Hydration performance of dioctahedral smectite saturated with Ba^{2+} and Cs^{+} cations: Quantitative XRD investigation

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Abstract The present paper aims at characterizing the hydration behavior in the case of dioctahedral smectite with different location charge (i.e. montmorillonite SWy-2 and beidellite SbId-1) exchanged by heavy metals ca < "(tions characterized by different valence (Ba^{2+} and Cs^{+}) generally coming from industrial waste and wastewater solution . The study was performed basing on the quantitative X-ray diffraction investigation. This method consists on the comparison between experimental patterns with a theoretical ones calculated from structural models and allows us to determine the relative proportions of different hydration states (dehydrated.0W, monohydrated.1W,or bihydrated.2W,) that can coexist within smectite structure .Furthermore, position and amount of both interlayer water molecules and heavy metals cations can be also, determined along the c* axis . Obtained qualitative and quantitative XRD analysis showed the possibility to distinguish diverse hydration behavior of each complex. The presence of the monovalent cation (i.e. Cs^{+}) in the interlayer space of both smectite restricts the water molecule intercalation that structures are dominated by two principal hydration states: 1 W and 0W. Whereas in the case of the bivalent cation (i.e. Ba^{2+}), the interlayer water amount retuned in the beidellite and montmorillonite structure is more important seen the presence of a major bihydrated layers types in their interlayer's spaces.

Keywords**: **dioctahedral smectite, cation valence, hydration behavior, heterogeneous.

Introduction

The problems related to the radioactive and industrial waste represent one of the most urgent priority in the recent years seen their harmful impact on the surface environments, both terrestrial and marine. Diverse methods are used to remove heavy metal ions from hazardous waste in order to limit their dissemination in the environment. The use of the natural clays such us smectite ,as sorbents ,is one of the most economic and efficiency proposed solution to resolve these problems[1–7].In fact, smectites are a main components mineral in soil characterized by diverse properties mainly its high sorption capacity, its low hydraulic conductivity, its important adsorption and/or ion exchange capacity and especially its capacity to swelling .Theses suitable properties make from this material a natural geological membrane preventing the migration of radionuclide and heavy metal ions .Diverse works focus their study on the hydration performance of smectites , in fact basing on X-ray diffraction (XRD) analysis different layer types were defined for smectite as function of the relative humidity : the dehydrated (0W, d_{001}) 9.7-10.2 Å), the monohydrated (1W, d_{001}) 11.6-12.9 Å), the bihydrated (2W, d_{001}) 14.9-15.7 Å), and the trihydrated (3W,d_{001}) 18-19 Å) layers[8-11].Recent studies prove the possibility that different hydration states/layer types coexist on the same smectite structure. [12-14].

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In the present work we aims at examining the hydration behavior of two dioctahedral smectite : the montmorillonite of Wyoming SWy-2 and the beidellite SbId-1 saturated with the monovalent Cs^+ and the bivalent Ba^{2+} cations characterized by the same ionic radius .This purpose was achieved by XRD investigation where the structural parameters related to the abundance, position and organization of exchangeable cation and water molecule in the interlamellar space are mainly determined basing on the XRD profiles modeling approach .

II. Materials and methods

A. Starting smectites

The montmorillonite of Wyoming SWy-2 and the beidellite SbId-1 are the two dioctahedral smectites selected for this work which are supplied by the Source Clay Minerals Repository Collection [15]. The montmorillonite exhibits a major octahedral charge whereas the SbId-1 represents a most substitutions in the tetrahedral sheet.

B. Pre-treatment and experimental procedure

A pre-treatment of the starting materials is performed at first time which consists to prepare a Na rich smectites suspensions then in second time, all the exchangeable site of both clays are saturated by Cs^+ and Ba^{2+} cations.The procedure used to perform the exchange process is detailed in the Fig.1.

C. X-ray diffraction

All experimental XRD patterns were obtained by reflection setting with a D8 Advance Bruker installation using CuKα radiation and monitored by EVA release software. The usual scanning parameters were 0.04 °2θ as step size and 6 s as counting time per step over the angular range 2-40 °2θ. The divergence slit, the two Soller slits, the antiscatter, and resolution slits were 0.5, 2.3, 2.3, 0.5, and 0.06°, respectively.

