



Selectivity of Na–montmorillonite in relation with the concentration of bivalent cation (Cu^{2+} , Ca^{2+} , Ni^{2+}) by quantitative analysis of XRD patterns

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ABSTRACT

This paper aims at characterizing the structural evolution and the selectivity of a dioctahedral smectite (i.e. Wyoming montmorillonite) saturated with two different couples of cations. A reference sample was prepared by saturation with Ca^{2+} , Cu^{2+} or Ni^{2+} . The clay was dispersed in solutions of (Ca^{2+} and Cu^{2+}) or (Cu^{2+} and Ni^{2+}). The quantitative analysis of XRD patterns is achieved using an indirect method based on the comparison of XRD experimental patterns to calculated ones. The XRD quantitative analysis shows that for low concentrations of cations the basal spacing value corresponds to Wy–Cu, whereas for high concentration the d_{001} spacing value can be attributed to Wy–Ca or Wy–Ni. At low concentrations, the exchangeable sites were saturated with low hydration-state cations (i.e. Cu^{2+}) which is characterized by one water layer, whereas at high concentrations, the clay fixes the cations with high hydration state (i.e. Ca^{2+} or Ni^{2+}) characterised by a two water layers.

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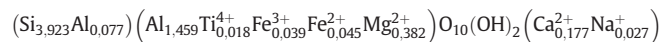
1. Introduction

Several study investigated the interaction between cations and clay mineral, but in general, authors focused on monoionic minerals (Pons et al., 1981; Ben brahim et al., 1983; Drits et al., 1984; Chang et al., 1997; Ben Rhaïem et al., 1998; Viani et al., 2002; Ferrage et al., 2005). However clays in soil are in contact with solutions which contain more than one cation. The behaviour of clay minerals in presence of several cations has been insufficiently investigated. The main objective of this study is to characterise the structural changes induced by the presence of heavy metal cations, especially the selectivity of a dioctahedral smectite (Wyoming montmorillonite) in presence of two pairs of cations: (Cu^{2+} , Ca^{2+}) and (Cu^{2+} , Ni^{2+}) at variable concentrations. One of the most effective methods for identifying and determining the structural characteristics is X-ray diffraction (XRD) analysis with both qualitative and quantitative interpretation. The structural characteristics were determined using an indirect method based on the comparison of the experimental ($00l$) reflections obtained from oriented films with reflections calculated from structural models.

2. Materials and methods

The montmorillonite fractions were prepared according to the classic protocol of extraction (Robert and Tessier, 1974). The $<2 \mu\text{m}$ fraction of montmorillonite (Wyoming, USA) as supplied by the Source Clay Minerals

Repository Collection. Its half cell structural formula, as obtained by electron microprobe (Ben Rhaïem, 1983), is:



The Na saturated clay minerals were prepared by dispersing suitable amounts of the montmorillonite several times in 1 N NaCl

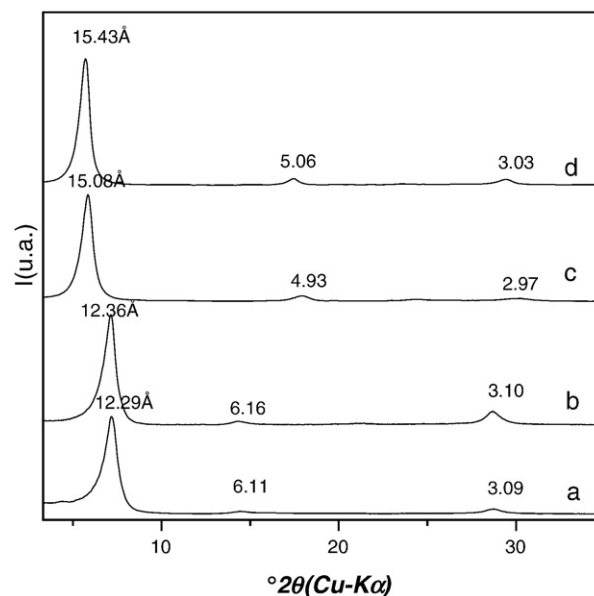


Fig. 1. Experimental XRD patterns of: Wy–Na(a), Wy–Cu(b), Wy–Ni(c), Wy–Ca(d).

