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EFFECT OF EXCHANGEABLE CATIONS ON THE PHYSICOCHEMICAL PROPERTIES OF SMECTITE

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1. Introduction

The absorption and adsorption properties of clay are functions of exchangeable cations and layer silicate structure. These processes are governed by the balance between attractive and repulsive forces arising from intermolecular and electrostatic interactions between the solution and solid phases in the suspension.

Many workers have studied the relation ship between physicochemical properties of clay and the effect of the nature of exchangeable cations. Total layer charge has been found to play a major role in the expansion properties of layer silicates [1, 2]. Net particle charge is the most important factor controlling clay dispersion for a range of pH and ionic strength values [3]. The effect of interlayer cations, net layer charge and charge location (octahedral or tetrahedral) are on the expansion properties of smectites [4–6]. The general conclusion was that the basal spacings of tetrahedrally-charged smectites were smaller then those of octahedrally-charged smectites under the same hydration and solution conditions.

The thermal treatment of smectites saturated with Li has been shown to reduce their layer charge as well as cause a decrease in exchangeable Li [7–8]. A similar reduction in charge has also been found when Mg^{2+} or Al^{3+} saturated clays were heated to 300°C [4, 9]. The mechanism of charge reduction was argued to be the migration of these cations of small radius into vacant octahedral sites to reduce the octahedral charge.
Other new studies [10], concerning interaction of water with exchangeable cations of smectite clay (Li-, Na-, Ca-, Mg-, Al-smectite) show that dehydratation involves desorption of the water molecules from its original adsorption site (oxygen surface of the clay or exchangeable cation) and diffusion of the desorbed molecule to the gaz phase. All data point to a strong cation dependence of the smectite-water interaction in parallel to what is observed or computed for water-cation interactions in the vapour or liquid phase [11]. It's reported that the weight loss of molecular water depending on the nature of the counter ion, the first water loss observed with all the samples (Li-, Na-, Ca-, Mg-, Al-smectite) takes place at temperature between 332 and 345K, the second water loss was observed for the smect-Li^{+}, smect-Ca^{2+}, smect-Ba^{2+}, smect-Mg^{2+} and smect-La^{3+} at 377–419 K temperature range, when smect-Mg^{2+} exhibit a third peak of water loss at 508±5K, this implies that the cation type is determinative for the total water content retained in smectite since the physical state of a clay charges with increasing water content; from solid to semi-rigid plastic then to gel and then finally to suspension.

In the present study, we investigate the effect of counter ions on the physico-chemical properties of a smectite clay collected from Zaghouan (North Est of Tunisia), then we reported the effect of heating at different temperatures (25-200-300-400°C) on the adsorption/absorption properties of smectite saturated with monovalent, divalent and trivalent cations.

2. Materials and experimental methods

2.1 Clay

The bentonite was used as clay in this study, obtained from Zaghouan (North-Eastern of Tunisia), it was prepared as described before [12–13]. The sample was characterized by X-ray diffraction, thermo gravimetric and FT-IR spectroscopic analyses. The chemical compositions of the clay was found to be as follows; 58.8% SiO_2, 3.95% MgO, 17.4% Al_2O_3, 0.84% K_2O, 0.28% CaO, 1.39 %Na_2O. The cation-exchange capacity (CEC) determined according to the ammonium acetate saturation method [14], the BET specific surface area (S_{BET}) and the total specific surface area (Ss) were also estimated. The most important properties of the used sample were illustrated in table 1.

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Table 1: Most important different properties of the used sample

$S_{BET}(m^2/g)$	$S_s(m^2/g)$	CEC méq/100g	$V_{tot}(cm^3/g)$
72,2	504	89	0,00581
structure Formula: $\mathbf{Ca_{0,043}Na_{0,404}K_{0,16}(Si_{7,56}Al_{0,44})(Al_{2,933}Fe_{0,678}Mg_{0,476})O_{22}}$			

2.2 Homoionic clays preparation

The homoionic Li^+-, NH_4^+-, K^+, Ca^{2+}-, Mg^{2+}-, Fe^{3+}- and A^{3+}- forms were obtained by ion exchanging the purified Na^+-form with the corresponding chlorides or nitrates (analytical grade) by repeated (seven times) exchange in 1% clay suspensions in 1N salt solutions at their natural pH, followed by many washing cycles (centrifugation and, when necessary, dialysis) until chloride-free. Later, the salt-free clay samples were dried at 60°C, powdered in a mortar and pestle, passing through a 60-mesh sieve to obtain finer grains before the experiments.

Homoionic smectites was heated at different temperature, analysis was carried out at a constant heating rate 100°C/h, from room temperature to 400°C, i.e. in a temperature domain where no dehydroxylation of the crystal structure takes place [15].

Characterization of synthesized clays included mineralogical analysis, measurement of CEC, pore volume and BET surface area was studies. The chemical analyses were obtained by using X-ray diffraction studies (Pillips goniometer, PW1730/10, using the Kα radiation of copper). The cation exchange capacities (CEC) were determined by Kjeldhal method [14] and BET surfaces area (S_{BET}) were measured by (N_2, BET) method. We reported also the results according to ATD- ATG, and AFM methods.

We give consequently the most important properties of synthesized clays.

