

# Structural Properties of Synthetic Na-Hectorite Exchanged with Heavy Metals

Karmous Mohamed Salah

Département de physique, Faculté des Sciences de Sfax Route de la Soukra km 4, Sfax, Tunisie.  
Email: karmoussalah@yahoo.fr

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## ABSTRACT

*The main objective of this study is to determine the structural characteristics of synthetic Na-Hectorite (H-Na) exchanged with heavy metals: Ni<sup>2+</sup>, Pb<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Co<sup>2+</sup> and Mg<sup>2+</sup> using quantitative analysis based on the comparison between the theoretical and experimental XRD patterns. The different complexes are not homogenous. The hectorite saturated by the lead and cadmium present a segregation distribution of the layers, where as the others complexes present a random distribution.*

**Keywords:** Hectorite, XRD, Heavy Metals, Simulation

## 1. Introduction

Heavy metal pollution occurs in many industrial wastewater such as those produced by metal-plating, finishing facilities, dyeing operations, mining and metallurgical engineering, electroplating, nuclear power plants, aerospace industries, battery manufacturing processes and glass production etc. The presence of heavy metals in the aquatic ecosystem has been of increasing concern because of their toxic properties and other adverse effects on natural waters quality, such as Ni, Cu, Zn, Cr, Cd and Pb.

The most important distinctive feature of clay minerals is their ability to balance with geochemical conditions. Clay mineral stability in changing environment is the function of their origin, structure, elementary cell charge and dispersion [1-3]. Heavy metal cations can be immobilized on silicates by two mechanisms: ion-exchange and chemisorption [4]. Ion-exchange involves a substitution of ions present in silicate crystalline lattice by metal ions from the solution. Ion exchange properties of smectites are connected with the presence of non-compensated negative charges [5]. Clay minerals (smectites) in soil play the role of a natural barrier.

In one hand, Pb (II) can be removed from aqueous/acidic solutions by using bentonite and natural sepiolite as an adsorbent [6,7]. The removal of Cu (II) from aqueous solution by using kaolinite, montmorillonite and their modified adsorbents [8]. In other hand, Ni(II) and Cu(II) were trapped in smectite structure using

ion-exchange mechanism [2,5].

Hectorite is one of the triocathedral subgroup of the smectite. The Mg (II) dominates the octahedral sites in both these minerals and a partial substitution of Li(I) for Mg(II) occurs in hectorite. Isomorphic substitution within the tetrahedral and/or octahedral sheets causes a negative charge on the layers, which is balanced by hydrated exchangeable cations in the interlayer space (mainly Ca<sup>2+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup>). The hydration states varies and depends on many factor related to the composition of the layers and the nature of the interlayer cation [2,3].

The work described in this paper was designed to study the possibility of trapping heavy metals into hectorite structure using XRD simulation.

## 2. Materials and Methods

### 2.1. Synthesis

The synthetic hectorite sample was prepared by hydrothermal treatment of hydrolyzed gels prepared by coprecipitation of Na, Mg, Al, and Si hydroxides at pH = 14, according to a slightly modified version of the gelling method of Hamilton and Henderson [9]. The source of Na was sodium carbonate, the sources of Al and Mg were titrated solutions of their nitrates. The source of Si was (C<sub>2</sub>H<sub>5</sub>O)<sub>4</sub>Si (TEOS). This resulting gel is slowly dried up to 200°C. It is then calcined at 600°C by further temperature increase. It is then introduced in Morey type externally heated pressure vessels in which the samples

are insulated from the vessel wall by a silver coating. The hydrothermal reactor was then heated at 400°C under a 1000 bar water pressure. Samples were recovered after four weeks. The started synthetic material has a structural formulae:  $[\text{Na}_{0.4}]^{\text{inter}}[\text{Mg}_{2.6}\text{Li}_{0.4}]^{\text{oct}}[\text{Si}_4]^{\text{tet}}\text{O}_{10}(\text{OH})_2 \cdot x \text{H}_2\text{O}$  ( $x$  is the number of water molecule per cation). Hectorite exchanged with  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Co}^{2+}$  were prepared by conventional ions exchanges reactions using respectively aqueous solutions of 0.1M of  $\text{CoCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{PbCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{ZnCl}_2$  and  $\text{NiCl}_2$ . Removal of excess chloride was performed by washing in distilled water until a negative  $\text{AgNO}_3$  test was obtained; the solids were deposited on glass slide to obtain an oriented aggregate; the samples are referred as H-Cd and H-Co, H-Ni, H-Zn, H-Mg and H-Pb.

