THERMAL TREATMENT OF SOME PURE SMECTITES

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ABSTRACT

Eight pure smectite samples (six montmorillonites and two nontronites) were analysed by DTA and TG. Seventeen derivatives of different exchangeable cations were prepared from one of these montmorillonites and thermally analysed. Montmorillonites show higher dehydroxylation temperatures than nontronites. Dehydration of the smectite derivatives studied gives DTA peaks markedly differing in temperature, intensity, width and number of peaks, depending on the type of exchangeable cation. TGA curves for the derivatives studied are also given.

INTRODUCTION

The thermal treatment of smectite minerals and their derivatives (including dehydration, dehydroxylation and phase transformation) is of great interest due to the recent wide applications of these minerals.

The effect of exchangeable cation type and clay lattice composition of different smectite minerals was previously studied [1–4]. Dehydration was reported to be strongly affected by the type of exchangeable cation. On the other hand, dehydroxylation is highly dependent on the structure and composition of the unit cell.

The present work aims to study the dehydration and dehydroxylation behaviour of some pure smectites and some other derivatives prepared from one of them.

EXPERIMENTAL

Materials

The crude smectite samples were thoroughly dispersed in distilled water ($S/L = 1:100$) using a high-speed agitator. After 24 h settling the upper layer of the suspension (5–10% of the total bulk) was decanted and collected. This agitation, settling and decantation process was repeated until electron

microscopy testing confirmed the presence of a pure smectite sample. The nontronite samples prepared are: Manito (U.S.A.) and Sampor (U.S.S.R.); the montmorillonite samples are: Polkville (U.S.A.), Arizona (U.S.A.), Ginovec (Yugoslavia), Askangel (U.S.S.R.), Pyzevsky (U.S.S.R.) and Jelsovy Potok (Czechoslovakia).

The other seventeen samples of different cationic derivatives were prepared from pure Jelsovy Potok montmorillonite (JP) by overnight soaking of the original sample in a 1 N chloride solution of the desired cation, using 5% pulp concentration. The prepared derivatives were washed and decanted five times with 0.1 N chloride solution. In order to facilitate filtration and washing of the highly dispersed slurries, ethyl alcohol was used as flocculant. Washing was repeated until a chloride-free filtrate was obtained. Samples were dried at 90°C to drive off absorbed alcohol and then subjected to hydration for 10 days at constant relative humidity in a vacuum desiccator containing a saturated solution of $Mg(NO_3)_2$. The derivatives prepared are $(NH_4)^+$, Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Fe^{3+} and Al^{3+}.

Techniques

The DTA experiments were carried out using a locally made apparatus with a dc amplifier (Leeds and Northrup type) and recorder (H & B poly Co.). The heating rate was kept at $2°C\ min^{-1}$. The recommendations of Mackenzie [3] and McAdie [5] were taken into account. TG was performed on an automatic thermobalance (Gebrüder Netzsch, Germany).

RESULTS

Chemical analysis and structural formula

Chemical analyses of the pure smectite samples investigated are given in Table 1. The structural formulae of smectites calculated according to Kelley's method [6] are depicted in Table 2. An example of these calculations is given in Table 3 for Askangel montmorillonite. It can be seen from Table 1 that the silica content in the nontronites studied is in the range 40–45%, whereas for montmorillonites, this range is 49–59%. Greater variation is shown in alumina and iron oxide contents where, for the nontronites, the ranges are 3–6 and 30–35%, respectively. For montmorillonites, the ranges are 16–20 and 1.6–6%, respectively.

The substitution between aluminium and both silica and iron took place in the octahedral and tetrahedral sheets [7]. From these results it can be seen that, for nontronites, the substitution of Si atoms by aluminium, taking place in the tetrahedral sheets, is more pronounced than in montmorillonites.

