

## NUCLEAR MAGNETIC RESONANCE (NMR) STUDY OF Cd<sup>2+</sup> SORPTION ON MONTMORILLONITE

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**Abstract**—<sup>113</sup>Cd solid-state nuclear magnetic resonance (NMR) was used to identify possible Cd<sup>2+</sup> adsorption sites in montmorillonite. The montmorillonite was treated with 0.1 and 1 M CdCl<sub>2</sub> aqueous solutions and samples with 13 and 8- $\mu$ m particle size were used. The data are consistent with a two-site model for sorption of Cd<sup>2+</sup> on montmorillonite. Cd<sup>2+</sup> is localized in the montmorillonite in two different sites: 1) in the interlayers as hydrated Cd<sup>2+</sup> and 2) on the external surface, probably with few H<sub>2</sub>O molecules hydrating to it. Cadmium is also adsorbed as CdCl<sup>+</sup> in the interlayer. Treatment with a 0.1 M CdCl<sub>2</sub> solution produces adsorption of free Cd<sup>2+</sup> in the interlayer whereas treatment with 1 M CdCl<sub>2</sub> resulted in adsorption of Cd<sup>2+</sup> in both the interlayer and on surface sites and the adsorption of CdCl<sup>+</sup> in the interlayer. A larger particle size favors Cd<sup>2+</sup> adsorption on the external surface whereas a smaller particle size favors Cd<sup>2+</sup> adsorption in the interlayer.

**Key Words**—Adsorption, Cadmium, Montmorillonite, Nuclear Magnetic Resonance.

### INTRODUCTION

The need for environmental remediation has increased interest in obtaining a fundamental understanding of sorption mechanisms for heavy metals on clay minerals. Information of interest includes how species bind to layer silicates, the chemical environment of the adsorbed species, and whether mobility is affected by processes such as complexation, thereby providing insight in how to trap contaminants inside a clay matrix and how contaminants pass through a clay matrix. Recent results have shown that solid-state nuclear magnetic resonance (NMR) can investigate the environments of exchangeable cations, although the technique has resolution and sensitivity limitations. Many isotopes of important elements, including <sup>15</sup>N (as NH<sub>4</sub><sup>+</sup>), <sup>23</sup>Na, <sup>25</sup>Mg, <sup>31</sup>P, <sup>39</sup>K, <sup>87</sup>Rb, <sup>113</sup>Cd, and <sup>133</sup>Cs can be studied in the clay matrix using NMR. Weiss *et al.* (1990) studied Cs-exchanged montmorillonite. They observed an isotropic peak ( $\delta_{iso}$ ) at  $-20$  ppm (probably due to interlayer hydrated Cs) moving to  $-10$  ppm when humidity changed to 100% relative humidity (R.H.). They also used <sup>133</sup>Cs NMR methods at temperatures from  $+80$  to  $-100^\circ\text{C}$  to show that Cs sorbed on hectorite has various chemical environments depending on the state of hydration. Fripiat (1990) used <sup>23</sup>Na NMR spectra of hydrated and dehydrated samples of Na-rich beidellite to probe the Na environment in smectite. He concluded that Na was sorbed in the interlayer ( $\delta_{iso} = -20$  ppm) and at the external clay surface ( $\delta_{iso} = -7$  ppm). Recently, Kim *et al.* (1996a) used <sup>133</sup>Cs magic angle spinning (MAS) NMR spectra to investigate the adsorption sites and atomic dynamics of Cs adsorbed on illite, kaolinite, bohemite, and silica gel. They confirmed that the Cs cation is adsorbed at sites on the mineral surface, where the cation-surface

bond is relatively strong (Stern layer) and at distant sites in the diffuse layer, where the Cs-surface bond is weaker (Gouy layer). Finally, Kim *et al.* (1996b) suggested that most Cs was exchanged in the interlayer of montmorillonite and showed a chemical shift of  $-12$  to  $-18$  ppm at ambient conditions.

Despite the considerable literature concerning <sup>113</sup>Cd NMR spectra of coordination compounds and proteins (*e.g.*, Armitage *et al.*, 1976; Summers, 1988), relatively few studies used NMR methods to probe the interaction between Cd and swelling phyllosilicates. Nevertheless NMR was used to study <sup>113</sup>Cd sorbed on montmorillonite by Bank *et al.* (1989). The MAS NMR spectra of <sup>113</sup>Cd in Cd-rich montmorillonite showed both a narrow signal (1 kHz) and a broad signal (6–9 kHz) which were interpreted as an edge site in interaction with the iron in the octahedral positions (narrow component) and an interlayer site with low chemical-shift anisotropy (broad component). Tinet *et al.* (1991) studied the anisotropy of the chemical-shift tensor for oriented samples of a Cd-rich montmorillonite. They attributed the chemical-shift anisotropy to interaction between interlayer Cd and hydroxyls in the hexagonal cavities, rather than a consequence of two or more chemical environments for Cd.

