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DEHYDRATION, DIFFUSION AND ENTRAPMENT OF ZINC IN BENTONITE

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Abstract—Interactions with bentonite are important in the chemical speciation and fate of heavy metals in soils and other ecosystems. The interactions of Zn with bentonite were studied using X-ray diffraction (XRD), dehydration, kinetic and sequential extraction procedures. The species and activity of Zn retained by bentonite were affected markedly by pH. The $Zn(OH)^+$ was retained by bentonite prepared at pH $\geq$ 6.9. The extent of dehydration of $Zn(OH)^+$-bentonite was higher than that for Zn-bentonite. At a relative humidity of 55.5%, the basal spacing of the $Zn(OH)^+$-bentonite was from 1.21 to 1.26 nm with 1 water sheet and that of the Zn-bentonite was 1.51 nm with 2 water sheets. The greater affinity of $Zn(OH)^+$ for bentonite than Zn was associated with a lower degree of hydration. When an aqueous suspension of Ca-bentonite was incubated with soluble Zn, the concentration of Zn retained by the Ca-bentonite was linearly related to the square root of time. The rate of the interaction was controlled probably by the interlayer diffusion and subsequently by the diffusion into the ditrigonal cavities in bentonite. The Zn retained by bentonite was dehydrated *in situ* so as to increase the bonding of Zn with surfaces of bentonite. With hydrothermal treatment the retained Zn could diffuse easily into the cavities and transform increasingly to the residual forms that are associated with the entrapped form.

Key Words—Bentonite, Entrapment, Interaction, Micropore Diffusion, Speciation, Zinc.

INTRODUCTION

Interactions of Zn with smectites, such as bentonite, are important in the chemical speciation and fate of Zn in soils and other ecosystems. The interactions involving surface complex formation (inner and outer sphere) have been studied frequently in the short term (days), but they have not been studied over relatively long terms (months). The long-term processes that decrease the activity and extractability of Zn retained by smectites are believed to be important in the availability of Zn added to soils and in the remediation of soils contaminated with Zn.

The species and activity of Zn, whether in solution or retained by smectites, are affected markedly by pH. High pHs generally result in greater specific adsorption of Zn (Farrah and Pickering 1976). The mechanism of the specific adsorption at high pH is believed to be associated with the formation of $Zn(OH)^+$ (Farrah and Pickering 1976; Tiller et al. 1984). Although Zn has a high degree of hydration (Pass 1973), in solution the Zn will increasingly form $Zn(OH)^+$ with increasing pH. Furthermore, proton dissociation from water molecules often takes place more readily in the intermicellar spaces than in bulk solutions (Farmer 1978; Tan 1993). Quirk and Posner (1975) postulated that at low pH, Zn can hydrolyze to $Zn(OH)^+$ at the surface of Fe oxides. And Frenkel (1974) reported that the degree of dissociation of a water molecule adsorbed on montmorillonite is 10^7 times higher than in liquid water. The reaction:

$$[Zn(H_2O)_n]^{2+} \rightarrow [Zn(OH)(H_2O)_{n-x-1}]^+ + xH_2O + H^+ \quad [1]$$

is promoted by partial dehydration, since the residual water molecules around Zn are more highly polarized and hence more acidic (Farmer 1978). The greater affinity of $Zn(OH)^+$ over Zn is apparently due to the lower degree of hydration of the former which leads to both steric and electrostatic favoritism in the sorption process.

Tiller and Hodgson (1962) postulated that the Zn unextractable with 2.5% HOAc is associated with the filling of lattice vacancies of layer silicates, but XRD analysis has failed to reveal any changes in the structure of the layer silicates (Reddy and Perkins 1974). Reddy and Perkins (1974) postulated that the Zn enters the interlayer spaces of the expanded lattice (due to hydration) and is trapped as the crystal lattice contracts upon drying. However, there is little direct evidence for lattice cavity entrapment of Zn by swelling layer silicates.

Few studies have been carried out to investigate the loss of activity and extractability of Zn at high pH over months and years. Interactions in the interlayer spaces, such as with ditrigonal cavities, may be responsible along with other processes such as dehydration of $Zn(OH)^+$ species. The objective of this study was to investigate the species, dehydration and interlayer diffusion and entrapment of Zn in ditrigonal cavities of bentonite.

MATERIALS AND METHODS

Hydration and Dehydration—Theory and Experiment

The cations with low hydration energies, such as K, NH_4^+ and Rb, are easy to dehydrate and tend to be entrapped in interlayer positions of swelling layer silicates (Dixon and Weed 1989). The free energy of sol-

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Table 1. Salts used to prepare saturated electrolyte solutions for constant water activity at 20 °C.