TABLE 1

Chemical analysis of pure smectite sample [nontronites: (I) Manito (U.S.A.); (II) Sampor (U.S.S.R.); montmorillonites: (III) Polkville (U.S.A.); (IV) Arizona (U.S.A.); (V) Ginovec (Yugoslavia); (VI) Askangel (U.S.S.R.); (VII) Pyzevsky (U.S.S.R); (VIII) JP (Czechoslovakia)]

	I	II	III	IV	V	VI	VII	VIII
SiO_2	40.41	45.40	50.61	51.72	49.55	50.72	49.09	58.58
Al_2O_3	5.72	2.99	17.97	16.70	16.73	16.18	16.76	20.44
Fe_2O_3	29.69	34.85	6.04	3.86	3.6	3.46	1.65	2.57
TiO_2	–	0.16	0.26	0.70	–	–	–	0.36
TiO	0.61	0.10	2.57	4.04	2.27	4.03	3.18	4.01
CaO	2.83	3.36	3.40	3.64	5.60	3.09	6.16	2.65
Na_2O	–	–	0.03	–	–	–	–	0.18
K_2O	–	–	–	–	–	–	–	0.20
Ignition loss	16.96	14.93	19.24	19.30	19.07	19.00	22.18	11.00

Complete substitution of Al by Fe in the octahedral sheets occurred only in the case of nontronites.

Differential thermal analysis (DTA)

The results of DTA of the eight pure smectite samples are represented by the curves in Fig. 1. Two peaks appear in the temperature range 50–250°C, attributed to the dehydration of interlayer water. The shape of the dehydration peaks is markedly influenced by the type of exchangeable cations present in the mineral studied. The double peaks may be related to the effect of calcium. The presence of other exchangeable cations (e.g., Na^+, K^+ or Mg^{2+}) has little effect, since they are present in relatively small amounts (Table 2). The change in shape of the dehydration peaks, due to the presence of different types of exchangeable cations, is also studied below.

TABLE 2

Chemical structure of pure smectite samples

Sample	Structure
I	$(Si_{6.93}Al_{1.07})(Al_{0.08}Fe_{3.83}Mg_{0.09})O_{20}(OH)_4 - Mg_{0.07}Ca_{0.52}$
II	$(Si_{6.90}Al_{1.10})(Al_0 Fe_{3.98}Ti_{0.02})O_{20}(OH)_4 - Mg_{0.02}Ca_{0.54}$
III	$(Si_{7.54}Al_{0.46})(Al_{2.69}Fe_{0.68}Mg_{0.61}Ti_{0.02})O_{20}(OH)_4 - Ca_{0.54}Na_{0.01}$
IV	$(Si_{7.67}Al_{0.33})(Al_{2.59}Fe_{0.43}Mg_{0.90}Ti_{0.08})O_{20}(OH)_4 - Ca_{0.58}$
V	$(Si_{7.67}Al_{0.33})(Al_{2.72}Fe_{0.42}Mg_{0.86})O_{20}(OH)_4 - Ca_{0.93}$
VI	$(Si_{7.79}Al_{0.21})(Al_{2.72}Fe_{0.40}Mg_{0.88})O_{20}(OH)_4 - Ca_{0.51}Mg_{0.04}$
VII	$(Si_{7.66}Al_{0.34})(Al_{2.74}Fe_{0.19}Mg_{1.06})O_{20}(OH)_4 - Ca_{1.03}$
VIII	$(Si_{7.78}Al_{0.22})(Al_{2.98}Fe_{0.26}Mg_{0.73}Ti_{0.03})O_{20}(OH)_4 - Ca_{0.38}Mg_{0.06}Na_{0.02}K_{0.02}$

TABLE 3

Determination of chemical formula of Askangel montmorillonite, based on the Kelley method [6]

	Percent-age	Gram-molecules of cations, A	Gram-equivalent of cations, B	Atoms/unit cell, C [a]		Charge, D
				First calcu-lation	Re-calcu-lation	
SiO_2 (60.09)	50.72	0.8441	3.3764	7.7884	7.7884	
				Al_2O_3	0.2116	− 0.2116
					8.0000	
Al_2O_3 (50.98)	16.18	0.3174	0.9522	2.9286	2.7170 [b]	
Fe_2O_3 (79.85)	3.46	0.0433	0.1299	0.3995	0.3995	
MgO (40.32)	4.03	0.1000	0.2000	0.9227	0.8835	− 0.8835
					4.000	− 1.0951
MgO					0.0392 [c]	+ 0.0784
CaO (56.08)	3.09	0.0551	0.1102	0.5084	0.5084	+ 1.0168
			4.7687			+ 1.0952

[a] $C = KA$; $K = 44/4.7687 = 9.22683$, where 44 is the equivalent of 20 oxygen atom + 4 hydroxyl groups (or $8\ Si^{4+} + 4Al^{3+}$).

