The water retention mechanism of a Cs^+ and Na^+ exchanged montmorillonite: effect of relative humidity and ionic radius on the interlayer

Marwa Ammar,[1] Walid Oueslati,[1,2,a)] Nejmeddine Chorfi,[3] and Abdesslem Ben Haj Amara[1]

[1]*UR 05/13-01: Physique des Matériaux Lamellaires et Nanomatériaux Hybrides (PMLNMH), Faculté des Sciences de Bizerte, Zarzouna 7021, Tunisia*

[2]*General Studies Department, College of Electronics and Communications, Technical and Vocational Training Corporation, TV Street, P.O. Box 2816, Jeddah 21461, Saudi Arabia*

[3]*Department of Mathematics, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia*

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Dioctahedral smectites are clay minerals that widely used as a crucial component for the edifice of natural barriers in industrial wastes and wastewater treatment. The hydration behaviours of these mineral types are very sensitive by environmental surroundings changes. The present work focuses the evolution of the interlayer water amount as a function of the relative humidity rates (RH), varied along a humidifying-drying cycle, in the case of two dioctahedral smectites with different charge location (i.e. Wyoming montmorillonite SWy-2 and Beidellite SbId-1). The CEC (i.e. cation exchange capacity) of the studied sample is saturated by two monovalent cations (i.e., Cs^+ and Na^+) characterized by a different ionic radius. The X-ray diffraction (XRD) profile modelling tools based on the indirect method that consist on the comparison of experimental *00l* reflections with other calculated from structural models is used to perform these aims. The qualitative XRD profile investigation suggests heterogeneous hydration behaviour at different stage of the cycle for all studied samples. The water content fluctuation, confirmed by the appearance of a hydration *hysteresis*, within the interlamellar space of diverse complexes is an irreversible process during the shrinking–rewetting sequence. Comparing to Na^+ cations, the presence of the Cs^+ ions in exchangeable sites of both smectite structures is accompanied by more orderliness of systems, which retunes the lowest water molecules amount over the applied cycle. © *2015 International Centre for Diffraction Data*.
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Key words: dioctahedral smectites, XRD profile modelling, shrinking–rewetting, water retention and hysteresis

I. INTRODUCTION

Dioctahedral smectites are 2:1 aluminosilicate clays with layered structure composed by two tetrahedral sheets sandwiching an octahedral ones. These clays type represents ones of the most important minerals in soils characterized by diverse properties mainly the high cation exchange capacity (CEC), the high specific surface area, high swelling ability, and metal absorption. These advantageous properties make smectite as a promising material in the context of engineered barrier for industrial and nuclear waste disposal (Atun and Bascetin, 2004; Malikova *et al.*, 2004; Oueslati *et al.*, 2007, 2009a, 2009b; Di *et al.*, 2008; Gupta and Bhattacharyya, 2008; Phothitontimongkol *et al.*, 2009; Cháveza *et al.*, 2010; Ammar *et al.*, 2013; Zamparas *et al.*, 2013). On the other hand, all the specific properties of smectite can be, significantly, altered by environmental perturbations. Indeed, Oueslati *et al.* (2012) studied the effect of an applied continuous, *in situ*, hydration–dehydration cycles using variation of %RH (relative humidity) on the cation exchange process of a dioctahedral smectite where results shows that the hydration behavior is affected by the number of hydration–dehydration cycle accompanied by a new organization of the interlamellar space of the host materials. Chalghaf *et al.* (2013) demonstrate that the intrinsic properties (i.e., CEC and the specific surface area) of Na-rich montmorillonite are affected by applying a hydrous strain. The same authors reveal the effect of the perturbation, created by varying pH solution and continuous heating cycle, in the cation exchange process in the case of Na-rich montmorillonite sample. Indeed, this perturbation type has an obvious effect on the selective exchange process for all stressed samples, in the case of bi-ionic solution with variable concentration. All previous cited studies are performed based on the X-ray diffraction (XRD) profiles modelling approach. In fact, the XRD has been a capital analysis method frequently used to study the hydration properties of these minerals. Following the evolution of the *00l* basal reflections position as a function of relative humidity in the case of smectites, the pioneering studies defined different layer type's corresponding to the penetration of 0, 1, 2, or 3 planes of water in the interlayer spaces (Bradley *et al.*, 1937; Mooney *et al.*, 1952; Norrish, 1954; Walker 1956; Cases *et al.*, 1992; Sato *et al.*, 1992; Moore and Reynolds, 1997). The recent studies prove that different hydration states usually coexist in the same smectite structure (Ferrage *et al.*, 2005a, 2005b, 2007; Oueslati *et al.*, 2007, 2009a, 2009b; Lanson, 2011). Such heterogeneities can be quantified using the XRD profile