Salt	Water activity (a_w)
P_2O_5	0.00
$LiCl \cdot H_2O$	0.12
$CaCl_2 \cdot 6H_2O$	0.35
$Ca(NO_3)_2 \cdot 4H_2O$	0.55
$NaNO_2$	0.65

From Denis et al. (1991).

vation of an ion may be calculated directly from the Born equation (Pass 1973):

$$\Delta G^\circ = \frac{LZ^2e^2}{8\pi\epsilon_0 r_i}\left(1 - \frac{1}{\epsilon_r}\right) \quad [2]$$

where: L = the Avogadro constant = 6.002×10^{23} mol^{-1}; Z = the numerical value of the charge on the ion; e = the magnitude of the electronic charge = 1.602×10^{-19} C; r_i = the radius of the ion (nm); ϵ_0 = the permittivity of a vacuum = 8.854×10^{-12} F m^{-1}; ϵ = the permittivity of the solvent (F m^{-1}); and ϵ_r = ϵ/ϵ_0 = the relative permittivity (also called the dielectric constant). Expressions for the hydration enthalpy and hydration entropy may be derived from this equation, which on substitution reduce to:

$$\Delta H^\circ = -69.9 \times 10^3 \frac{Z^2}{r_i} \quad \text{(nm J mol}^{-1}\text{)} \quad [3]$$

$$\Delta S^\circ = -4.10 \times \frac{Z^2}{r_i} \quad \text{(nm J K}^{-1}\text{ mol}^{-1}\text{)} \quad [4]$$

The ionic radii are often difficult to ascertain. Generally, the crystallographic radii r_c corrected by the additive term c, with a constant common value (0.085 nm for Pauling's ionic radii) for cations is used: $r_i = r_c + c$ (Koryta and Dvorák 1987).

Chinese white bentonite was provided by Commercial Minerals Limited, Victoria. Bentonite (5 g) was saturated with K, Ca, Mg and Zn by shaking for 4 h with 50 mL of 0.1 M KCl, $CaCl_2$, $MgCl_2$ and $ZnCl_2$ solutions, centrifuged and the supernatants decanted. The residues were washed twice for 1 h each time with 25 mL of distilled water. The pHs of the bentonite suspensions were adjusted with KOH/HCl to the appropriate values (initial pH) and the suspensions were allowed to stand overnight to achieve pH equilibrium; then the final pH was measured. The suspensions were centrifuged and the supernatants decanted. All the residues were air-dried at room temperature except the Mg-bentonites, which were dried at 40 °C for easy grinding. After grinding, some of the samples were stored in a desiccator for at least 1 week above a saturated solution of $Mg(NO_3)_2 \cdot 6H_2O$ to obtain constant relative humidity (55.5%) prior to XRD with a Siemens D1500 X-ray Diffractometer.

The chemical analysis of Zn-saturated bentonite at pH 5.6 was carried out by X-ray fluorescence (XRF) spectroscopy and the results were presented as follows: SiO_2 647 g kg^{-1}, Al_2O_3 205 g kg^{-1}, MgO 40 g kg^{-1}, K_2O 33 g kg^{-1}, Na_2O 11 g kg^{-1}, Fe_2O_3 7.7 g kg^{-1}, CaO 7.2 g kg^{-1}, TiO_2 1.8 g kg^{-1}, P_2O_5 0.4 g kg^{-1}, MnO 0.1 g kg^{-1} and ZnO 44.3 g kg^{-1}. The structural formula was obtained by calculation (Newman and Brown 1987; Bain and Smith 1994):

$$K_{0.51}Na_{0.26}Ca_{0.09}Zn_{0.40}(Al_{2.85}Fe(III)_{0.07}Ti_{0.02}Mg_{0.73})(Si_{7.9}Al_{0.1})O_{20}(OH)_4$$

The chemical composition and the formula of the bentonite suggest that the bentonite is a dioctahedral illite–smectite and the predominant charges are generated in octahedral sheets (Newman and Brown 1987).

The homoionic bentonite samples were incubated at a water activity (a_w) of 1.0 for 1 week and then placed in desiccators at water activities of 0, 0.12, 0.35, 0.55 and 0.65 (Table 1) at 20 °C for 1 week. The water contents of the samples at the different a_w were measured by weighing.

The bentonites saturated with Zn (Zn-bentonite) at different pHs were extracted with 1 M NH_4Cl, KCl, NaCl and LiCl solutions at pH 7.0 (twice), respectively. The solutions (200 mL) were added to the centrifuge tubes with Zn-bentonite (1 g) at different pHs and shaken for 24 h. After shaking and centrifuging, the supernatants were decanted and filtered. The second extraction was conducted by adding another 200 mL extractant to the residue from the previous extraction. After shaking for 24 h, the filtrates were obtained as before. Calculations were made to take into account the amount of Zn left over from the previous extraction. The filtrates were diluted 100 times for Zn analysis by atomic absorption spectrophotometry (Varian-Techtron AA-1475 series).