## 2.2. X-Ray Measurement and Simulation Principle

XRD patterns were recorded using a Brüker D8-advance using Cu-K $\alpha$  radiation (1.5406 Å). Data were recorded in the range 5° - 50°2 $\theta$  with a step of 0.02°2 $\theta$  and 0.05 s per step. The mineralogical and structural characteristics were determined by comparing the experimental X-ray patterns with the theoretical patterns calculated from structural models [10,11] and permits determination of the number and the position of the intercalated water molecules. The XRD patterns were calculated using the  $z$ -coordinates, where the origin of the atomic coordinates was taken at the basal oxygen atoms [2]. The diffracted intensity for a unit-cell along the 00 rod of the reciprocal space is given by the following expression [12]:

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

with  $L_p = \psi \frac{1 + \cos^2 2\theta}{\sin 2\theta}$  [12], where  $\psi$  is the orientation factor of the particles and where Re is the real part of the final matrix, Spur, the sum of the diagonal terms of the real matrix;  $M$ , the number of layers per stack;  $n$ , an integer varying between 1 and  $M - 1$ ;  $[\phi]$ , the structure factor matrix;  $[I]$ , the unit matrix;  $[W]$ , the diagonal matrix of the proportions of the different kinds of layers, and  $[Q]$  the matrix representing the interference phenomena between adjacent layers. For a system made up of two types of layers ( $A$  and  $B$ ) and a nearest neighbour interaction,  $[Q]$  takes the form:

$$\det Q = \begin{vmatrix} P_{AA} \exp(-2i\pi s d_A) & P_{AB} \exp(-2i\pi s d_A) \\ P_{BA} \exp(-2i\pi s d_B) & P_{BB} \exp(-2i\pi s d_B) \end{vmatrix} \quad (2)$$

where  $s$  is the modulus of the scattering vector;

$s = \frac{2 \sin \theta}{\lambda}$ ,  $d_A$  and  $d_B$  are the  $d$ -spacing of layer  $A$  and layer  $B$ , respectively, and  $P_{AB}$  is the conditional probability of passing from a layer  $A$  to layer  $B$ . The relationship between the different kinds of layer proportions and probabilities are given by:

$$W_A + W_B = 1, P_{AA} + P_{AB} = 1, P_{BA} + P_{BB} = 1 \\ \text{and } W_A P_{AB} = W_B P_{BA}.$$

The relationships between these probabilities and the abundances  $W_A$  and  $W_B$  of the different types of layers are given by Drits and Tchoubar [11]: 1) the segregation tendency is given by:  $W_A < P_{AA}$  and  $W_B < P_{BB}$ , 2) The total demixion is obtained for  $P_{AA} = P_{BB} = 1$ , 3) The regular tendency is obtained if:  $W_A < P_{BA} < 1$  and  $W_B < P_{AB} < 1$  and finally the limit between the last distribution labelled random distribution when  $W_A = P_{BA} = P_{AA}$  and  $W_B = P_{AB} = P_{BB}$ ; with  $\sum W_A = 1$ ,  $\sum P_{AB} = 1$ .

The overall fit quality was assessed using the unweighted  $R_p$  parameter [13]:

$$R_p = \sqrt{\frac{\sum [I_{obs}(2\theta_i) - I_{calc}(2\theta_i)]^2}{\sum I_{obs}(2\theta_i)^2}} \quad (3)$$

where  $I_{obs}$  and  $I_{calc}$  represent respectively measured and calculated intensities, at position  $2\theta_i$ , the subscript  $I$  running over all points in the refined angular range. This parameter is mainly influenced by the most intense diffraction maxima, such as the 001 reflection, which contains essential information on the proportions of the different layer types and on their layer thickness.

## 3. Results and Discussion

### 3.1. Qualitative Description of Experimental Patterns

**Figure 1** shows the evolution of the  $d(001)$  values measured on the experimental XRD patterns. The different values of the samples are listed also in the **Table 1** with the full width at half maximum intensity (FWHM) of the 001 reflection. The qualitative survey of diffractions patterns shows that in most of these diffractograms a dissymmetry with regard to the first order and it is very remarkable for the two complex H-Ni and H-Pb (**Figures 1(d), 1(e)**), for all the complexes the basal distances are all inferior to 15 Å except the H-Zn complex (**Figure 1(f)**) where the  $d(001)$  is equal to 15.58 Å. For superior orders, it is clear the presence of the 002-003-004-005 reflections (H-Zn), the 002 reflection decreases for the H-Cd, H-Co and H-Mg (**Figures 1(a) to (c)**) and this reflection disappears for the H-Ni and H-Pb (**Figures 1(d), 1(e)**),