[b] $2.717 = 2.9286 - 0.2116$.

[c] $0.0392 = 0.9227 - 0.8835$.

Other endothermic peaks were detected in the temperature range 400–750°C. These peaks were related to the dehydroxylation of heated samples. With nontronites, a single, sharp endothermic peak occurs in the temperature range 400–550°C with a maximum at ~ 490°C. The dehydroxylation peaks of montmorillonite samples are displayed at relatively higher temperatures ranging from 550 to 750°C with maxima at ~ 665°C, except JP montmorillonite which has a maximum at 695°C. These results are in good agreement with those of previous investigators [3,4] who concluded that increasing Fe^{3+} in the octahedral layers is accompanied by a dehydroxylation temperature change. It can be noted that the change in tetrahedral substitution has no influence on the decrease in dehydroxylation temperature. This result is also in agreement with those of Green-Kelley [8] and Cičel [9] but differs from that of Johns and Jonas [10]. It is worth mentioning that the dehydroxylation peaks of montmorillonite samples differ not only in temperature maxima, but also in size and shape of the peak. This may be attributed to the extent of substitution in octahedral aluminium by other cations, such as Fe^{3+} or Mg^{2+}. This can be explained by the change in energy of Me(VI)–OH bonds with the change in substituted octahedral Me(VI).
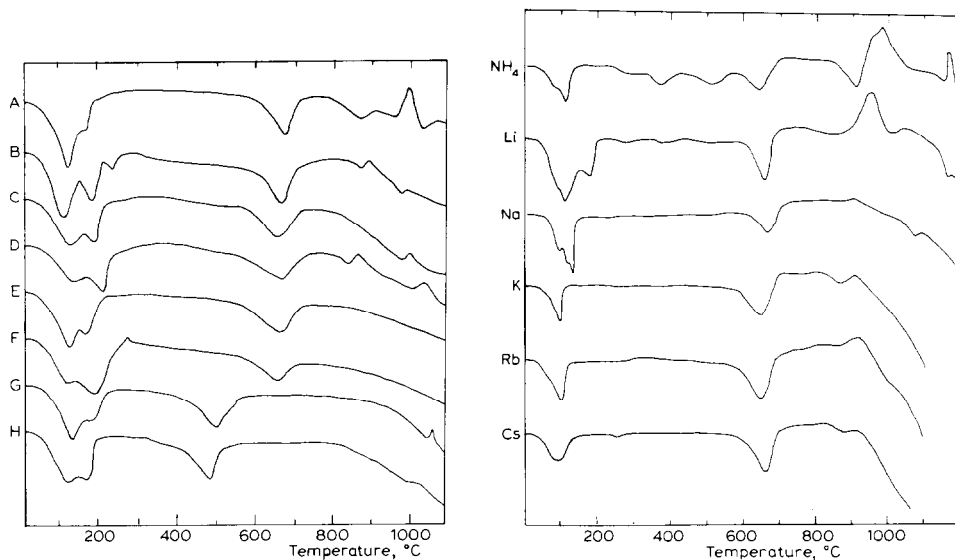
Fig. 1. DTA curves of pure smectite samples: (A) Jelsovy Potok montmorillonite; (B) Pyzevsky montmorillonite; (C) Ginovec montmorillonite; (D) Arizona montmorillonite; (E) Askangel montmorillonite; (F) Polkville montmorillonite; (G) Manito nontronite; (H) Sampor nontronite.

Fig. 2. DTA curves of monovalent derivatives.

