

## HEAVY-METAL UPTAKE BY A HIGH CATION-EXCHANGE-CAPACITY MONTMORILLONITE: THE ROLE OF PERMANENT CHARGE SITES

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### ABSTRACT

A High Cation Exchange Capacity (HCM) montmorillonite clay has been prepared by acetate treatment of Zenith clay. The HCM has been evaluated for metal-uptake from aqueous solutions. The present data show that the cation exchange sites can play a significant role in the adsorption of metals in smectite clays. A theoretical analysis scheme has been developed which shows that permanent-charge sites can become dominant in metal-uptake by clays. In addition, it was shown that the permanent charge can influence the ionic-strength sensitivity of the Point of Zero Charge of the clay.

**KEYWORDS:** Montmorillonite; CEC; Adsorption; Heavy metals; Surface Complexation Models; Permanent charge.

### 1. INTRODUCTION

Under certain environmental conditions, heavy metals might accumulate up to toxic concentrations and cause ecological damage. Heavy metals are often introduced to the environment through modern human activities. Montmorillonites are a class of layered aluminosilicate minerals with unique combinations of swelling and ion exchange properties that make them valuable nanostructures in diverse fields. Their structures consist of an octahedral alumina layer fused between two tetrahedral silica layers. Smectite clays have a cation exchange capacity, which depends on the substitution of low-valent atoms such as  $Mg^{2+}$  or  $Al^{3+}$  in the octahedral sheet, and  $Al^{3+}$  or  $Si^{4+}$  in the tetrahedral sites. As a consequence, the layers are negatively charged (Sposito, 1989; Sposito, 2004). Soluble heavy metals can be removed from the environment, by adsorption. Clay minerals are low cost sorbents and are highly valued for their adsorptive properties. Therefore, a number of studies performed using clays for heavy metal adsorption showed effectiveness in removing heavy metals or organic molecules from aqueous solutions (Ikhsan *et al.*, 2005; Barbier *et al.*, 2000; Bradbury and Bayens, 1999; Bayens and Bradbury, 1997). Adsorption of ions on clay minerals is controlled by two different mechanisms: (i) pH-independent adsorption, usually attributed to cation exchange in the intrer-layer and resulting from the electrostatic interaction between the ions and the permanent charge. (ii) a pH dependent adsorption, thought to result from the surface complexation reaction similar to those on oxides. Cation exchange has been found to be an important sorption mechanism for many clay minerals (Ikhsan *et al.*, 2005; Kraepiel *et al.*, 1999; Avena and De Pauli, 1998) with a number of studies suggesting that exchange sites are responsible for cation uptake at low pH. Adsorption models for clays based on surface complexation modeling (SCM) usually involving two distinct types of surface groups (1)  $X^-$  groups bearing a permanent charge with account to the cation exchange part of adsorption (2) amphoteric sites of SOH groups. Recently we have shown that the cation exchange capacity (CEC) of a Zn-containing montmorillonite (code name Zenith) can be increased by selective removal of Zn atoms from the clay lattice (Stathi *et al.*, 2009). According to this methodology treatment with acetate allows the production of clay materials with C.E.C up to 180meq/100g. This exceed by 200% the typical C.E.C

for smectites (Sposito, 1989; Sposito, 2004; Ikhsan *et al.*, 2005; Barbier *et al.*, 2000; Bradbury and Bayens, 1999; Stathi *et al.*, 2009). In the present work, we present a physicochemical theoretical and experimental study of the metal-binding properties of the High-CEC-Montmorillonite (herein termed HCM). The aim of the present work is (a) to evaluate the metal-uptake capacity of the HCM, (b) to study the role of permanent-charge-sites in the H-binding and metal-binding properties of the HCM, and (c) to develop a theoretical model describing the role of the permanent-charge sites.

