

INVESTIGATION OF MONTMORILLONITES TREATED BY UREA

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I. INVESTIGATION OF MONTMORILLONITES TREATED BY UREA SOLUTIONS

The behaviour of different clay minerals brought into contact with organic substances was studied in the last years by GREENLAND [1964, 1965], LAFFER, etc. The swelling of three-layer silicates of montmorillonite type in watery as well as in organic agents was studied by GORODNOV [1966], KERNS [1966], MANUILOVA [1966], HAZART [1965], HILTNER [1967], TAYLOR [1965], etc.

Several authors dealt with the interaction of different organic compounds and montmorillonites regarding the swelling of the clay mineral's lattice and the building in of the organic molecules into the lattice. WEISS [1961] dealt with kaolinite-urea, WADA [1959] studied the urea-montmorillonite systems, while SHIGA [1961] investigated the complexes of different cation-montmorillonites formed with urea and their derivatives. MORTLAND [1966] studied the structure of urea-montmorillonite complexes on the basis of their infrared absorption spectra.

Our primary aim was to produce *slowly acting* nitrogenous chemical fertilizer which are produced by utilizing clay minerals. The use of clay mineral was chosen because it is cheap, occurs in the soil and the intensive, motorized soil cultivation had the claim to *slowly acting chemical fertilizers*.

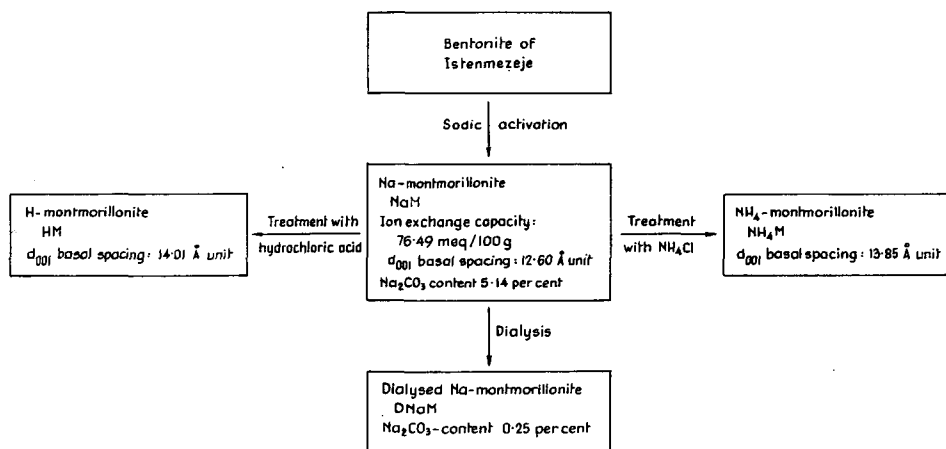


Fig. 1. Origin of the applied samples

Urea is applied on a large-scale for soil and sprinkling fertilizers as fast-acting nitrogen chemical fertilizer. The nitrogen content of the urea is the highest out of the nitrogen chemical fertilizers. In the course of natural biological fertilization urea falls into the soil. Our investigations were performed with clay minerals brought into contact with urea to determine the interaction of the clay minerals of three-layer structure and of the urea brought into contact with them. Na-montmorillonite (*NaM*) from the Istenmezeje bentonite was the starting material and from this sample H-, occasionally NH_4 -clay minerals were prepared (Fig. 1.).

With this cation-montmorillonite experiments were performed in test-tubes. 50 cg samples of air-dry montmorillonite were weighed and 20 ml urea solution of different concentration was added to each sample. The suspensions thus obtained were then held constantly at 30° C. After the certain observations the suspensions were shaken and let rest undisturbed till the next observation.

The concentration of the solutions being in contact with clay minerals was measured from time to time during several months, and the measure of gel-stage and rheological changes of the clay mineral were also registered. The degree of swelling was measured by the gel-volume while its thixotropic change was observed on the basis of its rheological behaviour in the course of tilting of the test-tube. The preparation method is discussed in the previous paper [LIBOR and GRABER, 1969].