Kinetics—Theory and Experiment

Bentonite saturated with Ca was prepared by shaking bentonite (20 g) with 100 mL 0.5 M $CaCl_2$ at pH 7.0 for 3 times, each for 24 h, and then the sample was washed twice with distilled water, air-dried and passed through a 100-mesh sieve.

The kinetics of the reaction of Zn with the Ca-bentonite (4 mg L^{-1} Zn in 0.01 M $CaCl_2$ in 1% suspension) was studied by monitoring the Zn concentration in solution while the suspension was continuously stirred. The concentration of Zn in solution decreases as Zn enters the Ca-bentonite because there is a limited volume of solution. For the diffusion from a limited source (such as a stirred solution of limited volume) into a plane sheet, the process can generally be expressed by the following equation (Crank 1975):

$$Y/Y_m = 1 - e^{T/\alpha^2}\,\mathrm{erfc}\sqrt{T/\alpha^2} \quad [5]$$

where Y is the amount of diffused Zn, Y_m is the total

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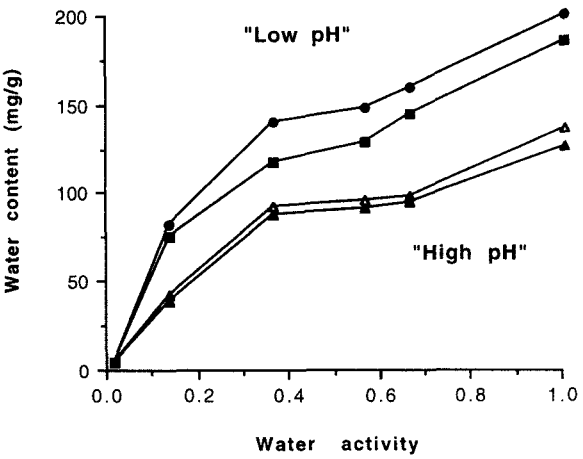


Figure 1. The water content of Zn-bentonite at different pHs as a function of water activity: (●) pH 5.6, (■) pH 6.3, (△) pH 6.9 and (▲) pH 8.8.

amount of Zn added to the suspension of bentonite, $T = Dt/l^2$, erfc is referred to as the error-function complement, D is a constant diffusion coefficient, $2l$ is the sheet thickness, t is time and α is a constant whose value can be given by the fraction of the total amount of Zn finally taken up by the Ca-bentonite ($F = 1/(1+\alpha)$).

If T/α^2 is small (<0.01), corresponding to small t, small D/l^2 and large α, $e^{T/\alpha^2} \approx 1$, thus one obtains:

$$Y/Y_m = 1 - \text{erfc}\sqrt{T/\alpha^2} = \frac{2}{\sqrt{\pi}}\frac{\sqrt{T}}{\alpha} - \frac{2}{3\sqrt{\pi}}\left(\frac{\sqrt{T}}{\alpha}\right)^3 + \frac{2}{10\sqrt{\pi}}\left(\frac{\sqrt{T}}{\alpha}\right)^5 + \ldots \quad [6]$$

The higher-order terms in Equation [6] can be neglected at small T/α^2; hence Equation [5] can be simplified to:

$$Y/Y_m = \frac{2}{\alpha\sqrt{\pi}}\sqrt{\frac{D}{l^2}}\sqrt{t} \quad [7]$$

If small values of α are required, corresponding to very high fractional uptakes of Zn by a plane sheet, it is convenient to reduce Equation [5] to:

$$Y/Y_m = 1 - \frac{\alpha}{\sqrt{\pi}\sqrt{T}} + \frac{1}{2\sqrt{\pi}}\left(\frac{\alpha}{\sqrt{T}}\right)^3 - \frac{3}{4\sqrt{\pi}}\left(\frac{\alpha}{\sqrt{T}}\right)^5 + \ldots \quad [8]$$

This is obtained from Equation [5] by substituting the asymptotic expansion for $e^{T/\alpha^2}\,\text{erfc}\sqrt{T/\alpha^2}$ when T/α^2 is large. If α is small, the higher-order terms in Equation [6] can be neglected at large values of time and Equation [5] can be simplified to:

$$Y/Y_m = \beta - \frac{\alpha}{\sqrt{\pi D/l^2}}\frac{1}{\sqrt{t}} \quad [9]$$

where $\beta = 1 + \S$ (§ is an error from the deletion of higher-order terms). A plot of Y/Y_m versus $1/\sqrt{t}$ should give a straight line with an intercept β and a slope $\alpha/\sqrt{\pi D/l^2}$. The value of α can be estimated by the equation, $\alpha = 1/F - 1$, where F is the fraction of the total amount of Zn finally taken up by the Ca-bentonite. In this experiment, the value of F is given by the equation $Y/Y_m = Ft/(t + t_{1/2})$, where $t_{1/2}$ is a constant; when $t \to \infty$, $Y/Y_m = F$.