## 2. MATERIALS AND METHODS

All solutions were prepared with analytical grade chemicals and purified water (milli-Q academic system) with a conductivity of demineralized water of 18.2 $\mu$ S and degassed prior to use. Solutions of Pb(NO<sub>3</sub>)<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub> and Zn(NO<sub>3</sub>)<sub>2</sub> (Aldrich >99.5%) were prepared at a concentration of 3mM and kept in a polyethylene container at pH <2. A buffer system of 10mM *N*-morpholino-ethanesulfonic acid, 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid, and tris-hydroxymethyl-aminomethane was used for all of the samples, which presented a significant buffer capacity at a pH range of 5-9, with an average value deviation from the adjusted initial value of up to 5%. The pH values were adjusted with small volumes of NaOH or HNO<sub>3</sub> (concentrations of 0.1 and 0.05 N). Screening experiments indicated that, under the conditions of our experiments, the buffer molecules caused no interferences on the adsorption.

The montmorillonite used in this work was from the Island of Milos with a code name Zenith-N and the following chemical composition Na<sub>0.63</sub>K<sub>0.07</sub>Ca<sub>0.11</sub>[Si<sub>7.75</sub>Al<sub>0.25</sub>]-{Al<sub>3.21</sub>Mg<sub>0.69</sub>Fe<sup>+3</sup><sub>0.05</sub>Ti<sub>0.05</sub>}O<sub>20</sub>(OH)<sub>4</sub>. The sample fractionated to <2 $\mu$ m by gravity sedimentation and purified by standard methods (King *et al.*, 1987). Sodium exchange samples were prepared by immersing the clay into 1M solution of sodium chloride. Cation exchange was complete by washing and centrifuging four times with sodium chloride. Then, the samples were transferred into dialysis tubes in order to obtain chloride free clays and dried at room temperature. As detailed in Stathi *et al.*, 2009 with no-acetate treatment the CEC was 80 meq/100g. After acetate treatment (Stathi *et al.*, 2009) a High CEC Montmorillonite was prepared with CEC 186meq/100g. This (HCM) material was used throughout the present work. After completion of the purification and saturation of zenith clay, 10mg of the sample suspended in 10 mL HNO<sub>3</sub> 65% incubated for 48h centrifuged and the supernatant analyzed by atomic absorption spectroscopy (Perkin Elmer AAS700). Full data have been presented by Stathi *et al.*, 2009.

### 2.1 Surface Charge Properties of Montmorillonite

The surface charge of montmorillonite suspensions were evaluated by two methods: potentiometric acid–base titrations (Schulthess and Sparks, 1986; Stathi *et al.*, 2006; Giannakopoulos *et al.*, 2006) and mass titration (Giannakopoulos *et al.*, 2006; Bourikas *et al.*, 2003).

*Potentiometric titrations:* Acid-base potentiometric titration was used to measure the surface proton adsorption. The ionic strength of the suspension was adjusted, before the titration experiment, at 0.01M with KNO<sub>3</sub>. A 12.5 mg of montmorillonite was suspended in a titration cell containing 12.5 mL of Milli-Q water to yield a montmorillonite concentration 1 g L<sup>-1</sup>. The suspension allowed to equilibrate (Swell) for 12 hours with continuous stirring. Then, the suspension was purged with N<sub>2</sub> for 30min prior to titration and divided into two equal portion, that is, one for acidimetric and one for alkalimetric titration. The acidimetric titration was done with 12.5 mM HNO<sub>3</sub> in the pH range 3.00-9.25 and the alkalimetric was done with 12.5 mM NaOH with pH range 9.25-10.50. In all titrations the Metrohm 794 Basic Titrino buret was used, and the pH was measured with Metrohm Pt-glass electrode (type 6.0239.100).

*Mass Titration.* The mass titration method was used to determine the point of zero charge (PZC) of the clay in two ionic strengths. A 5 mg portion of montmorillonite was added to 5 mL of Milli-Q water having a pH between 7.50 and 11.50. The initial pH of the solution was adjusted with HNO<sub>3</sub> or NaOH. After each addition of 5 mg of solid Laponite, the pH was measured with a Metrohm Pt-glass microelectrode (type 6.0222.100). The suspension was continuously stirred and purged by nitrogen gas. When equilibration was achieved (equilibration time 15 min), a new amount of montmorillonite was added. This procedure was continued until further montmorillonite additions did not change the pH of the solution. This pH value has been shown to be a good approximation to the PZNPC of oxide and clay surfaces (Kraepiel and Morel, 1999; Avena and De Pauli, 1998; Giannakopoulos *et al.*, 2006; Stathi *et al.*, 2009).