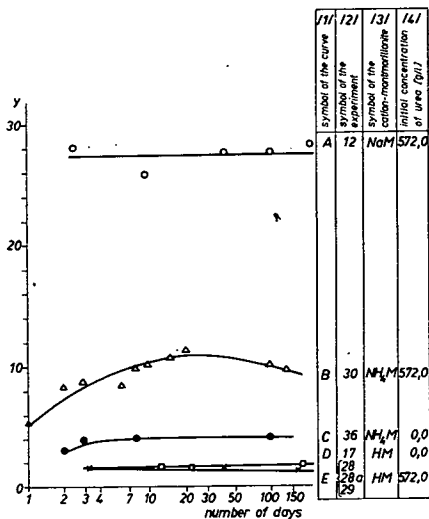


Fig. 2. Swelling of cation montmorillonites y = volume of the swelled gel taking the original volume as 1

Montmorillonites showed better swelling in concentrated urea solution than in distilled water. *NaM* shows the best swelling (it swells at about 28-times of its original volume) and *HM* swells least (Fig. 2.).

In accordance with literature data water plays significant role in swelling of montmorillonites (Table I. a. b.). LIBOR and GRABER [1969] proved that montmorillonites swell hardly or not at all in alcohol.

In distilled water the swelling of *NaM* was unmeasurable because of the total diffusive settlement which was due to the large-scale peptization of the gel.

The swelling of montmorillonite caused by the effect of water is influenced by the hydration of the interlayer cations of the lattice, by the surface charge density and by the osmotic feature of the system.

The building in of N-containing compounds into the lattice of montmorillonite depends on the quantity of water in the lattice [SWOBODA and KUNZE, 1965; TAHOUN and MORTLAND, 1966; etc.]. MORTLAND also demonstrated that the proton transfer capacity of the water of air-dry montmorillonites is greater than that of the H_3O^+ ion, depending on the quality of the exchangeable cations of the lattice.

TABLE I

a) Initial composition of experimental solutions I
Aqueous solutions

/1/ Serial number of experiment	/2/ Marking of cation montmorillonite	/3/ Initial concentration of urea solution g/l	/4/ M_1	/5/ M_2	
2	NaM	1,86	0,05	39,94	M_1 = urea g/clay mineral g M_2 = water g/clay mineral g
7	NaM	102,30	4,09	36,95	
12	NaM	572,10	22,88	23,11	
14	NaM	0,0	—	40,00	
17	HM	0,0	—	40,00	
23	HM	104,50	4,18	38,90	
27	HM	504,20	20,01	25,11	
34	NH_4M	0,0	—	40,00	
35	NH_4M	572,80	22,91	23,09	
37	DNaM	0,0	—	40,00	
38	DNaM	572,60	22,90	23,82	Admeasurement in experiments 1—57:0,5 g of cation-montmorillonite in each case.

b) Initial composition of experimental solutions II

42	NH_4M	0,0	—	31,54	In case of samples N° 42—45, 50—53 abs. alcohol, otherwise etanol of 96 per cent were used.
43	NaM	0,0	—	31,52	
44	HM	0,0	—	31,58	
45	DNaM	0,0	—	31,54	
46	NH_4M	0,0	—	32,16	
47	NaM	0,0	—	32,16	
48	HM	0,0	—	32,08	
49	DNaM	0,0	—	32,18	
50	NH_4M	49,4	1,58	30,54	
51	NaM	49,4	1,59	30,61	
52	HM	49,4	1,58	30,56	
53	DNaM	49,4	1,58	30,56	
54	NH_4M	90,2	3,00	32,34	
55	NaM	90,2	3,00	32,34	
56	HM	90,2	3,02	32,40	
57	DNaM	90,2	3,02	32,40	

Fig. 3. shows the process of thixotropy of the NaM. This process was completed during several days in concentrated urea solutions while it proved to be a long-lasting process in diluted solutions. HM did not swell under the experimental conditions thus thixotropy could not be observed.

Dissolving investigations were also performed from the gel swelled in concentrated urea solution to determine whether the montmorillonite swelled in diluted urea solution for a longer time possesses or not urea-retaining feature.

The watery gel was dried (above CaCl_2 , at room-temperature) and water was dropped on it. The quantity of dissolving urea was determined and the montmorillonite was dried again. This process was repeated several times always drying the sample. Granular and pulverized urea which does not contain clay mineral as well as urea mixed with quartz powder were also investigated.

The urea which did not contain clay mineral totally dissolved practically in two steps. The dissolving of urea from the *HM*-urea took place in about nine steps. The *NaM*-urea contained about 30 per cent of the original urea content after twelve steps (Table. II).

