

Zn sorption on Ca-illite and Ca-smectite: experiment and modelling

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Abstract. To predict Zn behaviour in soil, the retention properties of clay minerals plays a relevant role. In a continental environment, Ca is the main cation in solution. Soil reactivity may be reduced to sorption properties of Zn and Ca on illite and smectite, the major clay minerals in soil. With this assumption, a multi-site ion exchanger model has successfully been applied to the Zn sorption on Ca-illite and Ca-smectite. New batch experiments performed in this study enabled to collect sorption data for Zn on Ca-illite by concentration and pH isotherms. Zn sorption reversibility was then verified. These sorption data were modelled successfully with a multi-site ion exchanger (MSIE) formalism by using four sorption site types. Zn sorption isotherms on smectite were retrieved from literature and interpreted following the MSIE formalism. The obtained selectivity coefficients may be thereafter put into ion exchange models to describe the Zn sorption in natural environments.

1 Introduction

In the context of environmental monitoring of nuclear sites, or to evaluate the impact of metallurgic facilities, migration of Zn in soils, sediments and aquifers needs to be understood and well predicted. Migration of trace elements is partly governed by chemical sorption phenomena on mineral surfaces, especially on clay minerals known to have negatively surface charges compensated by cations [1]. Specific sorption sites are recognized for their high affinity for Zn on smectite and illite [2-3]. With this purpose, many sorption models consider sorption processes as ion exchange or surface complexation phenomena [1-5]. A multi-site ion exchanger model [4] using sorption property of pure smectite recently described with success the sorption of Zn on natural sediment under static conditions [5]. In this macroscopic approach, sorption sites are described by their sorption capacities (expressed in mol/kg of solid phase) and their affinity towards chemical elements. Any chemical and mineralogical assignment of the sorption sites is impossible by this sole macroscopic and thermodynamic approach. Sorption experiment data result from pH and concentration isotherms, which support the mineral retention properties.

Among the most abundant minerals in natural soils and sediments, illite and smectite are recognized to play a determining role in cation adsorption. Many studies were dedicated

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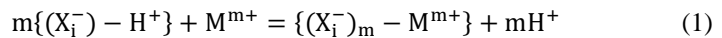
to characterize illite and smectite retention properties, mainly performed on sodic media. On the contrary, despite the extensive presence of Ca in the natural environment, Zn sorption on illite has never been studied in presence of Ca.

The purpose of this study was, (1) to assess the clay mineral exchange properties that drive the Zn uptake on those surfaces, (2) to evidence the affinity of Zn for these minerals and, (3) to discuss the relative role played by clay minerals in Zn adsorption by comparing their respective affinity towards Zn. Filling the data gap on Zn sorption onto Ca-illite, pH and concentration isotherms were acquired in batch experiments. Then, sorption and its reversibility were tested over a large pH range and Zn concentrations. A thermodynamic multi-site ion exchange model was used to interpret these new experimental data and those previously acquired on Ca-smectite [2] and Na-illite [3].

2. Multisite ion exchange model

The Multi-Site Ion Exchanger model is based on thermodynamics of chemical equilibria, and considers minerals as ion-exchangers described by negatively charged adsorption sites. For a complete description of the approach, readers can refer to [1-4, 5]. This theory is only based on a macroscopic description, and does not imply any structural hypothesis on minerals [4]. Thus, the exchange behaviour of each cation (here, Ca^{2+} and Zn^{2+}) has to be studied individually as a function of pH and concentration on purified clay minerals. Then, H^+ is taken as reference cations.

Classically, cation exchange between H^+ and M^{m+} for a given sites X_i^- is expressed by equation 1.