## 2.2 Sorption Experiments

The concentrations of metals in the aqueous phase were determined as described earlier (Giannakopoulos *et al.*, 2006) for clay suspensions at concentrations  $1 \text{ g L}^{-1}$  with an initial concentration of  $4.5 \mu\text{M}$  of metal ions.

Sorption pH-edge experiments were performed to measure the effect of pH on the metal uptake, as follows: zenith clay was suspended in polypropylene tubes containing a buffer system of 10mM MES (N-morpholino-ethanesulfonic acid), 10mM HEPES (4-(2-Hydroxyethyl)piperazine-1ethanesulfonic) was used at all of the samples. This system presented a significant buffer capacity at range pH: 5.0 to 8.5 with an average deviation from the adjusted pH value  $< 5\%$ . Screening experiments indicated that under the conditions of our experiments the buffer molecules caused no interferences on the adsorption phenomena. The pH was adjusted with small volumes of NaOH (0.1N) or  $\text{HNO}_3$  (0.05N) and each suspension was allowed to equilibrate (swelling) for 12 hours under continuous stirring. Then, a suitable volume of metal stock solution was added to yield a metal concentration of  $4.5 \mu\text{M}$ . The pH of the suspension was re-adjusted, if necessary, by using small amounts of  $\text{HNO}_3$  or NaOH. The sample was allowed to equilibrate at room temperature for 2h under stirring. Screening experiments showed that equilibrium metal-uptake equilibrium was attained within 40minutes (data not shown). The pH of each suspension was continuously monitored and readjusted if necessary. Typically, in the present experiment pH variations did not exceed  $\pm 0.1$  pH units. Finally, the sample was centrifuged and the supernatant solution was analyzed for metals.

## 3. THEORETICAL SURFACE COMPLEXATION MODELING

The results of all potentiometric titration and sorption experiment were modeled with a surface complexation model. Surface complexation models (SCM) can describe successfully adsorption of ions on charged surfaces by assuming that adsorption involves both a coordination reaction at specific surface sites and an electrostatic interaction between adsorbing ions and the charged surface. Extended SCM have been used previously to describe the adsorption of various ionic species onto a number of different substances (Dzombak and Morel 1990). In our modelling we have assumed two different populations of surface reactive sites. SOH sites represent amphoteric aluminol and silanol groups on the mineral edge. Proton exchange at these sites is modelled with following reaction



Permanent charge, cation exchange sites ( $\equiv\text{X}^-$ ) were also taken into account with reaction (3):



Initial estimate for the surface sites densities of  $\equiv\text{X}^-$  and  $\equiv\text{SOH}$  were obtained by optimizing the fit for the potentiometric titration curve. This modelling approach was adapted from previous successful applications for adsorption of metals and organics on kaolinite, montmorillonite (Ikhsan *et al.*, 2005; Barbier *et al.*, 2000; Bradbury and Bayens, 1999) and Laponite (Giannakopoulos *et al.*, 2006). Including more than one type variable charge surface sites *e.g.* as in the case of montmorillonite did not improve the fit. On the other hand, the inclusion of permanent charge cation exchange sites has effect of the adsorption data at acidic pH. The equilibrium constants ( $K_{\text{int}}^+$  or  $K_{\text{int}}^-$  refers to the reaction constant without the electrostatic correction) for the surface reactions are given by equations:

$$K_{\text{int}}^+ = \frac{[\equiv\text{SOH}_2^+]}{[\equiv\text{SOH}](\text{H}^+)} e^{\left[\frac{F\Psi_0}{RT}\right]} \quad (4)$$

$$K_{\text{int}}^- = \frac{[\equiv\text{SO}^-](\text{H}^+)}{[\equiv\text{SOH}]} e^{\left[\frac{-F\Psi_0}{RT}\right]} \quad (5)$$

where:  $\Psi_0$  is the electrostatic double layer potential;  $F$  is the Faraday constant;  $R$  is the gas constant; and  $T$  is the absolute temperature. The equilibrium constant of metal reacting with surface sites are expressed in the form

$$K_{(M^{+2})} = \frac{[\equiv SOM^+](H^+)}{[\equiv SOH](M^{+2})} e^{\left[\frac{F\Psi_0}{RT}\right]} \quad (6)$$

The theoretical calculation were performed using the software FITEQL (Herbelin and Westall, 1999) assuming a Diffuse Layer Model (Dzombak and Morel, 1990).