The objective of this study was: 1) to identify possible Cd<sup>2+</sup>-adsorption sites in montmorillonite; 2) to investigate the effect of Cd<sup>2+</sup> concentration in the treatment solution on Cd<sup>2+</sup> adsorption on montmorillonite; and 3) to investigate how particle size influences the adsorption of Cd<sup>2+</sup> on montmorillonite.

### EXPERIMENTAL

#### Clay preparation

The clay used in this study is a naturally occurring Mg- and Ca-rich montmorillonite obtained from En-

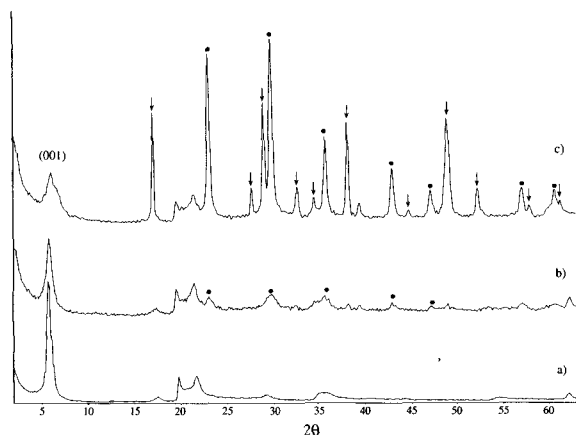


Figure 1. XRD patterns of a) untreated Westone montmorillonite; b) 1 M  $\text{CdCl}_2$ -treated non-dialyzed WA (Westone A); c) 1 M  $\text{CdCl}_2$ -treated dialyzed WA. Arrows indicate  $\text{CdOHCl}$  species; circles  $\text{CdCO}_3$  species.

lish China Clay, St. Austell, Cornwall (Westone L or WL).

The cation-exchange capacity (CEC) is 77 meq/100 g (modified method based on Chapman, 1965). The sample has a low Fe content (0.8 wt. %  $\text{Fe}_2\text{O}_3$ ) which prevents line broadening or variations in chemical shift owing to ferromagnetic impurities, especially  $\text{Fe}^{3+}$  (Bank *et al.*, 1989).

To determine whether Ca or Mg is the interlayer cation in the WL montmorillonite, the test of Green-Kelly (1953a) was used. This test differs from the Green-Kelly test (1953b) commonly used to distinguish between beidellite and montmorillonite and there is no Li saturation. The sample is pre-heated to 430°C and treated with glycerol for several hours. At this temperature, a single-layer glycerol complex of  $d(001) = 9.5 \text{ \AA}$  occurs if the interlayer cation is Li or Mg, whereas a two-layer glycerol complex of  $d(001) = 17.8 \text{ \AA}$  is formed for interlayer cations of Na, Ca, Sr, La, K, or Ba. The observed  $d$ -value for the WL montmorillonite after testing was 17.7 Å, implying that the interlayer cation was Ca.

Clay purity was obtained by X-ray diffraction (XRD) analysis (Siemens D5000,  $\text{CuK}\alpha$  radiation, graphite secondary monochromator, sample spinner). The  $d(001)$  of the untreated clay was  $15.1 \pm 0.3 \text{ \AA}$ . Brown and Brindley (1980) reported a similar spacing for a Ca-rich montmorillonite at 53% R.H., corresponding to two layers of  $\text{H}_2\text{O}$  molecules in the interlayer.

WL montmorillonite has a particle-size mode of 27.61  $\mu\text{m}$  (most frequently occurring size). Particle size was measured using a Malvern Instrument laser granulometer Master Size E Ver. 1.2. Subsamples with different particle sizes were obtained by grinding the sample in hexane for different periods of time. Two sets of samples with particle-size modes of 12.85 and

8.45  $\mu\text{m}$  were produced, labeled Westone A (WA) and Westone B (WB).

Treatments with  $\text{CdCl}_2$  solutions were performed by suspending 2 g of sample in 40 mL of  $\text{CdCl}_2$  solution. A solution of  $\text{CdCl}_2$  was used because this solution gives complete Cd saturation of the clay (Tinet *et al.*, 1991). All exchange reactions were performed at neutral pH and room temperature. Each suspension was stirred for 24 h and then centrifuged. The resulting solid was suspended in distilled water and centrifuged, and this procedure was repeated three times. Samples were dialyzed against distilled water until no  $\text{Cl}^-$  was detected in the solution using  $\text{AgNO}_3$ . The dialyzed samples were investigated by solid-state NMR.

#### Scanning electron microscopy (SEM) analysis

Clay purity and the effects of grinding on the shape of particles were determined by SEM (Cambridge Stereoscan S 360) equipped with an (LINK AN10000) energy dispersive spectrometer (EDS). Samples were sputter-coated with gold and mounted on carbon stubs. The working voltage was 21 kV.

