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DEHYDRATION AND DEHYDROXYLATION OF SMECTITES
I. DEHYDRATION AND DEHYDROXYLATION KINETICS

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A b s t r a c t. Thermal analysis was employed to investigate the dehydration and dehydroxylation kinetics of smectites. It has been found that these reactions are determined by the kind of interlayer cations, the amount and type of isomorphic substitution in the layers, and the resulting charge. The electric field generated by the charges of the tetrahedral sheet slackens the reaction between interlayer cations and water molecules, thus affecting the process of dehydration of smectites.

INTRODUCTION

Dehydration and dehydroxylation are the reactions of thermal dissociation, involving the removal of water combined in the structure of minerals and inorganic compounds in the form of H_2O molecules and OH groups.

Smectites display an endothermic dehydration peak between 40 and 300°C on DTA and DTG curves. Its temperature, size and shape, as well as the amount of water released in this process, depend on the exchangeable cation occupying the interlayer spaces in smectites (Hendricks 1940; Caillere, Henin 1944; Barshad 1948; 1950; Arens 1951). Mackenzie (1959) found a correlation between the temperature of the endothermic peak corresponding to the removal of interlayer water and the hydration energy of interlayer cations.

The endothermic effect of dehydroxylation of smectites begins above 500°C and its maximum temperature varies over a wide range. Page (1943) and Kelley (1943) noticed that when Al is the principal cation of the 2:1 octahedral sheet, hydroxylation water is removed at a lower temperature than in the case when Mg is the main cation. These authors were of the opinion that the introduction of Fe substituting for Al or Mg into the structure of a clay mineral lowers the temperature of endothermic dehydroxylation reaction and changes its magnitude (Kelley, Page 1943; Caillere, Henin 1947, 1948 a,b, 1949; Kulp 1951). Earley, Osthaus and Milne (1953) found a correlation between the dehydroxylation peak temperature and the amount of substitution of Al for Si in the tetrahedral sheet of a series of montmorillonites, in the range of 0.1–0.69 Al. According to Barshad (1950), Kerns and Mankin (1968), the

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exchangeable cation does not affect the dehydroxylation peak temperature of smectites, yet it influences to some extent the shape of DTA peak at 700–1000°C. Mackenzie and Bishui (1958) studied the Wyoming montmorillonites saturated with different cations and found that their dehydroxylation temperature is a parabolic function of the radius and ionic potential of the cations used. The studies of Horvath (1978) showed that the exchangeable cations of ionic radii comparable with that of Al accelerate dehydroxylation, occupying the vacant octahedral sites of a mineral during the process of dehydration. Jacobs and Defre (1961) studied the dehydroxylation kinetics of smectites saturated with different exchangeable cations and found that it is a first-order reaction of an activation energy of 226.9, 210.6 and 170.4 kJ/mol for Na^+, Ca^{2+} and H^+ smectites, respectively. The dehydroxylation rate varies depending on the kind of exchangeable cation in the following sequence: Li–K–Na–Mg–Ba–Ca–Sr.
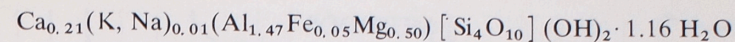
According to Bradley and Grim (1951), the removal of OH groups from montmorillonite at 500–700°C leads to the formation of montmorillonite anhydrite in which the Si–O sheets are similar to those in montmorillonite but the octahedral sheet is subject to re-arrangement. The octahedral coordination of aluminium is retained owing to the fact that oxygens left after dehydroxylation of the octahedral sheet shift from their original positions perpendicularly to the sheet plane (expansion of the unit cell along the „c" axis from 0.1 to 0.3 Å). Achar et al. (1966) observed that the dehydroxylation kinetics of smectites follows the mechanism of controlled diffusion of water. Pampuch and Wal (1971) distinguish two stages of dehydroxylation of montmorillonite: dehydroxylation proper and evaporation of the water formed. These stages are distinct under the conditions of dynamic heating during thermal analysis. Dehydroxylation proper occurs at lower temperatures, close to the dehydroxylation temperature of kaolinite. Water evaporation takes place at much higher temperatures, close to 700°C, as it is delayed by the diffusion length. At about 800°C, another endothermic peak appears, caused by the loss of residual OH groups and the structural breakdown of the anhydrous phase (Earley 1953; Bradley, Grim, Connell 1950). The studies of Barshad (1950) indicate that the high-temperature endothermic peak is affected by the kind of exchangeable cation.
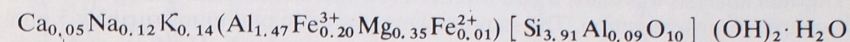
MATERIALS

Investigations were carried out on bentonites from Chmielnik, Milowice and Fintice (Czechoslovakia), a Russian bentonite of obscure origin, a montmorillonite from the Rudno melaphyres, the Kamienskoje beidellite (USSR) and a trans-Carpathian nontronite (USSR). The samples to be investigated were the $< 2\mu m$ fraction of these minerals, separated by sedimentation. X-ray and thermal analyses have shown that the Chmielnik, Fintice and Russian montmorillonites are typical dioctahedral Ca-montmorillonites, while the Milowice bentonite is a mixed-layer illite/montmorillonite with a very low proportion of illite layers. Montmorillonite from Rudno appeared to be a mixture of two minerals: montmorillonite (64 mol %) and saponite (36 mol %). This is indicated by the double (060) reflection on its X-ray diffraction pattern, with the line $d_{060} = 1.52$ Å corresponding to saponite and the 1.49 Å line being characteristic of dioctahedral montmorillonite. The Kamienskoje beidellite and the trans-Carpathian nontronite display reflections typical of dioctahedral smectites.