## 4. RESULTS AND DISCUSSION

### 4.1 Surface Charge of H.C. Zenith Montmorillonite

The mass titration experiments for a HCM sample are shown in Figure 1A for two values of ionic strength. In non buffered solution, the pH gradually changes with the addition of solid, asymptotically approaching a limiting value. Therefore the pH where the solid addition does not produce a pH shift, can be estimated by extrapolation.

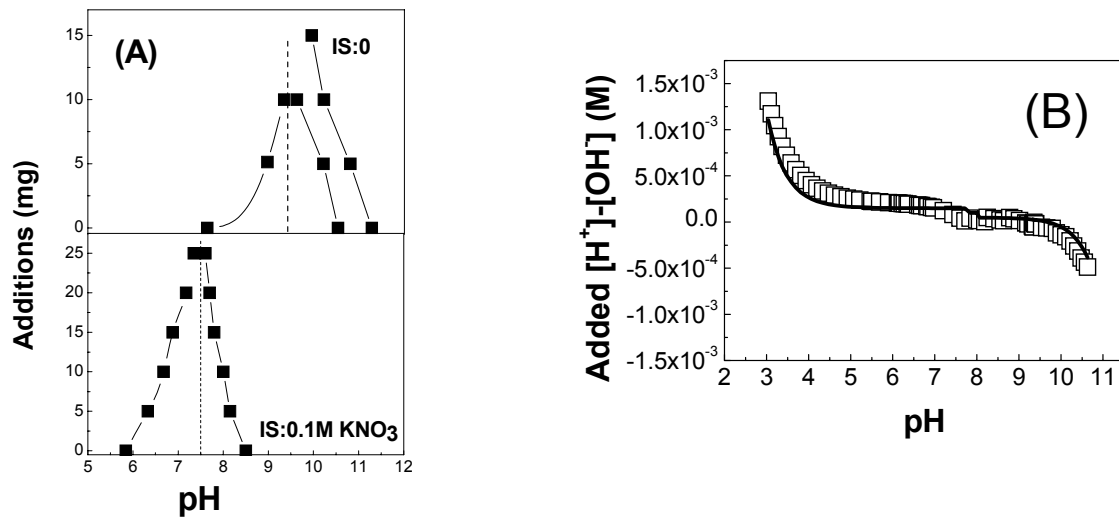


Figure 1. (A) Mass titration. (B) Potentiometric acid-base titration for the H.C.

The titration curve of a blank solution has been subtracted from the experimental data. Montmorillonite (open squares) experimental data (solid line) theoretical calculation using the protonation reactions described in Table 3

This value can be taken as a good approximation of the PZNC. For the HC-Zenith montmorillonite the data give PZNC 9.35 for IS=0 and PZNC 7.5 for IS=0.1 KNO<sub>3</sub>. Figure 1B shows potentiometric titration for a HCM sample at I.S.=0. The lines represent the best fit of experimental data using the following values for protonation constants  $\log K_{\text{intr}}^+ = 8.8$  and  $\log K_{\text{intr}}^- = -9.8$ . To verify the consistency between these values and the mass titration data we see that

$$\text{pH}_{\text{PZNC}} = \frac{1}{2} \left( \left| \text{p}K_{\text{intr}}^+ \right| + \left| \text{p}K_{\text{intr}}^- \right| \right) = 9.3 \quad (7)$$

which consistent with the value 9.35 from mass titration at I.S.=0. It is well known that montmorillonite particles carry two kinds of electrical charges a variable (pH dependent) charge resulting from proton adsorption/desorption reaction of surface sites SOH and a structural negative charge from X<sup>-</sup> sites resulting in from isomorphous substitution within the clay structure. The X<sup>-</sup> site concentration is intimately related with CEC of montmorillonite (200 meq/100g) and its result in values of permanent charge density  $\sigma_0 = F[X^-]/s = -47.9 \times 10^{-3} \text{ C/m}^2$ , for  $s = 300 \text{ m}^2 \text{ gr}^{-1}$ . Including  $\sigma_0$  value in the calculation of the PZNC, the formula of Kraepiel and Morel (1996).