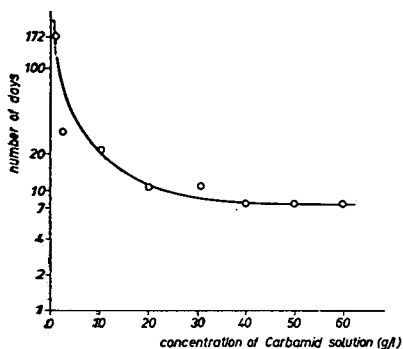


Fig. 3. Thixotropic time of Na-montmorillonite as a function of the concentration of urea

TABLE II

Investigation of urea-retaining capacity of NaM, HM and NH_4M

Sign of clay mineral	NaM	HM	NH_4M			
Number of dissolving steps	Dissolved urea in per cent*					
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	12	26	26	60	60	83
2	20	38	24	100	92	98
3	28	64	31		100	99
4	35	81	39			
5	41	89	49			
6	47	93	61			
7	52	94	71			
8	57	95	80			
9	59	97	89			
10	62		95			
11	68					
12	71					

* Concerning the initial quantity of urea.

(5) Urea was previously mixed with quartz powder, the quantity of which corresponded to that of the clay mineral content.

(6) Granular urea without clay minerals.

(7) Pulverized urea without clay minerals.

X-ray diffractometric base reflexion measurements were also done to determine the entering and binding forms of urea into the montmorillonite lattice. These measurements were done by GY. BÁRDOSSY*, with pulverized gels dried above CaCl_2 (Table III., Fig. 4.)

TABLE III

Change of the basal plane distance (d_{001}) of montmorillonites swelled in aqueous urea solutions

Sign of cation — montmorillonite	Original d_{001} Å	d_{001} Å swelled in aqueous urea solutions	Change of d_{001} Å
NaM	12,95	18,22	5,63
HM	14,04	13,51	—0,53

The elementary cell of the urea crystal is built up by two urea molecules (Fig. 5.). The "a" and "b" coordinates of the elementary cell are both 5.67 Å unit. While the base reflexion of the air-dry NaM swelled in diluted urea solution increased by 5.62 Å unit, it is presumable that the urea crystal layer, consisting of one elementary cell, lies between the basal spaces of the montmorillonite, the "c" axis of which is perpendicular to that of the montmorillonite lattice. In HM the d_{001} base reflexion decreased by 0,53 Å unit, urea did not enter the lattice.

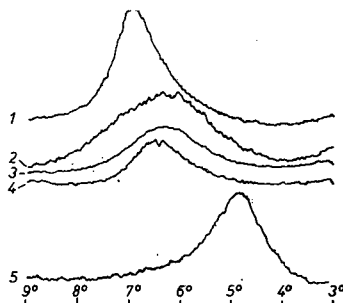
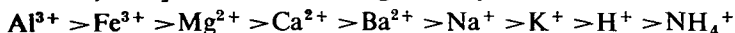


Fig. 4. X-ray-diffraction diagram of cation-montmorillonites 1. Original Na-montmorillonite, d_{001} spacing = 12.60 Å 2. Original NH_4 -montmorillonite, d_{001} spacing = 13.86 Å 3. Original H-montmorillonite, d_{001} spacing = 14,04 Å 4. Experiment No. 23. H-montmorillonite, previously swelled in 10 % urea solution d_{001} , spacing = 13,51 Å. 5. Experiment No. 7. Na-montmorillonite, previously swelled in 10 % urea solution, d_{001} spacing = 18,22 Å. Basis reflection is calculated according to the peak of basal spacing.

From these investigations it is obvious that the two cation-montmorillonites are of different behaviour. The influencing role of cations was emphasized by EMERSON [1963] and SHIGA [1961]. According to them the greater the charge of the exchangeable cations of the montmorillonite, it can bind the more organic molecules. The role

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of the exchangeable cations of the montmorillonite lattice, in connection with the swelling and urea-binding capacity of the lattice is probably influenced by its hydration capacity [NORRISH, 1954]. The relative charge density of the cations is the following:



From these data it is obvious that the charge density of the K^{+} , H^{+} and NH_4^{+} ions is the least and are about of same value. The charge density considerably influences the measure of the ions' hydration. The hydration energy, resp. the number of stronger bound water molecules of the ions of small relative charge density are least.

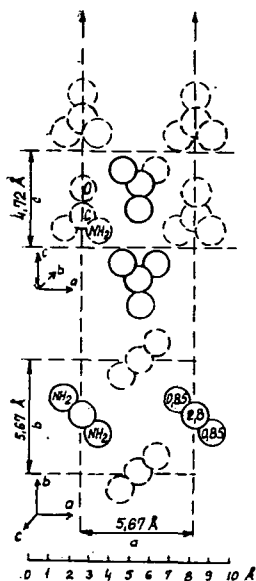


Fig. 5. Projection of urea.

