SORPTION OF HEAVY-METAL CATIONS BY Al AND Zr-HYDROXY-INTERCALATED AND PILLARED BENTONITE

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Abstract—The sorption of Cd, Cu, Pb, and Zn ions by Na-rich bentonite, Al and Zr-pillared Na-rich bentonite (Al-MX80, Zr-MX80), the uncalcined hydroxy-intercalated precursors (HAl, HZr-MX80), and commercial Al-pillared bentonite EXM 534 was investigated. Experiments were conducted in ultrapure water and artificial leachate with varying pH. The experiments were performed over periods to 30 wk. Sorption characteristics were described with one and two-site Langmuir isotherms. The non-exchangeable quantities of heavy metals were determined by fusion of the sorbents after ion exchange with ammonium acetate.

The sorption of Cd, Cu, Pb, and Zn by bentonite was dominated by cation exchange. In artificial leachate, the sorption was reduced due to competition with alkali and alkaline-earth cations. The sorption of Cu, Zn, and Pb at pH 4.9 and Cd at pH 6.9 by Al and Zr-hydroxy-intercalated and pillared MX80 was governed also by cation exchange. In contrast, the sorbed quantities of Zn at pH 6.9 exceeded the cation exchange capacity (CEC) of HAl, HZr, Al, Zr-MX80, and EXM 534 and were partially non-exchangeable. The increase of the sorption of Zn with pH and its independence of the ionic strength of the solution at neutral pH suggest a complexation of Zn ions to surface hydroxyl groups of the intercalated Al and Zr-polyhydroxo cations and pillars. This complexation is the dominating sorption mechanism. Removal of dissolved Zn from solution with time is attributed to surface precipitation. Al-hydroxy and pillared bentonites are considered potential sorbents of Zn ions from neutral pH aqueous solutions, such as waste waters and leachates.

Key Words—Heavy Metals, Intercalation, Montmorillonite, Pillared Clay, Sorption.

INTRODUCTION

Heavy metals represent a common class of environmental pollutants owing to their potential release during industrial use, mining, purification, processing, and waste disposal (Merian, 1991). The mobilization of heavy metal ions from waste and their transport via leachates can represent a threat to groundwater supplies. Arneth *et al.* (1989) investigated the contamination of aquifers from waste disposal sites and found contamination factors (mean concentration downstream/mean concentration upstream) of 4.7 for Cu and Zn, 5 for Pb, and >6.5 for Cd.

The main factors controlling migration of contaminated leachate from a waste disposal site into the surrounding environment are design and quality of the basal barrier (Rowe *et al.*, 1995). The most common components of waste disposal containment systems are naturally occurring clay deposits or compacted bentonite liners owing to their low hydraulic conductivity and their high sorption capacity for cations. The main constituent of bentonites is montmorillonite. Heavy metals are sorbed by this clay mineral via complexation on surface hydroxyl groups at the edges and via cation exchange at the negatively charged surface of the crystallites. The capacity of montmorillonite for surface complexation is considerably smaller than for electrostatic interactions. Only at high pH values and trace concentrations of heavy metals does specific sorption dominate (Van Bladel *et al.*, 1993). The neg-

ative surface charge of montmorillonite is caused by isomorphous substitution within the 2:1 layer. Depending on their size, charge, and competing cations in solution, sorbed cations can readily exchange. When two cations are present in equal amounts in the solution, the cation with the smaller atomic radius and/or higher charge is preferentially sorbed by the montmorillonite (McBride, 1994). Also the number of competing cations and ligands, *i.e.,* the ionic strength of the solution, determines the cation exchange reactions. Schmitt and Sticher (1986) investigated under laboratory conditions the sorption of Cd, Cu, and Pb in soils and reported a higher availability of these heavy metals when applied concurrently due to competition for the sorption sites. Asher and Bar-Yosef (1982) measured a decrease in the sorption of Zn by Ca-rich montmorillonite with increasing concentration of $KClO_4$ in the solution. Similarly, decreases in the sorption of Pb and Cd by montmorillonite with increasing quantities of Ca-cations in solution were reported by Griffin and Au (1977), Christensen (1984), and Inskeep and Baham (1983).

In leachates, the concentration of Ca is usually considerable. Brune *et al.* (1991) reported 70–4000 mg L^{-1} Ca for leachates from municipal solid waste landfills. Thus, the strong competition with Ca and other alkaline-earth and alkali cations prevents the sorption of high quantities of heavy metal cations by montmorillonite in waste disposal containment systems.

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Therefore, new materials must be tested with respect to their ability for chemically specific sorption. This should include a high selectivity for heavy metal cations, even in solutions of high salinity, and the fixation of these cations in a non-exchangeable way.

Pillared clays and their hydroxy-intercalated precursors may be able to meet these requirements. These materials were first described by Vaughan *et al.* (1979) and Lahav *et al.* (1978). The formation of pillared clays is summarized as follows. Initially, inorganic polyhydroxo cations are intercalated into the interlayers of 2:1 clay minerals. The resulting hydroxy-intercalated clays exhibit a $d(001)$-value to 20 Å and high surface areas (mostly 200–300 m^2 g^{-1}) owing to the formation of micropores between the intercalated complexes. The material has Brønstedt- and Lewis-type acidity. The calcination of the hydroxy-intercalated material is performed at temperatures between 300–500°C. The resulting $d(001)$-value and the microporosity of the pillared clay are smaller than those of the hydroxy-intercalated material. This is due to the transformation of the polyhydroxo cations by dehydration and dehydroxylation to rigid oxidic pillars of predominantly Lewis-type acidity (Vaughan, 1988). By varying the starting 2:1 clay mineral and the intercalated polyhydroxo cations, pillared clays with different physicochemical properties can be formed. These clay materials were reviewed by Vaughan (1988) and Kloprogge (1998).

Heavy metal cations can be sorbed specifically to oxide and hydroxide surface-water interfaces, such as silica and hydrous oxides of alumina (Hohl and Stumm, 1976; Schindler *et al.*, 1976; Stumm *et al.*, 1980). Our study focuses on whether sorption of montmorillonite for Cd, Cu, Pb, and Zn cations in a saline environment can be increased by the intercalation of polyhydroxo cations and oxidic pillars.

Bentonite MX80, containing 75 wt. % Na-rich montmorillonite, was the starting material for the preparation of hydroxy-intercalated and pillared clays. We did no fractionation or pretreatment because in industrial production of pillared clays, the bentonite is commonly used without purification. As sorbents, we used Al and Zr-pillared bentonites (referred to as Al-MX80 and Zr-MX80) and their hydroxy-intercalated precursors (referred to as HAl-MX80 and HZr-MX80) because these materials exhibit high thermal stability (Vaughan, 1988; Bartley, 1988), are easily produced, and are commercially available. For comparison, we included a commercial Al-pillared bentonite, EXM 534, in the investigations.

The intercalated Al-polyhydroxo cation is similar to the Al$_{13}$-Keggin molecule [AlO$_4$Al$_{12}$(OH)$_{24}$(H$_2$O)$_{12}$]$^{7+}$, referred to as Al$_{13}$ (Vaughan and Lussier, 1980). This molecule was described first by Johansson *et al.* (1960) from the structure of basic aluminum sulfate. Al$_{13}$ forms during base hydrolysis of aluminum salts

in aqueous solutions. In solutions of aluminum chloride, Al$_{13}$ is dominant at OH/Al-ratios between 1.5–2.5 (Schoenherr *et al.*, 1983). The quantity of Al$_{13}$ in the clay can be optimized by aging of the pillaring solution at elevated temperatures (Tokarz and Shabtai, 1985; Kloprogge, 1992; Gil and Montes, 1994). Al-hydroxy-intercalated montmorillonites exhibit an interlayer spacing ~9 Å, which corresponds to the size of the intercalated Al$_{13}$. This value decreases on calcination to ~8 Å (Pinnavaia, 1983). Although little is known about the structure of the oxidic pillars, measurements of Al-hydroxy-intercalated and pillared hectorite by solid state ^{27}Al NMR suggest that the distribution of the Al-atoms in the interlayers after calcination remains nearly unchanged, although some OH and H$_2$O-ligands are replaced by O atoms (Jones, 1988). Plee *et al.* (1985) reported from solid state ^{27}Al and ^{29}Si NMR measurements that linkages exist between Al-pillars and tetrahedral sheets of pillared beidellites. In smectites without tetrahedral substitutions, no linkages between Al-pillars and tetrahedral sheets were observed.