DTA records in the high temperature range (> 800°C) show peaks mainly due to the formation, transformation and crystallization of new phases. In the present investigation, it can be noted that for montmorillonites the endothermic peak obtained at ~ 800°C is followed by an exothermic peak at slightly higher temperature. Also, for the different smectites, there are great variations in these high-temperature peaks which may be attributed to the difference in clay composition.

The DTA records of the seventeen exchangeable cations prepared from JP montmorillonite are illustrated in Figs. 2 and 3. The variation occurring in these curves is mainly present in the dehydration peaks. While K^+, Rb^+ and Cs^+ derivatives manifest a single, well-defined endothermic peak at ~ 100°C, the Na^+ derivative shows three overlapped peaks at 100, 120 and 130°C. Similarly, Li^+ derivatives shows three overlapped peaks at 100, 110 and 180°C. These results contradict those found by some authors [2,3,8] who indicated that Na^+ and Li^+ montmorillonite derivatives showed one and two endothermic peaks, respectively, on dehydration. This contradiction may be attributed to the heating rate used, the change in relative humidities of such preparations [11] or to apparatus sensitivity. The DTA curve of the $(NH_4)^+$ derivative shows a single dehydration peak at 115°C with a shoulder at a slightly lower temperature.
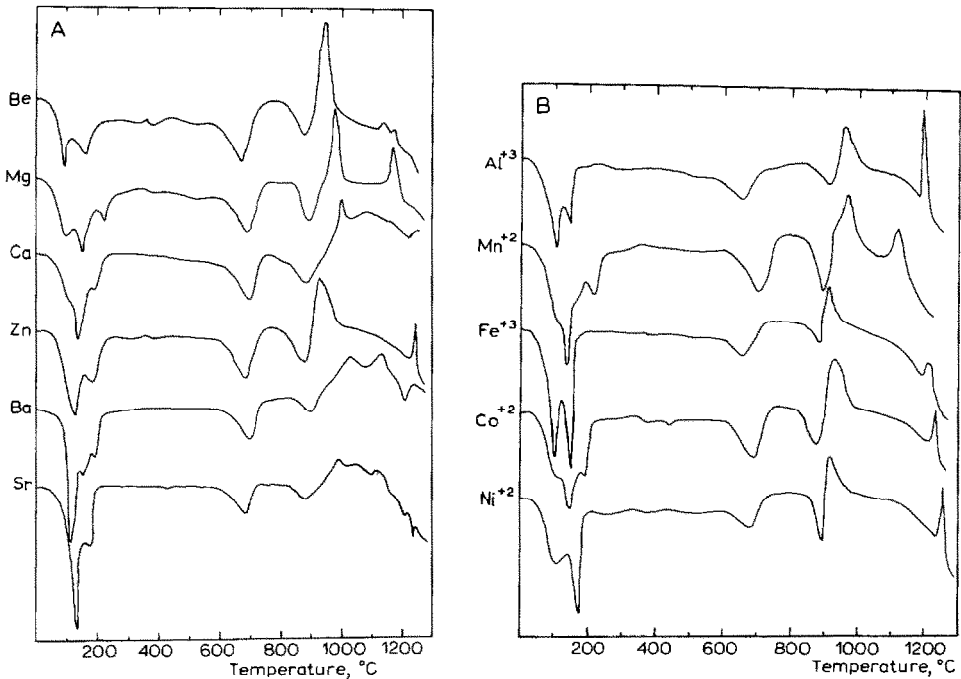
Fig. 3. DTA curves of multivalent montmorillonite derivatives.

Some divalent cation derivatives (Fig. 3) exhibit double dehydration peaks (Be^{2+}, Ca^{2+}, Sr^{2+}, Zn^{2+} and Ni^{2+}) while others show three overlapped peaks (Mg^{2+}, Ba^{2+} and Co^{2+}). These results deviate slightly from those obtained by Alexiads and Jackson [2] and Green-Kelley [8]. In the case of the Mn^{2+} derivative, three peaks are obtained at 120, 130 and 150°C with an extraordinary fourth peak at 215°C. The formation of this fourth peak may be related to the presence of some manganese hydroxides during the preparation of this derivative, which dissociate in such a temperature range. The trivalent derivatives, i.e., Fe^{3+} and Al^{3+}, show well-defined double peaks at 110 and 150°C.

