

Research Article

Selectivity of Na-Montmorillonite versus Concentration of Two Competitive Bivalent Cations (Cu^{2+} , Pb^{2+}): Quantitative XRD Investigation

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The goal of this paper is to examine, by quantitative XRD analysis, the effect of heavy metal cation concentrations (Pb^{2+} , Cu^{2+}) on the selectivity phenomenon in the case of dioctahedral smectite (i.e., Na-montmorillonite). The quantitative XRD analysis is achieved using an indirect method based on the comparison of experimental XRD profiles to those calculated using structural models. The obtained results show that for strong metals concentrations (i.e., 10^{-1}N), the host material presents heterogeneous structure characterized by interstratified hydration states between 1 W and 2 W (i.e., respectively, one and two water layer hydration state) attributed to Pb^{2+} cation. For low concentration, the d_{001} values investigation indicates that montmorillonite remains saturated with Na^+ characterized by homogeneous 1 W hydration state.

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1. Introduction

Montmorillonite is a clay mineral characterized by its capacity to exchange cations in the interlamellar space with others present in external solutions. Indeed, it is a clay mineral with “T-O-T” layer consisting of an octahedral sheet sandwiched by two tetrahedral sheets [1–3]. Isomorphic substitutions in octahedral and/or tetrahedral sheets commonly make the clay platelets negatively charged, which is compensated by exchangeable cation. These characteristics were controlled by the cationic exchange capacity (CEC) properties. Several works [4–10] studied the case where the starting sample is in contact with solutions containing only one metallic cation (i.e., monovalent or bivalent) and show a different hydration behavior related to the nature of exchangeable cation. The selectivity exchange problem was defined by the presence of several metallic cations in solution, which is the most realistic case if we want to apply clay properties in the context of industrial waste storage. This aim was approached by several research tasks [11–15]. Indeed, metal contamination is a persistent problem in many infected soils. The most commonly occurring metals are Cd^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} , Cr^{2+} , Zn^{2+} , and Hg^{2+} [16].

The various studies [17–22] related to the adsorption of heavy metals in clays indicated minor role of the CEC properties. Indeed, Alloway [23] shows that ionic exchange affinity increases with ionic valence and at the same charge value the cation with higher ionic radius was preferentially adsorbed (i.e., $\text{Pb}^{2+}(0.12\text{ nm}) > \dots > \text{Cu}^{2+}(0.072\text{ nm})$).

In this paper, we will study by investigation CEC properties, the selective exchange process of Na-montmorillonite in contact with solutions containing a couple of heavy metal cations (i.e., Cu^{2+} and Pb^{2+}) with variable concentrations. This study is coming in continuation with already established results in the case of reference samples (i.e., sample where exchangeable sites are saturated by one type of species) studied by Oueslati [10]. This work is divided into two complementary large shutters: qualitative and quantitative XRD analyses.

2. Materials and Methods

2.1. Samples. Montmorillonite fractions were prepared according to the classic protocol of extraction [24]. The $<2\ \mu\text{m}$ fraction of montmorillonite (Wyoming, USA) was

TABLE 1: d_{001} and FWHM of the 001 reflection are given respectively in Å and in $^\circ 2\theta$ -CuK α . The ξ parameter is calculated as the standard deviation of the $l \times (00l)$ values calculated for the Xi measurable reflections over the 2–35 $^\circ 2\theta$ CuK α angular range.

Normality	d_{001}	FWHM	ξ (Å)	Character
10^{-2} N	12.53	0.984	0.88	Interstratified
10^{-3} N	12.40	0.418	0.20	Homogeneous
10^{-4} N	12.36	0.413	0.11	Homogeneous

supplied by the Source Clay Minerals Repository Collection. Its half-cell structural formula, as obtained by electron microprobe, is: $\text{Si}_{3,923}\text{Al}_{0,077}(\text{Al}_{1,459}\text{Ti}_{0,018}^{4+}\text{Fe}_{0,039}^{3+}\text{Fe}_{0,045}^{2+}\text{Mg}_{0,382}^{2+})\text{O}_{10}(\text{OH})_2(\text{Ca}_{0,177}^{2+}\text{Na}_{0,027}^+)$.

The Na saturated smectites were prepared by dispersing suitable amounts of the montmorillonite several times in 1 N NaCl solution. The excess of chloride was removed by washing the clay in distilled water and by subsequent dialysis. In order to study selectivity process, we dispersed Na-montmorillonite in solutions containing 0.5 Cu $^{2+}$ and 0.5 Pb $^{2+}$. To investigate the concentration effect, we precede by dilutions until weak normality values 10^{-4} N. An oriented preparation was prepared by depositing a clay suspension on to a glass slide [25, 26].