In solutions of zirconyl chloride, the planar Zr-tetramer [Zr$_4$(OH)$_8$(H$_2$O)$_{16}$]$^{8+}$ is the dominant species, which can polymerize to larger units (Clearfield and Vaughan, 1956; Bartley, 1988). Based on the $d(001)$-values of Zr-hydroxy-intercalated montmorillonite of ~19 Å, Yamanaka and Brindley (1979) postulated that Zr-tetramers measuring 10 × 10 × 4.5 Å are intercalated with the plane of the molecule either perpendicular to the clay layers or as a double layer of flat lying complexes. In contrast, Burch and Warburton (1986) obtained $d(001)$-values of 13 Å suggesting that one sheet of flat-lying tetramers exists. After a 24 h reflux of the pillaring solution, $d(001)$-values of 20.5 Å were observed, possibly indicating the existence of larger polymers. Comparing the results of Yamanaka and Brindley (1979) and Burch and Warburton (1986), a higher degree of polymerization apparently produces increased $d(001)$-values of the Zr-hydroxy-intercalated products coupled with a considerable higher uptake of Zr.

Owing to the low sorption capacity of montmorillonites for heavy metal cations in a saline environment, we investigated the sorption behavior of Al and Zr-hydroxy and pillared bentonite. Owing to the intercalated polyhydroxo cations and pillars, these materials exhibit large oxide and hydroxide surfaces. These may favor surface complexation and thus, increase the sorption capacity for heavy metal cations, especially in saline solutions. The sorption isotherms of Cd, Cu, Pb, and Zn were obtained from batch experiments. To investigate the influence of competition between heavy metal, alkali, and alkaline-earth cations, the heavy metal cations were sorbed from both ultrapure water and an artificial leachate. The time-dependence of the sorption was studied from batch experiments lasting

Table 1. Physico-chemical properties of MX80, HAl-, Al-, HZr-, Zr-MX880, and EXM 534.

	MX80	HAl-MX80	Al-MX80	EXM 534	HZr-MX80	Zr-MX80
CEC (meq $(100g)^{-1}$) (pH 6.9)	76	52	45	40	55	45
Density (g cm^{-3})	2.70	2.56	2.65	2.59	2.47	2.60
Water content (wt. %)	7.7	13.8	5.3	5.0	11.5	4.9
BET surface area (m^2 g^{-1})	22	216	187	150	219	218
External surface area (m^2 g^{-1})	20	53	77	63	61	78
Total pore volume (μL g^{-1})	105	150	168	169	153	165
Micro pore volume (μL g^{-1})	1	73	49	39	71	63

either 3 d or 30 wk. After sorption, the non-exchangeable quantities of heavy metals were determined.

MATERIALS AND METHODS

Materials

For pillaring, the Wyoming bentonite MX80 (Bentonit International GmbH, Duisburg-Meiderich, Germany) was used. The material contained 75 wt. % Na-rich montmorillonite with the formula of $(Si_{3.96}Al_{0.04})(Al_{1.55}Fe^{3+}_{0.20}Fe^{2+}_{0.01}Mg_{0.24})O(OH)_2Na_{0.3}$ (Mueller-Vonmoos and Kahr, 1983). The remaining phases are quartz (15 wt. %), feldspar (5–8 wt. %) and illite, carbonate, kaolinite, pyrite, and organic carbon (all ≤ 2 wt. %) (Mueller-Vonmoos and Kahr, 1983). The cation exchange capacity (CEC) was 76 meq (100 g)$^{-1}$ and the surface area calculated after Brunauer,

Figure 1. X-ray diffractograms of MX80, HAl-, Al-, HZr-, Zr-MX80, and EXM 534.

Emmett, and Teller (BET-surface area; Brunauer *et al.,* 1938) was 22 m^2 g^{-1} (Table 1). The material was used in its natural state. The X-ray diffractogram is presented in Figure 1.

Also a commercial Al-pillared bentonite, EXM 534, which was supplied by Sued-Chemie AG (Moosburg, Germany), was investigated. As with the Al-pillared montmorillonite, this material contained quartz, feldspar, cristobalite, and illite. The X-ray diffractogram of EXM 534 is also presented in Figure 1, and its physico-chemical properties are listed in Table 1.

Preparation of HAl, Al, HZr, and Zr-MX80

The pillaring solution was prepared by adding dropwise 0.5 M NaOH to 0.2 M AlCl$_3$·6H$_2$O by vigorous stirring to an OH/Al ratio of 2.4. At this hydrolysis ratio, Al$_{13}$ is a major species in solution. At OH/Al ratios >2.5, Al$_{13}$ tends to aggregate to larger polymers (Furrer *et al.,* 1992). To accelarate the formation of Al$_{13}$, the solution was aged for 3 h at 90°C (Tokarz and Shabtai, 1985; Gil and Montes, 1994; Lahodny-Sarc and Khalaf, 1994), and then held overnight at room temperature. To quantify the amount of Al$_{13}$ in the pillaring solution, ^{27}Al NMR spectra were recorded with a Bruker DPX 250 spectrometer operating at 65.2 MHz (5.7 Tesla). The solutions were diluted 1:1 with D$_2$O and immediately measured. Solutions of aluminum chloride served as a reference for the chemical shift and as standards for the quantification. A background correction of the spectra was necessary owing to the presence of aluminum in ceramic parts of the probe. The amounts of aluminum monomers, tridecamers, and polymers were calculated using integrated intensities of the signals of four and sixfold aluminum as described by Kloprogge (1992).

The pillaring solution was slowly added under vigorous stirring to a 1.0 wt. % bentonite suspension to a ratio of 20 meq Al g^{-1} bentonite. The final suspensions were aged overnight at room temperature. Afterwards, the HAl-MX80 was separated by centrifugation and washed with deionized water until the supernatant was chloride-free as indicated by the AgNO$_3$ test. The product was dried at 40°C in air and gently ground in an agate mortar.

Al-MX80 was obtained by 5 h calcination at 400°C (Gil and Montes, 1994; Poncelet and Schutz, 1986) in
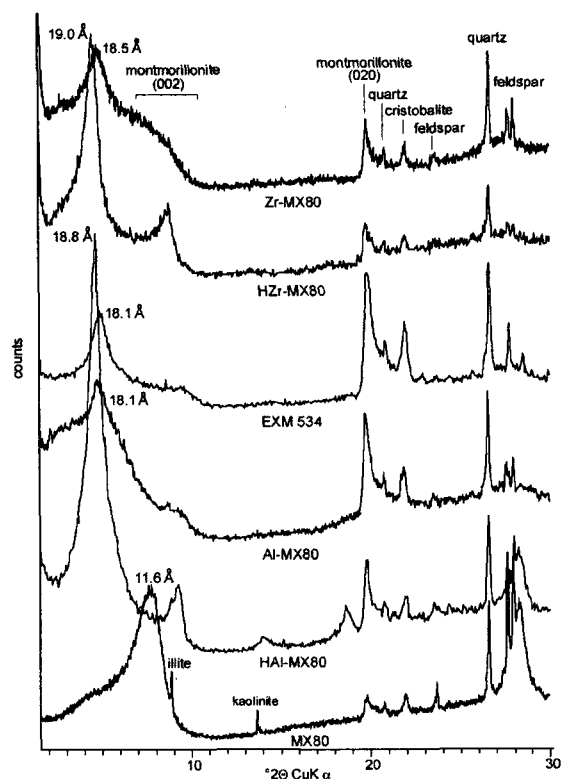
a furnace ("RP Economy-Pico") coupled with a Thermo-Computer TC 405 (Neue Kiag, Switzerland). Initially, the heating rate of the calcination was adjusted to 10°C min^{-1} because immediate heat exposure of the hydroxy-interlayered montmorillonite may result in an irregular stacking of the 2:1 layers (Zhu *et al.*, 1995).