Then, the equilibrium constant of this reaction is written as follow in equation 2:

$$K_{\text{M}^{m+}/\text{H}^+}^i = \frac{(\text{X}_i^- - \text{H}^+)^m (\text{M}^{m+})}{(\text{X}_i^- \}_m - \text{M}^{m+}) (\text{H}^+)^m} \quad (2)$$

$$K_{\text{M}^{m+}/\text{H}^+}^{i*} = \frac{[\text{X}_i^- - \text{H}^+]^m [\text{M}^{m+}] \gamma_{\text{M}^{m+}}}{[(\text{X}_i^- \}_m - \text{M}^{m+}) [\text{H}^+]^m \gamma_{\text{H}^+}} \quad (3)$$

where K^i is the selectivity coefficient, i is the type of sorption site. () and [] represent activities and concentrations of species, respectively. Species in solution are in mol.L^{-1} whereas adsorbed species are in mol.kg^{-1} (of dry clay mineral). f (in kg.mol^{-1}) is the activity coefficient of each adsorbed species and γ (in L.mol^{-1}) is the activity coefficient of the species in solution. All f are unknown and are included in the corrected selectivity coefficient $K_{\text{M}^{m+}/\text{H}^+}^{i*}$.

For cations such as Zn, the complexation in solution by OH^- must be taken into account. Consequently, $\text{Zn}(\text{OH})_2$ complex has been considered to calculate Zn^{2+} concentration at $\text{pH} > 8$, given that $[\text{Zn}^{2+}] = [\text{Zn}(\text{II})]/\alpha_{\text{Zn}}$ with $\alpha_{\text{Zn}} = 1.23$.

In this study, Zn sorption isotherms are acquired on purified illite and Zn sorption data acquired on Ca-smectite were retrieved from [4]. Selectivity coefficients between Ca^{2+} and Zn^{2+} can be determined using the ratio of both $K_{\text{Ca}^{2+}/2\text{H}^+}^i$ and $K_{\text{Zn}^{2+}/2\text{H}^+}^i$ selectivity coefficients.

3 Materials and experimental methods

3.1 Clay conditioning

In order to study Zn^{2+} exchange by only Ca^{2+} on clay sorption sites, illite was conditioned under homo-ionic Ca-form. Thus, illiteSA14(from Les Salins, France, close to le Puy en Velay) was initially purified by dissolving carbonate in 0.1M HCl solution and by sieving at 50 μm . Clay was dispersed in 1M $CaCl_2$ with a 1:10 solid/solution ratio, shaken for 24 h on an orbital shaker and centrifuged to replace the supernatant by a 1M $CaCl_2$ solution. The operation was repeated 5 times. Two similar operations were successively realized with 0.1M $CaCl_2$ and ethanol to eliminate residual salt. After centrifugation, conditioned clay material was left to air-dry for 2 days.

3.2 Sorption isotherm experiments

Two Zn sorption isotherms (pH dependent isotherm and concentration isotherm) were acquired on Ca-illite. Batch sets with 28centrifugation tubes were prepared by dispersing 0.11 g of Ca-conditioned illite in 5 ml of 0.01M $CaCl_2$ solution. In the case of pH isotherm, pH was adjusted for each tube to cover a range from 2 to 12 using HNO_3^- or $Ca(OH)_2$ solutions and tubes were shaken for a few hours. In case of concentration isotherm, 50 μL of $ZnCl_2$ stable solution ranged between 2M to $2 \cdot 10^{-7}M$ was added and pH was maintained to 6.5. Subsequently suspensions were spiked with ^{65}Zn by adding 70 μl of a solution $ZnCl_2$ dissolved in 0.1 M HCl, in order to introduce 9500 Bq in each tube. Then batches were shaken for 6 days. After centrifugation, the activity of 1ml aliquot of supernatant of each tube was measured by gamma counting and the total concentration in solution at equilibrium was measured by ion chromatography.

The concentration of adsorbed Zn is given by:

$$K_d = \frac{[\bar{M}]}{[M]} = \left(\frac{A_0}{A} - 1\right) \frac{V}{m} \quad (4)$$

where K_d is the solid-solution distribution coefficient, $[\bar{M}]$ and $[M]$ are respectively total concentration at equilibrium of adsorbed M and total concentration in solution of M, A_0 is the initial solution activity, A the activity at equilibrium in solution, m the total dry mass of solid and V the total volume of solution.