#### NMR analysis

$^{113}\text{Cd}$  solid-state NMR spectra were recorded on a Bruker MSL-300 spectrometer using single pulse excitation (SPE), cross polarization (CP), MAS, and dipolar decoupling (DEC). The relevant experimental parameters are: spinning speeds 4–5 kHz; contact time 10–12 ms; proton decoupler power level 55 kHz; and recycle delays of 1 and 4 s. To minimize interferences from spinning side bands for some spectra, a total side-band suppression (TOSS) was used. The CP sequence incorporated a 90° proton flip-back pulse immediately after the acquisition period to reduce the recycle delay necessary between scans. All MAS and CP-MAS NMR spectra were recorded on samples equilibrated at room humidity and are referred to a 0.1 M  $\text{Cd}(\text{ClO}_4)_2$  solution (Nolle, 1978).

## RESULTS

XRD and SEM analyses of WL montmorillonite showed that the clay mineral was the only mineral phase present in the sample (Figures 1 and 2). The XRD analysis of the Cd-treated montmorillonite equilibrated at room humidity showed  $d(001) = 15.3 \pm 0.3 \text{ \AA}$ , confirming the presence of a two-water-layer complex in the interlayer. XRD patterns of the  $\text{CdCl}_2$ -treated samples showed, in addition to the montmorillonite, the presence of two crystalline phases  $\text{Cd}(\text{OH})\text{Cl}$  and  $\text{Cd}(\text{CO}_3)$ , which apparently precipitated during the treatments (Figure 1c). The dialysis removed most of these salts (Figure 1b).

The  $^{113}\text{Cd}$  NMR MAS spectrum of the clay treated with 0.1 M  $\text{CdCl}_2$  showed one narrow peak at  $\sim -8$  ppm ( $-9.5$  ppm for sample WA and  $-7.3$  ppm for WB; Figure 3). No signal was observed using  $^{113}\text{Cd}$

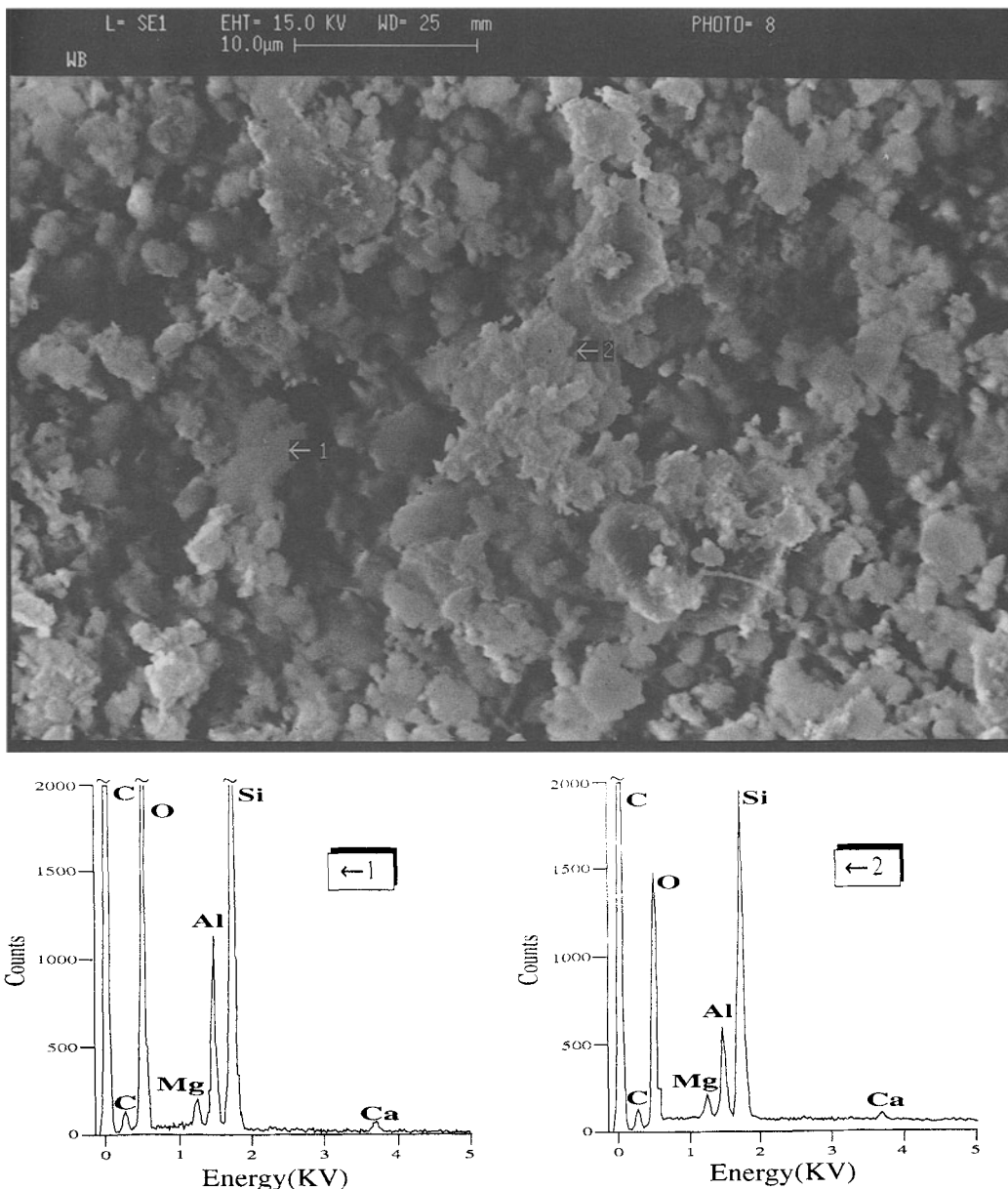


Figure 2. SEM photo of untreated Westone montmorillonite with EDS spectra of some particles. Arrows in the photo indicate the particles to which the EDS analyses refer.