$$\text{pH}_{\text{PZNC}} = \frac{1}{2} \left( \left| \text{p}K_{\text{intr}}^+ \right| + \left| \text{p}K_{\text{intr}}^- \right| \right) - \frac{1}{2.3} \left( \frac{F\Psi_{\text{PZNC}}}{RT} \right) \quad (8a)$$

$$\text{where: } \frac{F\Psi_{\text{PZNC}}}{RT} = 2 \text{arcsinh} \left( \frac{\sigma_0}{0.1174I^{\frac{1}{2}}} \right) \quad (8b)$$

gives a point of zero charge 9.19. Thus, the permanent charge has a nonzero effect on the PZNC of montmorillonite. All the surface charge properties of HCM zenith clay are summarized in Table 2.

Table 2. Physicochemical Parameters of High C.E.C Zenith Clay Used in this Study

CEC	186 meq / 100 g
PZNC	9.5 <sup>a</sup> , 9.19 <sup>*</sup>
K <sup>+</sup> <sub>int</sub>	8.8 <sup>a</sup>
K <sub>int</sub>	9.8 <sup>a</sup>
SOH concentration	3 mM g <sup>-1</sup>
X <sup>-</sup>	1.8 mM g <sup>-1</sup>
Partice size	200nm <sup>b</sup>

<sup>a</sup> via SCM and equation 1, <sup>\*</sup> This work via eq. 8a,b,  
<sup>b</sup> Stathi *et al.* (2009)

#### 4.2 Adsorption of metals

Adsorption of Pb, Cd, Cu and Zn versus pH are presented in Figures 2-5. The metal-uptake per Kg of HCM is listed in Table 3.

Table 3. Amounts (mmol kg<sup>-1</sup>) of Adsorbed Heavy Metals at pH=7.00

Pb	4.05
Cd	2.88
Cu	3.48
Zn	2.55

The data in Table 3 show that the HCM is characterized by a very high Pb-uptaking capacity. For the other metals high metal binding capacities are documented in Table 3, which exceed the capacities of other montmorillonites (Ikhsan *et al.*, 2005; Barbier *et al.*, 2000; Bradbury and Bayens, 1999; Bayens and Bradbury, 1997) including the reference Zenith clay (Balomenou *et al.*, 2008).

#### 4.3 Theoretical Speciation

The symbols in the figures represent experimental data and lines with open symbols are calculated using the parameters given in Table 4. The metal sorption edges were characterized by an initial sorption state where the uptake is stable. Taking into account the pKa values for the variable charge sites, Table 4, it is apparent that at acidic pH the prevailing positively surface charge sites  $\equiv\text{SOH}_2^+$  are not favorable for metal adsorption. On the other hand, assuming that the adsorption at low pH involves only the adsorption at  $\equiv\text{X}^-$  sites a consistent picture emerges, as shown from speciation schemes.

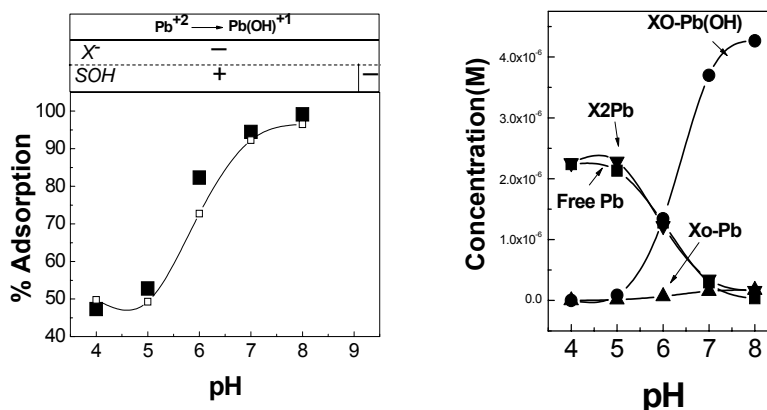


Figure 2. (Left) Adsorption of Pb on H.C. Zenith montmorillonite. Open symbols are theoretical calculations by using the parameters from Table 4 in FITEQL. At the top of the figures the Schindler-plot help the visualization of the charges of the interacting species as a function of the pH. (Right) Speciation analysis of the system clay- metal according to the calculations

