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MONTMORILLONITE-SALT INTERACTIONS AT 550°C

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Abstract—The reactions between montmorillonite and carbonates and hydroxides of Na, K and Li were studied at 550°C as a function of salt content and time. The reactions were found to be rapid with a half-time of 20–30 minutes. Good agreement was obtained between theoretical and experimental stoichiometric values for the clay-carbonate reaction. The 001 and 02,11 reflections of the products of the clay-salt reactions diminished in intensity and/or disappeared at and above the stoichiometric concentrations of the reactants.

Key Words—Carbonates, Hydroxides, Montmorillonite, Solid-state reaction.

INTRODUCTION

The isothermal solid-state reaction at 550°C between montmorillonite and sodium carbonate was found useful in the detection of montmorillonite in soil clays for which absence and/or weak basal reflections were observed in X-ray diffraction (XRD) traces (Helmy *et al.*, 1984). More information about that reaction, its mechanisms and its extent in the presence of other salts and clays were reported by Natale and Helmy (1989).

To gain more knowledge about montmorillonite/salt reactions at 550°C we tested the stoichiometry of the montmorillonite/Na_2CO_3 reaction. We studied the kinetics and the extent of the clay structure alterations produced in clay-salt interactions, and included in the study carbonates and hydroxides of Li and K. We also made use of a thermogravimetric balance, thus improving upon the overall precision of earlier weight determinations. The results of our study are reported here.

EXPERIMENTAL

The clay used in this study was a montmorillonite from Río Negro, Argentina (Natale and Mandolesi, 1985). Clay particles $< 2\ \mu m$ in diameter were obtained by sedimentation in water followed by centrifugation and air-drying. Samples were converted to the monoionic form by washing several times with a 0.1 M chloride of Li, Na or K. The clays were then washed several times with water until chloride was reduced considerably in the supernatant. The monoionic clays were then air-dried. Clay-salt mixtures were prepared by adding to 0.5 g samples 0.1 g of the respective carbonate or hydroxide salt dissolved in 1.5 ml of water. Clay pastes were well-mixed and left to dry in air. They were then pulverized, passed through a 200-μm sieve, and stored in bottles. In the case of the Na-clay, increasing amounts of Na_2CO_3 were added in order to study the effect of carbonate content on the clay-salt reaction.

The clay-salt reaction at 550°C was carried out using an automatic thermogravimetric balance Netsch GmbH Model (409/2). The heating rate was 10°C/min and the temperature (once attained) was maintained at 550°C for 2 hr. From the thermogravimetric curves the weight of the sample could be obtained as a function of time. The difference in weight between the sample at zero time (zero time is the time when a temperature of 550°C was reached) and its weight after two hours of heating at 550°C was taken to represent the complete reaction between salt and clay, i.e., $\alpha = 1$ in Eq. (2), below. This criterion was adopted because no change in sample weight was observed after the two-hour period.

XRD traces of the products of the salt-clay reaction were obtained using Ni-filtered CuKα radiation (Rigaku Danki geigerflex model D max 3C diffractometer).

RESULTS AND DISCUSSION

Stoichiometry of the clay/Na_2CO_3 reaction.

From the thermogravimetric data the amounts of carbonate consumed in the solid-state reaction were calculated. These are plotted as a function of the amounts added in Figure 1. As appears from the figure, the amounts consumed in the reaction increased as the content of carbonate increased in the clay/carbonate mixtures, and then reached a constant amount of 167.5 mg/g clay when the amount of Na_2CO_3 present in the mixtures exceeded 400 mg/g clay. Furthermore, in all cases a part of the carbonate in the mixtures did not react with the clay. This incomplete interaction between reactants is common in all solid-state reactions. It is usually attributed to the fact that complete contact between the two reactants cannot be achieved experimentally (Welch, 1955).

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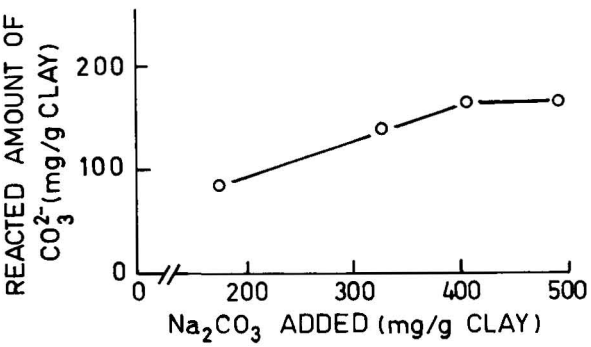


Figure 1. The amounts of Na_2CO_3 consumed per gram montmorillonite versus the amount added.