3. Result and discussion

3.1 Chemical Properties of synthesized clays (homoionics smectites)

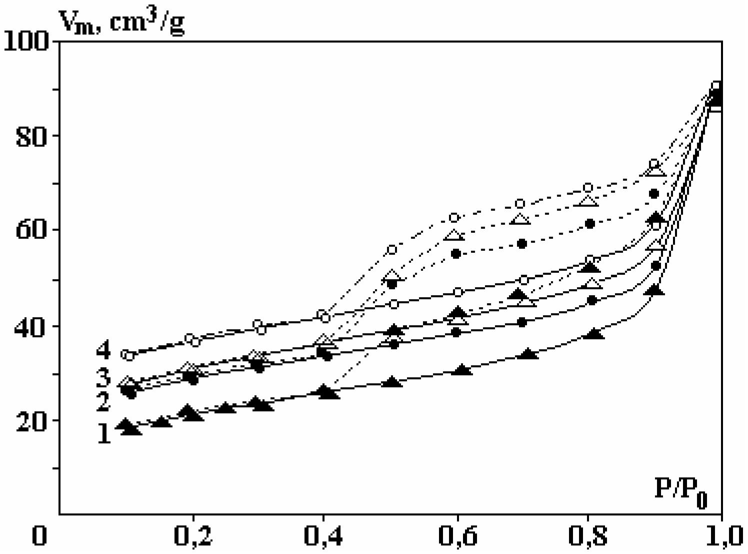
The cation exchange capacity of synthesized clays has been determined according to the ammonium acetate saturation method (table 2), the result show that CEC was function of the type of exchangeable cations, it increases in the following order: Na^+-smect> NH_4^+-smect> Fe^{3+}smect > Mg^{2+}-smect >Al^{3+}-smect > Ca^{2+}-smect> Li^+-smect> K^+-smect.

Table 2: Cation exchange capacity of homoinic smectite

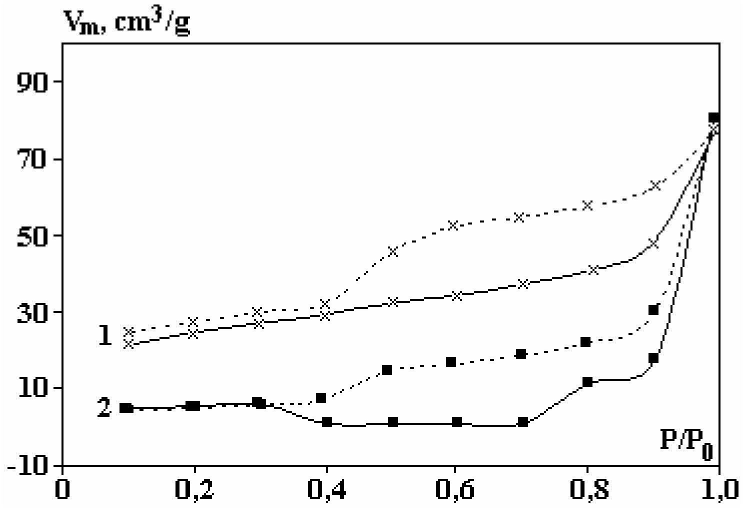
M^{n+}-smect	CEC (méq/100g of clay)	Ignition loss	CEC (méq/100g of calcined clay)
Na^+-smect	72	19	89
K^+-smect	32	7	34
NH_4^+-smect	77	9	85,55
Li^+-smect	63	10	69,23
Ca^{2+}-smect	60	11	70,58
Mg^{2+}-smect	69	15	77,52
Fe^{3+}-smect	72	8,52	78,7
Al^{3+}-smect	64	12	73

The BET Specifics Surfaces area (S_{BET}) and total pore volumes has been determined using the BET method [16]. The t-method of Halsey [17] was used for the determination of micropore volume in the presence of mesopores. This technique involves the measurement of nitrogen adsorbed by the sample at various low pressure values.

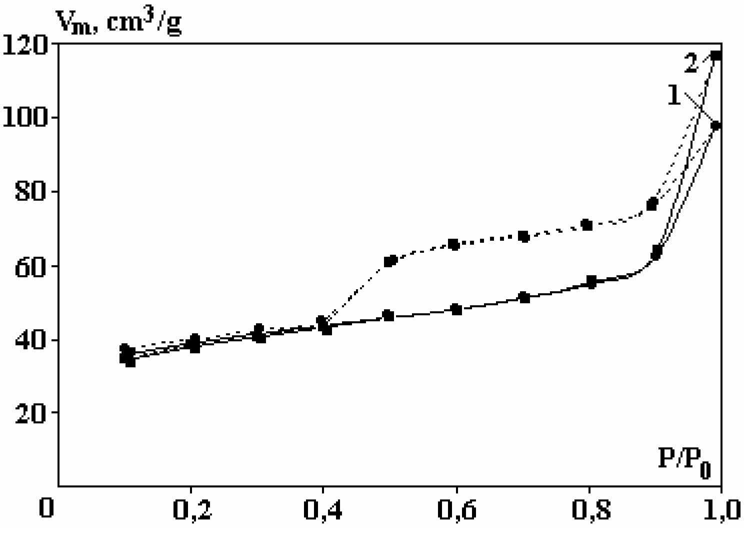
Representative nitrogen sorption isotherms are shown in figure1 they are of type II with H_2 hysteresis loops, as is typical for smectite clays that contain microporous networks of broad structure [18–19]. The surface area due to micropores, S_{mp}, was obtained from the difference (S_{BET} - S_{ex}). Reliable interpretation of these isotherms is limited to quantitative measurement of specific surfaces areas and total pore volumes, these data are provided in table 3 and figure 2.