1) Qualitative and quantitative investigation

The qualitative XRD analysis allows us to have a preliminary idea about the hydration state of the studied samples via the examination of position and the profile geometry related to the 001 reflexion (picks symmetry and/or asymmetry, d_{001} basal spacing values).In addition the calculation of the full width at half maximum intensity (FWHM) value and the irrationality indicator (ξ parameter) are used to characterize hydration heterogeneity is thus preferable, as recommended by Bailey [16]

However, the qualitative study cannot provide a detailed information about structural characteristic and determine quantitatively the relative proportions of the different layer types .Thus the quantitative analysis is crucial for the interpretation of the XRD profile of all studied complex. The theorotical XRD patterns were calculated using the z coordinates of Drits and Sakharov [17] and using the algorithms developed by [18]. The diffracted intensity was calculated according to the matrix formalism detailed by [19]. The relationships between the probabilities and the abundances Wi of the different types of layers are given by Drits and Tchoubar [19].

The structural models are calculated following also the strategy fitting detailed in the work of Ferrage et al. 2005[20].

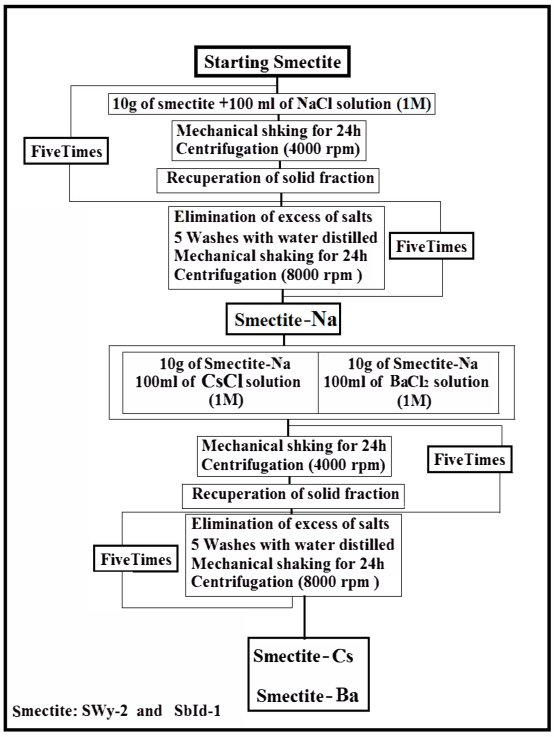

Fig.1: . Summary of the experimental protocol

III. Results

The best agreement between calculated and experimental XRD patterns produced by all studied samples are reported in Fig.2 .Different parameters deduced from the qualitative analysis including the d_{001} spacing values, the full width at half maximum intensity (FWHM) of the 001 reflection and the ξ parameter (i.e. which was calculated for 3 or 4 measurable reflections over the 2–40°2θ angular range) for all experimental patterns are illustrated in Table 1.

On the others hands ,we regroup in Table 2 all structural parameters used to achieve the modeling and reproduce experimental XRD patterns in the case of the homoionic

A. Case of SbId-1

1) Qualitative XRD investigation

The qualitative examination of both experimental patterns related to **SbId-1Ba** and **SbId-1-Cs**, shows a supplementary reflection ascribed to the presence of a 1:1 clay mineral fraction (Kaolinite) in starting sample (i.e. SbId-1).The XRD pattern produced by **SbId-1-Ba** complex is characterized by a dissymmetric 001 reflection (Fig.2.a) with a d_{001}=**14.58** Å signifying an interstratified hydration character between "1W and 2W" states with a major contribution of bihydrated layers [21]. This result can be confirmed by the height FWHM and ξ parameter values (i.e. 0.76 Å and 1.49) which proving an irrationality of the *00l* reflection positions. In the case of **SbId-1-Cs** specimens, the qualitative examination of the experimental patterns shows a symmetric 001 peaks shapes (Fig.2 b) situated at 2θ=7, 26° (d_{001}=12, 19Å) attributed to "1W" hydration state phase [21] .The homogenous hydration character is confirmed by the calculated ξ and FWHM values (i.e. 0.10 Å and 0.83) proving a rational series of the *00l* reflection positions.