Incubation and Extraction

Bentonite saturated with Ca^{2+} at pH 7.0 (1 g) was mixed with 20-mL aliquots of 4 mg L^{-1} Zn as $ZnSO_4$ in 0.01 *M* $CaCl_2$, and then incubated at 20 °C. After 1, 30, 60, 221 and 430 d, the suspensions were centrifuged and the concentrations of Zn in the supernatants as water-soluble Zn (WS-Zn) were measured. The Zn retained by the bentonite was extracted sequentially with 20 mL of 1 *M* $MgCl_2$ at pH 7.0 by shaking for 1 h ($MgCl_2$-Zn), 2 successive 1% Na-HCaEDTA in 1 *M* ammonium acetate at pH 8.3 by shaking for 2 h (EDTA-Zn), 0.5 *M* HCl by shaking for 2 h (0.5 *M* HCl-Zn), 6 *M* HCl by shaking for 2 h (6 *M* HCl-Zn) and H_2SO_4-$HClO_4$-HF mixture (residual Zn). Twenty grams of Ca-bentonite were added to 400 mL of 4 mg L^{-1} Zn ($ZnSO_4$) in 0.01 *M* $CaCl_2$ and the suspension was incubated at 20 °C for 120 d. Some of the suspension of bentonite with retained Zn was heated in a Teflon pressure vessel and some of the residue (bentonite with Zn) was heated in air at 200 °C for 12 h. After heating, 20 mL of the suspension was extracted sequentially using the method described above.

RESULTS AND DISCUSSION

Effects of pH on Species, Hydration and Extractability of Retained Zn

Although the Born equation is a rough approximation, it can be used to compare the hydration effect of Zn species. One expects the hydration enthalpy ($\Delta H°$) of $Zn(OH)^+$ to be less than that of Zn because of the lower charge and greater size of the former. The $-\Delta H°$ of Zn (r_c = 0.074 nm) is estimated to be 2056 kJ mol^{-1} while the $-\Delta H°$ of $Zn(OH)^+$ ($r_c \approx$ 0.21 nm) can be estimated to be about 237 kJ mol^{-1}, which is 8 times less than that of Zn and is less than the $-\Delta H°$ for K (322.1 kJ mol^{-1}) and Rb (292.8 kJ mol^{-1}) (Pass 1973). Thus one expects that $Zn(OH)^+$ has a low degree of hydration and dehydrates easily.

The water content of the Zn-bentonites at different a_w decreased with increasing pH (Figure 1). The degree of hydration of Zn-bentonite at the "high" pH was lower than that at the "low" pH. The formation of $Zn(OH)^+$ is probably responsible for the lower water content of Zn-bentonite at the "high" pH.

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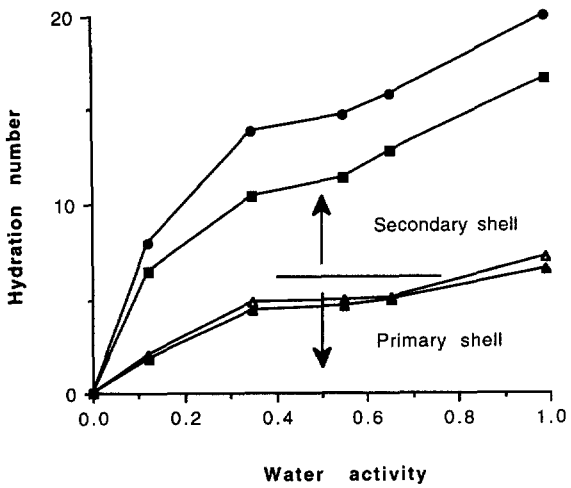


Figure 2. The hydration number of Zn retained by bentonite at different pHs as a function of water activity: (●) pH 5.6, (■) pH 6.3, (△) pH 6.9 and (▲) pH 8.8.