1 – Na$^+$-Smec; 2 – NH$_4^+$-Smec; 3 – Li$^+$-Smec; 4 – K$^+$-Smec



1 – Ca^{2+}-Smec; 2 – Mg^{2+}-Smec



1 – Al^{3+} -Smec ; 2 – Fe^{3+} -Smec

Fig.1. Nitrogen adsorption and desorption isotherms of synthesized clays

_____ *Adsorption* ------- *desorption*

Table 3: Physical data for synthesizes samples

Sample	S_{BET}(m^2/g)	$S_{ext(t-plot)}$(m^2/g)	S_{mp} (m^2/g)	V_{tot}(cm^3/g)
Na^+-Smect	72,2	61,5	10,7	0,00581
NH_4^+-Smect	93,8	65,92	27,88	0,0551
K^+-Smect	117	69,65	47,35	0,0264
Li^+- Smect	101	72,3	28,7	0,0158
Mg^{2+}-Smect	92	65,62	26,38	0,0112
Ca^{2+} -Smect	82	65,38	16,62	0,00921
Fe^{3+}-Smect	120	74	46	0,026
Al^{3+}-Smect	122	64,8	57,2	0,019

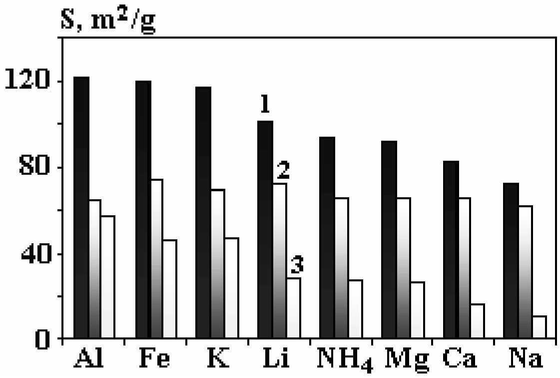


Fig. 2. Representative histograms of S_{BET}, S_{ext} and S_{mp}

3.2. Differential thermal analysis and thermogravimetric analysis (DTA-TGA)

DTA and TGA were merely used as complementary methods with respect to the other techniques. The interpretation [20] of the DTA-TGA curves of synthesizes clay samples (homoionic smectite), we give as example the DTA-TGA curve of Na homoionic smectite, leads to the following results (Figure 3):

- A significant endothermic peak between 130 and 180°C; these transformation are due to the removal of adsorbed and interlayer water from the clay mineral. The high intensity of the first peak confirms the presence of a swelling phase (smectite) interlayer stratified with non swelling clay (illite) [21].
- A small endothermic peak between 500 and 540 °C which corresponds to the loss of hydroxyl groups from the clay mineral structure (clay dehydroxylation).
- An endothermic peak between 930 and 997°C shows the formation of a phase at high temperature [22–23] characteristic of aluminum ferifere smectite.

Curves of TGA allow us to follow the weight loss of homoionic smectite samples (table 2). These curves show tow losses of weight of M^{n+}-smectite samples:

- The first loss of weight occurs between 30 and 130°C. These transformations are due to the removal of adsorbed and interlayer water from the clay mineral.
- The second loss of weight occurs at 526°C due to the removal of water composition from the clay mineral.

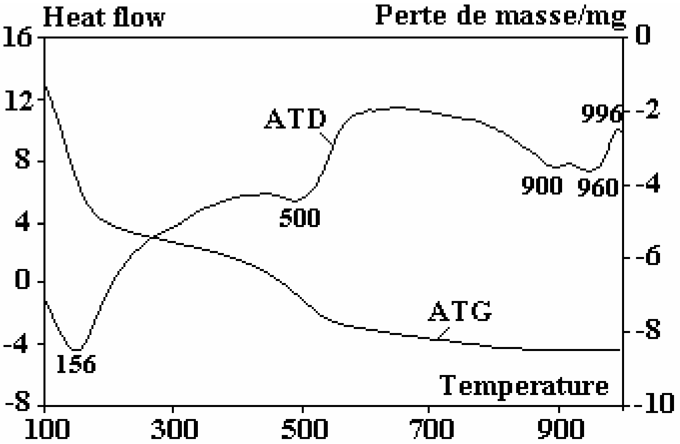


Fig.3 . DTA-TGA curves of Na homoionic smectite (Na^+-smect) sample

The weight loss result are given in table 4, it shows that the creep of smectite clays is not controlled by mobility of the individual water molecules but by the mobility of the interlayer cations surrounded by their hydratation shell, We compare our results to those obtained from a number of comparable homoionic smectites by DTA-TGA by other authors [9, 24–25].