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a)Author to whom correspondence should be addressed. Electronic mail: walidoueslati@ymail.com

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modelling procedure. Indeed, divers work use this method for determining the structural evolution, the relative proportions of the different layer types, and water content of natural or synthetic smectites. Ferrage *et al.* (2010) studied the evolution of interlayer water amount of synthetic saponites upon dehydration by the XRD profile modelling and water vapour adsorption/desorption isotherms and demonstrate a concordance between the results obtained through the two methods. On the other hand, the effect of the hydration sequence orientation on the structural properties of Hg exchanged montmorillonite is studied by fitting the experimental XRD patterns where the quantitative investigation shows that hydrous perturbation is accompanied by an irreversible gradual growth of the interlayer water molecules content (Ammar *et al.*, 2014a).

This work represents a continuation of the work of (Ammar *et al.*, 2014a) and aims to characterize the progress of interlayer water adsorption as a function of the relative humidity rates, which varied during a shrinking–rewetting cycle in the case of two dioctahedral smectites saturated by two different monovalent cations. The effect of ionic radius on the retention of interlayer water is investigated to better understand the hydration mechanism of samples when varying %RH. The study is carried out by the means of XRD analysis. This method consists on the comparison of experimental patterns recorded over the cycle to the calculated *ones*. The water amount evolution for different studied samples is derived from the *00l* quantitative XRD investigations.

II. EXPERIMENTAL

Two dioctahedral smectites, which differed by the charge location are selected for this study. The first specimen is the Wyoming montmorillonite SWy-2 originated from Wyoming-USA and the second is the beidellite SbId-1, extracted from Glen Silver Pit De Lamare Mine, Idaho. Both samples are supplied by the Source Clay Minerals Repository of The Clay Minerals Society (Moll, 2001). The experimental procedure of the ionic exchange processes used to saturate the exchangeable sites of the host materials by Cs^+ and Na^+ cations is performed according to a classical protocol (Tessier, 1984) detailed in the first part of this study (Ammar *et al.*, 2014a).The obtained specimens are referred as *SWy-2–Cs*, *SWy-2–Na*, *SbId-1–Cs*, and *SbId-1–Na*, respectively, for the montmorillonite and beidellite saturated by the Cs^+ and Na^+ ions. Oriented slides are prepared for different prepared complexes to be analysed by XRD along a hydration–dehydration cycle performed *in situ* by varying relative humidity rates. This task is achieved using a diffractometer installation, which is equipped with an Ansyco rh-plus 2250 humidity control device coupled to an Anton Paar TTK450 chamber. The shrinking–rewetting cycle is realized into process that can be resumed as follows: a dehydration phases is performed at first time by decreasing the RH rates from 80 to 10% RH and followed by a hydration process, by increasing the RH values from 10 to 80% RH (Ammar *et al.*, 2014b). A detailed description of the qualitative and quantitative XRD patterns investigations was presented in the first part of this study (Ammar *et al.*, 2014a). The profile modelling is achieved using calculated structural models with a water molecule distribution in accordance with the literature description (Sato *et al.*, 1992 and Oueslati et al., 2011). The X-ray profile modelling method is based on the algorithms developed by Sakharov *et al.* (1973) where the theoretical intensities were calculated according to the matrix formalism detailed by Drits and Tchoubar (1990).