The smaller size swelling and urea-binding capacity of the *HM* and *NH₄M* observed both by SHIGA [1961] and authors are possibly in connection with the smaller hydration ability which is connected to the charge density of low value of the H^{+} and NH_4^{+} ions.

The interaction of *HM* and *NaM* with the urea in watery agent is different and the dissimilarity between their cations is responsible for this difference. Urea penetrates the basal spaces of the lattice of *NaM*, and it does not that in case of *HM*.

To prove these facts derivatographic investigations were also performed. The prepared different cation-montmorillonites treated by urea as mentioned above were heated by a heating gradient of $10^{\circ}\text{C}/\text{min}$. To explain the thermal behaviour of the urea-containing clay minerals the derivatograms of the *HM* and *NaM* were also completed at the same temperature gradients (Figs. 6, 7). It was necessary to investigate the urea itself under the same conditions to explain the thermal behaviour of the montmorillonite-urea system.

II. THERMAL INVESTIGATION OF THE UREA

The chemical reactions taking place in the course of the thermal transformation of the urea pass off simultaneously in the certain thermal intervals. These reactions are influenced by the heating velocity of the reaction mixture and by the time spent on the temperature in question [KERNS, 1966; MORTLAND, 1968; etc.].

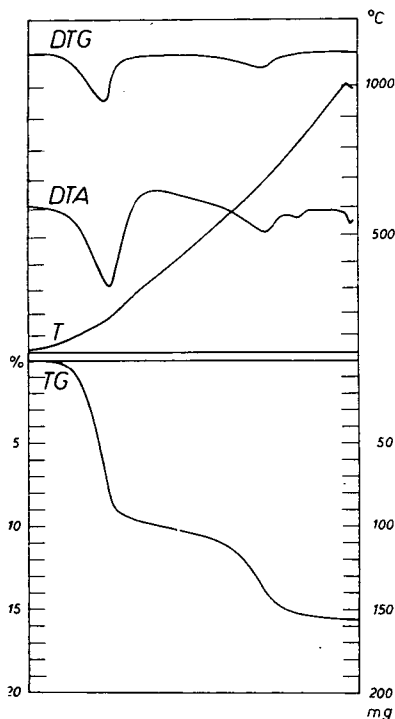


Fig. 6. Derivatogram of H-montmorillonite. Sample: 320 mg. T 1200 DTA 1/5, DTG 1/10, TG 50 mg.

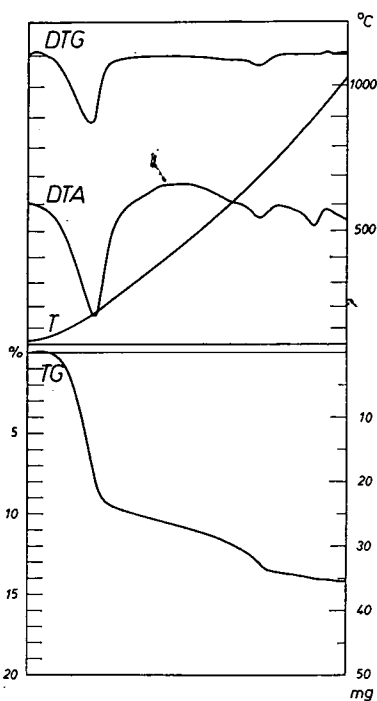


Fig. 7. Derivatogram of Na-montmorillonite. Sample: 1000 mg. T 1200, DTA 1/15, DTG 1/15, TG 200 mg.

Our derivatogram of urea was evaluated on the basis of the data of literature and we tried to explain the reactions which may be connected to the certain peaks of the DTA curve. As a result after melting the urea decomposes to cyanic acid and ammonia. The developing cyanic acid transforms with the urea to in situ nascendi biuret. Above 190 °C this melts and in the interval between 190 and 240 °C cyanic acid and ammonia forms from the biuret [SCHILTKNECHT 1963]. This transformation is connected to a loss of weight of 20 per cent. According to several authors above 190 °C biuret decomposes to urea and cyanic acid and the effect of further heating causes the formation of cyanuric acid and amide [GIGER, 1958]. At 225 °C besides these reactions cyanuric acid and ammonia develops from the urea [KINOSHITA, 1954; MALKINA and KASARNOVSKI, 1961].