Table 4: % loss of water

Sample: M^{n+}-smect	(%) waters hydratation loss	(%) waters constitution loss	(%)Total loss of water
Na^+- Smec t	13,5	4	17,5
Li^+-Smect	6,83	4,2	12,61
NH_4^+-Smect	9,58	5,5	15,1
K^+- Smect	11,4	4	15,5
Mg^{2+}-Smect	12,35	3,43	16,2
Ca^{2+}-Smect	12,17	3,32	15,5
Al^{3+}-Smect	15,13	4,5	19,6
Fe^{3+}-Smect	13,6	4,6	18,2

3.3. Atomic Force Microscopy AFM

Microtopography of the particles was achieved using atomic force microscopy images (AFM) and computerized image analysis describes a direct and quantitative study of the size and shape of synthesized clay (Figure 4).

AFM images were recorded on a nanoscope II instrument in contact mode and in a region of 5×5 µm^2 with a scan rate of 1Hz at 256 × 256 resolution, for sample preparation for AFM analysis. We use the method of Occelli *et al* [26]; Wafers were formed by pressing powders of samples at about 15 000 kPa and were glued onto steel disks with epoxy resin and when the glue had dried, the atomic force microscope tip was carefully guided to the middle of the wafer thus beginning the analysis.

Atomic Force Microscopy (AFM) reveals the network character and the development of morphology as a function of type of exchangeable cation, witch is noted by a variation in the value of the rugosity (table 5).

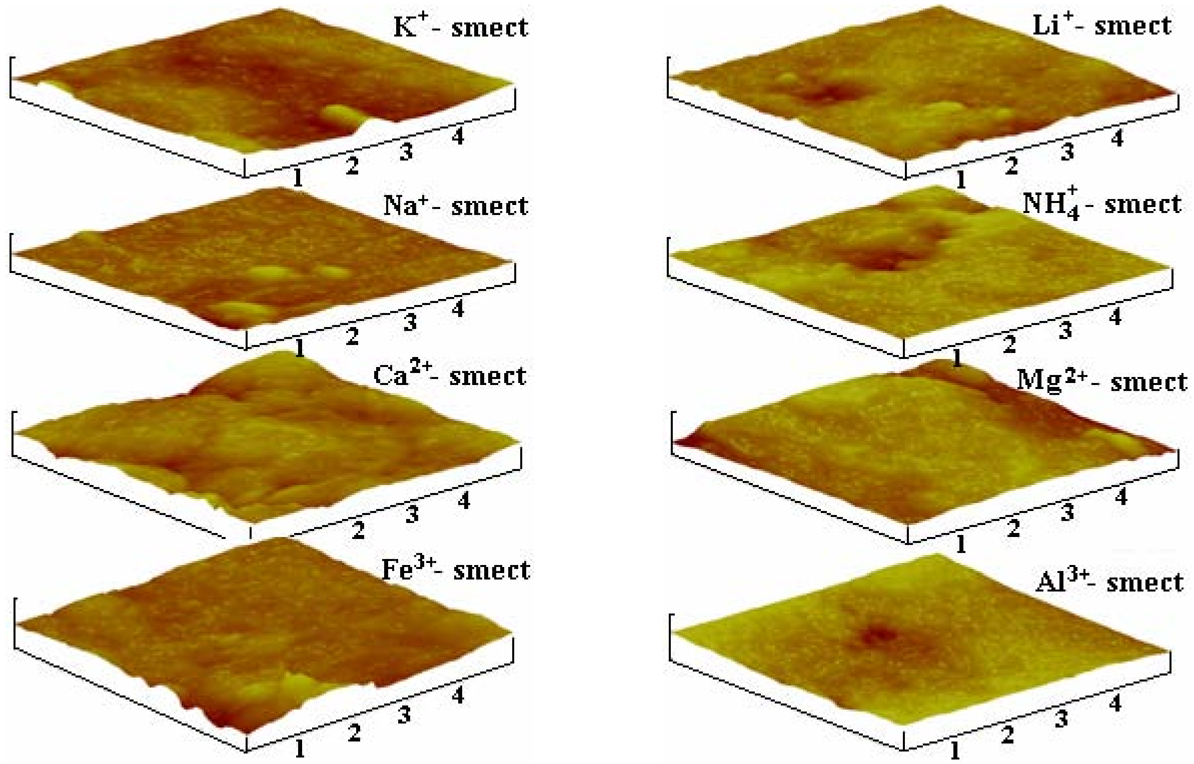


Fig.4. AFM images of homoionic clays

Table 5. Evolution of the regosity

M^{n+}-smect	Al^{3+}-smect	Fe^{3+}-smect	Mg^{2+}-smect	Ca^{2+}-smect	Na^{+}-smect	Li^{+}-smect	NH_4^{+}-smect	K^{+}-smect
Rq	70,7	97,2	84,3	109	107	61,2	74,7	119

3.4 Effect of heating

Physico-chemical properties of smectites depend upon their structures, their chemical compositions and the type of exchangeable cation. The variation of XRD patterns of Li^+-, Na^+-, NH_4^+-, K^+-, Mg^{2+}-, Ca^{2+}-, Fe^{3+}- and Al^{3+}-smectite (Figure 5-6) before and after heating and re-expansion after glycerol salvation was studied. Table 6 shows the swelling obtained for dry and glycerol solvated samples. The d_{001} spacing of Li^+- K^+- NH_4^+- and Na^+-smectite prior to heating correspond to a hydrated structure where the cations are located in the interlayer space and solvated by water molecules adsorbed from the atmosphere.