Zn sorption reversibility was investigated on Ca-illite. Reversibility is achieved when desorption K_d is equivalent to the adsorption K_d . In this case, H^+ and Ca^{2+} concentrations as well as the solid/solution ratio are maintained the same in sorption and desorption experiments.

4. Results and discussion

For illite and smectite adsorption is pH dependent. In case of illite, $\log K_d$ increase from 3 to 5 between pH 2.5 to pH 8 (Fig. 1) until it reaches a plateau with roughly constant $\log K_d$. This highlights the competition with protons and the progressive exchange with Zn on sorption sites, as the electrolyte Ca remain at constant concentration in the system. In figure 2, partitioning coefficients are expressed in function of Zn concentrations measured at sorption equilibrium in the supernatant at fixed pH. $\log K_d$ values for comparable pH and Zn concentrations are similar to those from pH isotherms in both experiments. Zn sorption reversibility is verified on Ca-illite. Illite and smectite have to be described as cation exchangers with four sites. Although, smectite expresses a larger cation exchange capacity

than illite (table 1), the estimated minor sites capacities (X_s and X_0) are close for both clay minerals, reaching 2.7 meq.kg^{-1} and 1.6 meq.kg^{-1} , respectively (table 1). They were estimated at 2 meq.kg^{-1} on a Ca-smectite [2] and on Na-illite [3] to model Zn sorption. The four sites considered in the model allow correct fitting of the illite experimental data (fig. 1 and 2). Individual site contributions show that the high reactive sites (X_0 and X_3) are dominant at pH below 4 (X_0) and up to 7 (X_3) in the Zn uptake. Between pH 4 to 7, the X_2 site contributes whereas the major site X_1 appears with a neglecting effect.

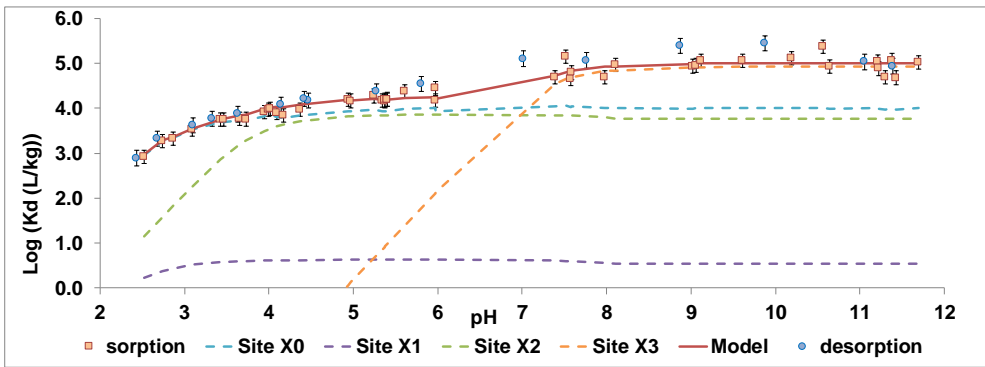


Fig. 1. Logarithm of the Zn distribution coefficient vs. pH at equilibrium on Ca-illite ($I=0.03M$) with introduced Zn concentration at $8.7 \cdot 10^{-6} M$ and the modelling outcome (redline). Contribution of the high-capacity site X_1 (violet dashed line) and the low-capacity site X_0 (blue dashed line), the minor site X_2 and X_3 (resp. orange and green dashed lines).