Intercalation of Zr-polyhydroxo cations was based on a study by Farfan-Torres *et al.* (1992). A 0.1 M solution of ZrOCl$_2$·8H$_2$O was refluxed for 2 h at 40°C and added dropwise to a 1.0 wt. % bentonite suspension with vigorous stirring. The Zr/clay ratio was 5 meq g^{-1}, which was similar to the Zr/clay ratios used by Farfan-Torres *et al.* (1992). The suspension was aged for 2 h at 40°C. Afterwards, the HZr-MX80 was separated by centrifugation and washed with deionized water to a chloride-free state. The product was dried at 40°C in air and gently ground in an agate mortar. Zr-MX80 was obtained after 5 h calcination at 300°C with a heating rate of 10°C min^{-1}. Calcination at 300°C results in well-ordered Zr-pillared montmorillonites whereas temperatures >300°C cause a partial collapse of the Zr-pillars (Bartley and Burch, 1985; Matthes and Madsen, 1996).

Analytical methods

The external surface areas and pore volumes were determined by N$_2$ adsorption and desorption in the range of p/p$_0$ 0.005–0.98 at −195.8°C (liquid N$_2$). The analyses were performed with a Micromeritics Gemini III 2375 apparatus. The BET surface area was determined in the range of p/p$_0$ from 0.005 to 0.25. The external surface area, the micropore, and total-pore volumes were calculated with the t-plot method using the standard isotherm of Harkins and Jura (1943) in the range of p/p$_0$ from 0.05 to 0.7. Prior to the measurement, the samples were dried overnight at 110°C and subsequently degassed for 24 h in a vacuum (0.15 mbar). The relative standard deviations, calculated from replications, were 1.8% (BET surface area), 3.0% (micropore volume), 1.6% (external surface area), and 1.7% (total pore volume). The density was measured by a Micromeritics helium gas displacement pycnometer "Accupyc 1330". The relative standard deviation was 0.3%. The CEC was determined on duplicate samples by the ammonium acetate method (MacKenzie, 1951) at pH 7. From replications, a relative standard deviation of 3.1% was calculated. The X-ray measurements were performed on oriented mineral aggregate specimens with a Philips diffractometer PW 1729/PW 1820 (CuKα radiation, diffracted beam monochromator, automatic divergence slit, receiving slit 0.1 mm, 40 kV, 30 mA, steps of 0.02 °2θ for 3 s).

Sorption experiments

Batch experiments were performed in sealed glass flasks with a suspension volume of 50 mL. The certified standard products TITRISOL Zn, TITRISOL Cu, and TITRISOL Cd (MERCK (Schweiz) AG, Dietikon, Switzerland) and solid Pb(NO$_3$)$_2$ were diluted with ultrapure water Milli-Q (Micropore SA) to stock solutions with a heavy metal concentration of 1 g L^{-1}. These stock solutions were then diluted in ultrapure water or artificial leachate to concentrations between 50–2000 μmol L^{-1}. The chemical composition of the artificial leachate was based on the composition of leachate at the waste disposal site at Koelliken, Switzerland (Hermanns, 1993). The leachate contained 1.094 g L^{-1} (NH$_4$)$_2$SO$_4$, 1.270 g L^{-1} K$_2$SO$_4$, 0.610 g L^{-1} NH$_4$Cl, 0.965 g L^{-1} CaCl$_2$, 10.168 g L^{-1} NaCl, and 3.810 g L^{-1} KCl. The ionic strength was 0.31, the conductivity was 30 mS cm^{-1}, and the pH was adjusted to 6.9 with NH$_3$.

The weight of the sorbents corresponded to 100 mg of material dried at 110°C and was calculated based on water contents to eliminate the effect of drying on the structure, especially on the polyhydroxo cations. The water content was determined on duplicate subsamples and calculated as follows: w = (m − m$_d$)/m$_d$, where m is the sample weight and m$_d$ is the sample weight after 12 h drying at 110°C. To each sample, 50 mL of the solution containing the heavy metal was added. The sorption isotherms of Cd were recorded at pH 6.9 ± 0.1. To avoid precipitation of Cu(OH)$_2$ and Pb(OH)$_2$, the sorption isotherms of Cu and Pb were recorded at pH 4.9 ± 0.1. To investigate the pH dependence of the sorption capacity of Al and Zr-hydroxy-intercalated and pillared MX80, the sorption of Zn was studied at pH 4.9 and 6.9. The pH was adjusted with 0.1 M HCl or 0.1 M NaOH. The suspensions were equilibrated on a shaking table at 130 oscillations min^{-1} at room temperature. The pH was monitored and readjusted if necessary. Reference solutions without any sorbent served as control samples. After 3 d, the suspensions were transferred into plastic vessels and centrifuged at 4500 g for 60 min to separate the solid from the solution. The supernatant was filtered (glass fiber filters, 0.5 μm) and acidified with HCl or HNO$_3$ (Pb). The concentrations of heavy metals were measured by flame atomic absorption spectroscopy (AAS) on a Perkin Elmer 1100 Atomic Absorption Spectrophotometer. The solid was washed by centrifugation until the conductivity of the supernatant was in the range of ultrapure water, and then dried at 40°C. For longer duration experiments, samples were equilibrated for 3 d on the shaking table and then stored at room temperature in a dark environment. The pH was measured several times and readjusted if necessary. After 30 wk, the samples were treated as described above. The relative standard deviations, calculated from replications, were 6.7% (Zn), 7.8% (Cu), 6.4% (Pb), and 5.6% (Cd).

The sorption isotherms were calculated using a non-linearized Langmuir equation (Kinniburg, 1986; Lang-
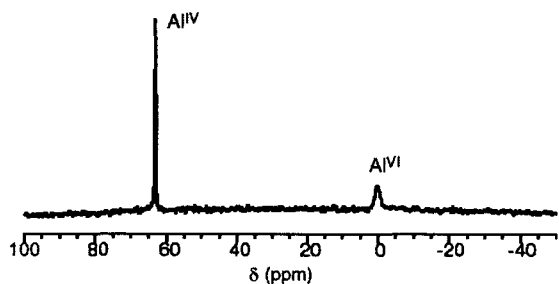
Figure 2. ^{27}Al NMR-spectrum of the 0.1 M Al-chloride pillaring solution (OH/Al-ratio 2.4).

muir, 1918), which can be applied to one and two-site models:

$$q = \sum_{i=1}^{n} \frac{cK_i}{1 + cK_i} q_{max,i} \qquad (1)$$

where K_i and $q_{max,i}$ are the affinity constant and the sorption maximum of the site i, respectively, n is the number of energetically different sorption sites, q is the sorbed concentration of the sample in μmol g^{-1}, and c is the aqueous equilibrium concentration, expressed in μmol L^{-1}. The parameters K_i and $q_{max,i}$ were determined by non-linear *least-squares* regression including a maximum uncertainty of the dissolved concentrations of 5%. Where feasible, the sorption behavior of the sorbents was described with one-site Langmuir isotherms, otherwise two-site isotherms were used.

Determination of the non-exchangeable portion of sorbed heavy metal ions

The ion exchange of the samples containing the heavy metals was based on the ammonium acetate method for the determination of the CEC. The pH of the 1 *M* solution of CH$_3$COONH$_4$ was adjusted with acetic acid to the pH of the sorption experiments, *i.e.,* 6.9 for Cd and Zn and 4.9 for Cu, Pb, and Zn. After ion exchange, samples were washed in ultrapure water as described above, dried, and ground in an agate mortar. Prior to decomposition, the samples were dried overnight at 110°C. After cooling in a desiccator, the samples were weighed in duplicate in silver crucibles, mixed with 2 g KOH, and heated until homogeneously melted. After cooling, the material was stepwise dissolved with ~40 mL of concentrated HCl and ultrapure water. Heavy metals were analyzed by flame AAS. The relative standard deviations, calculated from replications, were 7.1% (Zn), 7.3% (Cd), 10.4% (Cu), and 6.6% (Pb).