Lithium saturation and heating caused the bentonite (smectite) to develop hydrophobic character. Li-clay collapsed and remained un-expandable after being heated at 200-400°C (table 4). The XRD patterns of Li-clay after heating at 200–400°C exhibit a d_{001} reflection corresponding to 10Å, even after treatment by glycerol.

The high charge reduction guessed from the reduction of the amount of exchangeable cation (CEC) of Li-clay (witch decrease from 69,3 to 7 méq/100g), after heat treatment is in good agreement with previous work. Calvet and Prost [27] showed that the clay did not swell with water when the amount of exchangeable cation was lower than 50% of the original exchange capacity.

Table 6 : *Effect of thermal treatment on pH, CEC, and d_{001} spacing of synthesized clays (M^{n+}- smectite)*

Cation M-clay	Temperature of heating °C	d001		pH	CEC (meq/100g of clay)
		Dry	glycol		
Na	25	12,25	17,94	6,17	*89*
	200	11, 98	17,94	6,25	84
	300	11,1	17,6	6,43	80
	400	11,1	17,6	6,49	76
Li	25	12,06	17,2	6,05	*69,23*
	200	10,7	17,2	6,5	38
	300	10	10	6,63	16
	400	10	10	7	7
NH_4	25	12,1	16,67	6,2	*85,55*
	200	11,98	16,67	6,32	80
	300	11,98	16,6	6,35	76
	400	11,98	16,6	6,45	70
K	25	10,78	16,7	5,39	*34*
	200	10,6	16 ,7	5,42	28
	300	10,6	16,7	5,55	25
	400	10,6	10,6	5,76	12
Mg	25	14,7	16,97	5,85	*77,52*
	200	14,2	17,2	6,5	66
	300	13,2	17,2	6,64	43
	400	9,6	9,6	6,7	18
Ca	25	15,4	16,67	6,34	*70,58*
	200	15,2	17,67	6,48	60
	300	15,2	17,67	6,65	50
	400	15,2	17,67	6,83	45
Fe	25	14,7	18,4	4,98	*78,7*
	200	14,25	18,4	5,09	68
	300	12,82	18,4	5,11	53
	400	9,6	9,6	5,18	22
Al	25	15	16,7	4,89	*73*
	200	13,2	16,7	4,91	65
	300	13,2	16,7	4,97	58
	400	9,6	9,6	5,12	18