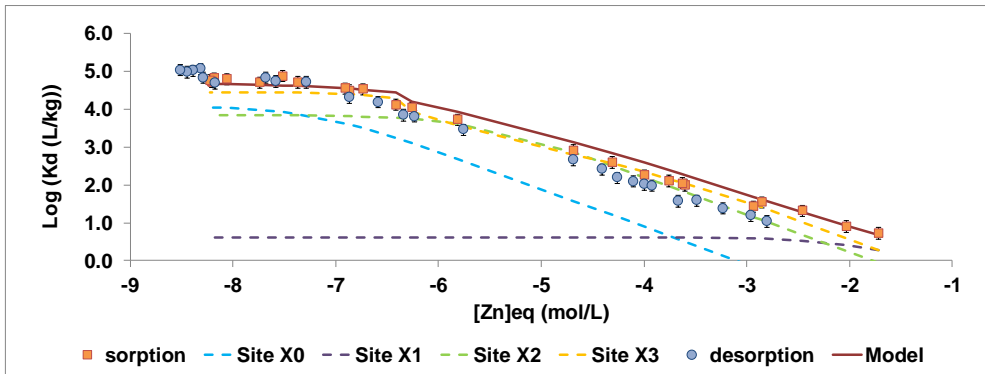


Fig. 2. Logarithm of the Zn distribution coefficient vs. the C_s concentration at equilibrium (pH=7.3) on Ca-illite ($I=0.03M$) and the modelling outcome (redline). Contribution of the high-capacity site X_1 (violet dashed line) and the low-capacity site X_0 (blue dashed line), the minor site X_2 and X_3 (resp. orange and green dashed lines).

Table 1. Site capacities CE_i and selectivity coefficients $K^{i_{2H^+}/Ca^{2+}}$ and $K^{i_{2H^+}/Zn^{2+}}$ of Ca-illite and Ca-smectite [2] determined and used in this study. The uncertainties given correspond to 1σ . "A" marks data issued from [1].

Mineral	Sites	CE_i (eq.kg ⁻¹)	$K^{i_{2H^+}/Ca^{2+}}$ ^A	$K^{i_{2H^+}/Zn^{2+}}$
Illite	X ₀	$1.6 \cdot 10^{-3}$	-0.40 ± 1.98	4.82 ± 0.75
	X ₁	0.13 ^A	-2.17 ± 0.07	-2.35 ± 2.23
	X ₂	0.04 ^A	-4.31 ± 0.272	-0.66 ± 0.61
	X ₃	0.07 ^A	-11.75 ± 0.21	-7.28 ± 0.12
Smectite	X _s	$2.7 \cdot 10^{-3}$	-0.22 ± 0.18	-2.22 ± 0.10
	X _a	0.39 ^A	-0.49 ± 0.49	-0.42 ± 0.37
	X _b	0.36 ^A	-4.35 ± 0.03	-4.08 ± 2.38
	X _c	0.14 ^A	-14.84 ± 0.06	-9.44 ± 0.45

Even that available data on Zn sorption were acquired at different ionic strength, sorption trends due to ionic competition and mineral dependence may be evidenced. Compared to pH sorption isotherm acquired on Na-illite [3], Zn sorption on Ca-illite is lower (Fig. 3) whatever the pH value. This expresses a larger competition between Zn and Ca compared to Na as previously observed on Cs sorption on smectite [6]. Considering the ionic strength difference, Ca-illite adsorbs more Zn than Ca-smectite [2] at $pH < 7$ and inversely at $pH > 7$. This confirms a larger X₀ affinity than the one of X_s.

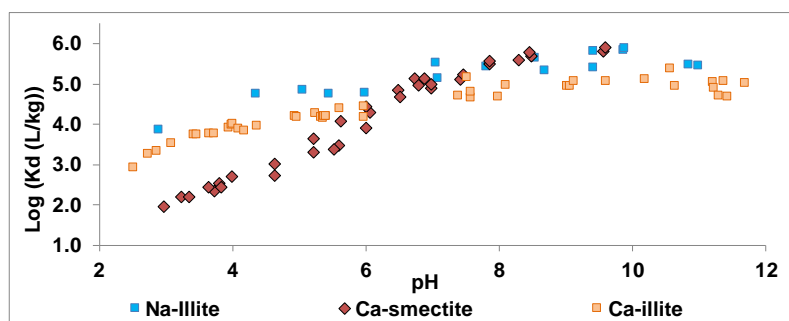


Fig. 3. Logarithm of the Zn distribution coefficient vs. pH at equilibrium on Ca-illite ($I=0.03M$, this study), on Ca-smectite ($[Ca(NO_3)_2]= 3.3 \cdot 10^{-3} M$ [4]) and on Na-illite ($[NaClO_4]= 0.1M$, [5]).

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