2.2. Experimental. The XRD patterns, of oriented and air-dried specimens, were obtained by reflection setting with a D8 Advance Bruker installation using Cu-K α radiation and equipped with solid-state detector. Intensities were measured at an interval of 2θ equal to 0.04° and 40–50 s counting time per step. The absolute precision of the Bragg angles was better than 2θ 0.01° over the whole angular range.

2.3. XRD Profile Modeling. Quantitative XRD analysis aims to determine structural parameters by comparing the experimental patterns with the theoretical intensities calculated from the matrix formalism given by Drits and Tchoubar [27]:

$$I_{00}(2\theta) = L_p \text{Spur} \left(\text{Re}[\emptyset][W] \left\{ [I] + 2 \sum_n^{M-1} \left[\frac{(M-n)}{M} \right] [Q]^n \right\} \right). \quad (1)$$

This method allowed us to determine the abundances (Wi), the mode of stacking of the different kinds of layers, and the mean number of layers per coherent scattering domain (CSD) [28, 29]. Within a CSD, the stacking of layers is described by a set of junction probabilities (P_{ij}). The relationships between these probabilities and the abundances (Wi) of the different types of layers are given by Drits and Tchoubar [27]. The XRD patterns were calculated using the z coordinates of Sakharov and Drits [30]. The origin of these coordinates was placed on the plane of surface Oxygen atoms [27]. The overall fit quality was assessed using the unweighted R_p parameter [31]:

$$R_p = \sqrt{\frac{\sum [I(2\theta_i)\text{obs} - I(2\theta_i)\text{calc}]^2}{\sum [I(2\theta_i)\text{obs}]^2}}. \quad (2)$$

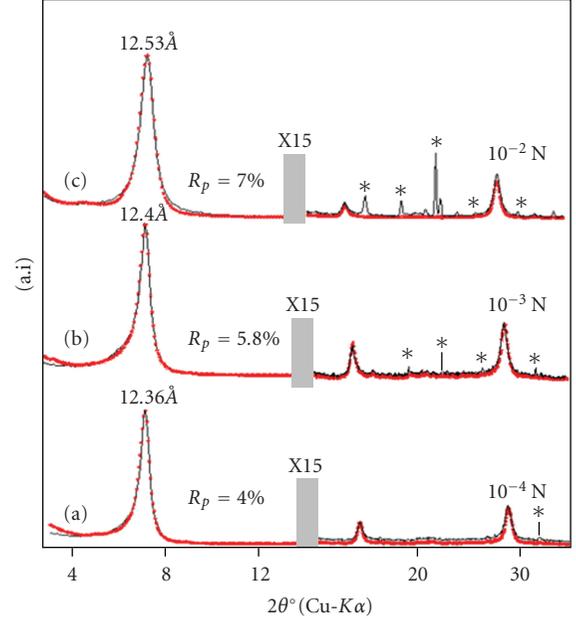


FIGURE 1: Best agreement between experimental (—) and theoretical (***) XRD patterns obtained for decreasing normality (i.e., 10^{-2} N(c), 10^{-3} N(b) and 10^{-4} N(a)) in the case of (0.5 Cu $^{2+}$ and 0.5 Pb $^{2+}$) solutions. d_{001} are given in(Å). R_p : goodness of fit parameter. The gray bar (Int X15) indicates a modified scale factor for the high-angle region. (*): Laurionite (PbOHCl) pat ref 74-2022(c).

R_p is mainly influenced by the most intense diffraction maxima, such as the 001 reflections, which contains essential information on the proportions of the different layer types and thickness.

3. Results

3.1. Qualitative XRD Investigation. We present in Figure 1 the different XRD patterns obtained from decreasing normality (i.e., 10^{-2} N \rightarrow 10^{-4} N) in the case of mixture containing 50% Cu(II), 50% Pb(II). We show supplementary reflection attributed to excess of salt in host solution identified by the Eva release software. We calculated for all experimental patterns the FWHM of the 001 reflection and the ξ parameter which was calculated as the standard deviation of the $l \times d(00l)$ values for all measurable reflections over the 2–35 $^\circ 2\theta$ angular range [5] (Table 1). In the case of 10^{-3} N and 10^{-4} N, the d_{001} values indicate quasi homogeneous 1W hydration state confirmed by a low FWHM and ξ parameter value (Table 1) [7]. For 10^{-2} N, we note heterogeneous hydration state characterized by an asymmetric 001 reflection profile with $d_{001}=12.53$ Å. This interstratified character traduced by irrationality of reflection position is accompanied by an increase of FWHM and ξ parameter values (Table 1).