RESULTS

Characterization of the Al- and Zr-hydroxy-intercalated and pillared bentonites

The ^{27}Al NMR spectrum of the Al-containing pillaring solution (Figure 2) exhibits a signal at a chem-

ical shift δ of 0.2 ppm corresponding to monomeric Al. The signal at 63.1 ppm is caused by four-coordinated Al. The Al$_{13}$ complex was 71% of the total dissolved aluminum phases, the dominant species in solution. Furthermore, 7% of the aluminum phases were monomeric Al and apparently 22% undetectable Al-polymers. These results are consistent with those of Kloprogge (1992). The X-ray diffractograms (Figure 1) show a $d(001)$-value of HAl-MX80 of 18.8 Å. Subtraction of the thickness of the 2:1 layer of 9.6 Å (McBride *et al.,* 1975) yields an interlayer separation of 9.2 Å corresponding to the size of Al$_{13}$. Consequently, this tridecamer is the predominant intercalated species (Pinnavaia, 1983; Vaughan, 1988). The interlayer spacing of HZr-MX80 of ~9 Å corresponds to that obtained by Yamanaka and Brindley (1979), who attributed the spacing to Zr$_4$-tetramers, either oriented perpendicular to the 2:1 layers or as a double layer of flat-lying complexes. Furthermore, the intercalation of the Al and Zr-polyhydroxo cations produces micropores between the complexes (Table 1).

The dehydration and dehydroxylation of the polyhydroxo cations during calcination produces a decrease of the $d(001)$-values to 18.1–18.5 Å (Figure 1) and micropore volumes to 39–63 μL g^{-1} (Table 1). The BET surface areas of the hydroxy-intercalated and pillared materials ranged from 150 to 219 m^2 g^{-1}. The CEC of the original bentonite was reduced from 76 meq g^{-1} to 40–55 meq g^{-1} (Table 1) owing to partial occupation of permanently charged sites by polyhydroxo cations and pillars and migration of protons from the pillars into the octahedral sheet of the montmorillonite. Considering the montmorillonite content of MX80 at 75% (Mueller-Vonmoos and Kahr, 1983), these data correspond well with Vaughan *et al.* (1979), Poncelet and Schutz (1986), Farfan-Torres *et al.* (1992), Gil and Montes (1994), and Lahodny-Sarc and Khalaf (1994).

Sorption experiments in ultrapure water

For dissolved heavy metal concentrations of <10 μmol L^{-1}, the hydroxy-intercalated and pillared bentonites sorbed similar or greater amounts of Cu, Cd, Pb, and Zn than the original MX80 (Figures 3 and 4). Above that concentration, this trend reverses. However, at pH 6.9, Al and Zr-hydroxy-intercalated and pillared MX80 sorbed as much Zn as MX80 (Figures 3a and 4a). Because of the reduced CEC of these sorbents (Table 1), the enhanced sorption of Zn under the given experimental conditions is attributed to the Al and Zr-polyhydroxo cations in the interlayers.

The sorption behavior of MX80 is described with one-site Langmuir isotherms. As indicated by logK-values between 4.0–4.3 (Table 2), MX80 shows similar affinities for each of the four heavy metals. The sorption maxima closely correspond to the CEC of 76 meq (100 g)$^{-1}$. The sorption was independent of the
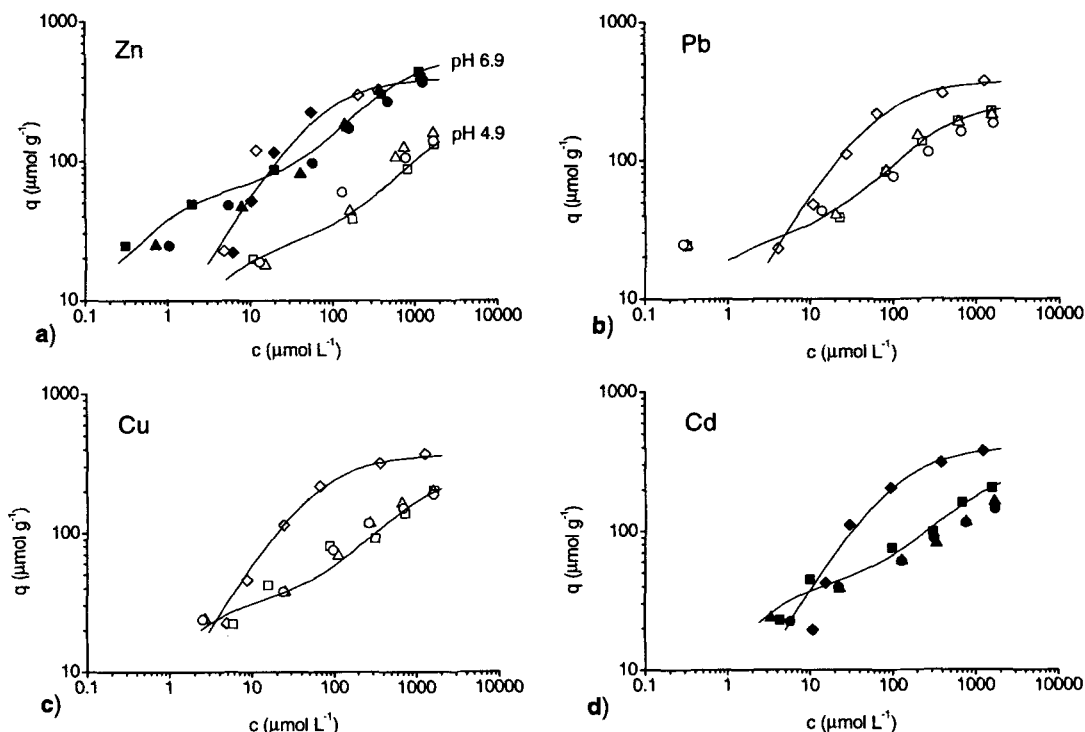
Figure 3. Sorption of (a) Zn, (b) Pb, (c) Cu, and (d) Cd by MX80 ($\Diamond$), HAl-MX80 ($\square$), Al-MX80 ($\triangle$), and EXM 534 ($\bigcirc$) after 3 d in aqueous suspension (q: sorbed quantity of heavy metal, c: equilibrium concentration of heavy metal in solution). The solid lines represent the fitted model curves of MX80 and HAl-MX80. Open symbol: pH 4.9, solid symbol: pH 6.9.

pH as shown for Zn (Figure 3a), and the amounts of non-exchangeable heavy metal cations were low (Table 3), which suggests the dominance of cation exchange on permanently charged sites.

A one-site Langmuir isotherm appeared to be inadequate to describe the sorption behavior of Al and Zr-hydroxy-intercalated and pillared MX80 because it underestimated sorption at low initial concentrations. Two-site Langmuir isotherms better described sorption. The langmuir constants for the sorption of Cd, Cu, Pb, and Zn (pH 4.9; Table 2) show that high-affinity sites exist with a small sorption maximum and that medium-affinity sites exist with a large sorption maximum. The sorbed heavy metal ions were readily exchangeable (Table 3).

Considerably higher amounts of Zn were sorbed at pH 6.9 (Figure 3a; Table 2). The chemical analyses of the fused sorbents after reexchange with CH_3COONH_4 show that ~33% of the Zn sorbed by HAl-MX80 and 25% of the Zn sorbed by Al-MX80 was non-exchangeable (Table 3). These results suggest a partially specific sorption of Zn-ions by pH-dependent sites of the intercalated Al-polyhydroxy cations and pillars at neutral pH.

The amounts of Zn sorbed by HAl and Al-MX80 after 30 wk exceeded the maxima predicted from the two-site Langmuir isotherms of 584 μmol g^{-1} and 485 μmol g^{-1}, respectively (Tables 2 and 3; Figure 5a).

Also, non-exchangeable Zn increased to 273.7 and 153.5 μmol g^{-1}, respectively (Table 3). In contrast, the sorption of Pb (Figure 5b) and Cu (Figure 5c) was constant with time. The decrease in the dissolved Cd concentration after 30 wk was probably caused by the precipitation of $CdCO_3$, since the experiments were not performed in an inert atmosphere (Figure 5d).