The crystallochemical formulae given below show the kind and extent of isomorphic substitution in the structure of the montmorillonites studied.
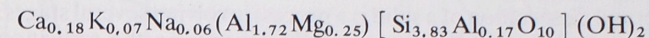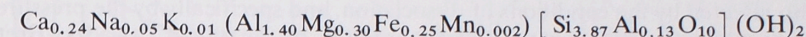
Chmielnik (Kulesza-Wiewióra 1976):

$$Ca_{0.21}(K, Na)_{0.01}(Al_{1.47}Fe_{0.05}Mg_{0.50})\left[Si_4 O_{10}\right](OH)_2 \cdot 1.16 \, H_2O$$

Milowice (Kulesza-Wiewióra 1976):

$$Ca_{0.05}Na_{0.12}K_{0.14}(Al_{1.47}Fe^{3+}_{0.20}Mg_{0.35}Fe^{2+}_{0.01})\left[Si_{3.91}Al_{0.09}O_{10}\right](OH)_2 \cdot H_2O$$

Fintice (Gregor, Cičel 1969):

$$Ca_{0.18}K_{0.07}Na_{0.06}(Al_{1.72}Mg_{0.25})\left[Si_{3.83}Al_{0.17}O_{10}\right](OH)_2$$

Russian (Wacławska 1978):

$$Ca_{0.24}Na_{0.05}K_{0.01}(Al_{1.40}Mg_{0.30}Fe_{0.25}Mn_{0.002})\left[Si_{3.87}Al_{0.13}O_{10}\right](OH)_2$$

Rudno (Wacławska 1978; Stoch, Żabiński 1977):
36 mol %

$$Ca_{0.017}K_{0.02}Na_{0.05}(Mg_{2.96}Fe_{0.04})\left[Si_{3.52}Al_{0.47}O_{10}\right](OH)_{1.95}$$

64 mol %

$$Ca_{0.23}K_{0.015}Na_{0.005}(Al_{1.53}Mg_{0.42}Fe_{0.05})\left[Si_{3.76}Al_{0.24}O_{10}\right](OH)_2$$
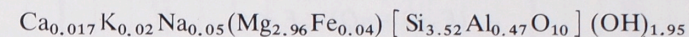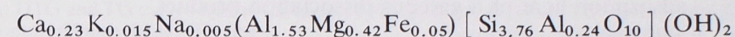
Nontronite (Wacławska 1978):

$$Ca_{0.07}Na_{0.18}K_{0.04}(Al_{1.17}Fe_{0.75}Mg_{0.12}Ti_{0.01})\left[Si_{3.57}Al_{0.43}O_{10}\right](OH)_2.$$
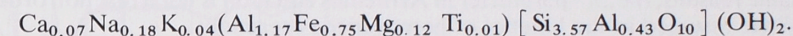
The smectites were converted into monoionic forms by saturating them with Na^+, K^+, Ca^{2+} or Mg^{2+} cations, using the method developed by Jackson (1958). The choice of these cations was influenced by the frequency of occurrence of specific sorption complexes in clay minerals. The bulk of clays occurring in Poland are in the Ca-form, with Mg^{2+}, K^+ and Na^+ appearing as exchangeable cations (Grabowska-Olszewska 1968).

The cation exchange was controlled by measuring the basal interplanar spacing d_{001} of montmorillonites on X-ray diffraction patterns. The resulting d_{001} values, dependent on the interlayer cation, are listed in Table 1. As appears from the table, air-dry smectites saturated with calcium or magnesium have the interlayer spacing $d_{001} \sim 15$ Å, corresponding to two monomolecular water layers. Smectites saturated with sodium or potassium show lower d_{001} values, corresponding to one monomolecular water layer. The intensity of basal reflections also depends on the kind of exchangeable cations and, according to Barshad's data (1949), is the highest for samples saturated with bivalent cations and decreases for smectites with Na^+ or K^+ cations occupying the exchange positions.

Table 1

Basal interplanar spacings d_{001} (Å) of smectites saturated with different exchangeable cations

Sample	Interlayer cations			
	K	Na	Ca	Mg
Rudno	12.6	12.9	15.3	15.2
Chmielnik	12.4	12.6	15.5	15.2
Milowice	12.1	12.2	15.6	14.4
Russian	12.4	12.6	15.5	14.9
Fintice	12.6	12.8	15.5	14.9
Beidellite	10.4	10.4	15.7	16.0
Nontronite	13.8	13.6	15.5	15.5

METHODS

Thermal analysis was made with a Mettler TA-2 thermoanalyser, taking 100 mg of each sample for investigation. The samples were placed in platinum crucibles 5 mm in diameter, and sintered α-Al_2O_3 was used as standard. Heating rate was 10°C/min., air flow 4 l/hr.

The thermal dissociation of a solid is a process involving several stages. Hence the activation energy determined experimentally depends on the activation energy of partial processes and is referred to as apparent activation energy. Activation energy is also affected by the conditions of dissociation, and specifically by the pressure of gaseous products, which is expressed, for example, by the rule of Zawadzki-Bretsznajder. The activation energy of thermal dissociation (E) is frequently much greater than the heat of this reaction (Q) (Prodan, Pawluczenko, Prodan 1976):

$$(E_2 \pm \lambda + mQ) < E < \infty$$

where E_2 – activation energy of the opposite reaction,
λ – adsorption heat of a gaseous dissociation product,
m – constant.

The results obtained for smectites are in good agreement with this relationship. For the same reasons, the „n" parameter in Arrhenius equation is not a reaction order in the sense assumed in the kinetics of homogeneous reactions.

The dedydration and dehydroxylation kinetics of the samples studied was determined from TG and DTG curves. Assuming that it can be described by Arrhenius equation referring to the reaction kinetics in homogeneous systems, the coefficient E of this equation (apparent activation energy) was determined with the method of Freeman-Carroll (1958). The relevance of this method in the determination of kinetic parameters of thermal dissociation had been confirmed by several authors (Michelson 1970; Chen 1974, 1975).

The method of Piłojan-Nowikowa (1967) was also used in the present study. The measurements of reaction kinetics with the methods of thermal analysis are subject to errors because of the non-isothermal conditions of measurements. If, however, they are carried out under standardized conditions, they may be useful in comparative studies, for example, for the determination of the effect of different factors on the process of thermal dissociation.