CP-MAS NMR for the WA and WB samples treated with 0.1 M CdCl<sub>2</sub>. The MAS NMR spectra of the 1 M CdCl<sub>2</sub>-treated samples are different from those obtained for samples treated with 0.1 M CdCl<sub>2</sub> solution (Figure 4). The spectra of the 1 M CdCl<sub>2</sub>-treated samples exhibit a broad peak at 119.5 ppm for the WA and at 112.5 ppm for the WB (average value 116 ppm) sample; their full width at half height (FWHH) ranges between 8–11 kHz. Other peaks in the spectra (Figure 4) are two narrow resonances occurring at -12.7, -41.9 and -10.9, -39.9 ppm, respectively for WA and WB (average values -11 and -41 ppm). The

FWHH of these resonance lines is 1–1.7 kHz. The signal area normalized per number of scans of the 1 M CdCl<sub>2</sub>-treated WA and WB samples suggests that the amount of Cd<sup>2+</sup> sorbed by the sample with the smaller particle size (WB) is roughly double that sorbed by the sample with the larger particle size (WA).

Recycle delays were measured for the WA samples treated with 1 M CdCl<sub>2</sub>. The broad peak at 119.5 ppm and the peak at -12.7 ppm relaxed quickly (1 s recycle delay was sufficient). The peak at -41.9 ppm relaxed more slowly and a different recycle delay (4 s) was needed to prevent partial saturation.

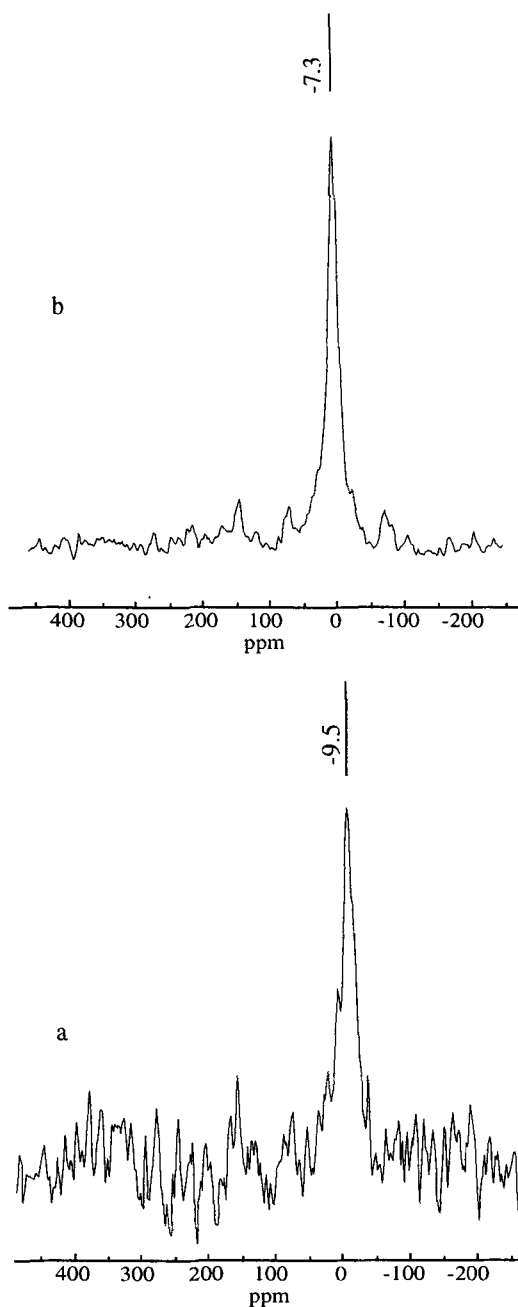


Figure 3.  $^{113}\text{Cd}$  MAS spectrum of the 0.1 M  $\text{CdCl}_2$ -treated a) WA (Westone A; particle size mode 12.85  $\mu\text{m}$ ) and b) WB (Westone B; particle size mode 8.45  $\mu\text{m}$ ). See text also.