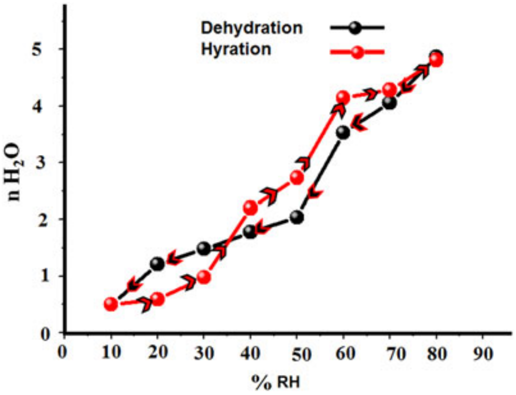

Figure 1. (Color online) Evolution of the interlayer water amount according to %RH variation in the case of SWy-2–Na complex.

III. RESULTS AND DISCUSSION

In the work of Ammar *et al.* (2014a), the XRD profile modelling has allowed, following the sequential evolution of different layer types abundances as a function of the %RH for divers studied complexes and showing that the transition from a homogeneous hydrated state to others ones on the crystal scale is a complex phenomenon. The relation between hydration heterogeneities and the number of mixed layer structure (i.e., MLS) used to calculate the XRD patterns are also investigated where the obtained results showed systematic heterogeneity hydration behaviour for all studied specimens at all the relative humidity rates and the nature of the interlayer cation (i.e., Cs^+ or Na^+). The main purpose of the present part is to characterize the evolution of the interlayer H_2O molecule upon the cycle and to determine a link between the %RH, the ionic radius of the exchangeable cation and the water amount rearranged in the structure of different complexes derived through the quantitative XRD investigation detailed in the first part.

A. Evolution of the water content over the shrinking–rewetting cycle

1. Case of the montmorillonite SWy-2

a. SWy-2–Na

The examination of the interlayer H_2O molecules progress as a function of the %RH rate in the case of *SWy-2–Na* complex (Figure 1) shows the appearance of two hysteresis where the first one extends between $35 \le \%RH \le 80$, whereas the second hysteresis is founded at the lowest humidity range between 35 and 10% RH (Figure 1). Indeed, the decrease of the RH values from 80 to 40% RH, along the dehydration process, is accompanied by a fast shift of the interlayer water amount. By against, a slowly changes is noted for the low relative humidity range. The gradual increase of the RH rates from the extremely dried condition (10% RH) during the second process is accompanied by a slow H_2O molecule intercalation growth proving the complex rehydration phenomenon, especially between 10 and 35% RH. In fact, the interlayer water amounts calculated in this RH range are fewer than those calculated along the dehydration process, which can be explained by a new structural reorganization in the interlayer space. A notable change in the water content is observed, when increasing the RH values to 40%, and continued to the almost saturated condition (80%). In fact, over this RH field, a fast insertion of the H_2O molecules in the interlamellar spaces is noted and accompanied by an important water amount during the hydration process than in the case of the dehydration procedure.

b. SWy-2–Cs

The progress of the interlayer water amounts along the dehydration procedure in the case of *SWy-2–Cs* complex (Figure 2) is performed along three steps. A gradual disappearance of the H_2O molecules from the interlamellar spaces is noted. In effect, a fast decreasing of the water contents is observed between 80≤ %RH ≤60 which is decelerated between 60≤ %RH ≤30.

A slow variation in the water amounts towards the lowest RH fields (Figure 2) is distinguished. A different behaviour is observed along the rehydration process and the progress of the interlayer water contents follows others different way along the dehydration procedure. Indeed, by growing the %RH values from 10 to 40, the insertion of the H_2O molecules in the structure seems to be hard which is confirmed by the slow water amount variation bringing appearance of a notable hysteresis with a big loop. On the other hand, the continued increase of the relative humidity from 50% RH to the end of the cycle is accompanied by a fast growth of the interlayer water molecule contents. During the studied cycle, the numbers of the H_2O molecules calculated through the dehydration process are more important than those determined over the hydration process. Furthermore, it is noted that the SWy-2–Cs complex loose water from the interlamellar spaces at the end of the applied cycle (Figure 2), which prove that material structural properties are affected by the continuous variation of the relative humidity rates.