RESULTS

Dehydration kinetics of smectites

The dehydration of smectites produces an endothermic peak between 40 and 300°C on DTA and DTG curves. When smectites contain bivalent cations at the exchange positions, a double or, in the case of Mg-montmorillonites, a triple endothermic peak appears on DTA and DTG curves. This indicates that the removal of interlayer water is a process involving several stages. Montmorllonites saturated with monovalent cations display a single dehydration peak, which testifies to the one-stage mechanism of this reaction (Figs. 1–3).

TG analysis has revealed that the amount of interlayer water and the dehydration temperature of smectites are determined by the kind of interlayer cation (Table 2). It has been found that the Ca- and Mg-forms contain the greatest and similar amounts of water. Thermal analysis of smectites with monovalent cations at the exchange positions has shown that the amount of hydration water is less for the K-form than for
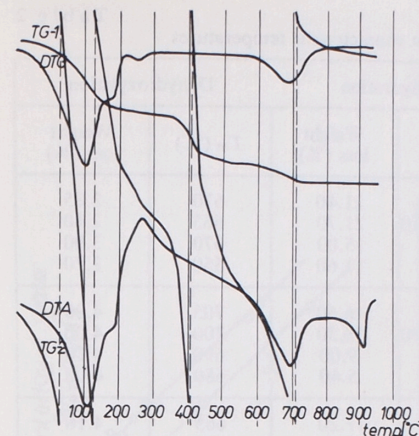

Fig. 1. DTA, DTG and TG curves for the Ca-form of montmorillonite from Milowice
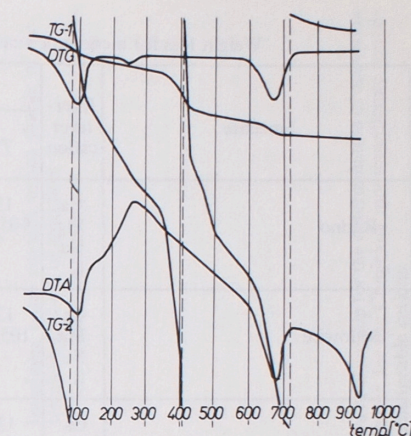

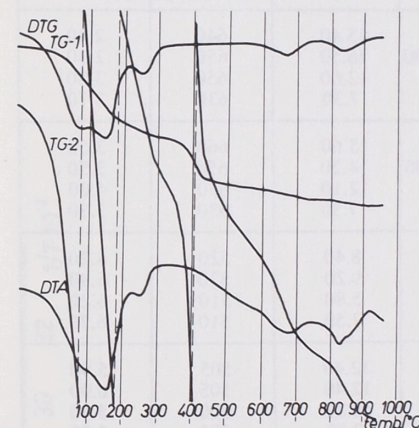Fig. 2. DTA, DTG and TG curves for the K-form of montmorillonite from Milowice

Fig. 3. DTA, DTG and TG curves for the Mg-form of montmorillonite from Milowice

the Na-form of the same smectite. The amount of interlayer water and dehydration temperature also depend on the extent of isomorphic substitution of Al for Si. Extensive substitution in the tetrahedral sheet is paralleled by the increase in density of the negative electric charge of the layer surface. This results in the increased energy of electrostatic bonds between the exchangeable cations and the layer, thereby decreasing the amount of water in the interlayer spaces (Fig. 4). An increase in the charge of the tetrahedral sheet from 0 to 0.5 reduces by half the amount of interlayer water when the strongly hydrated Ca^{2+} or Mg^{2+} cation occupies the exchange positions. If, however, the weakly hydrated Na^+ is the exchangeable cation, the above increase in charge reduces down to 30% the amount of water that can be accomodated by a montmorillonite showing practically no substitution in the tetrahedral sheet.

Furthermore, it has been noticed that the separation of peaks corresponding to the dehydration of montmorillonites with bivalent cations at the exchange sites is the more poronounced on DTA and DTG curves, the less isomorphic substitution of Al for Si takes place in the tetrahedral sheet. This behaviour accords well with the observations of Wiegman (1966).

Table 2

Weight loss for monoionic smectites at characteristic temperatures

Smectite	Interlayer cation	Dehydration		Dehydroxylation	
		Tm (°C)	Weight loss (%)	Tm (°C)	Weight loss (%)
Rudno	Ca	135,200	21.40	670	2.85
	Mg	105,155,240	21.70	665	2.40
	Na	140	15.00	670	3.00
	K	120	11.60	650	2.70
Milowice	Ca	130,180	16.60	705	4.00
	Mg	105,150,220	16.50	700	4.00
	Na	120	9.00	690	4.10
	K	105	5.40	680	4.00
Chmielnik	Ca	130,180	17.20	665	4.10
	Mg	105,155,220	18.00	665	3.90
	Na	135	15.50	680	3.70
	K	110	9.10	650	4.50
Russian	Ca	140,190	15.40	640	2.40
	Mg	110,150,200	16.50	650	2.30
	Na	125	12.00	650	3.00
	K	100	7.30	630	3.70
Fintice	Ca	120,180	15.00	660	3.50
	Mg	105,125,200	14.20	650	3.50
	Na	120	12.10	650	4.00
	K	100	7.30	630	3.70
Nontronite	Ca	100	8.40	520	6.20
	Mg	100	9.20	520	5.90
	Na	100	5.80	510	6.20
	K	90	7.50	510	6.70
Beidellite	Ca	110,170	12.40	505	5.90
	Mg	115	12.40	505	6.00
	Na	110	8.30	500	5.90
	K	105	7.80	505	5.70

The effect of exchangeable cations on the dehydration kinetics of smectites is reflected by the different inclination of straight lines on Freeman-Carroll plots. These plots, however, do not show the several stages of removal of interlayer water as DTA and DTG curves do. In this case, the method of Piłojan-Nowikowa appears to be more useful. On the $\ln\alpha - 2\ln T$ against $1/T$ plots, there are straight line regions corresponding to the several stages of dehydration (Fig. 5), and the apparent activation energy of each stage can be determined on their basis. By multiplying the partial activation energies of dehydration, determined with the method of Piłojan-Nowikowa, by the amount of water removed in each stage, expressed as the degree of decomposition α, and by summing the obtained values, the averaged values of activation energy were obtained, which are generally close to the values calculated by the method of Freeman-Carroll (Table 3). The apparent activation energy of dehydration of smectites varies from 15.1 to 26.4 kJ/mol and does not seemingly depend on the kind of exchangeable cations.