CP-MAS experiments were performed only on the WA sample (Figure 5). Two additional resonances at 105.9 and 71.7 ppm and a relatively broad peak at 0.26 ppm (FWHM = 3.819 kHz) dominate the CP-MAS spectrum. Neither the broad resonance at  $\sim 116$  ppm nor the  $\sim -11$ -ppm peak was observed. In contrast, the  $\sim -41$ -ppm peak was evident although only as a shoulder on the right side of the 0.26 peak, implying

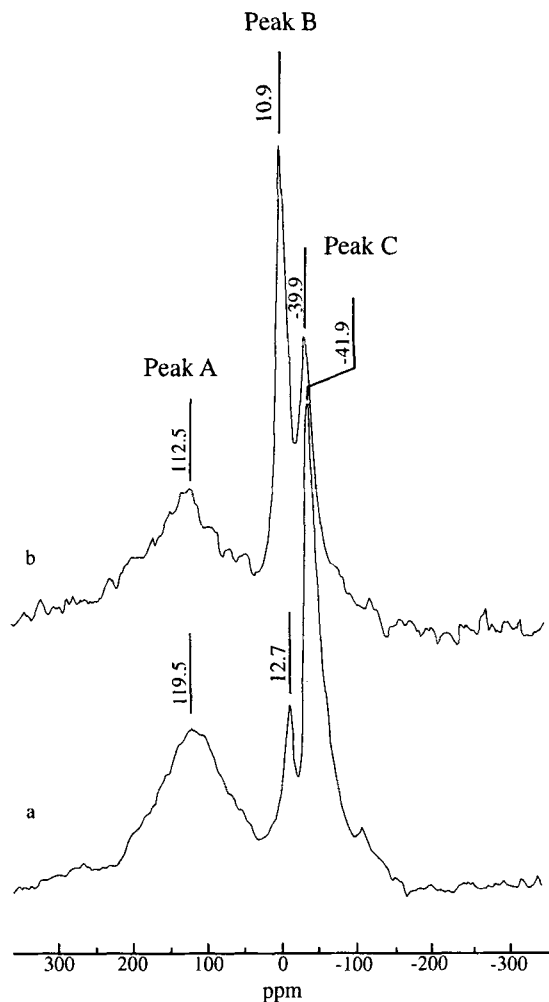


Figure 4.  $^{113}\text{Cd}$  MAS spectrum of 1 M  $\text{CdCl}_2$ -treated a) WA (Westone A; particle size mode 12.85  $\mu\text{m}$ ) and b) WB (Westone B; particle size mode 8.45  $\mu\text{m}$ ). Peak A: average value 116 ppm; Peak B: average value  $-11$  ppm; Peak C: average value  $-41$  ppm.

that the site producing the polarized component at  $\sim -41$  ppm relaxes at a significantly slower rate compared to the other sites. The CP-MAS experiments showed a loss in overall signal intensity with respect to the MAS experiments.

## DISCUSSION

### Peak assignments and structural environments

To explain the shape of the NMR signal observed for both WA and WB treated with 1 M  $\text{CdCl}_2$  solution, a multisite model for Cd sorption on montmorillonite was invoked. The chemical-shift value of the broad component ( $\sim 116$  ppm) suggests a cadmium-halide interaction in water. Chemical shifts near 100 ppm were observed for Cd-chloride species such as  $\text{CdCl}^+$  and  $\text{CdCl}_2$  in aqueous solutions (Ackerman *et al.*, 1979). As the speciation diagram generated using a

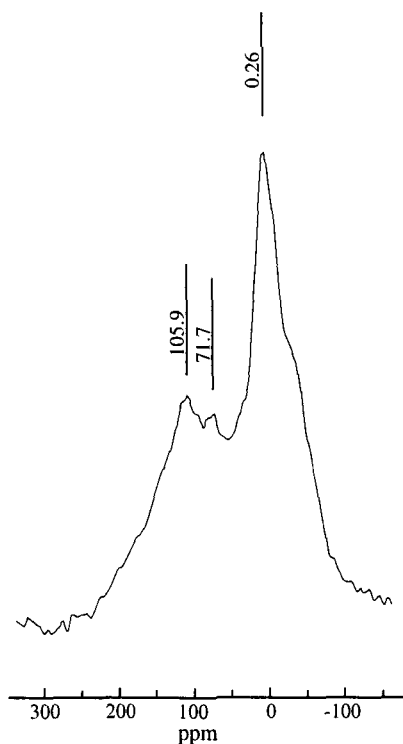


Figure 5. <sup>113</sup>Cd CP-MAS spectrum of 1 M CdCl<sub>2</sub>-treated WA (Westone A; particle size mode 12.85 μm).

computer program (HALTAFALL, Ingri *et al.*, 1967) suggests, in a 1 M CdCl<sub>2</sub> aqueous solution, the species present are Cd<sup>2+</sup> and CdCl<sup>+</sup> with a ratio [Cd<sup>2+</sup>]:[CdCl<sup>+</sup>] of 1:15 (Figure 6). CdCl<sup>+</sup> is the most abundant species, and this suggests that the CdCl<sup>+</sup> complex replaced Ca<sup>2+</sup> ions in the interlayer of the montmorillonite during treatment with a 1 M CdCl<sub>2</sub> solution.

The quick relaxation of the ~116-ppm broad component depicting the adsorbed CdCl<sup>+</sup> species (1 s recycle delay) indicates a localization in the interlayers. The hydration complexes of exchangeable cations, owing to the interaction with the clay surface through water ligands, show different dynamics relative to corresponding cations in solution (without the presence of clay particles) (Güven, 1992).