2. Case of the beidellite SbId-1

a. SbId-1–Na

The water contents variation upon the cycle calculated from the quantitative XRD investigation in the case of *SbId-1–Na* is represented in Figure 3. The examination of this figure showed a continuous decrease of the interlayer water amount which shift quickly from 80 to 10% RH with the RH values changes. The intercalation of the H_2O plane in the structure with increasing %RH rates during the hydration process was characterized by a slow evolution thus the water amounts calculated over this sequence is fewer compared to those calculated over the dehydration procedure. This hydration behaviour incites the appearance of the clear hysteresis, which spreads overall the explored %RH range (Figure 3). This result is probably explained by a structural fluctuation, created with the continuous RH rates changes, over the cycle, inducing a perturbation on the hydration behaviours of the studied specimens.

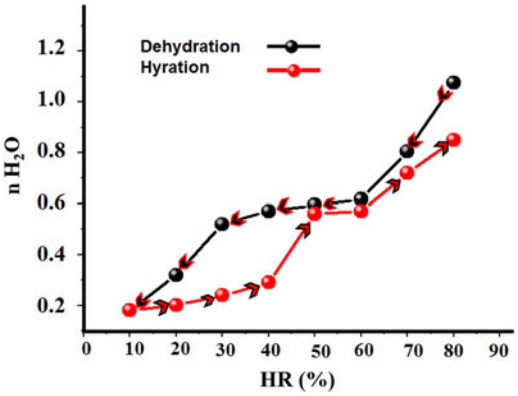

Figure 2. (Color online) Progress of the interlayer water amount according to %RH variation along shrinking–rewetting process in the case of SWy-2–Cs complex.

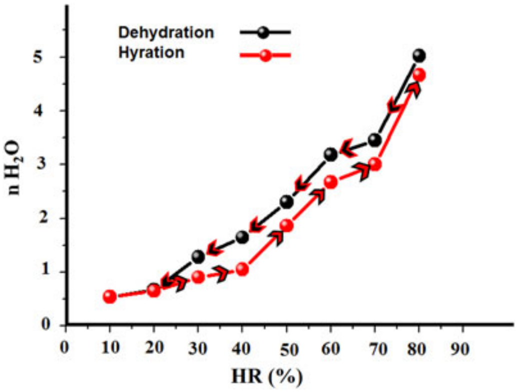

Figure 3. (Color online) Evolution of the interlayer water amount according to %RH variation in the case of the SbId-1–Na sample.

b. SbId -1–Cs

The variation of the interlamellar water amounts as function of the %RH values along the shrinking–rewetting cycle (Figure 4) in the case of *SbId -1–Cs* complex is characterized by the appearance of a clear hysteresis with a big loop founded at a wide RH range spreading between 80 and 10% RH. Indeed, by applying a dehydration procedure (Figure 4) the H_2O molecules disappears slowly from structure, but a brief shift is detected toward the lowest RH field between 20

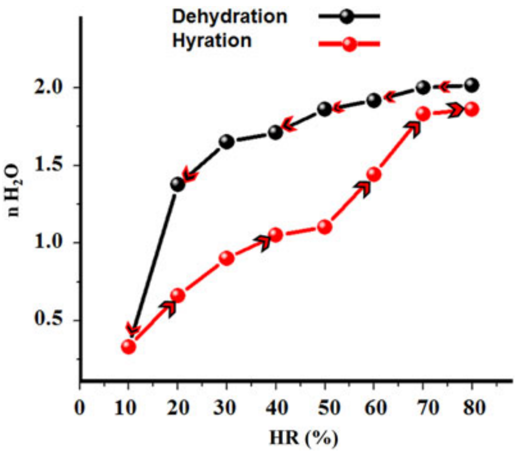

Figure 4. (Color online) Progress of the interlayer water amount according to %RH variation along the shrinking–rewetting process in the case of SbId-1–Cs sample.