Compared with Al-hydroxy-intercalated and pillared bentonite, the Langmuir constants of HZr and Zr-MX80 for each heavy metal showed higher sorption maxima of the high-affinity sites and similar or lower sorption maxima of the medium-affinity sites (Table 2). The sorbed Cu, Cd, Zn (pH 4.9), and Pb (Figure 4) did not significantly exceed the CEC of the sorbents, were readily exchangeable (Table 3), and did not notably increase with time (Figure 6). The decrease of dissolved Cd after 30 wk (Figure 6d) was an exception, which probably is due to the precipitation of $CdCO_3$. At pH 6.9, larger amounts of Zn were sorbed, which were partially non-exchangeable (Figure 4a; Table 3). However, HZr and Zr-MX80 sorbed less Zn than Al-hydroxy-intercalated and pillared bentonite. The non-exchangeable portions of 33.7 and 31.4 μmol g^{-1} were lower than those of HAl- and Al-MX80 at 134.6 and 95.2 μmol g^{-1}, respectively (Table 3). Also the increase of sorbed and non-exchangeable Zn with time was lower than that of Al-hydroxy-intercalated and pillared MX80 (Figure 6a; Table 3).
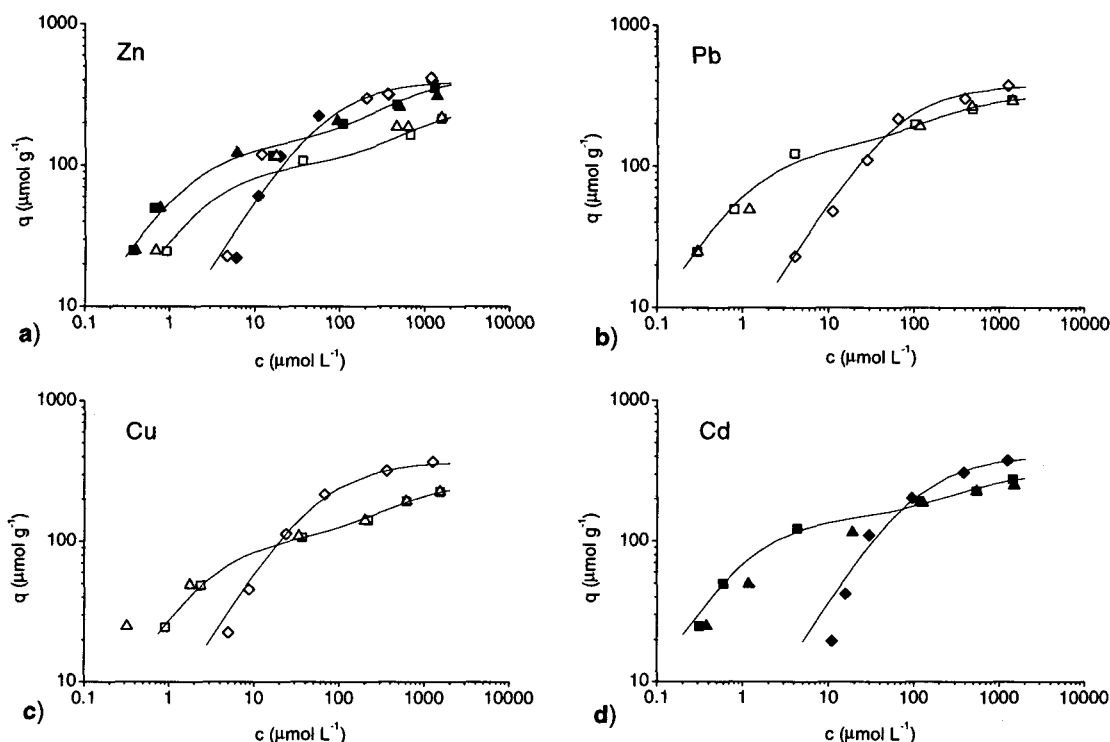
Figure 4.   Sorption of (a) Zn, (b) Pb, (c) Cu, and (d) Cd by MX80 (◇), HZr-MX80 (□) and Zr-MX80 (△) after 3 d in aqueous suspension (q: sorbed quantity of heavy metal, c: equilibrium concentration of heavy metal in solution). The solid lines represent the fitted model curves of MX80 and HZr-MX80. Open symbol: pH 4.9, solid symbol: pH 6.9.

Thus, Zn appears to be bound at the surfaces of Zr-polyhydroxo cations and pillars, although the affinity of the Zn-ions towards the Zr-polyhydroxo cations and pillars seems to be weaker than towards Al-polyhydroxo cations and pillars.

In Figure 7, the sorption isotherms of MX80, HAl, and HZr-MX80, representing the three groups of sorbents investigated, illustrate order of preference towards Cd, Cu, Pb, and Zn. Bentonite MX80 did not exhibit any preference nor was the sorption strongly pH dependent as shown for Zn (Figure 7a). Al-hydroxy-intercalated and pillared bentonite exhibited the following order of preference: Zn > Cd at pH 6.9, Pb $\approx$ Cu > Zn at pH 4.9 (Figure 7b). Zr-hydroxy-intercalated and pillared MX80 showed the same sequence at pH 6.9. However, at pH 4.9, preference was Pb > Cu $\approx$ Zn (Figure 7c).

Sorption experiments in artificial leachate

The sorption experiments in artificial leachate were restricted to Cd, Cu, and Zn because of the precipitation of $PbSO_4$ in the sulfate containing leachate. The results confirm the preference of Al-hydroxy-intercalated and pillared MX80 for Zn at neutral pH (Table 3). Despite the higher ionic strength of the solvent, the maximum amount of Zn sorbed by HAl, Al-MX80, and EXM 534 was nearly as high as in ultrapure water,

i.e., between 385.2–354.6 $\mu mol\ g^{-1}$. Also, the amount of non-exchangeable Zn of HAl and Al-MX80 were in the same range (Table 3). In contrast, the amount of Zn sorbed by HZr and Zr-MX80 was 68 and 63% of that in ultrapure water. The amount of non-exchangeable Zn in HZr-MX80 decreased from 33.7 to 8.8 $\mu mol\ g^{-1}$ (Table 3).

The maximum sorption of Cu by Al and Zr-hydroxy-interlayered and pillared MX80 decreased from 188.0–226.8 $\mu mol\ g^{-1}$ to 91.5–109.5 $\mu mol\ g^{-1}$, and the amount of sorbed Cd fell from 142.8–277.4 $\mu mol\ g^{-1}$ to 31.0–53.0 $\mu mol\ g^{-1}$. However, the original bentonite MX80 exhibited the maximum decrease of heavy metal sorption. Compared with the amounts of Zn (pH 6.9), Cu, and Cd sorbed in ultrapure water at initial concentrations of 2000 $\mu mol\ L^{-1}$, only 25, 33, and 7%, respectively, were sorbed in artificial leachate.

DISCUSSION

Sorption of heavy metal ions by the bentonite MX80

The sorption of Zn, Cu, Pb, and Cd by MX80 was described with one-site Langmuir isotherms. The calculated and measured maximum concentrations closely corresponded to the CEC of MX80. The residual heavy metal content in the samples after displacement of the sorbed heavy metals with NH_4^+ varied between 0.9–10.6 $\mu mol\ g^{-1}$, *i.e.,* for all elements investigated,

Table 2. Langmuir constants K and q_{max} and correlation coefficients R^2 for the sorption of Zn, Cu, Cd, and Pb (the numerals 1 and 2 refer to energetically unique sorption sites).