CP-MAS experiments performed on samples treated with 1 M CdCl<sub>2</sub> (Figure 5) suggest that the interlayer Cd-chloride species may occur in different local environments. The broad component at ~116 ppm observed in the MAS experiment of WA and WB (Figure 4) is replaced in the CP-MAS spectra by two broad components with chemical shifts of ~105 and ~71 ppm (Figure 5). The peak at ~105 ppm has a chemical shift matching that of CdCl<sub>2</sub> in water (Ackerman *et al.*, 1979) and the component at ~71 ppm has a chemical shift close to that observed for Cd interacting with one OH group within the hexagonal cavity (Tinet *et al.*, 1991; Laperche *et al.*, 1990). The presence of more

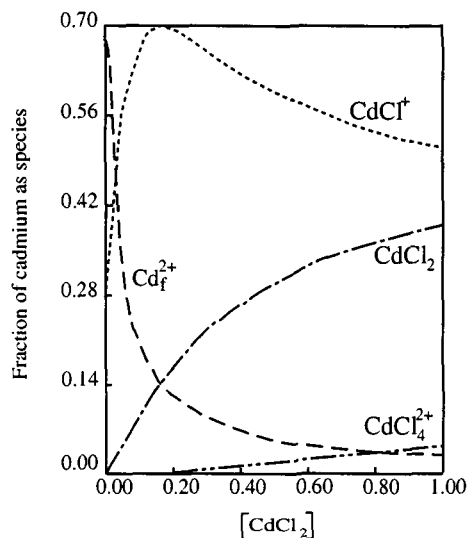


Figure 6. The calculated dependence of the mole fraction of cadmium present as various Cd species upon the total added CdCl<sub>2</sub> concentration.

than one chemical environment for interlayer Cd-chloride species may cause chemical-shift dispersion in the MAS experiments, which would account for the observed broadening of the peak at ~116 ppm (FWHH 8–11 kHz) in the <sup>113</sup>Cd MAS spectra of samples treated with 1 M CdCl<sub>2</sub> (Figure 4). The influence of paramagnetic nuclei, also responsible for broadening of the <sup>113</sup>Cd NMR signal (Bank *et al.*, 1989), is ruled out due to the low amount of octahedral iron present in the montmorillonite samples (0.8 wt. % of Fe<sub>2</sub>O<sub>3</sub>).

The resonance line at ~-10 ppm present in the MAS NMR spectra of samples treated with both 1 and 0.1 M CdCl<sub>2</sub> solutions (~-11 and ~-8 ppm, respectively; Figures 3 and 4) and the more shielded resonance line at ~-41 ppm, occurring only in the spectra for the 1 M CdCl<sub>2</sub>-treated montmorillonite (Figure 4) correspond, according to their chemical-shift values, to Cd which is predominantly coordinated to oxygen ligands (Ellis, 1983). The smaller peak width, as compared to the peak at ~116 ppm, along with the lack of spinning side bands indicates that the sites producing the ~-10 and ~-41-ppm resonances are well defined and quite symmetrical.

The shielding of the nuclei of exchangeable cations by their electron shells is affected by electron transfer with oxygen ions from the tetrahedral sheets; accordingly, the chemical shift of the exchangeable cations which strongly interact with the basal-oxygen ions is negative (Laperche *et al.*, 1990). In hydrated phases, where one or two H<sub>2</sub>O layers are present in the interlayers, shielding should be less efficient because the lattice-oxygen ions contribute less to the coordination of the exchangeable cations. Hence, in a two-layer hydrate, as in the montmorillonite, where the first coor-

dination shell of the exchangeable cation contains H<sub>2</sub>O molecules only, deshielding (no strong negative chemical-shift values) should be at a maximum. In this case, the interlayer cation is fully dissociated from the clay surface and has, accordingly, relatively free motion in the interlayer. Thus the narrow component at  $\sim -10$  ppm, occurring in montmorillonite treated with both 0.1 and 1 M CdCl<sub>2</sub> could then arise from Cd<sup>2+</sup> in the interlayer. The Cd<sup>2+</sup> is surrounded by H<sub>2</sub>O molecules and does not form complexes with the charged-surface functional groups (Ellis, 1983). Dynamics of the peak at  $\sim -10$  ppm (quick relaxation) are similar to that of the broad peak at  $\sim 116$  ppm produced by an interlayer species, and this also supports the assignment of the  $\sim -10$ -ppm resonance line to Cd<sup>2+</sup> in the interlayer. The two monolayers of adsorbed H<sub>2</sub>O present in the interlayer may thereby prevent motional averaging between the two chemical environments of Cd<sup>2+</sup> and CdCl<sup>+</sup>; hence, we observe two resonances depicting two unique interlayer-cadmium species.