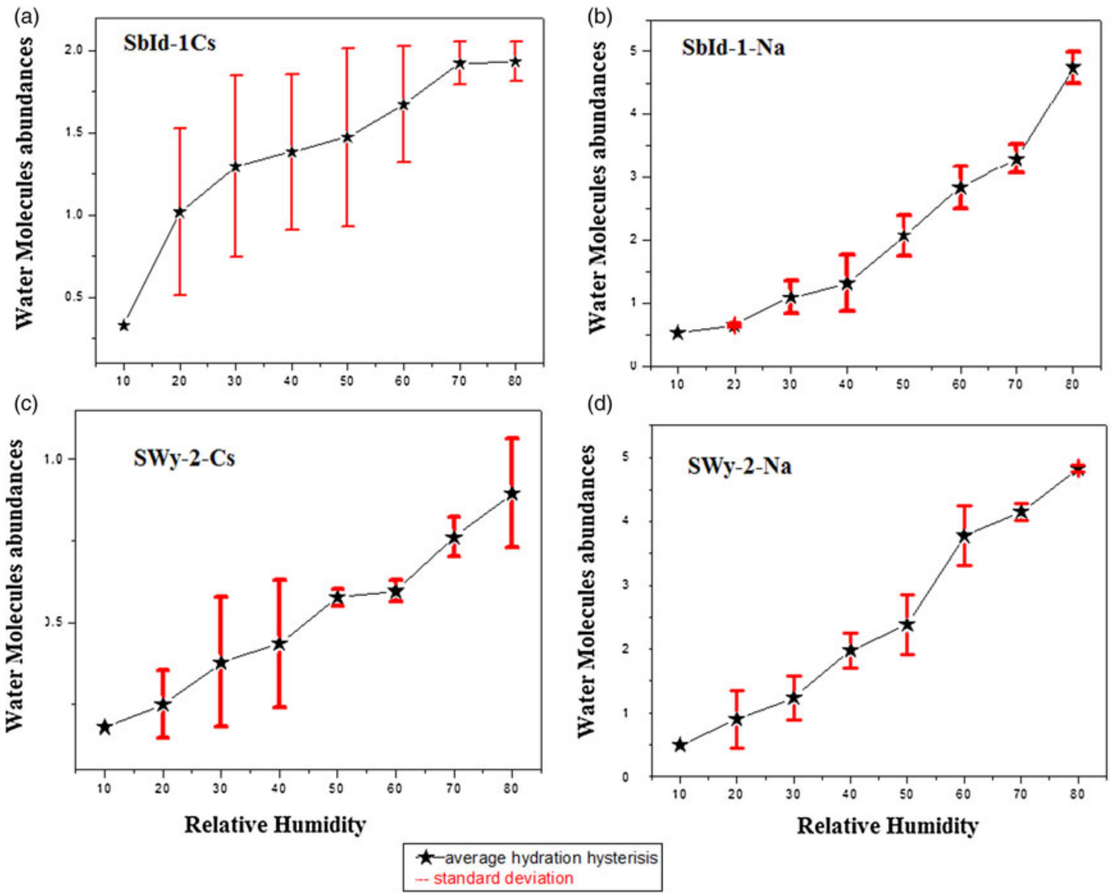

Figure 5. (Color online) Average hydration hysteresis (–*–) and the associated SD (——).

and 10% RH. Along the hydration sequence the interlayer water content is low respected and a different curve of the H_2O number evolution upon this process characterized by the truncated water amount at different explored RH values is observed.

The appearance of such hysteresis for different studied smectites is a result of the perturbation on the interlamellar water organization. In fact, the draining and filling of interlayer spaces by H_2O molecules is performed in an irreversible way, which can be explained by the structural fluctuation created within smectites structures. In addition, the opening of the interlamellar spaces become hard after decreasing the RH values to the almost dried condition (10% RH) which complicates the hydration procedure.