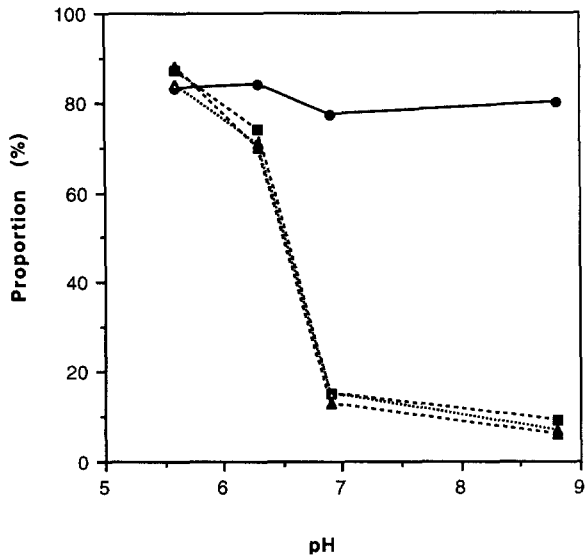


Figure 4. The proportion of Zn extracted with 1 *M* chloride solutions (twice) for Zn-bentonites prepared at different pHs: (●) NH_4Cl, (■) KCl, (△) NaCl and (▲) LiCl.

The hydration number (n), which is the number of H_2O molecules bound to a single ion, was estimated from the ratio of adsorbed water to Zn retained (H_2O molecules/Zn cation). At the "high" pH, n was found to be ≤ 7; thus the H_2O molecules probably existed only in the primary shell or coordination shell and would be bonded to Zn by ion dipole forces or coordinate bonds. At the "low" pH, n was always greater than that at the "high" pH and was from 7 to 20 at a_w from 0.12 to 1.00 respectively; here there were 2 shells in the hydration sphere—a primary shell and a secondary shell (Figure 2). The basal spacing (001) of $Zn(OH)^+$-bentonite at the "high" pH was from 1.21 to 1.26 nm with 1 water sheet; that of Zn-bentonite at the "low" pH was 1.51 nm with 2 water sheets; the basal spacings (001) of the bentonites saturated with K, Ca and Mg at high pH and low pH were found to be similar and were from 1.44 to 1.51 nm (Figure 3). Compared to K, Ca and Mg, the species and hydration of Zn retained and the basal spacing were markedly affected by pH.

The concentrations of Zn removed in 2 successive extractions with 1 *M* chloride solutions of some monovalent cations for Zn-bentonites prepared at different pHs are shown in Figure 4. The exchangeability of K, Na and Li markedly decreased with increasing of pH, but the percentage of Zn extracted successively by NH_4Cl solution showed little change with increasing of pH with respect to the other monovalent cations. The concentrations of Zn extracted with KCl, NaCl and LiCl solutions were high at pH 5.6 and 6.3 (from 70 to 88%) and low at pH 6.9 and 8.8 (from 6 to 15%). These results suggest that the $Zn(OH)^+$ retained by bentonites was difficult to exchange with K, Na and

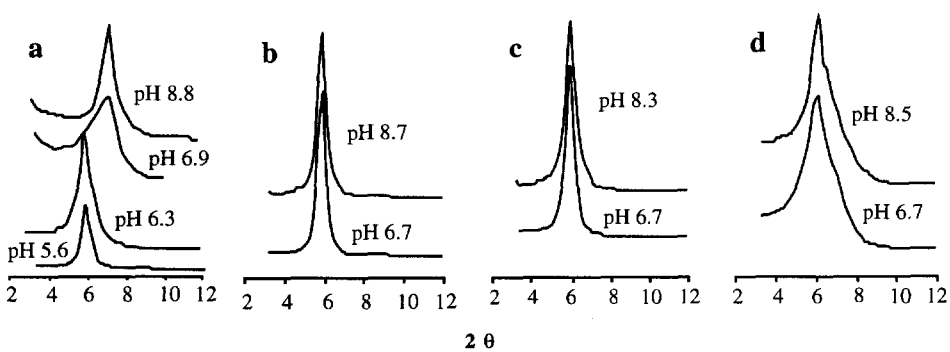


Figure 3. XRD patterns of the bentonites saturated with Zn (a), Ca (b), Mg (c) and K (d) at different pHs. At a relative humidity of 55.5%, the basal spacing (001) of the bentonite saturated with Zn at "high pH" (pHs 6.9 and 8.8) was from 1.21 to 1.26 nm; that of Zn-bentonite at "low" pH (pHs 5.6 and 6.3) was 1.51 nm; and those of bentonites saturated with Ca, Mg and K at different pHs were from 1.44 to 1.51 nm.

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Table 2. Characteristics of Zn-bentonite at different pH.

	"High"	"Low"
Species	$Zn(OH)^+$	Zn
Ionic radius (nm)	≈0.21	0.074
Zn retained (g kg^{-1})	67.3	37.7
Water in interlayer	1 sheet	2 sheets
Basal spacing (nm)	1.21–1.26	1.51
Extractability†	low	high

† In 1 *M* KCl, NaCl and LiCl.

Li, and that the affinity of $Zn(OH)^+$ for bentonites was higher than for Zn.