Variation of exchangeable cations causes a slight shift in temperature at which dehydroxylation starts. Changes in peak maxima range from 645 to 705°C.

On the other hand, deviations in the endothermic–exothermic peaks are clearer at temperatures > 850°C. For Na^+, K^+, Rb^+ and Cs^+ derivatives, these successive peaks are of lower magnitude and occur in the temperature range 830–950°C. An intense exothermic peak is noted at 950°C in the case of the Li derivative. These successive peaks are more obvious in the case of multivalent derivatives, and are displayed in the temperature range 850–950°C. Light divalent derivatives (Be^{2+} and Mg^{2+}) also show an intense exothermic peak at about 950°C and this intensity decreases as the

cationic weight (or radius) increases (Fig. 3A). Other derivatives (Al^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+} and Ni^{2+}) show similar peaks in that temperature range (850–950°C), where the endothermic–exothermic peaks are of nearly the same intensity (Fig. 3B). At higher temperatures (> 1150°C) most of these derivatives show a sharp exothermic peak which may be attributed to the interaction of these cations with other metal oxides during spinel and silicate formation [3].

Based on the above results, the following general assumptions can be made.

(i) The number of peaks in the dehydration region may be related to the presence of different types of water molecules attached to the montmorillonite flakes by different bonding energies. It was considered by Boenisch [12] that the water of hydration could be classified into three main kinds: liquid (or free), surface (adsorbed on the clay flake surfaces), and hydrated (attached by the exchangeable cations). The first two kinds are easily removed from the interlamellar spaces at temperatures below 100°C. The last kind is directly held by the free cations (exchangeable cations) with higher bonding energies than the other two kinds. Accordingly, dehydration of the second type occurs at temperatures higher than 100°C, dependent on cation–water bonding energy. The present study shows derivatives containing cations with weak bonding energy and a single peak on dehydration at 100°C, e.g., K, Rb and Cs derivatives. The second group of derivatives is that of high bonding energy which exhibits three peaks on dehydration (the third peak occurs at > 180°C), e.g., Li^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Mn^{2+} and Co^{2+}. The third group of derivatives acquires moderate bonding energy and complete dehydration is performed below 180°C with only two peaks being obtained, e.g., Na^+, Be^{2+}, Zn^{2+}, Sr^{2+}, Al^{3+}, Fe^{3+} and Ni^{2+}.

(ii) Precisely speaking, the heavy alkalies (K^+, Rb^+ and Cs^+), showing a single peak on dehydration (at 100°C), do not contain oriented (hydrated) water molecules. This phenomenon was also predicted by TG studies, where low weight loss values are obtained on dehydration. One may assume that these cations are firmly held on the montmorillonite surfaces in the absence of hydrated water molecules, which could separate the cation from the clay surface. Consequently, the electrostatic attractive force between the cation and the negatively charged surface of montmorillonite are too strong for them to be easily separated.

Thermogravimetric analysis

The results of TG analysis of the bentonite derivatives studied are given in Figs. 4 and 5. These results show that dehydration of monovalent derivatives is almost complete at ~ 100°C. The weight loss of these derivatives decreases from 14.5 to 6.6 for derivatives of Li, Na, K, Rb and Cs, respectively. For the multivalent derivatives studied, containing di- or trivalent ex-
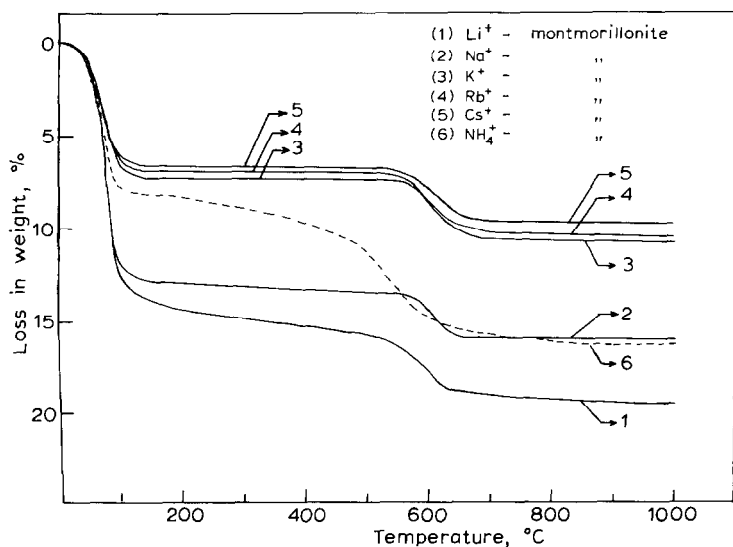
Fig. 4. TG curves of monovalent cationic derivatives of Jelsovy Potok montmorillonite.