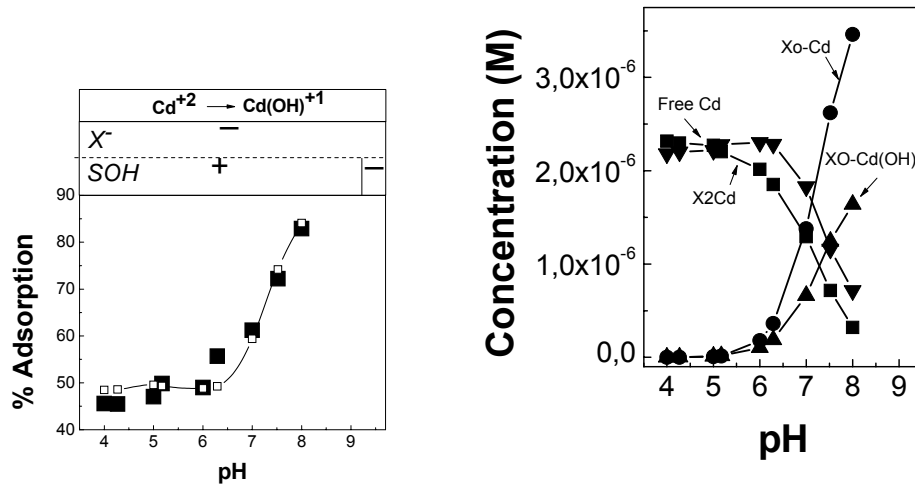


Figure 3. (Left) Adsorption of Cd on H.C. Zenith Zenith montmorillonite. Open symbols are theoretical calculations by using the parameters from Table 4 in FITEQL. (Right) Speciation analysis of the system clay- metal according to the calculations

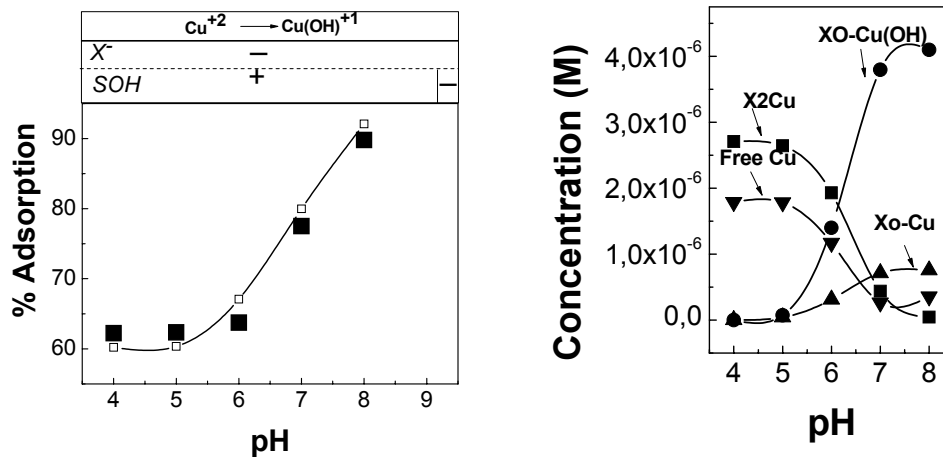


Figure 4. (Left) Adsorption of Cu on H.C. Zenith Zenith montmorillonite. Open symbols are theoretical calculations by using the parameters from Table 4 in FITEQL. (Right) Speciation analysis of the system clay- metal according to the calculations