Because of the formation of Zn ammine complexes at high pH ($Zn(NH_3)^{2+}$ > 90% at pH ≥ 7.0), the exchangeability with NH_4^+ was higher than for K, Na and Li. It is considered that NH_4^+ can exchange with Zn and $Zn(OH)^+$ species adsorbed with bentonites and the exchange reaction between $Zn(OH)^+$ and NH_4^+ may be represented as follows:

$$\text{Bentonite-Zn(OH)} + 2NH_4^+ \rightleftharpoons \text{Bentonite-}NH_4 + Zn(NH_3)^{2+} + H_2O \quad [10]$$

There was twice as much Zn retained at the "high" pH than that at the "low" pH (Table 2) which supports the idea that the species of Zn retained were $Zn(OH)^+$ at the "high" pH, and Zn at the "low" pH.

The greater affinity of $Zn(OH)^+$ for bentonite was associated with the lower degree of hydration with respect to Zn (Table 2). The $Zn(OH)^+$ retained by bentonite was dehydrated partially at the "high" pH and some behaved as specifically sorbed Zn. One assumes that $Zn(OH)^+$ in the interlayer space was coordinated directly with oxygen ions of the siloxane surface on 1 layer and formed hydrogen bonding between hydroxyl and oxygen on the siloxane surface of the opposite layer. In contrast, the Zn retained at the "low" pH behaved as readily exchangeable cations and existed in the interlayer with 2 water sheets.

Diffusion and Entrapment of Zn

The concentration of Zn taken up and retained by Ca-bentonite increased with time (Figure 5). A plot of the proportion of Zn retained by Ca-bentonite (Y/Y_m) versus the square root of time shows conformity with the diffusion model from Equation [5] with D/l^2 = 2.03 × 10^{-5} d^{-1} (or 2.35 × 10^{-10} sec^{-1}) and α = 4.52 × 10^{-3} (Figure 5). This result suggests that the interaction of Zn with bentonite was a diffusion rate-limiting process. In the well-stirred system, film diffusion is most unlikely to be rate-limiting; the rate of the process was probably controlled by interlayer diffusion and subsequently by the diffusion into the ditrigonal cavities in bentonite.

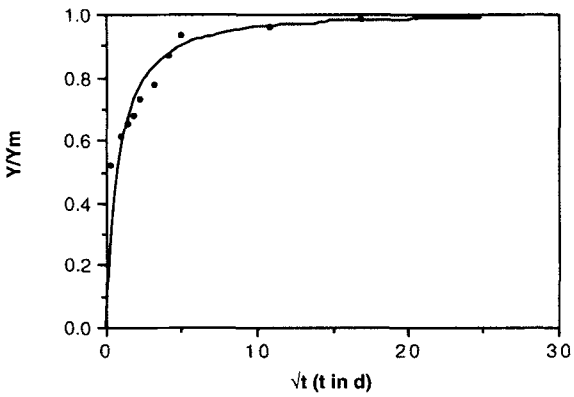


Figure 5. A plot of measured proportion (Y/Y_m) of Zn retained (Y) by bentonite from a well-stirred solution of limited volume to the added Zn (Y_m) against the square root of time $\sqrt{t}$ (points) and theoretical diffusion curve (solid line) of Equation [5] with D/l^2 = 2.03 × 10^{-5} d^{-1} and α = 4.52 × 10^{-3}. The value of D/l^2 was derived from the experimental data Y/Y_m versus $1/\sqrt{t}$ (t > 2 d) using Equation [9]. The correlation coefficient (R) was 0.978, which was significant at the level of probability P > 0.001. The experimental data show approximate conformity with the diffusion model, Equation [5].

The concentrations of Zn in water-soluble, exchangeable ($MgCl_2$), and EDTA-extractable fractions decreased while the concentrations of Zn extracted by 0.5 *M* HCl, 6 *M* HCl and the residual Zn increased with incubation time (Table 3).

The Zn in residual forms plus the Zn extracted with 6 *M* HCl, which was considered to be associated with the entrapped form, increased with incubation time. Assuming the Zn in residual forms plus the Zn extracted with 6 *M* HCl in the Ca-bentonite treated at 200 °C for 12 h is equal to the maximum of Zn in

Table 3. The transformation of Zn added (80 mg kg^{-1}) to Ca-bentonite at pH 7.0 and effects of heating (mg kg^{-1}).

Fraction	Incubation time (d)					Control	Heating (200 °C, 12 h)	
	1	30	60	221	430	20 °C	In air	In water
Water-soluble	3.6	1.3	1.2	1.0	0.5	0.5	0.5	0.2
$MgCl_2$-Zn	28	10	8.1	5.0	5.9	9.1	4.9	0.7
EDTA-Zn	35	29	25	15	17	20	28	3.0
0.5 *M* HCl-Zn	12	31	34	33	34	36	33	18
6 *M* HCl-Zn	3.1	10	12	14	14	9.4	12	17
Residual Zn	n.d.†	n.d.	n.d.	12	8.7	3.9	5.5	45

† n.d. = not detected (<0.1 mg kg^{-1}).