The peak at  $\sim -40$  ppm (a chemical environment more shielded than that depicted by the  $\sim -10$ -ppm resonance) indicates a strong interaction of the Cd species with basal-oxygen ions in smectite (Laperche *et al.*, 1990). Relatively strong negative chemical shifts characterize the dehydrated phase of Cd-rich vermiculite and are caused by the absence of H<sub>2</sub>O molecules shielding Cd from the influence of structural-oxygen ions (Laperche *et al.*, 1990). Because only two-layer hydrated phases are present in our samples (Figure 1a), the  $\sim -40$ -ppm component may depict Cd on the external surfaces of montmorillonite, consistent with the interpretation of Tinet *et al.* (1991) and Bank *et al.* (1989). Dynamics (slow relaxation and low cross-polarization rate) of the  $\sim -40$ -ppm peak depicting Cd<sup>2+</sup> suggest the Cd species is not surrounded by many H<sub>2</sub>O molecules. Relaxation is often caused by coupling to nuclei that are not an inherent part of the molecule of interest (as the water protons around the exchangeable cations) and such coupling is a function of the concentration of the active nuclei (Stebbins, 1988). At room humidity, the Cd on the sites at the external basal surface will be more hydrated than the Cd sorbed on edge sites because the latter will likely form inner-sphere complexes with Al-OH groups (Sposito, 1989). The higher hydration expected for basal-surface sites relative to the edge sites suggests that the sites producing the  $\sim -40$ -ppm resonance are edges and not basal sites.

For the CP-MAS technique, the signal from nuclei closer to the protons <sup>1</sup>H is preferentially enhanced relative to the signal from nuclei that are distant from the protons. Therefore the signal from the anhydrous phases is eliminated (Kirkpatrick, 1988). This may explain the 0.264-ppm resonance line that appears only from the CP-MAS technique. This resonance line may be due to Cd<sup>2+</sup> which is surrounded by many H<sub>2</sub>O

molecules, probably in the interlayers, but further analysis at different relative humidities is needed to assign this line.

We propose a multisite-sorption model for montmorillonite treated by CdCl<sub>2</sub>: 1) interlayer sites where hydrated Cd<sup>2+</sup> and CdCl<sup>+</sup>, respectively producing the  $\sim -11$  and  $\sim 116$ -ppm resonance lines, are adsorbed and 2) external surface sites where Cd<sup>2+</sup>, producing the  $\sim -40$ -ppm resonance line, is adsorbed.

#### *Effects of solution concentration*

The concentration of the solution used to treat the Westone clay affects the type of Cd species sorbed and the type of adsorption sites. Cd<sup>2+</sup> replaces Ca<sup>2+</sup> ions from the interlayer and Cd<sup>2+</sup> is adsorbed on the external surface when montmorillonite is treated with a 1 M CdCl<sub>2</sub> solution. On the other hand, Cd<sup>2+</sup> apparently replaces Ca<sup>2+</sup> from the interlayer only for samples treated with a 0.1 M CdCl<sub>2</sub> solution to produce NMR MAS spectra with only the peak at  $\sim -8$  ppm, which we assigned to Cd<sup>2+</sup> in the interlayer (Figure 3).

A possible explanation for the adsorption of Cd<sup>2+</sup> only in the interlayer of the 0.1 M CdCl<sub>2</sub>-treated montmorillonite may be the stronger affinity of interlayer sites for divalent cations with respect to monovalent cations. The number of Cd<sup>2+</sup> and CdCl<sup>+</sup> cations in a 0.1 M CdCl<sub>2</sub> solution is about the same (Figure 6). Furthermore Cd<sup>2+</sup> is adsorbed in the interlayer to a larger extent than CdCl<sup>+</sup>. By contrast, CdCl<sup>+</sup> is the predominant species in the more concentrated 1 M CdCl<sub>2</sub> solution and therefore interlayer Ca<sup>2+</sup> ions are substantially replaced by CdCl<sup>+</sup> for montmorillonite treated with a 1 M CdCl<sub>2</sub> solution. A greater affinity of Ca ions for inner-tactoid surfaces was suggested by Shainberg and Kemper (1966) and Banin and Lahav (1968). However, Schramm and Kwak (1982) demonstrated that redistribution of ions on the surfaces occurs during ion-exchange reactions in montmorillonite. Before the breaking of tactoids, the exchanging ions show preference for external surfaces, although the region surface coverage is small. Once the tactoids dis-aggregate, there is little distinction between external and internal surfaces and apparently approximately equal preference for all surfaces (Schramm and Kwak, 1982). As Ca is exchanged by ions with strong preferential binding, *e.g.*, Mg, there is apparently an equal preference for all surfaces although Mg- and Ca-rich montmorillonite forms different size tactoids (Schramm and Kwak, 1982). The same behavior can be suggested for Cd where preferential binding is stronger than that of Mg: the preference for both external and internal surfaces is apparently equal during Cd-exchange reactions and Cd<sup>2+</sup> can also adsorb on inner surfaces.