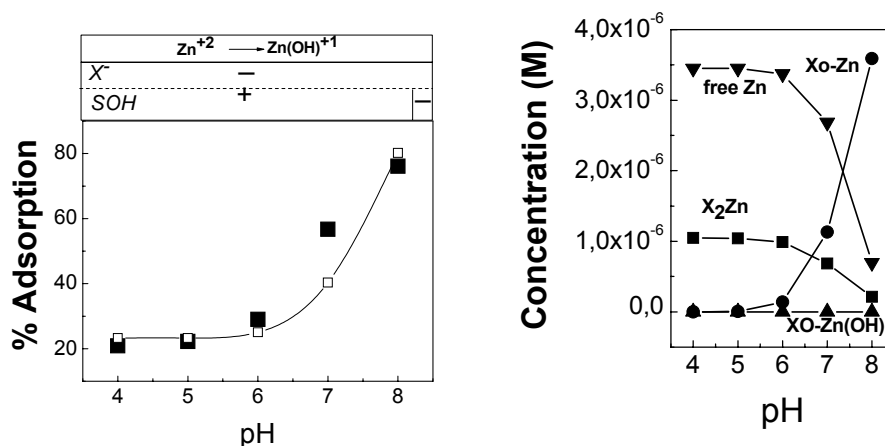


Figure 5. (Left) Adsorption of Zn on H.C. Zenith Zenith montmorillonite. Open symbols are theoretical calculations by using the parameters from Table 4 in FITEQL. (Right) Speciation analysis of the system clay- metal according to the calculations

The present data show that the cation exchange sites can play a significant role in the adsorption of metals in smectite clays. This can be significant in cases where the CEC sites of a clay have significant concentration. In low-CEC clays i.e. such as kaoline CEC ~ 20 meq/100g (Sposito, 1989) the contribution of the permanent-charge sites is practically zero. Barbier *et al.* (Barbier *et al.*, 2000) reported that the adsorption of Pb ions on Na-montmorillonite, CEC ~ 80 meq/100g, is primarily via cation exchange, while surface hydroxyl groups seem to play a secondary role. Our present data reveal clearly that permanent-charge sites can become dominant in metal-uptake by clays. In addition it was shown that the permanent charge can influence the ionic-strength sensitivity of the PZC of the clay.

Table 4. Solution and Surface reactions for High CEC Zenith Montmorillonite

	LogK	Reference
<b>Dissociation of Water</b>		
$H_2O \leftrightarrow H^+ + OH^-$	14	
<b>Hydrolysis of Metals</b>		
$Pb^{+2} \leftrightarrow Pb(OH)^+ + H^+$	7.70	Baes and Mesmer (1986)
$Cd^{+2} \leftrightarrow Cd(OH)^+ + H^+$	10.0	Baes and Mesmer (1986)
$Cu^{+2} \leftrightarrow Cu(OH)^+ + H^+$	5.60	Baes and Mesmer (1986)
$Zn^{+2} \leftrightarrow Zn(OH)^+ + H^+$	9.80	Baes and Mesmer (1986)
<b>Protonation of Zenith Clay</b>		
$SOH \leftrightarrow SO^- + H^+$	-9.80	Stathi <i>et al.</i> (2009)
$SOH + H^+ \leftrightarrow SOH_2^+$	8.80	Stathi <i>et al.</i> (2009)
<b>Sorption of metals onto zenith clay</b>		
$X + Pb^{+2} \leftrightarrow [X_2Pb]$	4.31	This work
$X + Cd^{+2} \leftrightarrow [X_2Cd]$	4.28	This work
$X + Cu^{+2} \leftrightarrow [X_2Cu]$	4.51	This work
$X + Zn^{+2} \leftrightarrow [X_2Zn]$	3.80	This work
$SOH + Pb^{+2} \leftrightarrow [SOPb]^+ + H^+$	5.50	This work
$SOH + Cd^{+2} \leftrightarrow [SOCd]^+ + H^+$	4.80	This work
$SOH + Cu^{+2} \leftrightarrow [SOCu]^+ + H^+$	5.95	This work
$SOH + Zn^{+2} \leftrightarrow [SOZn]^+ + H^+$	4.52	This work
$SOH + Pb(OH)^{+1} \leftrightarrow [SOPb(OH)] + H^+$	1.50	This work
$SOH + Cd(OH)^{+1} \leftrightarrow [SOCd(OH)] + H^+$	2.60	This work
$SOH + Cu(OH)^{+1} \leftrightarrow [SOCu(OH)] + H^+$	1.90	This work
$SOH + Zn(OH)^{+1} \leftrightarrow [SOZn(OH)] + H^+$	0.60	This work

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