That the amount of carbonate consumed cannot exceed 167.5 mg/g clay will be clear from the following theoretical considerations.

At relatively high temperatures, for example at 550°C or less, the protons associated with the structural-OH groups of the clay migrate to surfaces and/or boundaries where they combine with carbonate anions according to the reaction:

$$2\ H^+ + CO_3^{2-} \rightarrow CO_2 + H_2O. \qquad (1)$$

In this reaction, two protons are needed for each carbonate decomposed. The structural formula for montmorillonite contains four hydroxyl groups, and the clay used in this study had the following chemical composition (Natale and Mandolesi, 1985):

$$(Si^{4+}_{7.83}, Al^{3+}_{0.17})^{IV}(Al^{3+}_{3.00}, Fe^{3+}_{0.35}, Mn^{3+}_{0.05}, Mg^{2+}_{0.61})^{VI} O^{2-}_{20}(OH)^-_4,$$

with a formula weight of 716. Stoichiometry requires, therefore, that each gram of this clay can consume no more than 167.5 mg/g of carbonate.

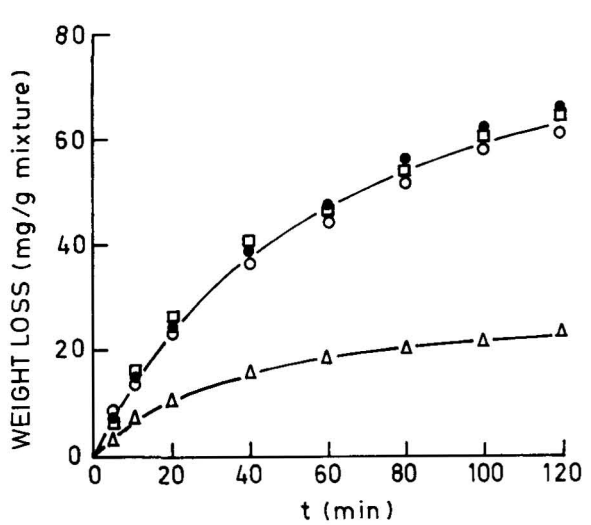


Figure 2. Weight loss (mg/g mixture) versus time for mixtures of montmorillonite and Na_2CO_3 heated at 550°C: (△) 0.16; (□) 0.33; (○) 0.41; (●) 0.49 g/g clay.

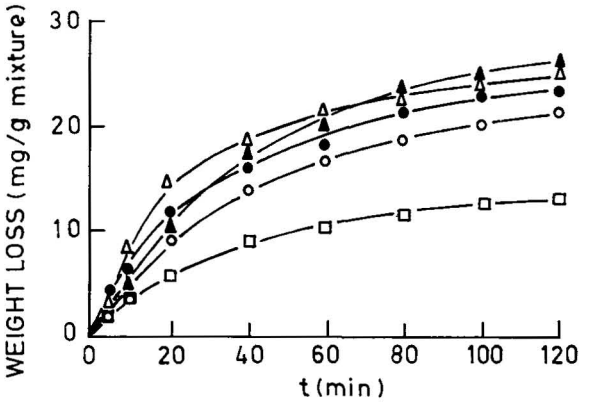


Figure 3. Weight loss (mg/g mixture) versus time for mixtures of montmorillonite and salts: (●) Na_2CO_3; (○) K_2CO_3; (□) LiOH; (△) NaOH; (▲) KOH (0.20 g/g clay).

The experimental data of Figure 1 are thus in excellent agreement with the theoretical value since the curve in Figure 1 reaches a maximum at the value of 168 mg carbonate per g clay, and is found to flatten above that value, indicating also that no reaction other than that given by Eq. (1) has taken place.