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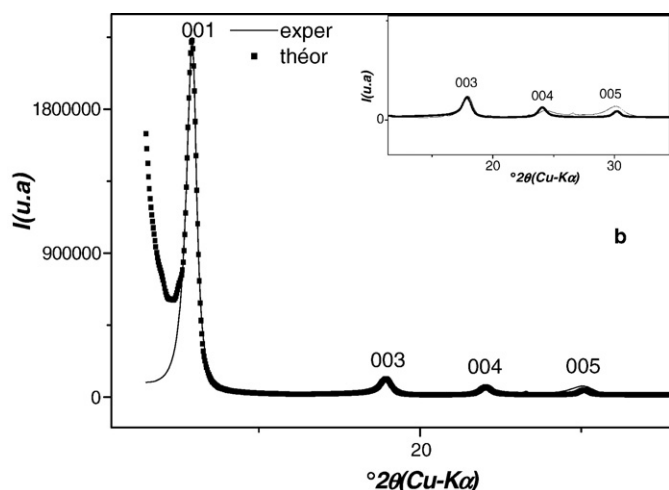


Fig. 2. Comparison between experimental and calculated XRD patterns of Wy-Ni.

solution. The samples were then exchanged with 1 N calcium chloride, nickel chloride or cooper chloride solution yielding Wy-Ca, Wy-Ni and Wy-Cu. The excess of chloride was removed by washing the clay in distilled water and by subsequent dialysis. To study the selectivity of the montmorillonite, we dispersed the Wy-Na in three solutions containing (0.5Cu²⁺,0.5Ca²⁺), (0.2Cu²⁺, 0.8Ca²⁺) and (0.5Cu²⁺, 0.5Ni²⁺). The total normality of the solution varied from 1 N to 10⁻³ N.

The XRD pattern of oriented and air-dried specimen were obtained by reflection setting with a D8 advanced Bruker installation using Cu-Kα 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 equal 0.01° over the whole angular range.

An oriented preparation was prepared by depositing the montmorillonite dispersion on a glass slide. For qualitative identification, XRD patterns were recorded on air-dried and we used EVA release software. The quantitative analysis aims to determine the structural parameters by comparing the experimental patterns with the theoretical intensities calculated from the matrix expression (Drits and Tchoubar, 1990; Ben Rhaiem et al., 1998):

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

Where Re indicates the real part of the final matrix; Spur, the sum of the diagonal terms of the real matrix; L_p, the Lorentz-polarization factor; M, the number of layers per stack; n, an integer varying between 1 and 1-M-1; [Φ], 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 between adjacent layers. This method allowed us to determine the

Table 1

Structural parameters for the reference samples: n, Zn number and position of exchangeable cations per half unit cell, W₁, W₂ mass abundance for layer 1 and layer 2; P_{ij}, P_{ji} succession law between layer 1 and layer 2, M: layer number per stacking, * absence of second phase (homogeneous hydration state)

Samples	d ₀₀₁ (Å)	Cation	n	Zn (Å)	W ₁	P _{ij}	M
					W ₂	P _{ji}	
Wy-Na	12.30	Na ⁺	0.33	09.80	1.00	1.00	8
	*	*	*	*	0.00	0.00	
Wy-Cu	12.36	Cu ²⁺	0.17	10.00	1.00	1.00	8
	*	*	*	*	0.00	0.00	
Wy-Ni	15.08	Ni ²⁺	0.17	11.80	0.92	0.95	7
	17.80	Ni ²⁺	0.17	13.30	0.08	0.58	
Wy-Ca	15.43	Ca ²⁺	0.16	10.90	0.92	0.95	8
	18.15	Ca ²⁺	0.16	12.85	0.08	0.58	