#### *Effects of particle size*

Particle size does not affect the species of Cd sorbed on montmorillonite or the type of sites they occupy,

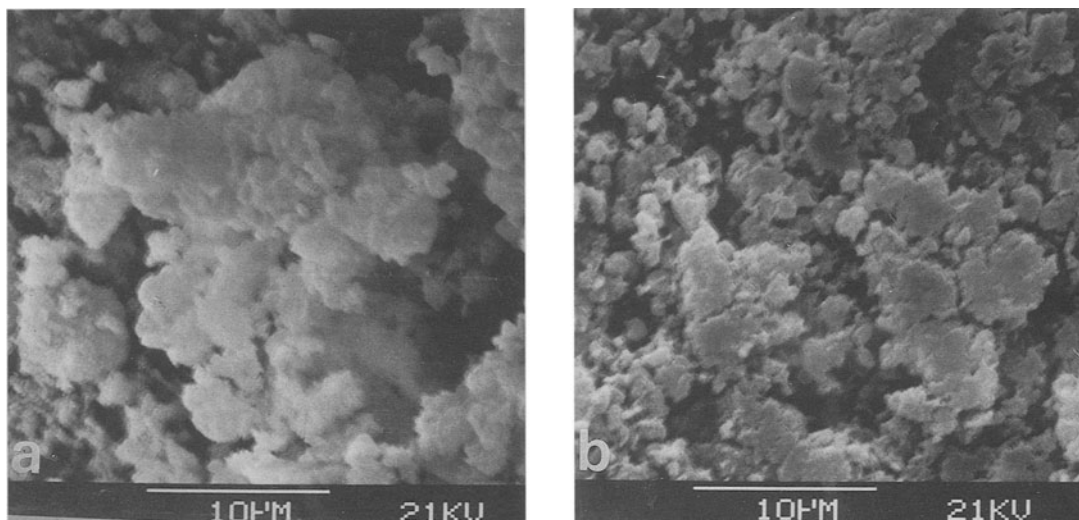


Figure 7. a) Sample WA (untreated Westone A, particle size mode 12.85  $\mu\text{m}$ ). Aggregates of clay platelets. b) Sample WB (untreated Westone B, particle size mode 8.45  $\mu\text{m}$ ). Clay particles after the grinding procedure.

but particle size does influence the relative amounts of  $\text{Cd}^{2+}$  sorbed on both external (basal and/or edges) and internal surfaces (Figure 4). The  $\text{CdCl}^+$  sites have the same distribution in both WA and WB samples (in the NMR spectra of both samples the peak originating from the  $\text{CdCl}^+$  sites represents  $\sim 60\%$  of the total spectrum-signal area normalized per number of scans) suggesting that differences in particle size do not affect the distribution of  $\text{CdCl}^+$  sites. However, the relative intensity of the peaks assigned to  $\text{Cd}^{2+}$  adsorbed in the interlayer ( $\sim 11$  ppm) and  $\text{Cd}^{2+}$  adsorbed on the external basal surface and/or edges ( $\sim 40$  ppm) is influenced by particle size. In the WA sample, the  $\sim 11$ -ppm peak is less intense (12% of the total spectrum-signal area normalized per number of scans) than the  $\sim 40$ -ppm peak (28% of the total spectrum-signal area normalized per number of scans) whereas the contrary is observed for the WB sample. This suggests that adsorption of  $\text{Cd}^{2+}$  in the interlayer is greater for samples with smaller particle size, whereas adsorption of  $\text{Cd}^{2+}$  on the external surface is greater for samples with larger particle size.

SEM investigations showed that the reduction in particle size results in the disaggregation of aggregates (Figure 7). In montmorillonite some large aggregates commonly do not disperse in water owing to coatings (Shomer and Mingelgrin, 1978). Large size makes these aggregates an important fraction of the bulk of the clay ( $\leq 20\%$ ). Reducing the particle size by grinding may disaggregate these samples.

Because the disaggregation of the clay is important in the exchange process, the presence of non-dispersible aggregates may account for the differences observed between the NMR spectra of 1 M  $\text{CdCl}_2$ -treated WA and WB (Figure 4).  $\text{Cd}^{2+}$  may be preferentially

adsorbed on the external surfaces of the non-dispersible aggregates in the sample with the larger particle size (WA). In the sample with the smaller particle size (WB), where disaggregation occurs and dispersement is made possible by grinding, the interlayer of a larger number of quasicrystals was made accessible to  $\text{Cd}^{2+}$ , and  $\text{Cd}^{2+}$  was able to replace  $\text{Ca}^{2+}$  ions.

#### ACKNOWLEDGMENTS

The authors are grateful to the Chemistry Department of the Queen Mary College, London, and to the Institute of Research on Clays of the National Research Council (Italy) for technical support. We thank P. Barrie of the URLIS solid-state NMR service in the Chemistry Department of the University College (London) for his assistance in the use of the NMR equipment, A. Destradis from the "Centro di Microscopia" of the University of Basilicata for assistance in the use of the SEM equipment, and V. Summa from the Institute of Research on Clays for granulometric analyses. We also thank J. Cuadros for critically reading the manuscript, G. Piccarreta and M. Schiattarella for constructive comments, and B. Molloy for language assistance.

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(Received 3 November 1997; accepted 22 May 1999; Ms. 97-098)