Kinetics of the montmorillonite/salt reaction

The results of the effect of time on the clay-salt reactions are given in Figures 2 and 3 where the fraction reacted is plotted as a function of time. For all salts studied the reaction was relatively more rapid in the beginning and slowed down with time. This behavior is typical of solid-state reaction. The reason for the slowdown is attributed to the formation of a layer of products at the interface. The movement of the reacting ions through such a layer allows the reaction to proceed and the layer is expected to increase in thickness as the original clay crystal structure is altered. Therefore, diffusion of ions (Na and H, for example) becomes slower with time and the reaction rate diminishes. Added to this factor is the expected decrease in the surface of contact as the reaction proceeds due to the consumption of the anions of the salts.

Table 1. Rate constants of the reaction (k) and times for completion of half reaction of montmorillonite with carbonates and hydroxides of Li, Na and K.

Salt	g salt/ g clay	k (sec^{-1})	t 0.5 (min)
Na_2CO_3	0.16	$(5.5 \pm 1.2) \times 10^{-4}$	21.6 ± 3.9
	0.20	4.5 ± 1.2	27.3 ± 5.7
	0.33	4.2 ± 0.4	28.1 ± 2.9
	0.41	4.1 ± 0.5	28.8 ± 3.3
	0.49	4.0 ± 0.4	28.9 ± 2.5
K_2CO_3	0.20	3.8 ± 0.7	31.1 ± 5.4
LiOH	0.20	4.8 ± 0.5	24.4 ± 2.6
NaOH	0.20	5.2 ± 1.2	23.0 ± 4.4
KOH	0.20	4.7 ± 0.9	25.1 ± 4.4

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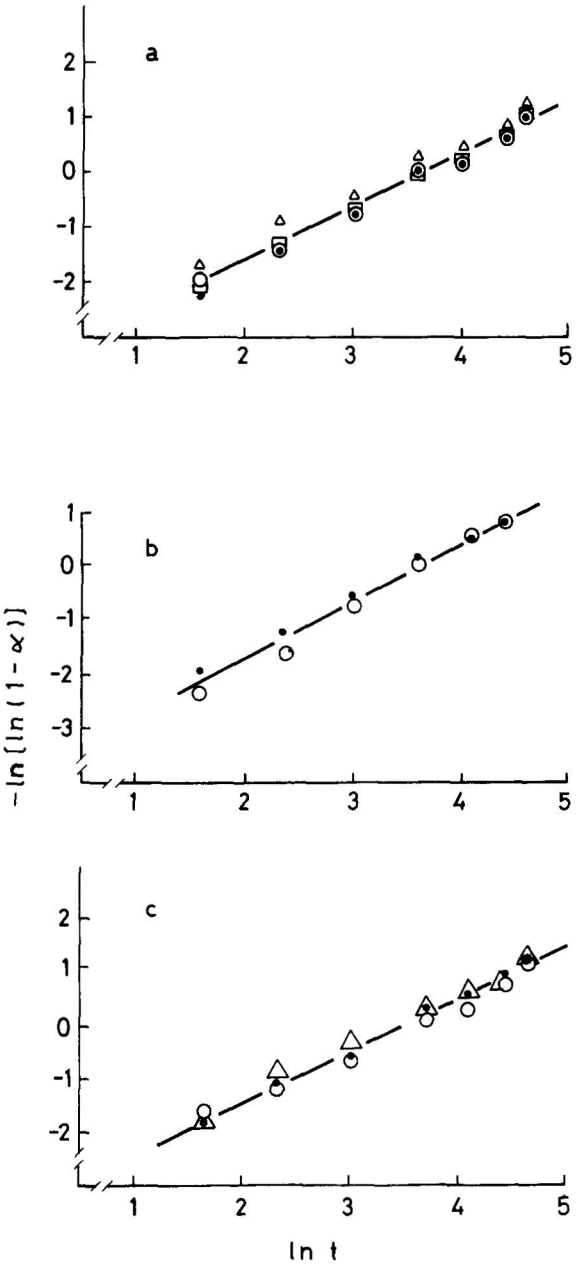


Figure 4. (a) Plots of $-\ln \ln (1 - \alpha)$ versus ln t for mixtures of montmorillonite and Na_2CO_3: (△) 0.16; (□) 0.33; (○) 0.41; (●) 0.49 g salt per g clay. (b) Same as in (a) but for Na_2CO_3 (●) and K_2CO_3 (○) (0.20 g/g clay). (c) Same as in (a) but for LiOH (●), NaOH (△), and KOH (○) (0.20 g/g clay).