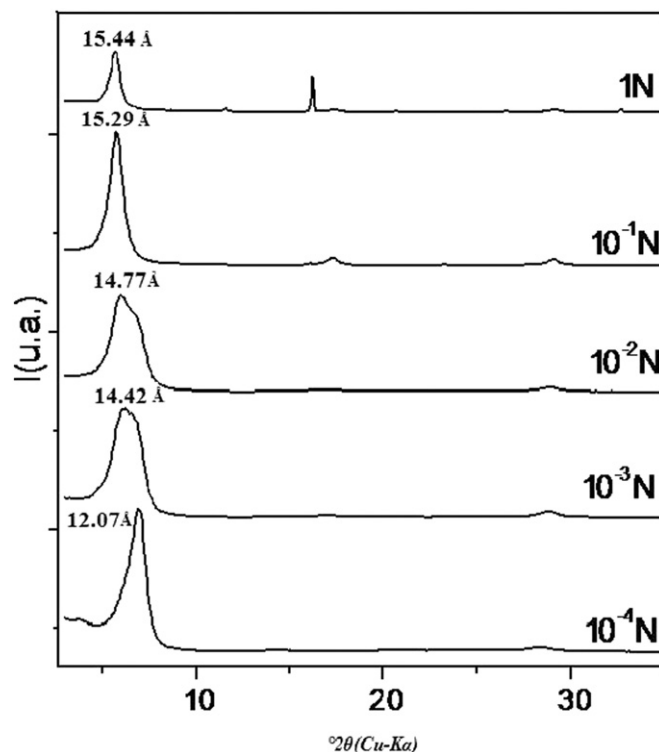


Fig. 3. XRD patterns of Wy-Na dispersed in solutions with molar fractions 0.5 Ca²⁺ and 0.5 Cu²⁺ with normality from 1 N to 10⁻⁴ N.

abundances (W_i), the mode of stacking of the different kinds of layers and the mean number of layers per coherent scattering domain (CSD) (Mering, 1949; Ben Rhaiem et al., 2000). 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 W_i of the different types of layers are given by (Drits and Tchoubar, 1990):

$$\sum W_i = 1, \sum P_{ij} = 1, \sum W_i P_{ij} = W_j$$

Where P_{ij} is the probability of an i layer to be followed by a j layer. The XRD patterns were calculated using the z coordinates of

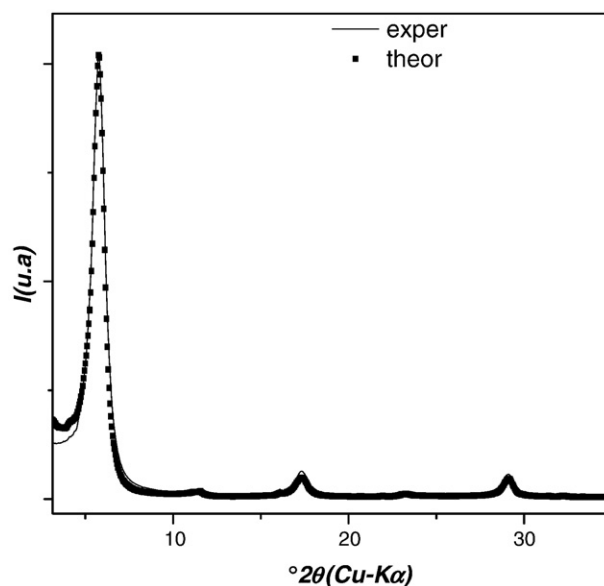


Fig. 4. Comparison between experimental and calculated XRD patterns at 10⁻¹ N solutions.

Table 2

Structural parameters for Wy–Na dispersed in solutions of molar fractions 0.5 Ca²⁺ and 0.5 Cu²⁺ (* absence of second phase (homogeneous hydration state))

Normality	<i>d</i> ₀₀₁ (Å)	Cation	<i>n</i>	Zn (Å)	<i>W</i> ₁	<i>P</i> _{ij}	<i>M</i>
					<i>W</i> ₂	<i>P</i> _{ji}	
1 N	15.44	Ca ²⁺	0.17	10.20	1.00	1.00	6
	*	*	*	*	0.00	0.00	
10 ⁻¹ N	15.29	Ca ²⁺	0.17	9.60	1.00	1.00	7
	*	*	*	*	0.00	0.00	
10 ⁻² N	15.20	Ca ²⁺	0.17	10.20	0.77	0.85	6
	12.37	Cu ²⁺	0.16	9.75	0.23	0.50	
10 ⁻³ N	15.10	Ca ²⁺	0.16	10.40	0.77	0.85	5
	12.31	Cu ²⁺	0.16	9.87	0.23	0.50	