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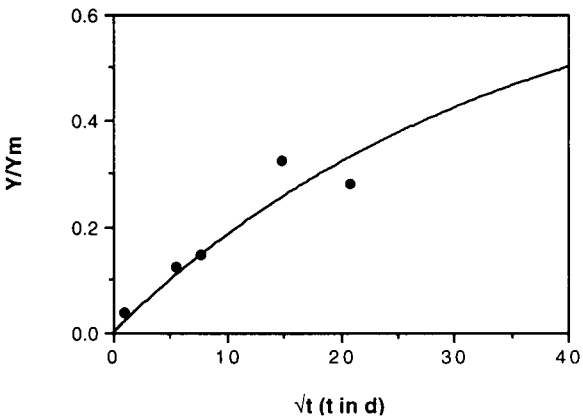


Figure 6. A plot of measured proportion (Y/Y_m) of Zn in residual forms and extracted with 6 *M* HCl (Y) to the added Zn (Y_m) against the square root of time $\sqrt{t}$ (points) and theoretical diffusion curve (solid line) of Equation [5] with $D/l^2 = 3.12 \times 10^{-5}\ d^{-1}$ and $\alpha = 0.29$. The value of D/l^2 was derived from the experimental data Y/Y_m versus $\sqrt{t}$ ($t < 30$ d) using Equation [7]. The experimental data show approximate conformity with the diffusion model, Equation [5].

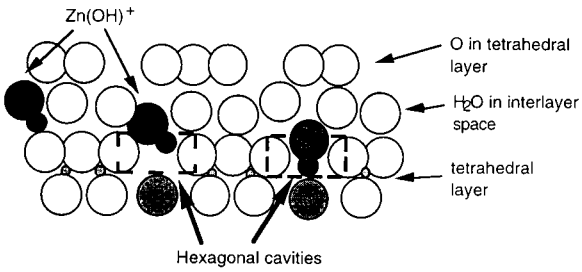


Figure 7. Cross-sectional view of the possible locations of $Zn(OH)^+$ retained by bentonite at "high" pH.

residual forms plus the Zn extracted with 6 *M* HCl in the Ca-bentonite incubated with Zn at 20 °C, then the change in the proportion of Zn in residual forms and extracted with 6 *M* HCl to the added Zn with time can be described by the diffusion model (Equation [5]) with $D/l^2 = 3.12 \times 10^{-5}\ d^{-1}$ (Figure 6). These results suggest that diffusion in the interlayer space and into cavities, and then further to the bottom of cavities, led to decreases in the activity and extractability of the Zn retained by the bentonite over a relatively long time.

When the bentonite with retained Zn was dehydrated by heating in air at 200 °C, the exchangeable Zn transformed to EDTA-Zn, which is considered to be associated with the specifically adsorbed Zn. The results suggest that the Zn retained by bentonite was dehydrated *in situ* which increased the bonding of Zn to the interlayer surfaces of the bentonite. With hydrothermal treatment, the adsorbed Zn may continue to diffuse into the cavities and increasingly transform into the residual forms that are analogous with the entrapped form (Table 3).

The migration of relatively small cations, such as Li, Mg, Zn, Ni, Cu(II) and Fe(III), from the interlayer space into the crystalline matrix of dioctahedral smectites occurs on heating at temperatures around 200 to 300 °C, but the final location taken by migrating cations in heated smectite is uncertain. The migration of Li in montmorillonite was studied by IR spectroscopy and it was suggested that the nonexchangeable Li is likely to be found in the bottom of the ditrigonal cavities (Calvet and Prost 1971). Ben Hadj-Amara et al. (1987) examined cation migration in Ni-exchanged beidellite using X-ray modeling techniques; their results suggested that Ni migrated into the vacant octahedral sites. Luca and Cardile (1989) studied the Fe(III) migration in smectites using electron spin resonance, Mössbauer spectroscopy, and magnetic susceptibility measurements; no evidence for the penetration of Fe(III) into the vacant octahedral sites of montmorillonite was found. However, the penetration of Zn into the vacant octahedral sites of smectites is unlikely under field conditions where the temperatures and degree of desiccation are relatively low when compared with the conditions referred to above.

Although saponite (trioctahedral) is different in structure from bentonite (dioctahedral), the Zn in water-soluble, exchangeable ($MgCl_2$) and EDTA-extractable fractions was transformed or transferred into Zn extracted with 0.5 *M* HCl, 6 *M* HCl and residual Zn with heating. The similar heating effects on the retention of Zn by both bentonite and saponite suggest that the bottom of the ditrigonal cavities in bentonite is the likely final site for Zn migration.