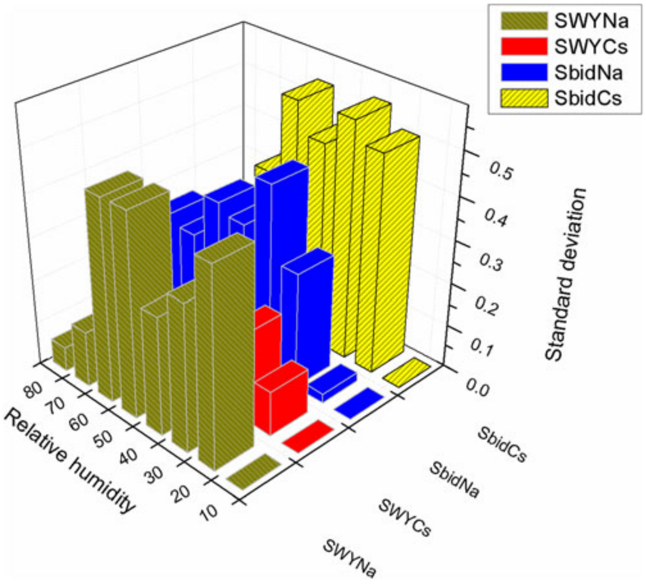

Figure 6. (Color online) Stacked histogram of the hydration SD.

B. Influence of ionic radius on water retention mechanism

The results deduced through the quantitative XRD analysis shows that the dioctahedral smectites selected for this study (i.e. SWy-2 and SbIb-1) present a different hydration behaviour along the shrinking–rewetting cycle. The size of exchangeable cations is an important factor on determining the amount of water that can be retained in the structure at different %RH rates over the cycle. In fact, the evolution of interlayer water content according to %RH rate the in the case of SWy-Na and SWy-2–Cs [Figures 5(c) and 5(d)] showed clearly that the presence of Na^+ cations in exchangeable montmorillonite sites enables the intercalation of the H_2O molecules more than in the case of Cs^+ cation along the explored RH field. This result is confirmed by the use of the calculated hydration standard deviation (SD) for all specimens, reported in Figure 5. The SD is also useful when comparing the dispersion of two separate data sets that have approximately the same average. The dispersion of the measurements around the mean is narrower in the case of a data set whose SD is smaller. Usually, such an assembly includes comparatively fewer high values or lower values. One selected randomly from a data set whose SD is low may be closer to the average one element of a data set whose SD is higher. By exploiting the given stacked histogram (Figure 6), which focuses the evolution of the SD parameter vs. %RH in the case of all studied complexes, a raised hydration fluctuation is noted in the case of Cs+ cation. This result is interpreted by the effect of the charge location on the exchange process. This problem disappears for the sodium cation and a similar hydration fluctuation is noted in both studied complexes. On the other hand, the investigation of the SD evolution in the case of in the case of SbId-1–Na and SbId-1–Cs, showed that the retained interlayer water amount structures are substantially similar at 80% RH value, whereas a small difference is observed from 30% RH to the almost saturated condition 70% RH [Figures 5(a) and 5(b)].

These results are in accordance with literature value which demonstrate that the presence of Na cations with a low ionic radius in both dioctahedral smectites structures allows insertion of H_2O molecules unlike the Cs^+ ions characterized by a huge size, which restrict the penetration of water in the interlamellar spaces and the hydration of the structures.

IV. CONCLUSION

This paper reports on a detailed the progress of the interlamellar water amount as a function of the relative humidity rates in the case of two dioctahedral smectites saturated by Cs^+ and Na^+ cations along the shrinking–rewetting cycle. The main results obtained through quantitative XRD investigation show that the continuous variation of the RH rates over the cycle leads to a strong perturbation on the water content within the interlamellar spaces and thus affected their evolutions, which explain the appearance of the clear hysteresis of the explored %RH range for different samples. Moreover, the results suggest that the water retention mechanism of both smectites depends mainly on the size of the interlayer cations. The presence of Cs^+ cations in exchangeable sites restricts the intercalation of H_2O molecules in the structures of both of the studied samples, which keeps the lowest water amount all over the cycle.

