a clay mineral can be represented by the half reaction



where M = metal ion or ion pair with charge m

X = the clay mineral

$\text{MX}_m$  = metal-clay complex.

Assuming that the actual activity of  $\text{X}^-$  is unity and the activity of the adsorbed metal ion to be equal to its mole fraction (N) on the adsorbent (implying an ideal

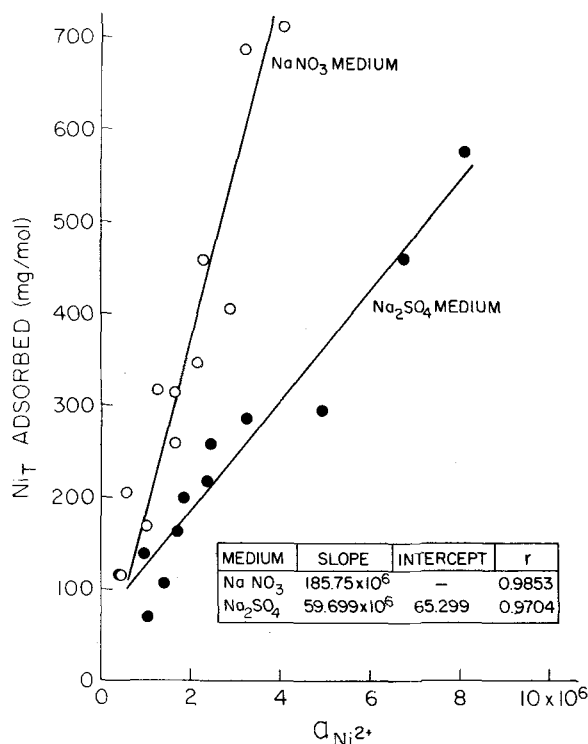


Figure 3. Ni adsorption on Na-kaolinite as a function of  $Ni^{2+}$  activity in  $NaNO_3$  and  $Na_2SO_4$  media.

mixture of solutes on the adsorbent), the equilibrium constant ( $K$ ) for the reaction can be written as:

$$K = N/a \quad (2)$$

where  $N$  = activity of adsorbed ion (=mole fraction) and  
 $a$  = ion activity in equilibrium solution.

Eq. (2) can be written as:

$$N = Ka \quad (3)$$

By plotting  $N$  as the dependent and  $a$  as the independent variable, one can obtain  $K$  from the slope of the line.

The standard free energy of adsorption ( $\Delta G_{ads}^0$ ) for a reaction such as Eq. (1) can then be computed from the relationships:

$$\Delta G_{ads}^0 = -RT \ln K \quad (4)$$

where  $R$  = gas constant ( $8.3147 \times 10^{-3}$  kJ/deg mole) and  
 $T$  = absolute temperature.

The calculated  $\Delta G_{ads}^0$  value for  $Ni^{2+}$  on kaolinite was  $-27$  kJ/mole.

### CONCLUSIONS

Increasing ionic strength decreases Ni adsorption on kaolinite. More Ni was adsorbed on Na-kaolinite than

on Ca-kaolinite. Adsorption of Ni is depressed to a greater degree when  $SO_4^{2-}$  is the dominant anion in solution instead of  $NO_3^-$ . This difference in adsorption can be attributed to higher concentrations of adsorbing species ( $Ni^{2+}$  and  $NiNO_3^+$ ) present in  $NO_3$  media in comparison to  $SO_4$  media in which only  $Ni^{2+}$  was the adsorbing species.

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**Резюме**—Изучалась адсорбция Ni(II) каолинитами, насыщенными Ca и Na, в равновесных растворах с общими концентрациями Ni, изменяющимися от 118 до 946  $\mu\text{г/л}$ . Дополнительные электролиты, используемые в этих экспериментах были 0,005, 0,01, 0,025, и 0,5 M  $\text{Ca}(\text{NO}_3)_2$ ; 0,002 и 0,005 M  $\text{CaSO}_4$ ; 0,01 и 0,1 M  $\text{NaNO}_3$ ; и 0,005 и 0,05 M  $\text{Na}_2\text{SO}_4$ . Образование ионов в равновесных растворах определялось с помощью компьютерной программы ГЕОХИМ. Подсчитанные концентрации и активности  $\text{Ni}^{2+}$  при равновесии коррелировались с общим количеством Ni, адсорбированным каолинитом. Увеличивающаяся ионная сила вызвала уменьшение адсорбции Ni. Адсорбция Ni из растворов была больше, когда  $\text{NO}_3^-$  был главным анионом. На основании данных адсорбции в среде  $\text{SO}_4^{2-}$  была вычислена стандартная свободная энергия адсорбции иона  $\text{Ni}^{2+}$  каолинитом, равная  $-27$  кДж/моль.

**Resümee**—Die Adsorption von  $\text{Ni}^{2+}$  durch Ca- und Na-gesättigte Kaolinite wurde in Lösungen nahe dem Gleichgewicht untersucht, die Gesamt-Ni-Konzentrationen im Bereich von 118 bis 946  $\mu\text{g/liter}$  hatten. Als Hilfselektrolyte wurden in diesen Experimenten verwendet: 0,005, 0,01, 0,025, und 0,5 M  $\text{Ca}(\text{NO}_3)_2$ ; 0,002 und 0,005 M  $\text{CaSO}_4$ ; 0,01 und 0,1 M  $\text{NaNO}_3$  sowie 0,005 und 0,05 M  $\text{Na}_2\text{SO}_4$ . Die Verteilung der Ionenarten in den Gleichgewichtslösungen wurde mit dem Computerprogramm GEOCHEM berechnet. Die berechneten  $\text{Ni}^{2+}$ -Konzentrationen und -Aktivitäten bei Gleichgewicht wurden mit dem Gesamt-Ni, das durch Kaolinit adsorbiert war, korreliert. Eine zunehmende Ionenstärke bewirkt eine abnehmende Ni-Adsorption. Die Ni-Adsorption aus den Lösungen war größer, wenn  $\text{NO}_3^-$  das vorherrschende Anion war. Aufgrund der Adsorptionsdaten bei  $\text{SO}_4^{2-}$ -Medium wurde die Freie Energie der  $\text{Ni}^{2+}$ -Adsorption an Kaolinit mit  $-27$  kJ/mol berechnet.

**Résumé**—L'adsorption de Ni(II) par des kaolinites saturées de Ca et Na a été étudiée dans des solutions équilibrantes avec des concentrations totales de Ni s'étendant de 118 à 946  $\mu\text{g/litre}$ . Des électrolytes de fond utilisées dans ces expériences étaient 0,005, 0,01, 0,025, et 0,5 M  $\text{Ca}(\text{NO}_3)_2$ ; 0,002 et 0,005 M  $\text{CaSO}_4$ ; 0,01 et 0,1 M  $\text{NaNO}_3$ ; et 0,005 et 0,05 M  $\text{Na}_2\text{SO}_4$ . La spéciation d'ions dans les solutions d'équilibre a été calculée par le programme d'ordinateur GEOCHEM. Les concentrations et activités de  $\text{Ni}^{2+}$  calculées à l'équilibre ont été apparentées à Ni total adsorbé par la kaolinite. La force ionique croissante a résulté en une adsorption décroissante de Ni. Lorsque  $\text{NO}_3^-$  était l'anion dominant dans les solutions, l'adsorption de Ni était la plus élevée. En se basant sur les données d'adsorption dans un milieu  $\text{SO}_4$ , on a calculé que l'énergie libre standard d'adsorption de l'ion  $\text{Ni}^{2+}$  sur la kaolinite était  $-27$  kJ/mole.