Cations pH	Constants correlations	MX80 1	HAl-MX80 1	HAl-MX80 2	Al-MX80 1	Al-MX80 2	EXM 534 1	EXM 534 2	HZr-MX80 1	HZr-MX80 2	Zr-MX80 1	Zr-MX80 2
Pb	$\log K$ (M^{-1})	4.2	6.3	3.6	6.1	3.6	6.1	3.4	5.9	3.7	5.8	3.7
pH 4.9	q_{max} ($\mu mol\ g^{-1}$)	375	27	235	30	210	41	178	135	183	122	193
	R^2	0.986	0.993		0.991		0.990		0.994		0.999	
Cu	$\log K$ (M^{-1})	4.3	5.8	3.1	5.8	3.4	5.8	3.4	5.6	3.3	5.7	3.3
pH 4.9	q_{max} ($\mu mol\ g^{-1}$)	369	32	250	33	211	34	184	104	164	103	167
	R^2	0.998	0.981		0.996		0.995		0.998		0.995	
Zn	$\log K$ (M^{-1})	4.3	5.3	2.7	5.0	3.1	4.9	3.0	5.6	3.0	5.7	3.5
pH 4.9	q_{max} ($\mu mol\ g^{-1}$)	362	26	231	13	208	38	150	99	176	107	126
	R^2	0.989	0.996		0.992		0.995		0.992		0.990	
Zn	$\log K$ (M^{-1})	4.2	6.2	3.4	6.1	3.6	6.1	3.4	5.8	3.3	5.9	3.7
pH 6.9	q_{max} ($\mu mol\ g^{-1}$)	394	62	522	30	455	44	415	139	290	130	182
	R^2	0.986	0.998		0.995		0.999		0.992		0.994	
Cd	$\log K$ (M^{-1})	4.0	5.5	3.3	5.6	3.0	5.6	3.4	5.9	3.4	5.7	3.8
pH 6.9	q_{max} ($\mu mol\ g^{-1}$)	403	47	200	35	192	36	183	146	159	125	138
	R^2	0.990	0.990		0.992		0.994		0.993		0.996	

Table 3. Sorbed and non-exchangeable Zn, Cu, Pb, and Cd in aqueous and artificial leachate suspensions after 3 d and 30 wk[1]. Initial concentration 2000 $\mu mol\ L^{-1}$.

Cations pH	Sorbent	Aqueous suspension Sorbed ($\mu mol\ g^{-1}$)	Aqueous suspension Non-exchangeable ($\mu mol\ g^{-1}$)	Leachate suspension Sorbed ($\mu mol\ g^{-1}$)	Leachate suspension Non-exchangeable ($\mu mol\ g^{-1}$)
Zn	MX80	393.8	10.6	97.1	4.6
pH 6.9	HAl-MX80	438.2	134.6	385.2	101.0
	HAl-MX80[1]	692.7	273.7	n.d.	n.d.
	Al-MX80	396.0	95.2	360.0	87.5
	Al-MX80[1]	612.0	153.5	n.d.	n.d.
	EXM 534	364.8	n.d.	354.6	n.d.
	HZr-MX80	351.0	33.7	237.9	8.8
	HZr-MX80[1]	468.1	38.0	n.d.	n.d.
	Zr-MX80	309.8	31.4	195.3	n.d.
Zn	MX80	374.8	3.2	n.d.	n.d.
pH 4.9	HAl-MX80	132.3	3.3	n.d.	n.d.
	Al-MX80	157.5	n.d.	n.d.	n.d.
	EXM 534	137.8	n.d.	n.d.	n.d.
	HZr-MX80	212.6	1.4	n.d.	n.d.
	Zr-MX80	216.8	n.d.	n.d.	n.d.
Cu	MX80	369.8	4.3	123.6	n.d
pH 4.9	HAl-MX80	203.2	5.8	109.5	n.d.
	Al-MX80	195.7	n.d.	94.5	n.d.
	EXM 534	188.0	n.d.	94.8	n.d.
	HZr-MX80	226.4	3.7	107.9	n.d.
	Zr-MX80	226.8	n.d.	91.5	n.d.
Pb	MX80	371.8	3.5	n.d.	n.d.
pH 4.9	HAl-MX80	226.3	1.9	n.d.	n.d.
	Al-MX80	209.8	n.d.	n.d.	n.d.
	EXM 534	182.9	n.d.	n.d.	n.d.
	HZr-MX80	294.4	1.6	n.d.	n.d.
	Zr-MX80	289.3	n.d.	n.d.	n.d.
Cd	MX80	377.8	0.9	25.9	n.d.
pH 6.9	HAl-MX80	202.7	1.8	40.9	n.d.
	Al-MX80	160.5	n.d.	31.0	n.d.
	EXM 534	142.8	n.d.	47.2	n.d.
	HZr-MX80	277.4	2.3	53.0	n.d.
	Zr-MX80	250.4	n.d.	50.2	n.d.

the sorption process was governed by reversible cation exchange reactions. These results are consistent with those of Stadler and Schindler (1993) and Lothenbach (1996).

Sorption of heavy metal ions by HAl- and Al-MX80

The sorption of Cu, Zn, Cd, and Pb by Al-hydroxy-interlayered and pillared MX80 is well described by two-site Langmuir isotherms. The Langmuir constants indicate that few high-affinity sites and many medium-affinity sites exist. The increase of q_{max} with pH (see sorption of Zn, Table 2) indicates that both high and medium affinity sites include pH-dependent charged sites, *i.e.*, hydroxyl groups. The OH groups are located on the edges of the montmorillonite crystallites and on the intercalated polyhydroxo cations and pillars. Whereas the sorbed Cd, Cu, Pb, and Zn (pH 4.9) roughly corresponded to the CEC of the sorbents and were almost entirely exchangeable, the amount of Zn sorbed at pH 6.9 was considerably higher. The strong pH-dependence of both sorption and non-exchangeable Zn suggests the complexation of Zn ions to surface OH groups of the intercalated Al_{13}-polyhydroxo cations at neutral pH. Furrer *et al.* (1992) reported the deprotonation of Al_{13} to be similar to the third deprotonation reaction of the Al^{3+} hexaquo complex: $0.5\ Al(H_2O)_4(OH)_2^+ = 0.5\ Al(OH)_4^- + H^+ + H_2O$ with a pK value of 6.7 at an ionic strength of 0.1 M. The partial or complete deprotonation of Al_{13} is a prerequisite for the complexation of heavy metals. Based on Furrer *et al.* (1992), our data suggest bonding of Zn by HAl-MX80 at pH 6.9, but not at pH 4.9.