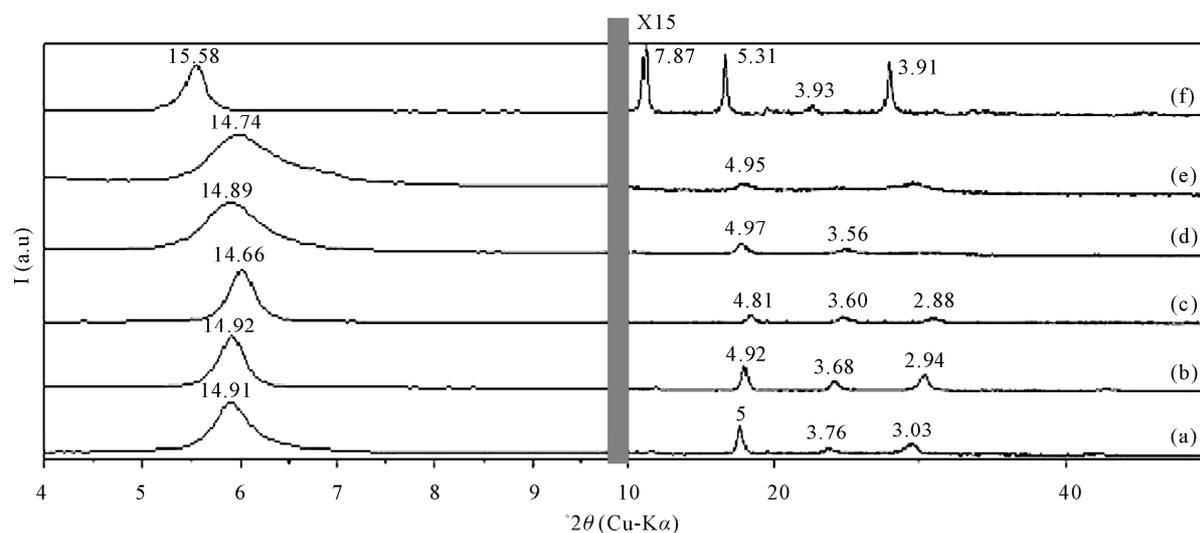


Figure 1. XRD patterns of the Hectorite saturated by: (a) Cd, (b) Co, (c) Mg, (d) Ni, (e) Pb and (f) Zn.

Table 1. The different basal distance of the hectorite complexes and their respective FWHM.

Complexes	$d_{001}(\text{Å})$	FWHM
H-Cd	14.91	0.416
H-Co	14.92	0.278
H-Pb	14.74	0.690
H-Ni	14.89	0.590
H-Mg	14.66	0.276
H-Zn	15.58	0.221

the 003-004 and 005 reflections decreases for all the complexes H-Cd, H-Co (**Figures 1(a), 1(b)**) and these orders had a weak intensity for the H-Mg, H-Ni and H-Pb (**Figures 1(c)-(e)**). We can conclude that all the complexes present a bilayer water in the interlayer space; now we will try to determine the number and the position of the water molecules surrounding the different cations and show if our complexes are homogenous or not. Looking at the FWHM values (**Table 1**), we remark that the biggest values are attributed to the H-Pb and H-Ni complexes and for the others these values are still so similar.

### 3.2. Quantitative Description of Some Complexes

The hydration state of smectites has been described using four layer types of different layer thickness and corresponding to the most common hydration states reported for smectites in non-saturated conditions: dehydrated layers (0 W, layer thickness  $\sim 9.6 - 10.1 \text{ Å}$ ), monohydrated layers (1 W, layer thickness  $\sim 12.3 - 12.7 \text{ Å}$ ), and bi-hydrated layers (2 W, layer thickness  $\sim 15.1 - 15.8 \text{ Å}$ ) and trihydrated (3 W, layer thickness  $\sim 18 - 19 \text{ Å}$ ) layers, the

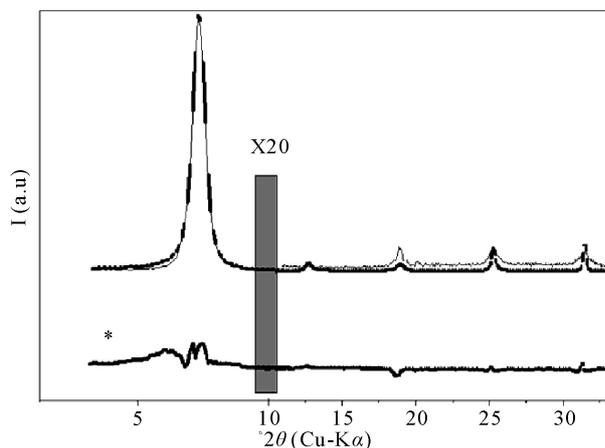
latter being less common [14,15].

H-Mg: The first remark to mention is that the H-Mg is not totally homogenous, we try to determine the different phases which exist in the complexes and this using the quantitative study of the XRD pattern. The best agreement (**Figure 2**) between the theoretical and experimental pattern is obtained with an abundance of:  $W_A = 0.912$ ,  $W_B = 0.0880$  and the respective probabilities are:  $P_{AA} = 0.912$ ,  $P_{AB} = 0.0880$ ,  $P_{BA} = 0.912$ ,  $P_{BB} = 0.0880$ , the major phase (phase A) is a bilayer one characterised by a basal distance of  $15.2 \text{ Å}$ , the second phase (phase B) is so minor and characterised by a basal distance of  $18.44 \text{ Å}$ .