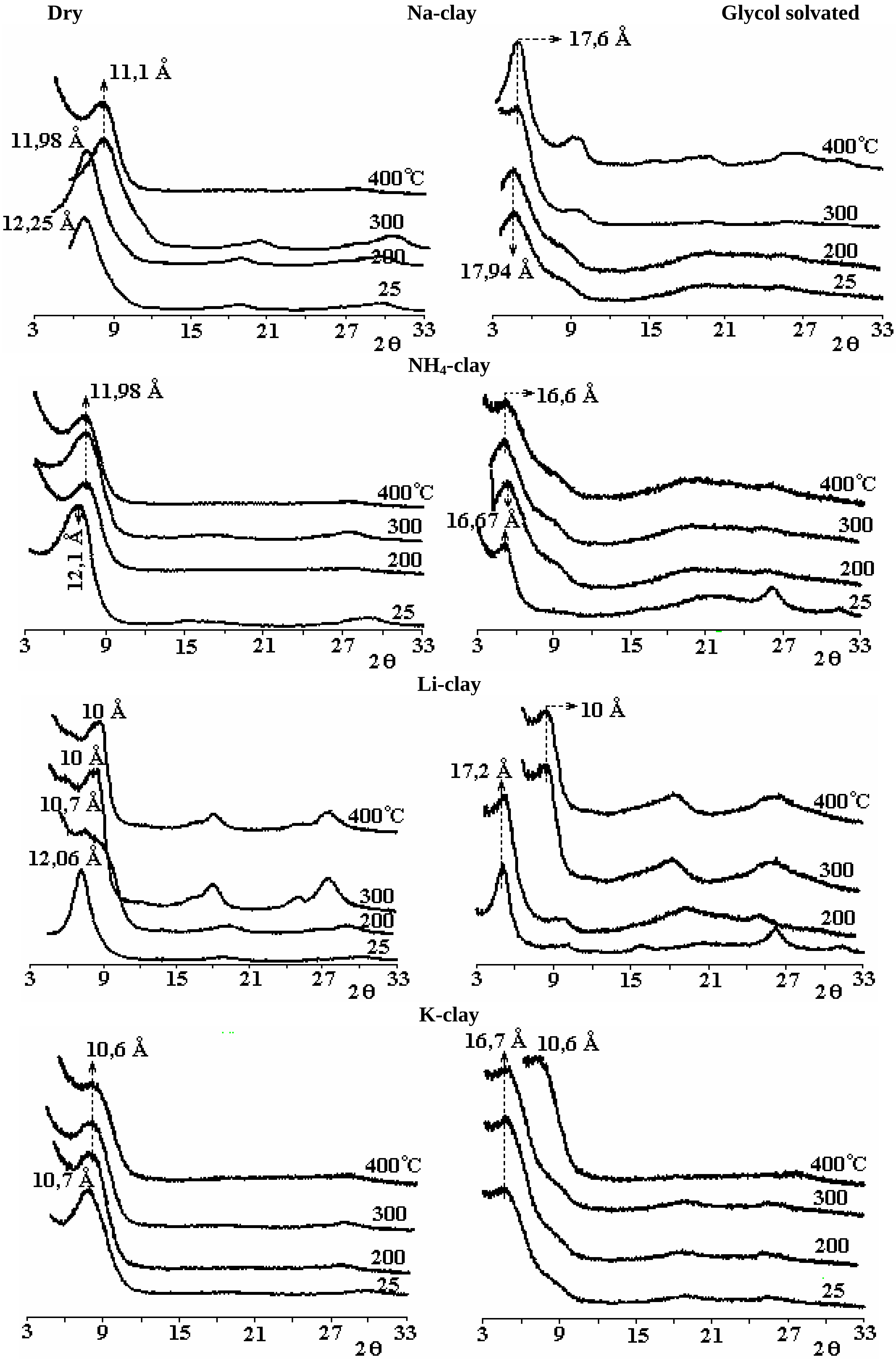
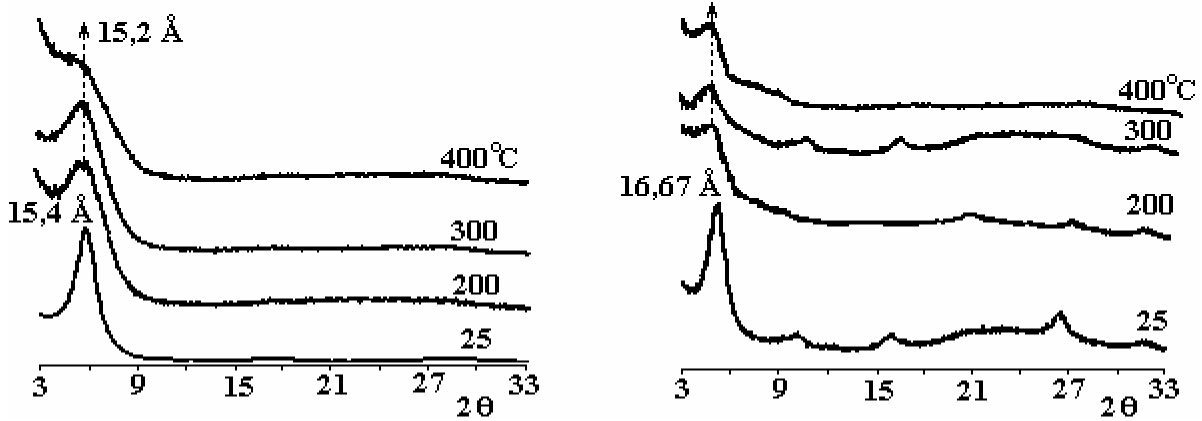
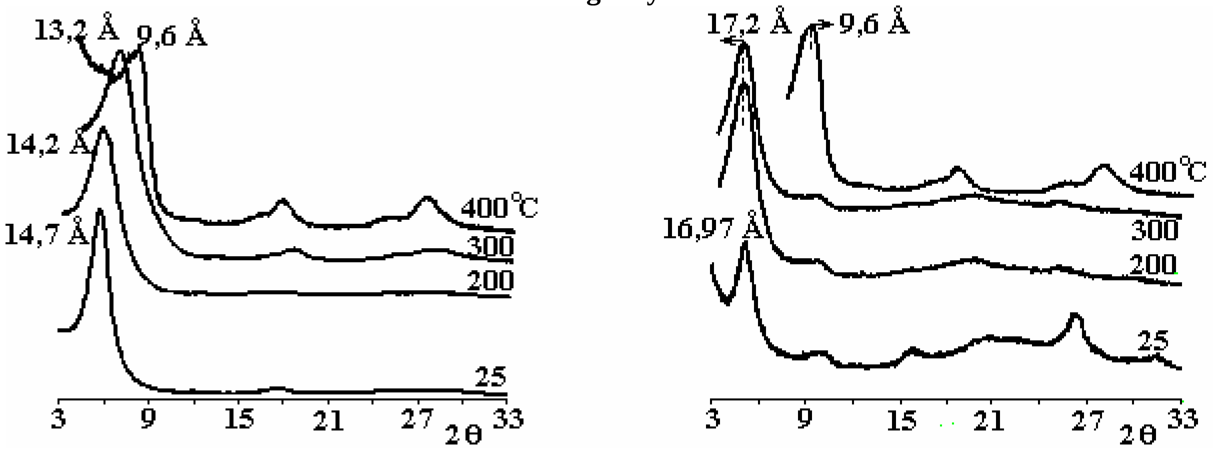


Fig.5. XRD patterns of the smectite saturated with Li, K, NH_4 and Na at different temperatures. The dry samples (left) and those glycol solvated (right)