Fig. 4. Interlayer water content versus charge of the tetrahedral sheet of smectites

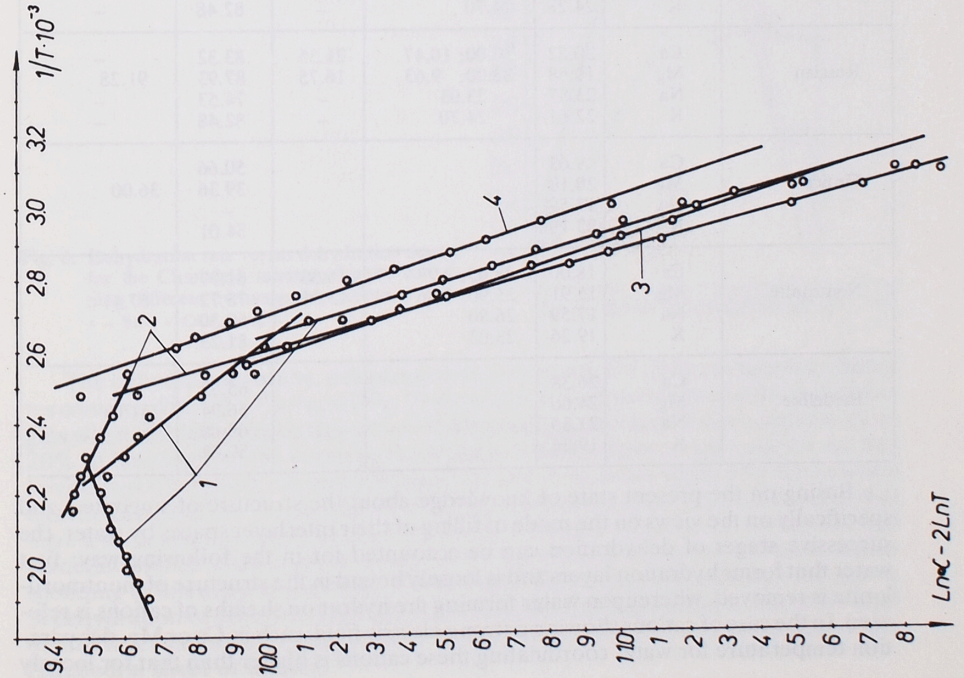1 – Ca – and Me-forms of smectites, 2 – Na-form of smectites

Fig. 5. Piłojan-Nowikowa relationship for the determination of activation energy of dehydration for the Chmielnik montmorillonite containing different exchangeable cations
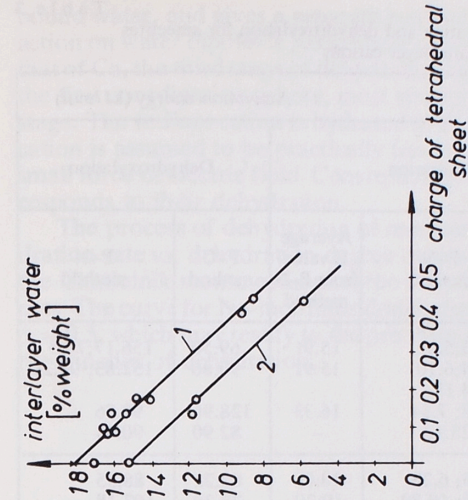
1 – Mg, 2 – Ca, 3 – K, 4 – Na

Table 3

Apparent activation energy of dehydration and dehydroxylation for smectites with different interlayer cations

Kind of reaction		Activation energy (kJ/mol)				
Smectite	Exchangeable cation	Dehydration			Dehydroxylation	
		F–C method	P–N method	Average E value from P–N method	F–C method	P–N method
Rudno	Ca	15.07	27.63; 5.02	15.91	69.50	156.17; 76.5
	Mg	16.75	32.24; 6.70 4.19	15.91	90.86	152.83; 98.20
	Na	17.59	37.68; 7.54	16.33	128.96	90.86
	K	25.54	25.12	–	82.90	90.44
Milowice	Ca	17.17	30.15; 6.28	20.09	82.22	88.35
	Mg	15.07	32.66; 10.89 2.93	19.29	78.30	107.18
	Na	25.12	26.38	–	129.80	113.47
	K	23.44	29.31	–	161.20	132.05
Chmielnik	Ca	21.77	30.98; 3.35	16.75	69.09	45.64
	Mg	15.07	32.66; 10.88 3.35	15.91	66.15	47.31
	Na	23.87	24.28	–	119.33	142.78
	K	24.28	24.70	–	82.48	–
Russian	Ca	20.52	36.00; 10.47	21.35	83.32	–
	Mg	19.68	33.00; 9.63	16.75	87.93	91.28
	Na	23.87	23.03	–	74.53	–
	K	22.61	24.70	–	82.48	–
Fintice	Ca	9.63			50.66	
	Mg	20.10			39.36	36.00
	Na	17.59			–	
	K	22.19			54.01	
Nontronite	Ca	18.00	28.05; 3.77	16.33	61.97	
	Mg	15.91	25.96; 5.86	15.91	78.72	67.41
	Na	17.59	26.80		60.30	
	K	19.26	23.03		81.23	
Beidellite	Ca	26.38			65.32	
	Mg	24.66			56.94	51.08
	Na	21.35			69.08	
	K	19.26			59.04	

Basing on the present state of knowledge about the structure of smectites, and specifically on the views on the mode of filling of their interlayer spaces by water, the successive stages of dehydration can be accounted for in the following way: first water that forms hydration layers and is loosely bound in the structure of montmorillonite is removed, whereupon water forming the hydration sheaths of cations is released. In the case of cations showing a strong electric field, such as Ca or Mg, dehydration temperature for water coordinating these cations is higher than that for loosely

bound water, and gives a separate peak on the DTA curve. If Mg is present, whose action on water dipoles is particularly strong because of the smaller ionic radius than that of Ca, the third stage of dehydration takes place. It is feasible that water forming the first coordination sphere, most strongly bound to the cation, is removed at this stage. The sodium cation is hydrated in an insignificant degree, while the potassium cation is assumed to be practically free of the hydration sheath because of the very small force of electric field. Consequently, only a single peak on thermal curves corresponds to their dehydration.