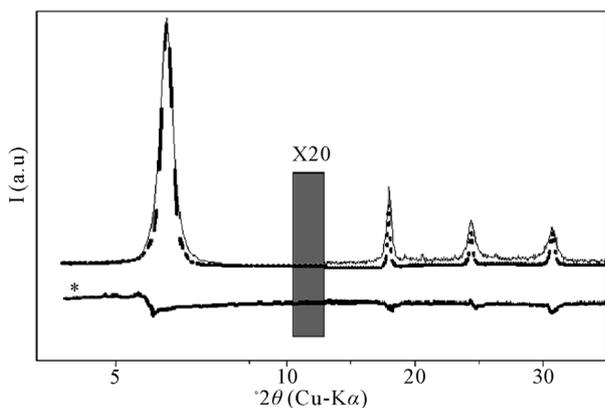
This agreement is obtained with a Rp factor equal to 3.5%. This result converges to the results found by Skipper [16] and Greathouse [17] using Monte Carlo simulation concluded that the  $\text{Mg}^{2+}$  cations are systematically octahedrally coordinated in 2W smectites and located in the mid-plane of the interlayer.

H-Cd and H-Co: The H-Cd complex is characterised by a basal distance situated at  $14.91 \text{ Å}$ . The best agreement between theoretical and experimental pattern is obtained using with an abundance of:  $W_A = 0.78$ ,  $W_B = 0.22$  and the respective probabilities are:  $P_{AA} = 0.9$ ,  $P_{AB} = 0.1$ ,  $P_{BA} = 0.35$ ,  $P_{BB} = 0.65$  (**Figure 3**). With A is a bilayer hydrated state ( $d_{001} = 15.2 \text{ Å}$ ) and B is a one hydrated layer ( $d_{001} = 12.4 \text{ Å}$ ) The Rp factor is equal to 6.2%.

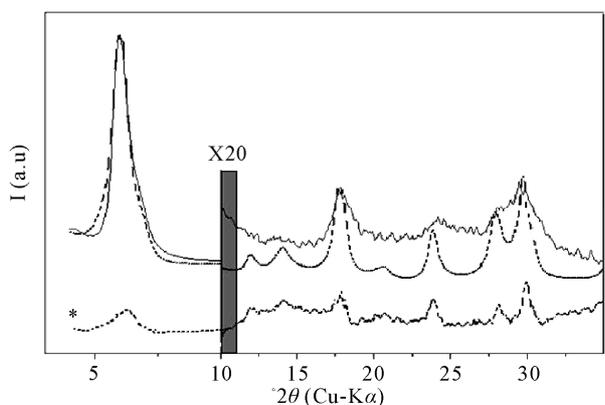
H-Pb: The  $d_{001}$  basal distance appears at  $14.91 \text{ Å}$ . The complex is not homogenous; the abundance of each phase are  $W_A = 0.6$ ,  $W_B = 0.4$  where A is a bilayer hydrated state ( $d_{001} = 15.2 \text{ Å}$ ), and B is a one hydrated layer ( $d_{001} = 12.4 \text{ Å}$ ), the respective probabilities are  $P_{AA} = 0.8$ ,  $P_{AB} = 0.2$ ,  $P_{BA} = 0.3$ ,  $P_{BB} = 0.7$ . The best agreement between calculated and experimental XRD patterns is re-



**Figure 2.** The best agreement between theoretical (---) and experimental (—) pattern of the H-Mg complex, (\*): represents the difference between theoretical and experimental patterns.



**Figure 3.** The best agreement between theoretical (---) and experimental (—) patterns of the H-Cd complex (\*): represents the difference between theoretical and experimental patterns.



**Figure 4.** The best agreement between theoretical (---) and experimental (—) patterns of the H-Pb complex; (\*): represents the difference between theoretical and experimental patterns.

ported on the **Figure 4**.

These results obtained from XRD simulation of different Hectorite complexes shows the possibility to trap heavy metals cations in interlayer space; these hydrated cations causes regular or random distribution of layers; this is lead us to consider that Hectorite can be a good natural barriers for heavy metals cations.

#### 4. Conclusions and Discussion

This study allows to study the structural and hydration properties of the synthetic hectorite exchanged with heavy metals, the hectorite saturated by the lead and cadmium present a segregation distribution of the layers, where as the others complexes present a random distribution of layers.

The nature of change in layer distribution is due to the difference between heavy metals cations, in fact,  $Pb^{2+}$  cations are less hydrated and more strongly connected with ion-exchange surface centers as compared to zinc cations [18].

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