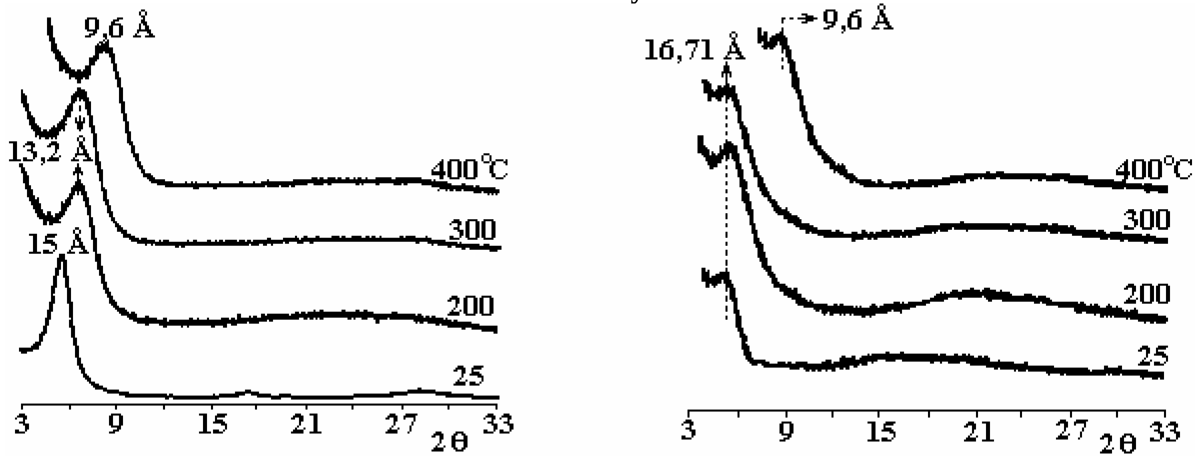
Ca-clay



Mg-clay



Al-clay



Fe-clay

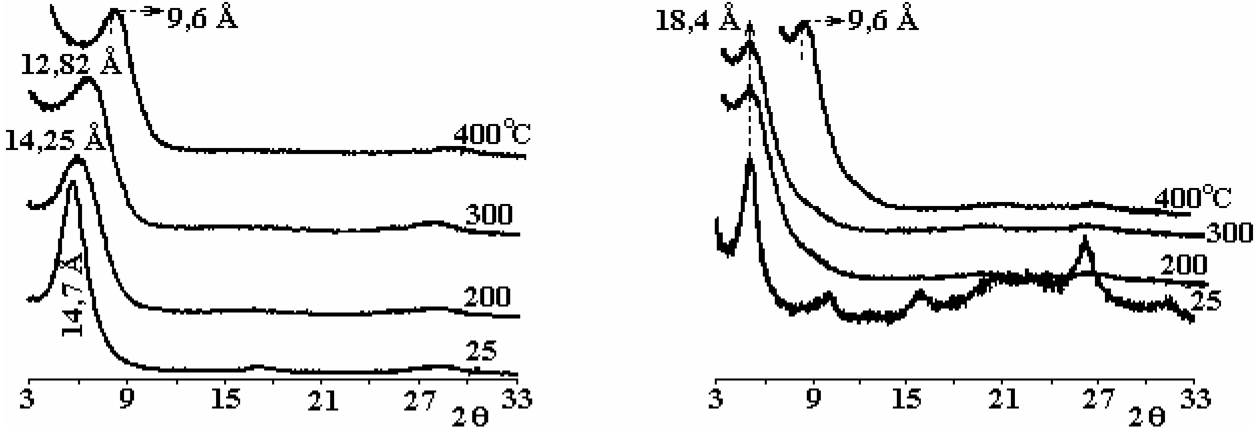


Fig.6. XRD patterns of smectite saturated with Ca, Mg, Fe and Al at different temperatures. The dry samples (left) and the glycol solvated (right)

No differences were detected between XRD patterns of Na-clay heating at 200°C-400°C and 25°C (unheated). Even after thermal treatment (up to 400°C), the hydrated sodium ions remained in the interlayer as re-hydrated sodium ions remained in the interlayer as reflected by d_{001} spacings (fig6, table 6). As a result of glycerol salvation, d_{001} spacing of treated clays increased to 17,6 Å, indicating swelling even after heating to 400°C. This behavior, as for the charge characteristics, is opposite to that of Li-clay.

The d_{001} spacings of K-clays heating to 300°C and after glycerol salvation were similar to those of Na-clays. Expansion in d_{001} spacing of K-clays after glycerol salvation is observed even after heating at 200 or 300°C (table 6). Thus, it appears that K^+ does not migrate into the lattice sites, the interlamellar K^+ remaining exchangeable. Heat treatment only reduces the amount of exchangeable K^+. Apparently, K^+ in the interlayer space is progressively fixed or strongly bonded to the surface -O or –OH groups with increasing temperature.