The process of dehydration of montmorillonites is well illustrated by the dehydration rate *vs.* dehydration degree curves (Fig. 6). As appears from the curves for the Chmielnik montmorillonite, the dehydration of its Na-form is a one-stage process. The curve for Na-montmorillonite shows an inflexion at the dehydration degree $\alpha = 0.5$, which may testify to the presence of two kinds of water, slightly differing in the kinetics of dehydration.
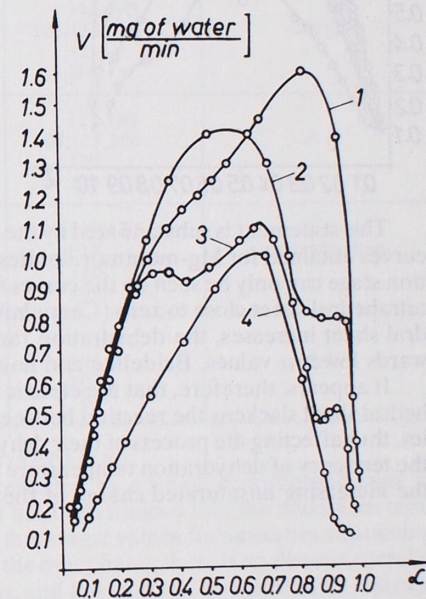

Fig. 6. Dehydration rate versus dehydration degree for the Chmielnik montmorillonite containing different exchangeable cations
1 – Na, *2* – Ca, *3* – Mg, *4* – K

The dehydration rate vs. dehydration degree curves for different montmorillonites converted into the Ca-form (Fig. 7) show that the second stage of dehydration begins when the dehydration degree $\alpha = 0.8$ is attained, and therefore comprises about 20% of interlayer water. It can be observed as a distinctly separate stage for the Milowice and Chmielnik montmorillonites, i.e. the ones characterized by the smallest electric charge of the tetrahedral sheet. It is less pronounced for motmorillonites that have a somewhat greater charge (Fintice and Russian), whereas for nontronite and beidellite, which show a great charge in the tetrahedral sheet, the inflexion corresponding to this dehydration stage is very slight. This means that although the course of dehydration of smectites depends in the first place, as is generally held, on the kind of interlayer cation, the effect of these cations is modified by the electric field of the tetrahedral sheet of a layer.
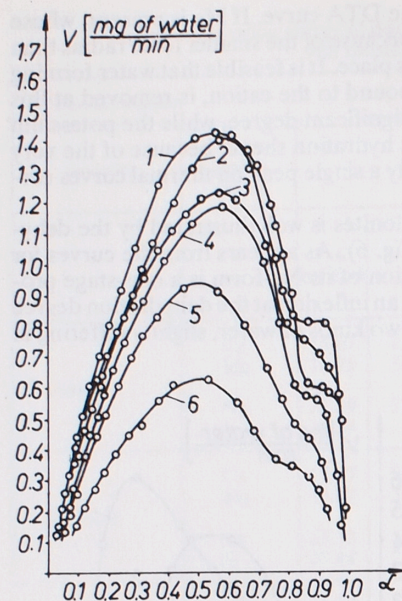
Fig. 7. Dehydration rate versus dehydration degree for different montmorillonites converted into Ca-form

1 – Chmielnik, *2* – Milowice, *3* – Russian, *4* – Fintice, *5* – beidellite, *6* – nontronite

This statement is substantiated by the dehydration rate vs. decomposition degree curves obtained for Mg-montmorillonites (Fig. 8), as the pronounced third dehydration stage can only be seen on the curves for montmorillonites with the charge of the tetrahedral sheet close to zero (Chmielnik, Milowice). As the charge of the tetrahedral sheet increases, the dehydration rate maximum of the second stage shifts towards lower α values. Beidellite and nontronite show one-stage dehydration only.

It appears, therefore, that the electric field generated by the charges of the tetrahedral sheet slackens the reaction between the interlayer cations and water molecules, thus affecting the process of their dehydration. This thesis is further supported by the tendency of dehydration temperature (DTA peak temperature) to decrease with the increasing unsaturated charge of the tetrahedral sheet (Table 4).
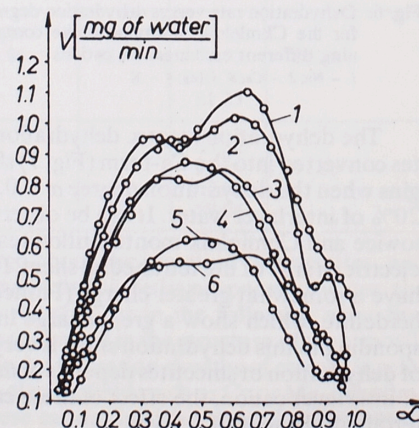

Fig. 8. Dehydration rate versus dehydration degree for different montmorillonites converted into Mg-form

1 – Chmielnik, *2* – Russian, *3* – Fintice, *4* – beidellite, *5* – nontronite, *6* – Milowice

Table 4

Dehydration temperature for smectites with different interlayer cations

Smectite	Exchangeable cation	Dehydration temperature	Charge of tetrahedral sheet per unit chemical formula or half unit cell
Chmielnik	Ca	130,180	0.00
	Mg	105,155,220	
	Na	135	
	K	110	
Milowice	Ca	130,180	−0.09
	Mg	105,150,220	
	Na	120	
	K	105	
Russian	Ca	140,190	−0.13
	Mg	105,150,200	
	Na	125	
	K	105	
Fintice	Ca	120,180	−0.17
	Mg	105,125,200	
	Na	120	
	K	100	
Beidellite	Ca	110,170	not determined
	Mg	115	
	Na	110	
	K	105	
Nontronite	Ca	100,160	−0.43
	Mg	100	
	Na	100	
	K	90	

Dehydroxylation kinetics of smectites

The dehydroxylation of smectites is reflected by a single endothermic peak at about 700°C on DTA and DTG curves. It has been noticed that the maximum temperature of dehydroxylation reaction has the lowest values for smectites containing the potassium ion in interlayer spaces. On the other hand, there is no distinct correlation between dehydroxylation temperature and the kind of other interlayer cations.