Table 3

Structural parameters for Wy–Na dispersed in solutions of molar fractions 0.2 Ca²⁺ and 0.8 Cu²⁺

Normality	<i>d</i> ₀₀₁ (Å)	Cation	<i>n</i>	Zn(Å)	<i>W</i> ₁₁	<i>P</i> _{ij}	<i>M</i>
					<i>W</i> ₂₁	<i>P</i> _{ji}	
1 N	15.45	Ca ²⁺	0.17	10.60	0.90	1.00	8
	12.40	Cu ²⁺	0.17	09.80	0.10	0.00	
10 ⁻¹ N	15.40	Ca ²⁺	0.17	10.60	0.80	1.00	8
	12.38	Cu ²⁺	0.17	09.86	0.20	0.00	
10 ⁻² N	15.20	Ca ²⁺	0.14	10.20	0.70	0.70	5
	12.37	Cu ²⁺	0.17	10.00	0.30	0.30	
10 ⁻³ N	12.80	Cu ²⁺	0.16	09.80	0.77	0.89	8
	15.00	Ca ²⁺	0.15	11.80	0.23	0.36	

Drits (1975). The origin of these coordinates was placed on the plane of surface Oxygen atoms (Drits and Tchoubar, 1990).

3. Results and discussion

3.1. Reference samples

The XRD patterns produced by Wy–Na and Wy–Cu (Fig. 1a, b) showed two 001 reflections at 12.29 Å and 12.36 Å and rational series of 001 reflections. Thus these samples are homogeneous and characterised by a one water layer (Oueslati et al., 2006). In the case of Wy–Ni and Wy–Ca, XRD patterns (Fig. 1c and d) are characterised by *d*₀₀₁ spacing of 15.08 Å and 15.43 Å respectively and irrational series of 001 reflections indicating the interstratified character. These samples have a two water layer hydration state on average.

The best agreements between experimental and theoretical profile in the case of Wy–Ni are reported in Fig. 2. The structural parameters summarised in Table 1 show that Wy–Na and Wy–Cu are characterised by one water layer whereas Wy–Ni and Wy–Ca had a two water layer

structure on average. In the average all samples contained 8 layers per stacking.

3.2. Structure and selectivity

3.2.1. Solutions containing Cu²⁺ and Ca²⁺

In the case of (0.5 Ca²⁺, 0.5 Cu²⁺) solutions (Fig. 3) the position of the 001 reflection shifts from 15.44 Å to 12.07 Å when decreasing the concentration from 1 N to 10⁻⁴ N. This indicates a transition of the hydration state from two to one water layer. For 10⁻² N and 10⁻³ N, we notice a broadening and a splitting of the 001 reflection in two peaks around 14.77 Å and 12.81 Å. This means that for within this range of concentrations, the samples are heterogeneous and composed of one and two water layer structures. In Fig. 4 we reported an example of agreement between experimental and calculated intensities produced in the case of 10⁻¹ N. The structural parameters (Table 2) show that for high concentrations (1 N to 10⁻¹ N), the interlamellar space is occupied by two layer of water molecules and the exchangeable sites are saturated with Ca²⁺. At low concentrations (<10⁻⁴ N), Cu²⁺ occupies the exchangeable sites and the basal spacing corresponds to one water layer. For intermediate concentrations, the samples are interstratified with interlayer spaces containing Cu²⁺ ions and Ca²⁺. These two types of layers are stacked in a random fashion. Within the range of concentration expected, the mean number of layers per stacking remained unchanged (≈6 layer per stack). The same behaviour was