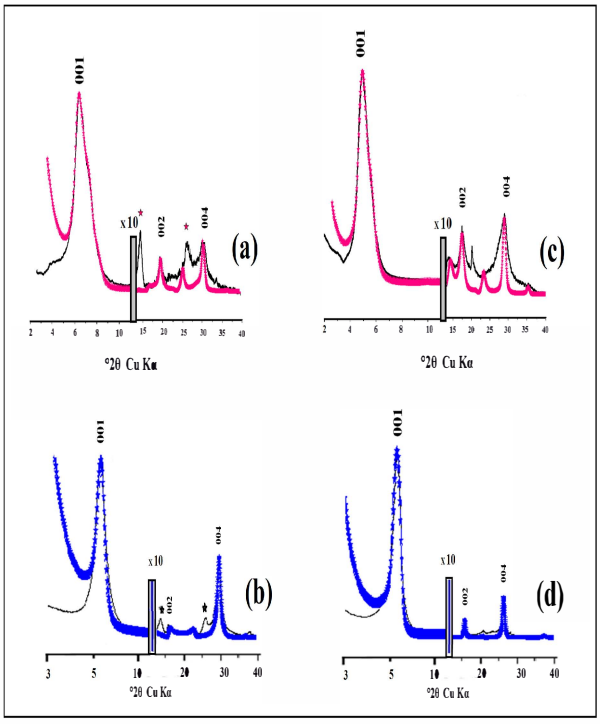

Fig.1: Summary of the experimental protocol

2) XRD profile modeling:

In order to achieve the modeling and obtain the best fit in the case of **SbId-1-Ba**, the contribution of three MLSs types were consistently used where the theoretical proposed model is characterized by a main structure contain the three layers hydration states types with a significant proportion of 0W layers (0W:1W:2W ratio respectively13.75:29.75:56.50). The number of layers per stack is 8 and others structural parameters used in simulations are illustrated in Tables 2.

The quantitative analysis prove the heterogeneity hydration character in the case of **SbId-1-Cs** complex and disagree the qualitative analysis .In fact ,the best fit is achieved using two MLSs types exhibiting random interstratifications between 1Wand 0W layers. The full structure involves 0W:1W ratio respectively 16:84.

B. Case of SWy-2

1) Qualitative XRD analysis

In the case of **SWy-2-Ba** complex, the qualitative examination of the experimental patterns show that the (001) reflection is characterized by a dissymmetric profiles (Fig. 2.c) with a d_{001} =14.94 Å corresponding to a quasi-homogeneous 2 W hydration state and indicate an interstratified hydration states in structure [21]. This preliminary result is confirmed by investigating the ξ and FWHM parameter values (i.e. 0.97 Å and 1.55), showing an irrationality of the 00l reflection positions.

On the others hands, the XRD pattern related to **SWy-2-Cs** sample is characterized by d_{001}=12.36 Å indicating the insertion of one water sheet in the interlayer space. The peaks symmetry description, ξ parameter and FWHM value (i.e. 0.23 Å and 0.67) confirm the obtained rational reflections series and suggest the homogeneous hydration state character [21].

Table1: Qualitative XRD investigation

Samples	d001(A°)	FWHM (°2θ)	ξ ,Xi	Caracter
SbId-1-Ba	14.58	1.49	0.76,3	I
SbId-1-Cs	12.19	0.83	0.10,4	H
SWy-2-Ba	14.94	1.55	0.97,3	I
SWy-2-Cs	12.36	0.67	0.05,4	H

2) XRD profile modeling

The qualitative estimation suppose the heterogeneity hydration character in the presence of SWy-2-Ba sample and predict an homogeneous hydration behavior for SWy-2-Cs, whereas the quantitative study prove the hydration heterogeneity character for both complex .