The TG analysis of different ionic forms of the smectites studied has shown that for the same smectite, the kind of exchangeable cation has no effect on the amount of water combined as OH groups in hydroxyls removed on heating. The content of water combined as OH groups in smectites is lower than theoretical and averages 3.5 wt.%, depending on isomorphic substitution in the structure. The main determinant of the actual content of this water seems to be the extent of isomorphic substitution in the octahedral and tetrahedral sheets and the resulting charge of the layer. The increasing charge decreases the amount of water removed during the second endothermic reaction, also decreasing the dehydration temperature (Fig. 9).

The removal of OH groups from smectites is a one-stage process, irrespective of the kind of exchangeable cation. For the Rudno smectite alone, which is a mixture of two minerals, two intersecting curves were obtained for the Mg- and Ca-forms, pointing to two stages of dehydroxylation. This is because saponite decomposes at a so-
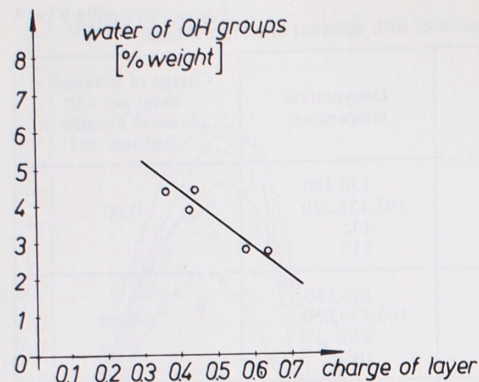
Fig. 9. Hydroxyl water content versus layer charge in smectites

mewhat higher temperature than montmorillonite, and the DTA peaks of the two minerals overlap only partially. It also seems that the kind of exchangeable cation has no marked effect on the apparent activation energy of dehydroxylation (Table 3). Irrespective of the kind of exchangeable cation, the apparent activation energy of dehydroxylation is lower for smectites than for minerals of the kaolinite series.

The relationship between the dehydroxylation rate and the degree of decomposition of smectites is presented in figures 10 and 11. It will be seen from the plots that the interlayer cation does have some effect on dehydroxylation. For example, the curve for the Chmielnik montmorillonite shows that when Mg, Ca or Na is the interlayer cation, the maximum dehydroxylation rate is attained at $\alpha \sim 0.75$; however, when the interlayer cation is K, this maximum shifts to 0.65. This means that dehydroxylation rate begins to decrease already at a lower degree of decomposition of montmorillonite.

The dehydroxylation rate *vs.* α curves for different montmorillonites saturated with potassium cations show that there is a relationship between the shift of the dehydroxylation rate maximum and the charge of the tetrahedral sheet. This shift is in-
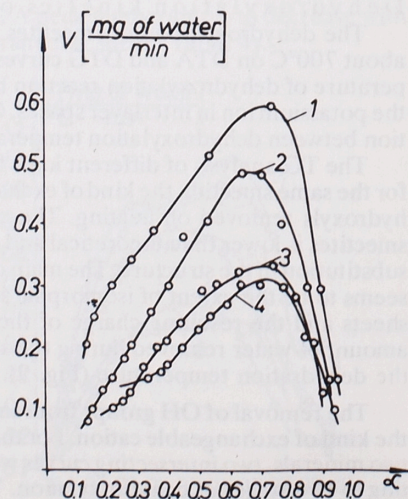

Fig. 10. Dehydroxylation rate versus decomposition degree for the Chmielnik montmorillonite containing different exchangeable cations
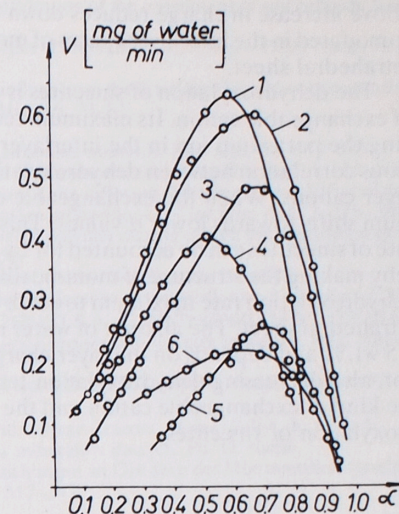*1* – Na, *2* – K, *3* – Ca, *4* – Mg

Fig. 11. Dehydroxylation rate versus decomposition degree for montmorillonites converted into K-form
1 – nontronite, *2* – Milowice, *3* – Chmielnik, *4* – beidellite, *5* – Fintice, *6* – Russian

significant for montmorillonites characterized by a small charge (Chmielnik, Milowice) and very pronounced (to $\alpha \sim 0.5$) for beidellite and nontronite, which have the greatest charge.

The slower rate of dehydroxylation of montmorillonites under the influence of potassium can be accounted for by potassium closing the interlayer spaces and making the structure of montmorillonite similar to that of mica, thereby hindering the removal of water being formed in this process.