changeable cations, the weight loss values do not differ greatly between these derivatives, and range between 15 and 18%.

It is also observed from these results that for both monovalent and multivalent derivatives of the same group, the amount of hydrated water and the slope of TG curves increase with decreasing ionic radius, e.g., Li
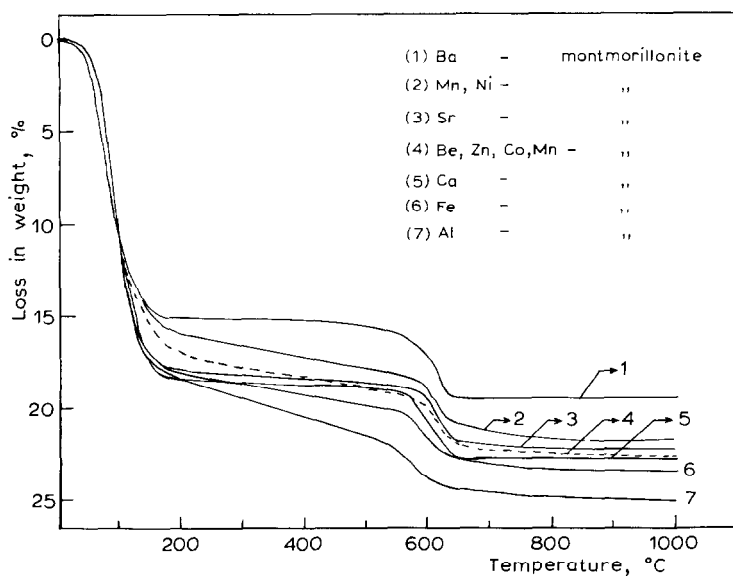

Fig. 5. TG curves of multivalent cationic derivatives of Jelsovy Potok montmorillonite.

TABLE 4

Electronegativities and slope of TG curve

Exchange-able cation	Pauling's electro-negati-vities	Slope of TG curve at 200–500°C (% loss °C^{-1}) ×10^{-3}	Exchange-able cation	Pauling's electro-negati-vities	Slope of TG curve at 200–500°C (% loss °C^{-1}) ×10^{-3}
Li$^+$	1.00	3.15	Sr^{2+}	0.95	1.9
Na$^+$	0.95	1.6	Ba^{2+}	0.89	1.9
K$^+$	0.82	1.3	Mn^{2+}	1.55	6.7
Rb$^+$	0.82	1.3	Zn^{2+}	1.65	6.7
Cs$^+$	0.79	1.3	CO^{2+}	1.88	6.7
Be^{2+}	1.57	6.7	Ni^{2+}	1.91	6.7
Mg^{2+}	1.31	7.7	Fe^{3+}	1.83	10.7
Ca^{2+}	1.00	1.9	Al^{3+}	1.61	7.3

derivatives for the monovalent derivatives of groups Ia, and Be and Mg for the multivalent derivatives of group IIa.

There also appears to be a relationship between the slope of the TG curves (in the temperature range 200–500°C) and the electronegativity of the exchangeable cation. According to Pauling's [13] electronegativity scale, in which fluorine is given an arbitrary standard value of 4, elements which have values above unity exhibit relatively high slope values. The relationship is given in Table 4.

From these TG curves it is observed that the dehydroxylation process of all these derivatives always starts at ∼ 550°C, which is quite reasonable since they were all prepared from the same original bentonite.

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