Among the divalent cations, d_{001}, spacing of unheated (25°C) clays (table6) indicated that interlayer divalent cations were more hydrated than K^+. Spacings for Al^{3+}-clays and Fe^{3+}-clays were also consistent with substantial cation hydration. Heating to 300°C did not result in any substantial collapse of d_{001} spacing, which upon glycerol salvation expanded with d_{001} spacings ranging from 16,7 to 18,4Å. However, on heating at 400°C, Mg^{2+}-, Fe^{3+}- and Al^{3+}-clays collapse to a d_{001} spacing of 9,6Å and did not expand with glycerol salvation (fig2). These results are consistent with migration of Mg, Fe and Al from the interlayer space to the vacant octahedral sites. From literature [3, 27] we reported that when Mg-montmorillonite and Ca-montmorillonite were heated at 400°C, Mg^{2+} ions could migrate into the structure while Ca^{2+} ions could not. Alternatively, it can be suggested that these cations are strongly bonded to the clay surfaces while still remaining in the interlayers.

Results show that peak intensity reduced with increasing temperature (Fig.5 and Fig.6). The extent of peak intensity reduction was similar to the cation exchange capacity reduction. For Li^+-, Mg^{2+}-, NH_4^+-, Fe^{3+}- and Al^{3+}-clays, after heating at 400°C, the cation exchange capacity reduction was drastic and the intensity of d_{001} peaks was also very low.

The thermal treatment of smectite saturated with monovalent divalent and trivalent cation has been show to reduce the cation exchange capacity (CEC) and to affect hydrophobic character of Li^+-, K^+-, Mg^{2+}-, Fe^{3+}- and Al^{3+}-clays suggesting that these cations becomes non-exchangeable.

In general, results corroborate that this clay, collected from Zaghouan, urbanized a good capacity to up take these toxics metals [28] from wast-water since its frequent appearance in waste streams from many industries, and to maintain them even at high temperature, witch rang form 200 to 400°C in this study.

The pH of suspension in distilled water has been measured before and after heating, the results shows that pH depend upon the nature of cation. Among monovalent cationic clays, Li^+-, Na^+- and NH_4^+-clays had higher pH values than K-clays. Furthermore, divalent cationic clays had higher pH values than Fe^{3+}- and Al^{3+}-clays (table 6). In the suspension of unheated clays (25°C), the dissociation of cations and subsequent hydrolysis reactions led to the changes in H^+ concentration. For Fe^{3+} and Al^{3+}, even though the dissociated ions were very low, strong hydrolysis reactions released more H^+ ions and the pH was 4,89 and 4,98 respectively for Fe^{3+}- and Al^{3+}-clays. Upon thermal treatment, the pH increased for all cationc clays, suggesting that the cations are more strongly bound to the clay surface [3]. This is clearly shown in the increase of cation exchange capacity (CEC) with increase in temperature of heating (table 6).

Conclusion

The effect of exchangeable cation noted a good progress in exchangeable properties of synthesized clay comparatively with the Na homoionic smectite form, means good exchangeable properties; adsorption and absorption, except the K homoionic clay witch present the lowest CEC and S_{BET}, consequently the lowest exchangeable properties.

Upon thermal treatment, the bonding characteristics change according to the size of the cations. Smaller cations (ionic radius < 0,7Å), Li, Mg, Fe and Al apparently migrate to the octahedral vacant sites. This result in severe cation exchange capacity reductions and the cation becomes non-exchangeable. This process occurred even at 200°C for Li^+-clays.

Larger cations Na, NH_4, K and Ca apparently do not migrate to lattice sites on thermal treatment.

The thermal treatment of smectite saturated with monovalent divalent and trivalent cation has been show to reduce the cation exchange capacity (CEC) and to affect hydrophobic character of Li^+-, K^+-, Mg^{2+}-, Fe^{3+}- and Al^{3+}-clays suggesting that these cations becomes non-exchangeable.

Results corroborate that this clay, collected from Zaghouan, urbanized a good capacity to remove toxics metals [28] from wast-water, since this problem has received considerable attention in recent years due primary to concern that those toxic metals in the waste streams can be readily adsorbed by marine animals and directly enter the human food chains, thus presenting a high health risk to consumers.

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Summary

The effect of exchange cations (M^{n+}: Li^+, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, and Al^{3+}), and thermal treatment on the physicochemical properties of smectite was investigated. Before thermal treatment, unheated (25°C) M^{n+}-smectite showed increased d_{001} spacing on glycol solvation, after heating at 300°C or above (400°C) d_{001} spacing on glycol solvation of Al-, Fe-, Mg-, Li-smectite decrease and reached 10Å, however, d_{001} of Ca^{2+}-, Na^+- and NH_4^+-smectite increase upon glycol salvation indicated that d_{001} varied with the nature of exchangeable cation and the temperature of heating. The results generally suggested that: d_{001} of homoionic smectite before and after heating at various temperatures depended upon the nature of exchangeable cation. The cation exchangeable capacities (CEC) and the BET surfaces area (S_{BET}) were functions of the type of exchangeable cations, since S_{BET} drop off in the following order: Na^+-smect>Ca^{2+}-smect>Mg^{2+}-smect>NH_4^+-smect>Li^+-smet>K^+-smect >Fe^{3+}-smect>Al^{3+}-smect. Finally we have noted a good progress in exchangeable properties of synthesized clay comparatively with the Na homoionic smectite form, except the K homoionic clay witch present the lowest CEC and S_{BET}, consequently the lowest exchangeable properties.