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Ammar, M., Oueslati, W., Ben Rhaiem, H., and Ben Haj Amara, A. (**2013**). “XRD profile modeling approach tools to investigate the effect of charge location on hydration behavior in the case of metal exchanged smectite,” Powder Diffr. **28**(S2), 284–300.

Ammar, M., Oueslati, W., Ben Rhaiem, H., and Ben Haj Amara, A. (**2014a**). “Quantitative XRD analysis of the dehydration–hydration performance of (Na + , Cs+) exchanged smectite,” Desalination Water Treat. **52**, 4314–4333.

Ammar, M., Oueslati, W., Ben Rhaiem, H., and Ben Haj Amara, A. (**2014b**). “Effect of the hydration sequence orientation on the structural properties of Hg exchanged montmorillonite: quantitative XRD analysis,” J. Environ. Chem. Eng. **2**, 1604–1611.

Atun, J. G. and Bascetin, E. (**2004**). “Adsorption of barium on kaolinite, illite and montmorillonite at various ionic strengths,” Radiochim. Acta **91**, 223–228.

Bradley, W. F., Grim, R. E., and Clar, G. F. (**1937**). “A study of the behavior of montmorillonite on wetting,” Z. Kristallogr. **97**, 260–270.

Chalghaf, R., Oueslati, W., Ammar, M., Ben Rhaiema, H., and Ben Haj Amaraa, A. (**2013**). “Effect of temperature and pH value on cation exchange performance of a natural clay for selective (Cu^{2+}, Co^{2+}) removal: equilibrium, sorption and kinetics,” Progr. Nat. Sci.: Mater. Int. **23**, 23–35.

Cháveza, M. L., Pablob, L., and Garcíaa, T. A. (**2010**). “Adsorption of Ba^{2+} by Ca-exchange clinoptilolite tuff and montmorillonite clay,” J. Hazard. Mater. **175**, 216–223.

Cases, J. M., Berend, I., Besson, G., Franqois, M., Uriot, J. R., Thomas, F., and Poirier, J. E. (**1992**). “Mechanism of adsorption and desorption of water vapor by homoionic montmorillonite.1.The sodium exchanged form,” Langmuir **82**, 2730–2739.

Drits, V. A. and Tchoubar, C. (**1990**). *X-ray Diffraction by Disordered Lamellar Structures: Theory and Applications to Microdivided Silicates and Carbons* (Springer-Verlag, Berlin), 371 pp.

Di, X., Zhou, X., and Wang, X. (**2008**). “Adsorption and desorption of Ni^{2+} on Na-montmorillonite: effect of pH, ionic strength, fulvic acid, humic acid and addition sequences,” Appl. Clay Sci. **39**, 133–141.

Ferrage, E., Lanson, B., Malikova, N., Plançon, A., Sakharov, B. A., and Drits, V. A. (**2005a**). “New insights on the distribution of interlayer water in bi-hydrated smectite from X-ray diffraction profile modeling of 00l reflections,” Chem. Mater. **17**, 3499–3512.

Ferrage, E., Lanson, A., Sakharov, B. A., and Drits, V. A. (**2005b**). “Investigation of smectite hydration properties by modeling of X-ray diffraction profiles. Part 1. Montmorillonite hydration properties,” Am. Miner. **90**, 1358–1374.

Ferrage, E., Kirk, C. A., Cressey, G., and Cuadros, J. (**2007**). “Dehydration of Ca-montmorillonite at the crystal scale. Part I: structure evolution,” Am. Miner. **92**, 994–1006.

Ferrage, E., Lanson, B., Micho, L. J., and Robert, J. L. (**2010**). “Hydration properties and interlayer organization of water and Ions in synthetic Na-smectite with tetrahedral layer charge. Part 1. Results from X-ray diffraction profile modelin,” J. Phys. Chem. C **114**, 4515–4526.

Gupta, S. S. and Bhattacharyya, K. G. (**2008**). “Immobilization of Pb(II), Cd (II) and Ni(II) ions on kaolinite and montmorillonite surfaces from aqueous medium,” J. Environ. Manag. **87**, 46–58.