In fact, the fitting of the experimental XRD patterns produced by **SWy-2-Ba** was achieved assuming presence of two MLSs with variable abundance including different contribution of 1W and 2W layers types randomly distributed within smectite crystallites. The first particle present a major proportion of the bihydrated layers (1W:2W ratio 15:85) while the second one contains mostly 1W layers (1W:2W ratio 65:35). The structure present in total (1W:2W ratio respectively 47:53). Table2 illustrate the principal structural parameters characterizing the calculated model.

For **SWy-2-Cs** complex, the quantitative analysis confirm the qualitative analysis, thus the experimental XRD pattern are reproduced using one homogeneous phase containing 1W layer with an average of 8 layer per stacking. (Table2).

Table 2: Optimum structural parameters used for modeling XRD patterns

Samples	2W L.T	2W nH2O	2W ZH2O	2W Z C.C	1W L.T	1W nH2O	1W ZH2O	1W Z C.C	0W L.T	0W Z C.C	Abundance of Layers types 0W/1W/2W (%)	$\overline{M}$
SbId-1Ba	15.00	5	10.70 11.20	11.20	12.30	2.5	9.70	9.70	10.20	9.00	13.75/29.75/56.50	8
SbId-1-Cs	-	-	-	-	12.16	2.5	9.50	9.65	10.20	9.00	16/84/0	9
SWy-2-Ba	15.50	4	11.40 14.60	12.20	12.20	1	10.30	10.30	-	-	0/47/53	8
SWy-2-Cs	-	-	-	-	12.30	1.5	9.50	9.50	-	-	0/100/0	8

IV. Discussion

The quantitative analysis prove that all studied specimens, with the exception of **SWy-2-Cs**, are characterizing by the coexistence of diverse hydrations states in their structure thus the hydration heterogeneity is the main deduced character for theses samples where the number of the MLSs types exhibiting used to obtain the best fit in the case of the beidellite (i.e. **SbId-1-Ba** and **SbId-1-Cs**) were more important comparing to **SWy- 2 -Ba and SWy- 2 – Cs** thereby the theatrical structure models related to the beidellite are more complex and heterogeneous than for montmorillonite . This result is in accordance with work [22]showing the increased of the hydration heterogeneity ,at different relative humidity (RH) conditions, in the case of the beidellite structure (SbId-1) compared to the montmorillonite (SAz-1) saturated by the bivalent cations Sr- and/or Ca. On the others hand an obvious influence of the valence cation on the crystalline swelling for the studied dioctahedral smectites can be detected through both qualitative and quantitative investigation. Indeed, the montmorillonite and beidellite display a notable difference in the hydration behavior as function of the earth metal cation present in the exchangeable sites:

In the case of **SbId-1-Cs** and **SWy-2-Cs** structures are dominated by the monohydrated layers types (i.e. 1W) devoid from the bihydrated layers types (i.e.2W), whereas the location of the bivalent cation (i.e.Ba2+) in interlayer spaces of both dioctahedral smectites is accompanied by the insertion of the water molecules that both structure of **SbId-1-Ba** and **SWy-2-Ba** are characterized by the presence of the monohydrated and a major proportion of bihydrated layers types.

Acknowledgements

Acknowledges W. O. for the fruitful discussions about smectite hydration, her main contribution in the XRD modeling approach.

Conclusion

The hydration behavior of the montmorillonite **SWy-2** and the beidellite **SbId**-1 saturated with Ba^{2+} and Cs^{+} was studied by modeling of X-ray diffraction patterns.

The obtained qualitative and quantitative results showed an obvious effect of the cation valence on the hydration performance of both smectite.

The modeling prove that the optimum structure models of **SbId-1-Cs**, **SbId-1-Ba** and **SWy-2-Ba** are determined assuming presence of several MLSs within smectite crystallites that all structures are characterized by heterogeneous hydration behaviors, whereas the structure model related to SWy-**2-Cs** complex is described by a homogenous hydration state.

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