The sorption of Zn by Al-MX80 and EXM 534 was also pH-dependent. This indicates complexation on pH-dependent charged sites, *i.e.*, edge sites of the montmorillonite crystallites and hydroxyl groups associated with the pillars. At present, little is known about the structure of these oxidic pillars.[27] Al solid
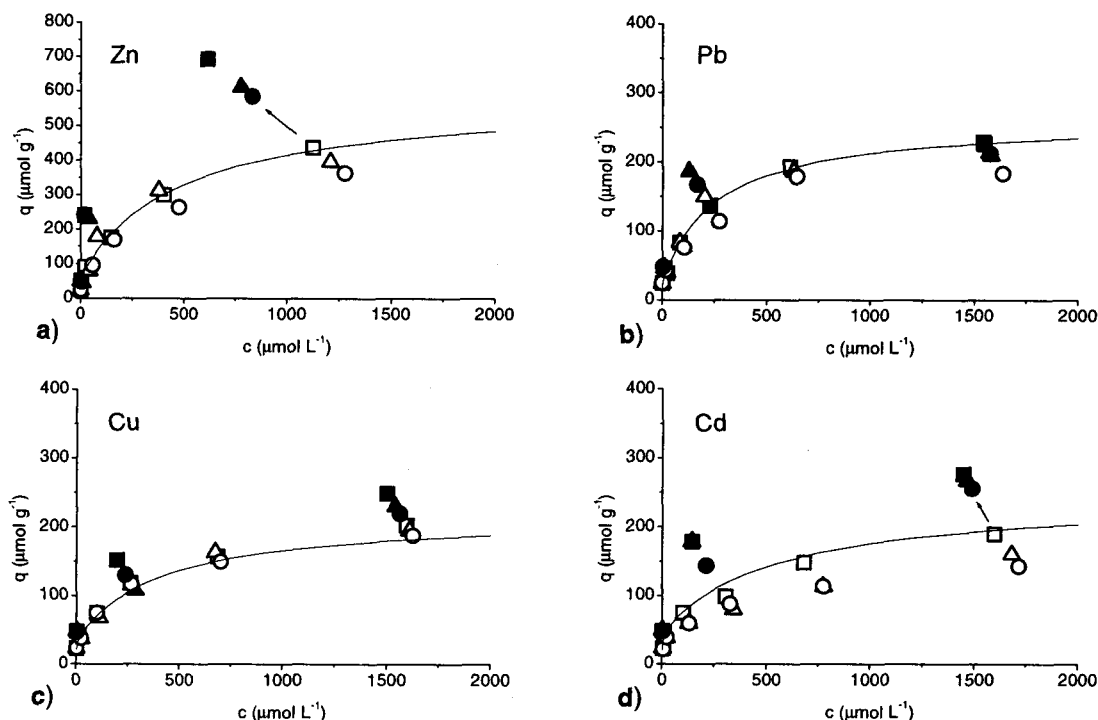
Figure 5. Sorption of (a) Zn, (b) Pb, (c) Cu, and (d) Cd by HAl-MX80 (□), Al-MX80 (△), and EXM 534 (○) after 3 d (open symbols) and 30 wk (solid symbols) in aqueous suspension (q: sorbed quantity of heavy metal, c: concentration of heavy metal in solution). The solid line represents the fitted model curve of HAl-MX80.
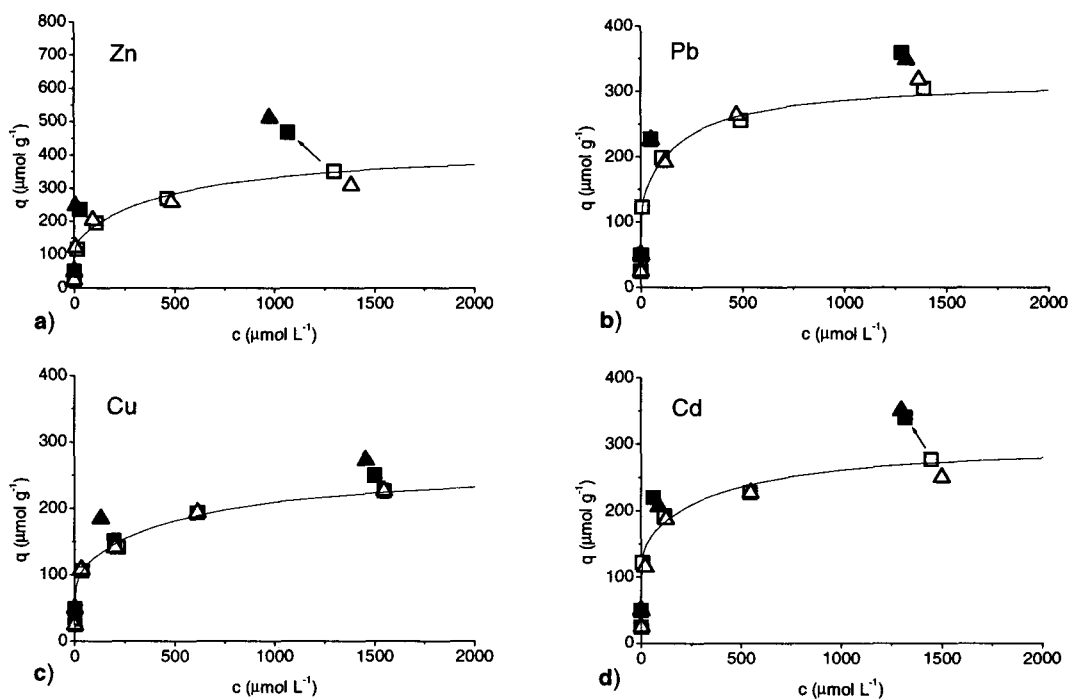

Figure 6. Sorption of (a) Zn, (b) Pb, (c) Cu, and (d) Cd by HZr-MX80 (□) and Zr-MX80 (△) after 3 d (open symbols) and 30 wk (solid symbols) in aqueous suspension (q: sorbed quantity of heavy metal, c: equilibrium concentration of heavy metal in solution). The solid line represents the fitted model curve of HZr-MX80.
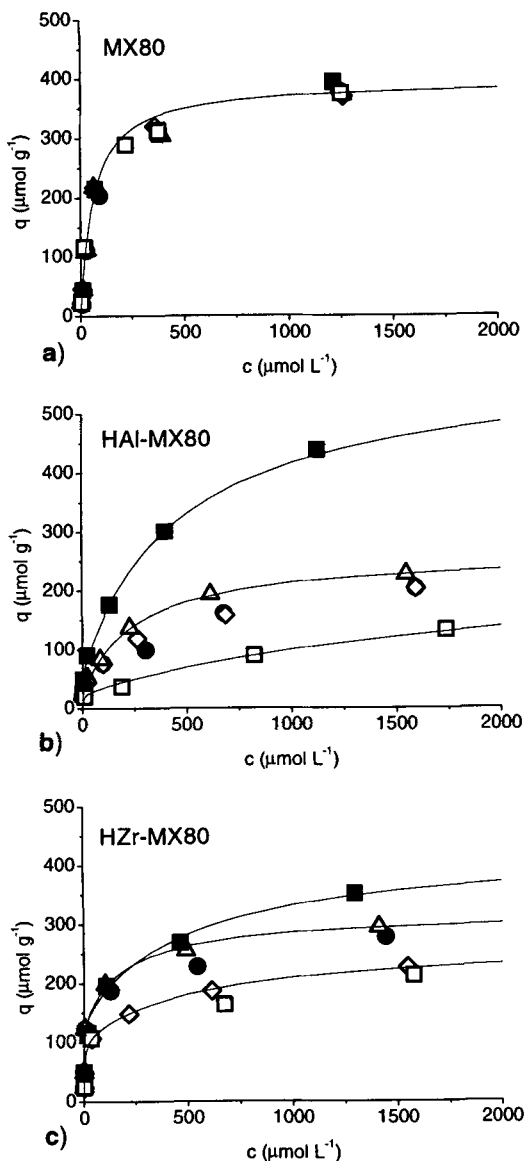
Figure 7. Selectivity of (a) MX80, (b) HAl-MX80, and (c) HZr-MX80 for Zn (□), Pb (△), Cu (◇), and Cd (○) after 3 d in aqueous suspension (q: sorbed quantity of heavy metal, c: equilibrium concentration of heavy metal in solution). The solid lines represent the fitted model curves. Open symbol: pH 4.9, solid symbol pH 6.9.

ally with a maximum temperature of 500°C for water loss (Occelli and Tindwa, 1983; Pinnavaia *et al.*, 1984). Thus, the Al-pillars are probably hydrous aluminum oxides. Sorption studies showed that metal ions in the surface layer of metal oxides have a reduced coordination number and, thus, behave as Lewis-acids (Stumm *et al.*, 1980). In the presence of H_2O, the surface metal ions tend to coordinate water molecules, which upon hydrolysis, form a hydroxylated surface where heavy metals can be sorbed via surface complexation (Stumm *et al.*, 1980; Schindler, 1981). Therefore, we believe that the high quantities of Zn sorbed and immobilized by Al-MX80 and EXM 534 are attributed to the complexation of Zn with OH groups coordinated to the surface of the oxidic pillars. Compared with HAl-MX80, the amount of Zn sorbed and immobilized by Al-MX80 and EXM 534 is lower, which corresponds to lower sorption maxima of the high and medium-affinity sites. Evidently, during calcination, the number of sorption sites is reduced owing to dehydration and dehydroxylation of the polyhydroxo cations, which is accompanied by a decrease in pillar height, surface area, and micropore volume (Figure 2; Table 1).