3.2. Quantitative XRD Investigation. To simulate the XRD pattern related to low normality (i.e., 10^{-4} N) (Figure 1(a)),

TABLE 2: Structural parameters deduced from quantitative XRD analysis. Exch.cation: exchangeable cations, Z_n : coordinates of the exchangeable cations (i.e., the origin of these coordinates was placed on the plane of surface Oxygen atoms [27]), $Z_{H_2O}(\text{\AA})$: coordinate of the water molecule sheets, M: the number of layers per stack W_A, W_B : abundances of the different types of layers.

Sample	Layer Thickness (\AA)	Exch.Cation	Z_n (\AA)	Z_{H_2O} (\AA)	$W_A W_B$	Character	M
10^{-2} N	12.4–15.4	Pb ²⁺	9.8	9.8	0.91	Interstratified	6
	12.4	Cu ²⁺	11.2	9.4–13.7	0.09	Homogeneous	
10^{-3} N	12.3	Na ⁺	9.5	9.5	0.96	Homogeneous	8
	12.4–15.4	Pb ²⁺	11.4	9.4–13.7	0.04	Interstratified	
10^{-4} N	12.4	Na ⁺	9.8	9.8	1.00	Homogeneous	8

we suppose that the host material maintains her interlamellar cation (i.e, Na⁺) and the cationic exchange process is not triggered due to the low population number of exchangeable species in the solution. For this reason, we used structural theoretical model containing one layer type saturated by Na⁺ cation regularly stacked (Table 2).

For 10^{-3} N, the best agreement between theoretical and experimental XRD patterns (i.e., $R_p = 5.8\%$) was obtained using 96% of homogeneous (1W) hydration state (i.e., Na⁺ saturated phases) and 4% of interstratified (1W-2W) hydration state (i.e., Pb²⁺ saturated phases) stacked randomly (Figure 1(b)). This quantitative result was interpreted by a minor contribution of Pb²⁺ in the cationic exchange process due to its low abundance (Table 2).

For 10^{-2} N (Figure 1(c)), the 001 reflections are situated at $2\theta = 7.20$ indicating probably a partially saturation of the CEC sample with Pb²⁺ cation. The best agreement (i.e., $R_p = 7\%$) can be obtained by supposing presence of two types of layers saturated respectively by Pb²⁺ and Cu²⁺ stacked with segregation tendency (Table 2). For all studied samples, we note weak fluctuation of the number of layers per stack.

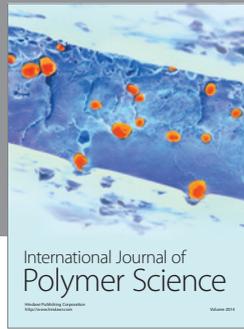
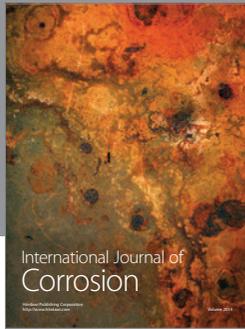
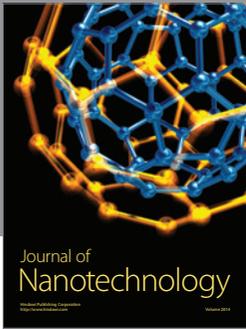
4. Conclusion

In this study we attempt to determine the effect of solution concentration on the natural selective exchange process for dioctahedral smectites. This problem is usually encountered if we want to apply clay properties in the context of industrial waste storage. We choose two competitive heavy metal cations (i.e., Pb²⁺ and Cu²⁺), since these cations occur frequently with variable concentration within household waste. The results obtained in this regards showed that: for low concentration and by using XRD profile investigation, we demonstrate that the clay remains saturated with Na⁺ cation and the clay CES (i.e., cationic exchange selectivity) is in favor of Na⁺ cation which is characterized by low hydration state. For high concentration, clay fixes the Pb²⁺ cations which are characterized by an interstratified hydration state ($d_{001} = 12.53 \text{\AA}$). This result is in accordance with sorption selectivity study in different soils [32–34] which is demonstrated that, at variable pH solution, the selectivity soil order for some studied heavy metal cations (i.e., Cu²⁺, Zn²⁺, Cd²⁺, Mg²⁺ and Pb²⁺) is usually in favor of Pb²⁺ cation.

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