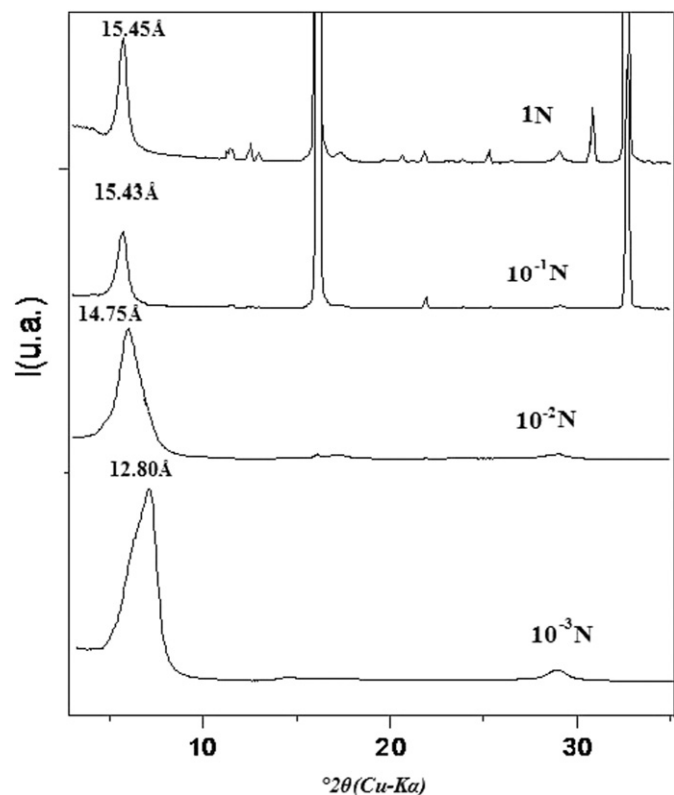


Fig. 5. XRD patterns of Wy–Na dispersed in solution with molar fractions 0.2 Ca²⁺ and 0.8 Cu²⁺ with normality from 1 N to 10⁻³ N.

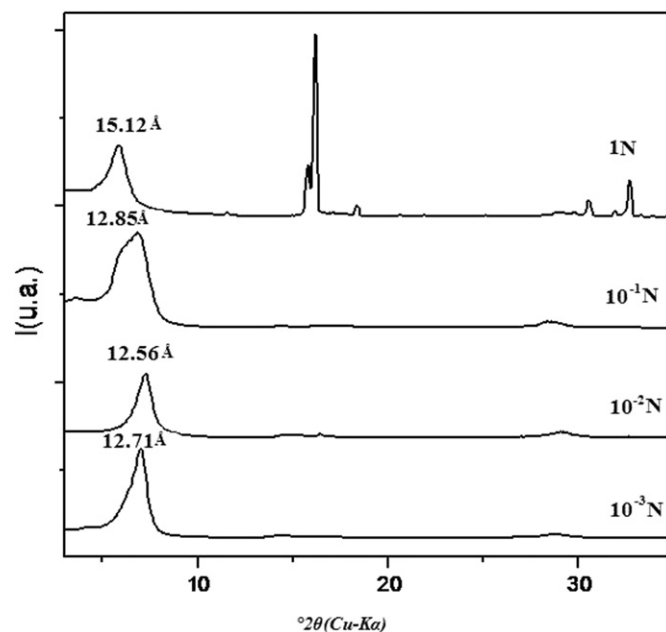


Fig. 6. XRD patterns obtained for decreasing normality from 0.5 N to 0.5.10⁻³ N in the solutions of molar fractions 0.5 Cu²⁺ and 0.5 Ni²⁺.

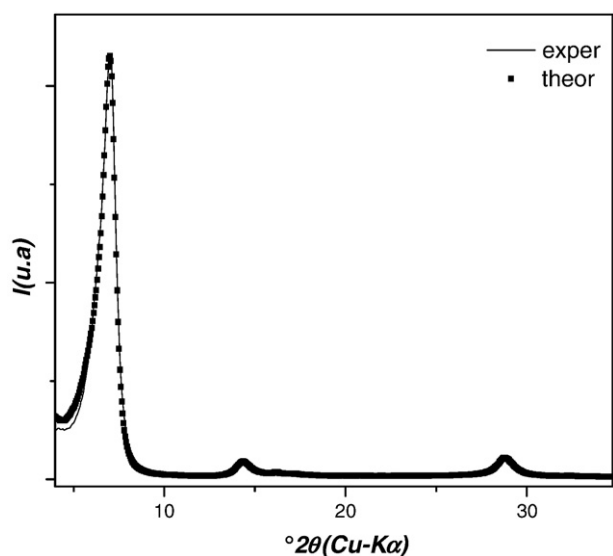


Fig. 7. Comparison between experimental and calculated XRD patterns in 10^{-3} N solutions.

observed when Wy–Na was dispersed in solution containing 0.2Ca^{2+} and 0.8Cu^{2+} (Fig. 5, Table 3).