DISCUSSION

The thermal properties of smectites are determined by the kind of exchangeable cations in the interlayer spaces, and the type and extent of isomorphic substitution within the layers. Depending on the kind of interlayer cation (valency), dehydration is a process involving one or several stages. This can be accounted for by the successive removal of water forming hydration layers and loosely bound in the structure of montmorillonite, and subsequently of water forming the hydration sheaths of cations. There seems to be no correlation between the apparent activation energy of dehydration and the kind of exchangeable cations. The process of dehydration of smectites is also determined by the electric field of the tetrahedral sheet, which slackens the reaction between the interlayer cations and water molecules (a decrease in the temperature of DTA dehydration peak). As the charge of the tetrahedral sheet increases, the maximum rate of the second stage of dehydration shifts towards lower α values. The amount of water released during dehydration depends on the kind of exchangeable cation and the charge of the tetrahedral sheet. In smectites with a small or medium $(0-0.2)$ charge of the tetrahedral sheet and containing calcium as the exchangeable cation, the water loss varies over a narrow range, averaging 16 wt.%. For beidellite and nontronite, which have a charge of 0.43, it is less, being 12 and 19 wt.% respectively. The increase in charge of the tetrahedral sheet from 0 to 0.5 reduces by half the amount of interlayer water when strongly hydrated Ca^{2+} or Mg^{2+} ions occupy the exchange positions. In the presence of the weakly hydrated Na^+ ion, the

above increase in charge reduces down to 30% the amount of water that can be accomodated in the interlayer spaces of montmorillonite showing no substitution in the tetrahedral sheet.

The dehydroxylation of smectites is a one-stage process, irrespective of the kind of exchangeable cation. Its maximum temperature is the lowest for smectites containing the potassium ion in the interlayer spaces. On the other hand, there is no obvious correlation between dehydroxylation temperature and the kind of other interlayer cations. When the exchangeable cation is K, the dehydroxylation rate maximum shifts towards lower α values. This effect of potassium on the dehydroxylation rate of smectites can be accounted for by potassium closing the interlayer spaces, thereby making the structure of montmorillonite similar to that of mica. The shift of the dehydroxylation rate maximum towards lower α values depends on the charge of the tetrahedral sheet. The amount of water removed in the form of OH groups averages 3.5 wt.% and depends on the layer charge. The increasing charge reduces this amount, also decreasing dehydroxylation temperature. There is no correlation between the kind of exchangeable cation and the amount of water released during the dehydroxylation of smectites.

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Irena WACŁAWSKA

DEHYDRATACJA I DEHYDROKSYLACJA SMEKTYTÓW
I. KINETYKA DEHYDRATACJI I DEHYDROKSYLACJI

Streszczenie

Kinetyka procesu dehydratacji i dehydroksylacji smektytów jest uwarunkowana rodzajem kationów w ich przestrzeniach międzypakietowych oraz ilością i rodzajem podstawień izomorficznych w pakietach i wynikającej stąd wielkości ich ładunku.

Do badań wybrano smektyty różniące się ładunkiem pakietu, które przeprowadzono w formy monojonowe, nasycając je kationami Na^+, K^+, Ca^{2+} i Mg^{2+}. Krzywe TG i DTG wykonane na termoanalizatorze TA-2 firmy Mettler posłużyły do określenia ilości wody oddanej w procesie dehydratacji i dehydroksylacji smektytów, jak również do wyznaczenia parametrów kinetycznych tych procesów metodą Freemana-Carrolla oraz Piłojana-Nowikowej.

Ilość wody oddawanej w czasie dehydratacji zależy od rodzaju kationu wymiennego oraz ładunku warstwy tetraedrycznej pakietu. Dla smektytów o ładunku 0–0,2 wobec Ca^{2+} jako kationu wymiennego jej zawartość wynosi średnio około 16% wag.. Wzrost ładunku warstwy tetraedrycznej do 0,5 zmniejsza do połowy ilość wody międzypakietowej gdy w pozycjach wymiennych znajdują się silnie zhydratyzowane kationy Ca^{2+} lub Mg^{2+}. W obecności jonu Na^+, wspomniany wzrost ładunku zmniejsza do 30% ilość wody międzypakietowej. W zależności od rodzaju kationu w przestrzeniach międzypakietowych proces dehydratacji przebiega jedno- lub kilkustopniowo. Nie stwierdzono wyraźnej zależności między wartością pozornej energii aktywacji dehydratacji, a rodzajem kationów wymiennych. Ładunek warstwy tetraedrycznej pakietu osłabia oddziaływanie kationów międzypakietowych na drobiny wody, co przejawia się obniżeniem temperatury dehydratacji oraz przesunięciem maksimum szybkości drugiego etapu dehydratacji w stronę mniejszych wartości α.

Ilość wody oddawanej w formie grup OH w smektytach wynosi średnio 3,5% wag. i ulega zmniejszeniu wraz ze wzrostem ładunku pakietu. Nie stwierdzono wpływu rodzaju kationu wymiennego na ilość wody oddawanej w czasie dehydroksylacji smektytów. Proces dehydroksylacji smektytów, niezależnie od rodzaju kationu wymiennego, przebiega jednostopniowo, a temperatura jego maksimum osiąga najniższe wartości jedynie w obecności potasu jako kationu międzypakietowego. W obecności potasu zaobserwowano również przesunięcie maksimum szybkości dehydroksylacji smektytów do niższych wartości α, co można tłumaczyć tym, że potas zmniejszając szybkość dehydroksylacji zamyka przestrzenie międzypakietowe i upodabnia strukturę smektytu do struktury miki.