At high pH, Zn retained by bentonite existed as $Zn(OH)^+$. The shape of $Zn(OH)^+$ is probably egg-shaped and although the size of $Zn(OH)^+$ seems to be bigger than the cavities in the tetrahedral layer of bentonite, the egg-shaped $Zn(OH)^+$ may fit neatly into the cavities. The possible forms of Zn retained by bentonite at "high pH" (Zn sorbed on the external surface, in the interlayer space and in ditrigonal cavities) are shown in Figure 7.

CONCLUSIONS

The species, activity and extractability of Zn retained by bentonite are affected markedly by pH. Hydroxy Zn ($Zn(OH)^+$) was retained by bentonite prepared at pH $\geq$ 6.9. The lower degree of hydration of $Zn(OH)^+$ relative to Zn gives rise to greater affinity of $Zn(OH)^+$ for bentonite than Zn. The basal spacing of $Zn(OH)^+$-bentonite was from 1.21 to 1.26 nm with 1 water sheet; that of Zn-bentonite was 1.51 nm with 2 water sheets at a relative humidity of 55.5%. The Zn in $Zn(OH)^+$-bentonite was less readily exchangeable with 1 *M* solutions of KCl, NaCl and LiCl and $MgCl_2$ than with 1 *M* NH_4Cl, which extracted about 80% of the $Zn(OH)^+$ retained by bentonite. Complexation of Zn with ammonia is probably responsible for the su-

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periority of NH_4Cl. The activity and extractability of Zn retained by bentonite decreased over a relatively long time. The decreases were probably due to interlayer diffusion and entrapment of Zn in ditrigonal cavities; hydrothermal treatment probably increases the extent and rates of these processes. The behavior of Zn observed here can be related to that in soils containing smectites and it may be used to advantage where Zn pollution has occurred and it is necessary to decrease the activity and mobility of the Zn in soils.

REFERENCES

Bain DC, Smith BFL. 1994. Chemical analysis. In: Wilson MJ, ed. Clay mineralogy: Spectroscopic and chemical determinative methods. London. Chapman & Hall. p 300–332.

Ben Hadj-Amara A, Besson G, Tchoubar C. 1987. Caractéristiques structurales d'une smectite dioctaèdrique en fonction de l'ordre-désordre dans la distribution des charges électriques: Études des reflexions *001:* Clay Miner 22:305–318.

Calvet R, Prost R. 1971. Cation migration into empty octahedral sites and surface properties of clays. Clays Clay Miner 19:175–186.

Crank J. 1975. The Mathematics of diffusion. Oxford Univ Pr. 414 p.

Denis JH, Keall MJ, Hall PL, Meeten GH. 1991. Influence of potassium concentration on the swelling and compaction of mixed (Na, K) ion-exchanged montmorillonite. Clay Miner 26:255–268.

Dixon JB, Weed SB. 1989. Minerals in soil environments (2nd ed). Madison, WI: Soil Sci Soc Am 1244 p.

Farmer VC. 1978. Water on particle surfaces. In: Greenland DJ, Hayes MHB, eds. The Chemistry of soil constituents. New York: J. Wiley. p 405–448.

Farrah H, Pickering WF. 1976. The sorption of zinc species by clay minerals. Aust J Chem 29:1649–1656.

Frenkel M. 1974. Surface acidity of montmorillonites. Clays Clay Miner 22:435–441.

Koryta J, Dvorák J. 1987. Principles of electrochemistry. Great Britain: J. Wiley. 447 p.

Luca V, Cardile CM. 1989. Cation migration in smectite minerals: Electron spin resonance of exchanged Fe^{3+} probes. Clays Clay Miner 37:325–332.

Newman ACD, Brown G. 1987. The chemical constitution of clays. In: Newman ACD, ed. Chemistry of clays and clay minerals. London Mineral Soc. London: Longman. p 1–128.

Pass G. 1973. Ions in solution (3): Inorganic properties. Oxford: Clarendon Pr. 101 p.

Quirk JP, Posner AM. 1975. Trace element adsorption on mineral surfaces. In: Nicholas DJD, Egan AR, eds. Trace elements in soil-plant-animal systems. New York: Academic Pr. p 95–107.

Reddy MR, Perkins HF. 1974. Fixation of zinc by clay minerals. Soil Sci Soc Am Proc 38:229–231.

Tan KH. 1993. Principles of soil chemistry (2nd ed). New York: Marcel Dekker. 362 p.

Tiller KG, Gerth J, Bruemmer G. 1984. The relative affinity of Cd, Ni and Zn for different soil clay fractions and goethite. Geoderma 34:17–35.

Tiller KG, Hodgson JF. 1962. The specific sorption of cobalt and zinc by layer silicates. Clays Clay Miner 9:393–403.

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