3.2.2. Solutions containing Cu^{2+} and Ni^{2+}

In solutions containing 0.5Cu^{2+} and 0.5Ni^{2+} the position of the 001 reflection was shifted from 15.12 \AA to 12.71 \AA when decreasing the concentration from 0.5 N to $0.05\text{ }10^{-3}\text{ N}$ (Fig. 6). This indicates a transition of the hydration state from two to one water layer. In the case of 0.5 N the sample are characterized by a reflection at $2\theta=5.89^\circ$ ($d_{001}=15.12\text{ \AA}$). The irrationality of the reflexion position for these sample indicate the interstratified character. A supplementary reflection appears in the diffraction pattern due to excess of Cooper chloride and Nickel chloride in starting solution. At $0.5\cdot 10^{-1}\text{ N}$ broadening and a splitting of the 001 reflection in two peaks around 12.85 \AA indicates heterogeneity of the sample consisting of interlayer spaces of Ni^{2+} with two water layers and of interlayer spaces with Cu^{2+} characterized by one water layer. At 10^{-2} N to 10^{-3} N the XRD patterns were characterised by a reflection respectively at 12.71 \AA and 12.56 \AA attributed to Cu^{2+} ion in the interlamellar space and an irrational position of reflection indicating the interstratified character. Experimental and calculated XRD patterns in the case of 10^{-3} N are shown in Fig. 7 and Table 4.

The structural parameters showed that at 0.5 N the exchangeable sites were saturated by Ni^{2+} cations with two water layers. For intermediate concentrations from $0.5\cdot 10^{-1}\text{ N}$ to $0.5\cdot 10^{-2}\text{ N}$, the samples are again interstratified.

For low concentrations the d_{001} spacing corresponds to Wy–Cu and the sample was homogeneous. The mass proportion (i.e. W_{ij}) as well as the probability of succession between layers (i.e. P_{ij}) varies according to the concentration of the cations and decreases with dilution process indicating demixion tendency. At high concentrations montmorillonite fixes Ni^{2+} preferentially, and for low concentrations a tendency was observed to fix either Cu^{2+} .

The average number of layers per particle varies from 6 to 10 and that explains the reduction in the half width semi height as well as the reorganization of the layers within the particle.

4. Conclusion

The XRD pattern of montmorillonite saturated by Na^+ , Cu^{2+} , Ca^{2+} and Ni^{2+} showed the basal spacings: 12.29 \AA , 12.36 \AA , 15.43 \AA and 15.08 \AA . In the case of Ca^{2+} and Ni^{2+} the sample were characterised by two water layers and in the presence of Na^+ and Cu^{2+} the sample were characterised

Table 4

Structural parameters for Wy–Na dispersed in solutions of molar fractions 0.5Cu^{2+} and 0.5Ni^{2+}

Normality	d_{001} (Å)	Cation	n	Zn (Å)	W_{11}	P_{ij}	M
					W_{21}	P_{ji}	
10^{-1} N	12.10	Cu^{2+}	0.17	10.2	0.77	0.89	6
	14.88	Ni^{2+}	0.16	10.8	0.23	0.36	
10^{-2} N	12.36	Ca^{2+}	0.17	09.5	0.93	0.98	8
	15.06	Ni^{2+}	0.16	11.0	0.07	0.65	
10^{-3} N	12.40	Cu^{2+}	0.17	09.8	0.85	0.92	10
	15.50	Ni^{2+}	0.16	10.6	0.15	0.45	

by one water layer. To studied the selectivity in ($\text{Cu}^{2+}, \text{Ca}^{2+}$) and ($\text{Cu}^{2+}, \text{Ni}^{2+}$) solutions. At low concentrations the d_{001} spacing corresponded to Wy–Cu whereas for high concentration, the d_{001} spacing could be attributed to the Wy–Ca or Wy–Ni. at low concentration exchangeable sites were saturated with low hydration-state cations (i.e. Cu^{2+}) one water layer. At high concentration, montmorillonite fixes the cations with high hydration state (i.e. Ca^{2+} or Ni^{2+}) two water layers.

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