OBJAŚNIENIA FIGUR

Fig. 1. Termogram montmorillonitu Milowice, przeprowadzonego w formę wapniową
Fig. 2. Termogram montmorillonitu Milowice, przeprowadzonego w formę potasową
Fig. 3. Termogram montmorillonitu Milowice, przeprowadzonego w formę magnezową
Fig. 4. Zależność zawartości wody międzypakietowej od ładunku warstwy tetraedrycznej smektytów
     1 – Ca i Mg-smektyty, 2 – Na-smektyty
Fig. 5. Zależność Piłojana-Nowikowej dla wyznaczenia energii aktywacji dehydratacji montmorillonitu Chmielnik, zawierającego różne kationy wymienne
     1 – Mg, 2 – Ca, 3 – K i 4 – Na
Fig. 6. Zależność szybkości oddawania wody hydratacyjnej od stopnia odwodnienia montmorillonitu Chmielnik, zawierającego różne kationy wymienne
     1 – Na, 2 – Ca, 3 – Mg i 4 – K
Fig. 7. Zależność szybkości oddawania wody hydratacyjnej od stopnia odwodnienia różnych montmorillonitów, przeprowadzonych w formę wapniową
     1 – Chmielnik, 2 – Milowice, 3 – Rosyjski, 4 – Fintice, 5 – beidellit, 6 – nontronit
Fig. 8. Zależność szybkości oddawania wody hydratacyjnej od stopnia odwodnienia różnych montmorillonitów, przeprowadzonych w formę magnezową
     1 – Chmielnik, 2 – Rosyjski, 3 – Fintice, 4 – beidellit, 5 – nontronit, 6 – Milowice
Fig. 9. Zależność zawartości wody hydroksylowej od ładunku pakietu smektytu
Fig. 10. Zależność szybkości dehydroksylacji od stopnia rozkładu montmorillonitu Chmielnik, zawierającego różne kationy wymienne
     1 – Na, 2 – K, 3 – Ca, 4 – Mg
Fig. 11. Zależność szybkości dehydroksylacji od stopnia rozkładu montmorillonitów, przeprowadzonych w formę potasową
     1 – nontronit, 2 – Milowice, 3 – Chmielnik, 4 – beidellit, 5 – Fintice, 6 – Rosyjski

Ирена ВАЦЛАВСКА

ДЕГИДРАТАЦИЯ И ДЕГИДРОКСИЛАЦИЯ СМЕКТИТОВ
I. КИНЕТИКА ДЕГИДРАТАЦИИ И ДЕГИДРОКСИЛАЦИИ

Резюме

Кинетика процесса дегидратации и дегидроксилации смектитов обусловлена видом катионов в их межпакетных пространствах, а также количеством и видом изоморфных замещений в пакетах и возникающей в следствие этого величины заряда. Для исследований были отобраны смектиты, отличающиеся зарядом пакета, которые были приведены к моноионовым формам путем насыщения их катионами Na⁺, K⁺, Ca²⁺, Mg²⁺. Кривые ТГ и ДТГ, выполненные на термоанализаторе ТА-2 фирмы Меттлер, дали возможность определить количество воды, отданной в процессе дегидратации и дегидроксилации смектитов, а также определить кинетические параметры этих процессов по методу Фримана-Каролла и Пилояна-Новиковой.

Количество воды, отдаваемое в процессе дегидратации, зависит от вида обменного катиона и заряда тетраэдрического слоя пакета. Для смектитов с зарядом 0-0,2 и обменным катионом Ca^{2+} ее содержание составляет в среднем около 16 вес.%. Увеличение заряда тетраэдрического слоя до 0,5 вызывает уменьшение количества межпакетной воды наполовину, когда обменными катионами являются интенсивно гидратированные катионы Ca^{2+} или Mg^{2+}. В присутствии иона Na^+ возрастание заряда вызывает уменьшение количества межпакетной воды на 30%. В зависимости от вида катиона в межпакетном пространстве процесс дегидратации бывает одно- или нескольскоступенчатый. Не обнаружено четкой зависимости между величиной мнимой энергии активации дегидратации и видом обменных катионов. Заряд тетраэдрического слоя пакета ослабляет действие межпакетных катионов на молекулы воды, что характеризуется понижением температуры дегидратации и перемещением максимума скорости второго этапа дегидратации в сторону меньших величин α.

Количество воды, отдаваемой в форме группы ОН в смектитах, составляет в среднем 3,5 вес.% и подлежит уменьшению по мере увеличения заряда пакета. Влияния вида обменного катиона на количество воды, отдаваемой в процессе дегидроксилации смектитов, не обнаружено. Процесс дегидроксилации смектитов, независимо от вида обменного катиона, одноступенчатый, а температура его максимума достигает самых низких величин только в присутствии калия как межпакетного катиона. В присутствии калия наблюдалось перемещение максимума скорости дегидроксилации смектитов к более низким величинам α, что может объясняться тем, что калий, уменьшая скорость дегидроксилации, замыкает межпакетные пространства и вызывает сходство структуры смектитов со структурой слюды.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Термограмма монтмориллонита из Миловиц, приведенного в кальциевую форму
Фиг. 2. Термограмма монтмориллонита из Миловиц, приведенного в калиевую форму
Фиг. 3. Термограмма монтмориллонита из Миловиц, приведенного в магниевую форму
Фиг. 4. Зависимость содержания межпакетной воды от заряда тетраэдрического слоя смектитов
Фиг. 5. Зависимость Пилояна-Новиковой для определения энергии активации дегидратации монтмориллонита из Хмельника, содержащего разные обменные катионы
     1 – Mg, 2 – Ca, 3 – K, 4 – Na
Фиг. 6. Зависимость скорости отдачи гидратационной воды от степени обезвожения монтмориллонита из Хмельника, содержащего разные обменные катионы.
     1 – Na, 2 – Ca, 3 – Mg, 4 – K
Фиг. 7. Зависимость скорости отдачи гидратационной воды от степени обезвожения разных монтмориллонитов, приведенных в кальциевую форму
     1 – Хмельник, 2 – Миловице, 3 – Русский, 4 – Финтице, 5 – Бейделлит, 6 – Нонтронит
Фиг. 8. Зависимость скорости отдачи гидратационной воды от степени обезвожения разных монтмориллонитов, приведенных в магниевую форму
     1 – Хмельник, 2 – Русский, 3 – Финтице, 4 – Бейделлит, 5 – Нонтронит, 6 – Миловице
Фиг. 9. Зависимость содержания гидроксиловой воды от заряда пакета смектита
Фиг. 10. Зависимость скорости дегидроксилации от степени разложения монтмориллонита из Хмельника, содержащего разные обменные катионы
     1 – Na, 2 – K, 3 – Ca, 4 – Mg
Фиг. 11. Зависимость скорости дегидроксилации от степени разложения монтмориллонитов, приведенных в калиевую форму
     1 – Нонтронит, 2 – Миловице, 3 – Хмельник, 4 – Бейзеллит, 5 – Финтице, 6 – Русский