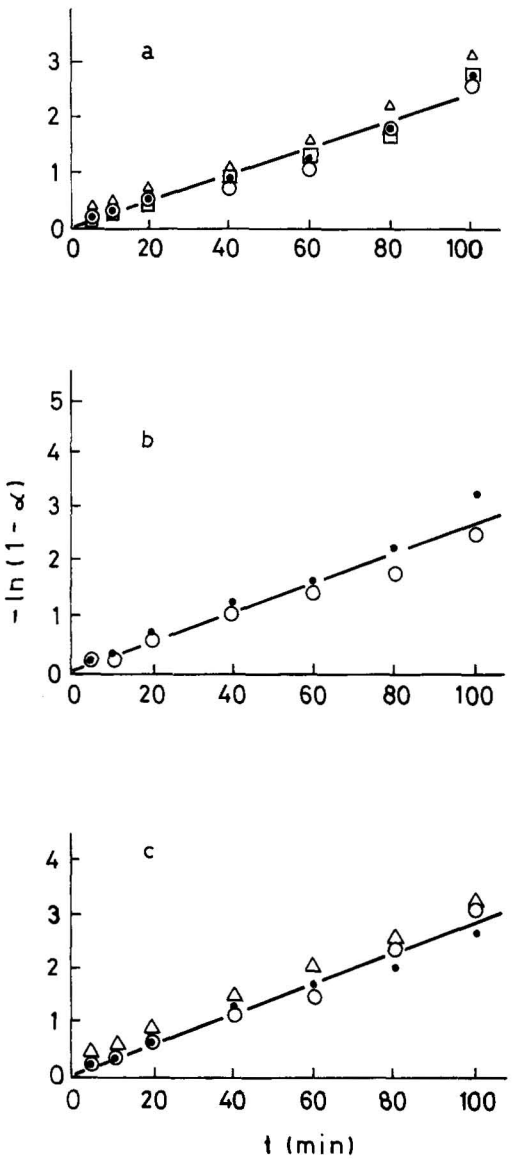


Figure 5. (a) Plots of $-\ln (1 - \alpha)$ versus time for mixtures of montmorillonite and Na_2CO_3: (△) 0.16; (□) 0.33; (○) 0.41; (●) 0.49 salt per g clay. (b) Same as in (a) but for Na_2CO_3 (●) and K_2CO_3 (○). (c) Same as in (a) but for LiOH (●), NaOH (△), and KOH (○) (0.20 g/g clay).

As mentioned above, carbonates and hydroxides of Li, Na and K were used in this study. The salt content in the clay-salt mixtures was 200 mg/g, except for Na_2CO_3 where contents varied from 160–490 mg/g clay. The results of the clay-salt reactions are plotted in Figure 4 according to the straight-line equation:

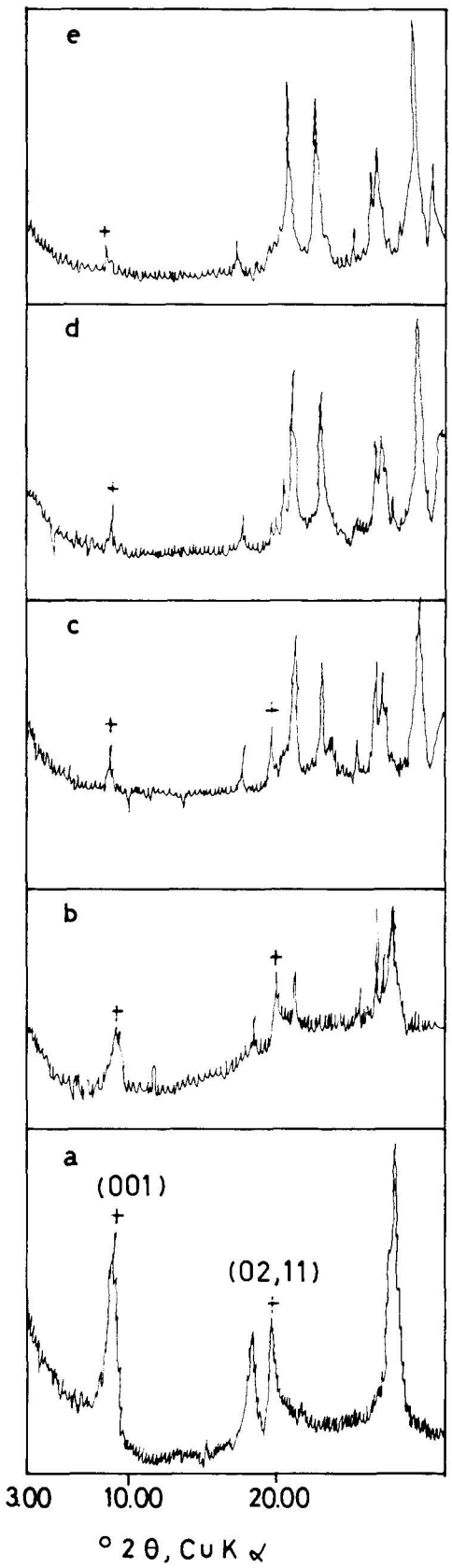
$$-\ln \ln(1 - \alpha) = \ln B + m \ln t, \qquad (2)$$

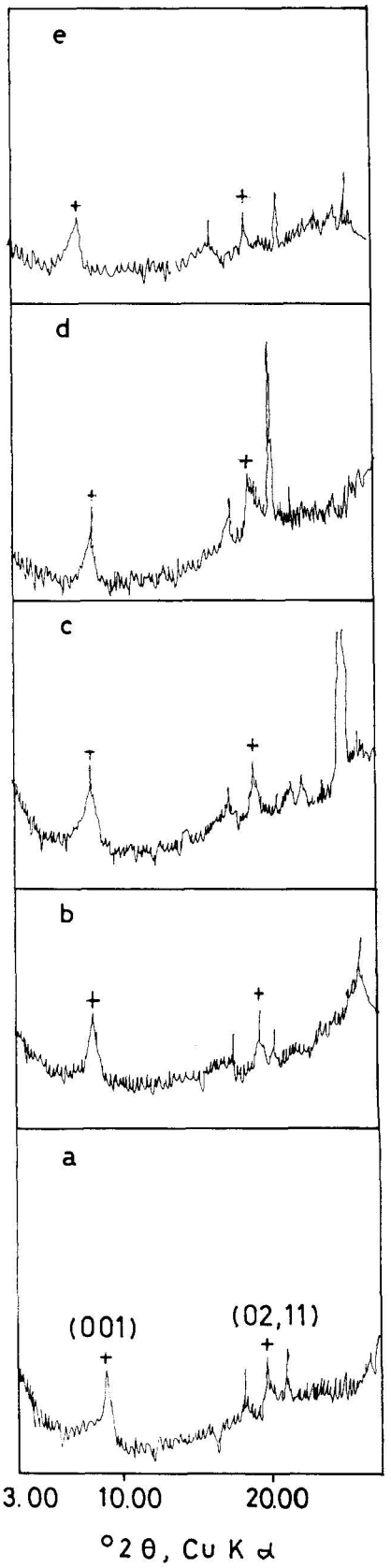
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Figure 6. XRD traces of montmorillonite heated for 2 hr at 550°C (a), and heated in the presence of different amounts of Na_2CO_3; 0.16 (b); 0.33 (c); 0.41 (d); 0.49 (e) g salt per g clay.

Figure 7. XRD traces of montmorillonite heated for 2 hr at 550°C in the presence of: 0.16 (g/g clay) of Na_2CO_3 (a); 0.20 (g/g clay) of K_2CO_3 (b); 0.20 (g/g clay) of LiOH (c); 0.20 (g/g clay) of NaOH (d); 0.20 (g/g clay) of KOH (e).