Kukkadapu and Kevan (1988) studied the sorption of Cu by Al-pillared montmorillonite at pH 7 by electron spin resonance and reported irreversible chemisorption of Cu^{2+} to the hydroxyl groups of the Al_{13}-pillars. Comets and Kevan (1993) investigated the coordination of Cu sorbed by Al_{13} and Zr_4-pillared montmorillonite by electron spin echo modulation spectroscopy. They found that Cu was sorbed strongly by Al_{13}-pillared montmorillonite and that Cu was coordinated to one water molecule and five oxygen atoms of an Al_{13}-pillar. Hohl and Stumm (1976) reported surface complexation of Pb on hydrous γ-Al_2O_3. In contrast, however, our experiments did not reveal significant specific interactions between Cu, Pb, or Cd and the Al-polyhydroxo cations and pillars. Obviously at pH 4.9, the surface complexation of Cu and Pb was inhibited by insufficient deprotonation of the Al-polyhydroxo cations and H_2O molecules coordinated on the surface of the pillars, respectively.

At neutral pH, Zn was partially immobilized by Al-hydroxy-intercalated and pillared bentonite, whereas the sorbed Cd was almost entirely exchangeable. This is attributed to the low affinity of Cd towards Oh groups as indicated by the high pK_1-value of 10.1 (Smith and Martell, 1976). Our results correspond to those of Keizer and Bruggenwert (1991) on the sorption of Cd by clay-aluminum hydroxide complexes. Lothenbach (1996) studied the dependence of the sorption of Cd, Cu, and Pb by Al_{13}-intercalated montmorillonite on the pH. Lothenbach reported decreasing dissolved concentrations of Cd above pH 7, and for Cu and Pb above pH 5. Hence, the sorption maxima of these elements probably increase at higher pH.

state NMR analyses of Al-hydroxy-interlayered hectorite before and after calcination showed that the relative atomic positions of aluminum in the interlayers were hardly affected by calcination. Thus, the structure of the Al-pillar is analogous to the polyhydroxo cation in that the bridging OH groups and H_2O molecules are replaced with oxygen atoms (Jones, 1988). By using differential scanning calorimetry (DSC) and differential thermal analysis (DTA), dehydration and dehydroxylation of the polyhydroxo cations appear gradu-

Since sorption is a surface phenomenon, the bonding of cations on hydrous metal oxides is a rapid process, provided that the sorption sites are readily accessible (Kinniburg and Jackson, 1981). In the model of Kinniburg (1986), which is an extension of the approach of Langmuir (1918), the sorption reaches a maximum after the formation of a monolayer of sorbate at the surface of the sorbent. However, our results show that the sorption of Zn at pH 6.9 did not reach a maximum, but increased with time beyond the modeled maximum concentrations of the two energetically different sites. This effect is explained by surface-precipitation (Farley *et al.,* 1985). Apart from the rapidly occurring monolayer sorption, this model also includes the slow sorption of multilayers. The composition of the precipitating phase varies continuously between that of the sorbate and a pure precipitate of the sorbing cation. Lothenbach (1996) also observed an increase in the sorption of Zn with time by montmorillonite coated with aluminum hydroxide and Al_{13}-intercalated montmorillonite. The author measured the influence of the dissolution of the binding agents on heavy metal remobilization. For the montmorillonite coated with aluminum hydroxide, dissolved Al and Zn showed a positive linear correlation. Lothenbach interpreted this as partial incorporation of Zn in the aluminum hydroxide structure, because Zn was only remobilized by dissolution of the hydroxide. For Al_{13}-intercalated montmorillonite, Lothenbach concluded that the Zn ions only marginally enter the structure of the polyhydroxo cations and are sorbed mainly near or at surface sites. These observations are consistent with our suggestion that the increasing sorption of Zn by Al-hydroxy-intercalated and pillared bentonite is attributed to surface precipitation.

Preferences of the Al-hydroxy-interlayered and pillared bentonite were Zn > Cd at pH 6.9 and Pb ≈ Cu > Zn at pH 4.9. These sequences are consistent with the results of Kinniburg *et al.* (1976), who studied heavy metal sorption on hydrous aluminum oxides. They also correspond to the affinity predicted from the pK_1-values of the metals (10.1 for Cd, 7.7 for Cu and Pb, and 9.0 for Zn; Smith and Martell, 1976).

Sorption of heavy metal ions by HZr and Zr-MX80

The sorption of Cu, Zn, Cd, and Pb by Zr-hydroxy-interlayered and pillared bentonite is also well described with two-site Langmuir isotherms. Compared with Al-hydroxy-interlayered and pillared MX80, the high-affinity sites of HZr and Zr-MX80 showed higher maximum sorption capacities. Similar to Al-hydroxy-intercalated and pillared MX80, the sorption maxima of both sites increased with pH as shown for the sorption of Zn (Table 2). Consequently, both sites as defined from the Langmuir isotherm must include sites that are pH-dependent. With exception of edge sites of the montmorillonite, pH-dependent sites are

located on the surface of the intercalated Zr-tetramers. The Zr atoms can hydrolyze independently to form polyhydroxo cations with the general formula $[Zr_4(OH)_{8+n}(H_2O)_{16-n}]^{(8-n)+}$ (Yamanaka and Brindley, 1979). The pH-dependent sites of the oxidic pillars are generated by hydrolysis of water molecules, which are coordinated on the surface of the pillars (Stumm *et al.,* 1980).

The Cd, Cu, Pb, and Zn ions (pH 4.9) were sorbed in the range of the CEC and almost entirely exchangeable, which suggests the dominance of cation exchange. However, at pH 6.9, Zn was sorbed beyond the CEC of HZr and Zr-MX80, although the sorbed and non-exchangeable amounts were less than for HAl- and Al-MX80. Evidently, the interactions between Zn and the intercalated Zr-polyhydroxo cations and pillars are weaker. This observation corresponds to the results of Comets and Kevan (1993), who studied the specific binding of Cu^{2+} by Zr_4 and Al_{13}-pillared montmorillonite using electron spin echo modulation spectroscopy. According to Comets and Kevan, Cu ions are coordinated to three H_2O molecules and three oxygen atoms of a Zr_4-pillar or to one H_2O molecule and five oxygen atoms of a Al_{13}-pillar. Comets and Kevan (1993) concluded that Cu ions are bound less strongly to Zr_4 than to Al_{13}-pillars.

At neutral pH, Zr-MX80 sorbed lower amounts of Zn than HZr-MX80. This is attributed to the dehydration and dehydroxylation of the Zr-polyhydroxo cations during calcination of HZr-MX80, which causes a decrease in surface area, micropore volume (Table 1) and thus, specific sorption sites.

At pH 6.9, HZr and Zr-MX80 showed the same sorption preference as the Al-hydroxy-interlayered and pillared bentonites, *i.e.,* Zn > Cd. However, at pH 4.9, the preference was Pb > Cu ≈ Zn. Obviously, the "softer" non-transition metal Pb was preferentially sorbed by the Zr_4-complex than the "harder" acids Zn and Cu. These preferences are roughly consistent with the affinity sequence of divalent metals for oxide surfaces based on the "softness" of the cations, Pb > Cu > Zn (McBride, 1991). Evidently, the binding of metal cations to oxide and hydroxide surfaces is a complex process, determined by the electrostatic and electron-sharing properties of both, sorbate and sorbent.

CONCLUSIONS

The sorption of Cd (pH 6.9), Cu (pH 4.9), Pb (pH 4.9), and Zn (pH 4.9) by Al and Zr-hydroxy-intercalated and pillared bentonites is governed by cation exchange. However, the higher and partially non-exchangeable quantities of Zn sorbed by these materials at pH 6.9 indicate the dominance of surface complexation of Zn-ions with hydroxyl groups of the Al and Zr-polyhydroxo cations and pillars. Thus, Al and, to a lesser degree, Zr-hydroxy-intercalated and pillared bentonites exhibit a high affinity for Zn ions, which is

independent of the ionic strength of the solvent. Consequently, the high sorption capacity of Al-hydroxy-intercalated and pillared bentonite remains nearly unaffected in saline solutions, whereas the sorption capacity of the original bentonite decreases due to competition between the heavy metal, alkali, and alkaline-earth cations. It is concluded that especially Al-hydroxy-interlayered and Al-pillared bentonites are potential sorbents for the removal of Zn from aqueous solutions, *e.g.,* municipal and industrial waste waters and leachates, at neutral pH.

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