Lanson, B. (**2011**). “Modelling of X-ray diffraction profiles: investigation of defective lamellar structure crystal chemistry,” EMU Notes Miner. **11**, 151–202.

Malikova, N., Marrya, V., Dufrechea, J. F., and Turqa, P. (**2004**). “Na/Cs montmorillonite: temperature activation of diffusion by simulation,” Curr. Opin. Colloid Interface Sci. **9**, 124–127.

Moll, W. F. (**2001**). “Baseline studies of the clay minerals society source clays: geological origin,” Clays Clay Mine **49**, 374–380.

Mooney, R. W., Keenan, A. G., and Wood, L. A. (**1952**). “Adsorption of water vapor by montmorillonite. II. Effect of exchangeable ions and lattice swelling as measured by X-ray diffraction,” J. Am. Chem. Soc. **74**, 1331–1374.

Moore, D. M. and Reynolds, R. C. (**1997**). *X-ray Diffraction and the Identification and Analysis of Clay Minerals* (Oxford University Press, New York), pp. 322.

Norrish, K. (**1954**). “The swelling of montmorillonite,” Discuss. Faraday Soc. **18**, 120–133.

Oueslati, W., Karmous, M. S., Ben Rhaiem, H., Lanson, B., and Ben Haj Amara, A. (**2007**). “Effect of interlayer cation and relative humidity on the hydration properties of a dioctahedral smectite,” Z. Kristallogr. Suppl. **2**(26), 417–422.

Oueslati, W., Ben Rhaiem, H., Lanson, B., and Ben Haj Amara, A. (**2009a**). “Selectivity of Na–montmorillonite in relation with the concentration of bivalent cation (Cu^{2+}, Ca^{2+}, Ni^{2+}) by quantitative analysis of XRD patterns,” Appl. Clay Sci. **43**, 224–227.

Oueslati, W., Meftah, M., Ben Rhaiem, H., and Ben Haj Amara, A. (**2009b**). “Selectivity of Na-montmorillonite versus concentration of two competitive bivalent cations (Cu^{2+}, Pb^{2+}): quantitative XRD investigation,” Adv. Mater. Sci. Eng., **2009**, Article ID 385673.

Oueslati, W., Ben Rhaiem, H., and Ben Haj Amara, A. (**2011**). “XRD investigations of hydrated homoionic montmorillonite saturated by several heavy metal cations,” Desalination **271**, 139–149.

Oueslati, W., Ben Rhaïem, H., Lanson, B., and Ben Haj Amara, (**2012**). “Effect of relative humidity vconstraint on the metal exchanged montmorillonite performance: an XRD profile modeling approach,” Appl. Clay Sci. **261**, 396–404.

Phothitontimongkol, Th., Siebers, N., Sukpirom, N., and Unob, F. (**2009**). “Preparation and characterization of novel organo-clay minerals for Hg (II) ions adsorption from aqueous solution,” Appl. Clay Sci. **43**, 343–349.

Sakharov, B. A. and Drits, V. A. (**1973**). “Mixed-layer kaolinte–montmorillonite: a comparison observed and calculated diffraction patterns,” Clays Clay Miner. **21**, 15–17.

Sato, T., Watanabe, T., and Otsuka, R. (**1992**). “Effects of layer charge, charge location, and energy change on expansion properties of dioctahedral smectites,” Clays Clay Miner. **40**, 103–113.

Tessier, D. (**1984**). “Etude expérimentale de l’organisation des matériaux argileux. Hydratation, gonflement et structure au cours de la dessiccation et de la réhumectation”. Thèse Université de Paris VII, Publication INRA Versailles, (France).

Walker, G. F. (**1956**). “The mechanism of dehydration of Mg-vermiculite,” Clays Clay Miner. **4**, 101–115.

Zamparas, M., Deligiannakis, Y., and Zacharias, I. (**2013**). “Phosphate adsorption from natural waters and evaluation of sediment capping using modified clays,” Desalination Water Treat. **51**, 2895–2902.