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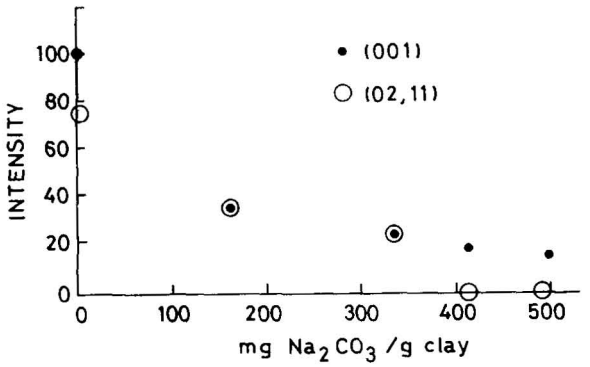


Figure 8. Intensity of the (001) and (02,11) XRD reflections of montmorillonite/Na_2CO_3 mixtures heated at 550°C for 2 hr.

where α is the fraction transformed at time, t, and B and m are constants. According to Brindley *et al.* (1967), Hancock and Sharp (1972) and Beretka and Brown (1983) Eq. (2) is the basic formula for comparing kinetic data of solid-state reactions. The value of m is characteristic of the mechanism that determines the transformation as diffusion-controlled, first-order controlled, or phase-boundary controlled. The values of m obtained varied between 0.87 and 1.11. The reactions studied, therefore, were first-order, and/or diffusion-controlled. Here we will treat the clay-salt reaction as first-order controlled since it offers the advantage of obtaining from the experimental results (Figure 5) the rate constant and also the times to complete half the reactions. This treatment is also in agreement with the chemistry of the reaction as expressed in Eq. (1).

The rate constants and the half-times for the clay-salt reactions are given in Table 1. The data in the table indicate that the clay-salt reactions are rapid with similar values for the rate constants for all the salts used. The half-time of the reactions is of the order of 20–30 minutes.

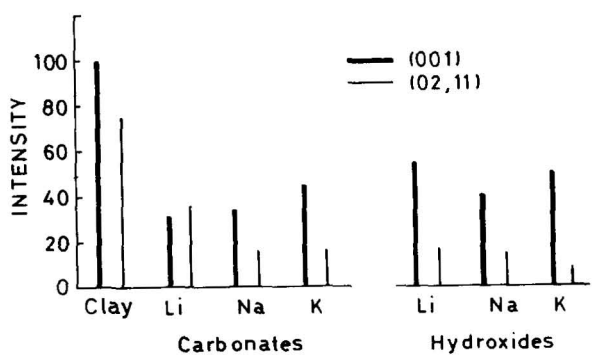


Figure 9. Intensity of the (001) and (02,11) XRD reflections of montmorillonite/salt mixtures heated at 550°C for 2 hr. The intensities obtained for the calcined clay (salt-free) are also shown.

The similarities in the values of the rate constants of carbonates and hydroxides deserve some comment since the hydroxides studied have melting points below 550°C. The clay-salt reactions in such cases were liquid/solid-state. Liquid/solid reactions are expected to be more rapid than solid/solid reactions because of the greater mobilities of ions in the liquid state. The results of the present study, however, indicate that this factor was not very important in determining the kinetics of the clay-salt interaction.

X-ray powder diffraction

The XRD traces of the products of the montmorillonite/salt reactions at 550°C are given in Figures 6 and 7. The effect of the carbonate content of the clay-carbonate mixture on the intensity of the 001 and 02,11 XRD reflections is shown in Figure 8. As may be seen, these intensities decrease gradually with the increase in carbonate content, and the 02,11 reflection disappears completely when the stoichiometric amounts of carbonate and clay have reacted. The reason for these observations is that the reaction given by Eq. (1) produces a charge imbalance; the clay structure loses positive charges (the protons). This creates a diffusion potential that forces the movement of the alkali cations into the crystal along the electrical potential created by the movement of protons in the opposite direction. The diffusion of the alkali cations into the clay crystal requires a drastic change in oxygen packing. This is because of size and high coordination numbers with oxygen in silicates, i.e., 8- to 12-fold coordination. The presence of the alkali cations, therefore, produces a distortion of the clay structure and a loss of the crystallographic properties of the clay causing the disappearance of the XRD reflections of the mineral.

No important differences in the XRD traces were observed due to the different salts used, and it appears that at 200-mg salt content the carbonates and hydroxides of Li, Na and K diminish the 001 and 02,11 XRD reflections of montmorillonite to about the same extent. This is shown by the traces in Figure 7 and the intensities given in Figures 8 and 9.

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