Strong endothermal change can be observed between 220 and 240 °C which is connected to large loss of weight (about 10.5 per cent). At temperatures between

240 and 260 °C a loss of weight of 14.7 per cent results. Then the biuret transforms with cyanic acid into cyanuric acid and cyanic acid is trimerized to cyanuric acid [MALKINA and KASARNOVSKI, 1957; SCHILTKNECHT, 1963]. Besides these reactions the biuret and cyanic acid have also possibly a reaction during which amelide forms parallel with water loss [WERNER, 1923]. The water formed in such a way reacts with the presenting cyanic acid during which carbon dioxide and ammonia forms [LIENHARD, 1954; SCHILTKNECHT, 1963]. These may cause the observed change of weight. In the course of the thermal decomposition of urea it hardens at 250 °C [SCHILTKNECHT, 1963], which is preceded by strong gas formation. This latter reaction connected to strong gas formation takes place also at this temperature. The thermal gradient curve of the derivatogram remains constant in the course of the reaction and this indicates the strongly endothermal change of it (Fig. 8.).

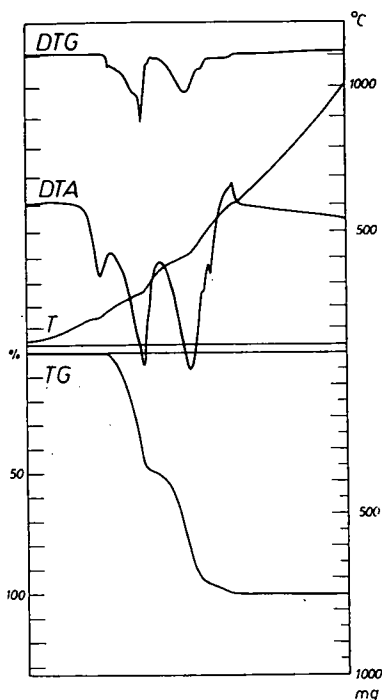


Fig. 8. Derivatogram of urea. Sample: 750 mg. DTA 1/20, DTG 1/15, TG 1000 mg, T 1200° C.

According to SCHILTKNECHT [1963] chain-polymer develops between 240 and 260 °C, which is insoluble in water. Therefore it is possible that there are simultaneous reactions. On the basis of the derivatogram only 4 per cent of loss of weight occurred in the interval of 260 to 280 °C. In this temperature interval possibly polymerization reactions form the main reactions. In the course of these reactions cyanuric acid [MALKINA and KASARNOVSKI, 1961; SCHILTKNECHT, 1963], amelide, amelina, melamine [KINOSHITA, 1954] and melam [FINKELSTEIN and ZAGRANICHNI, 1955] developed. The reaction is connected with exothermal reaction and this relates to the formation of greater quantity of the cyanuric acid [SCHILTKNECHT, 1963]. This exothermal

reaction is shown by the peak of the DTA curve at 300 °C. After melting above 380 °C the polymeric compounds decompose to cyanic acid [FINKELSTEIN and ZAGRANICHNI, 1955; HUNN, 1959; LIENHARD, 1954, SCHILTKNECHT, 1963].

Further five transformations have to be taken into consideration. Out of these changes there are three endothermal (at 420, 480, 520 °C) and two exothermal peak maximums (at 580 and 600 °C). The endothermal peak of 420 °C is in connection with the greatest loss of weight (42 per cent). This may be caused considerably by the leaving of ammonia and carbon dioxide which are the final decomposition products. The explanation of the endothermal processes pertaining to the peaks of 480 and 520 °C and connected to the loss of weight, as well as of the processes pertaining to 500 and 600 °C need further investigations. In literature there are data of the thermal change of urea only up to 500 °C. The loss of weight reaches 100 per cent at 600 °C.*

III. THERMAL INVESTIGATIONS OF MONTMORILLONITES AND THOSE OF UREA CONTENT

The derivatogram of the recorded pure *HM* and *NaM* (Figs. 6, 7) agrees well with the data of literature.

In case of the derivatograms of the urea-containing *HM* and *NaM*, however, there are characteristics which have to be explained.

In case of the urea-containing *NaM* (Fig. 9. and Table IV.) peak maxima characteristic of urea can be registered at 140, 250, 410 and 540 °C, and the characteristic peak maximums of pure *NaM* also occur at 690 and 820 °C. It is obvious from these facts that the common presence of the two materials has no significant influence on their thermal decomposition.

TABLE IV

Loss of weight of urea-containing Na-montmorillonite on the basis of its derivatogram

Temperature and character of peak maximums °C	Loss of weight pertaining to a given temperature °C per cent		Loss of weight pertaining to the temperature interval °C per cent	
140 endoth.	160	3,45	0—160	3,45
	195	14,42	160—195	10,97
220 endoth.	230	21,14	195—230	6,72
	300	31,43	230—300	10,29
250 endoth.	320	33,71	300—320	2,28
	360	36,57	320—360	2,86
	450	46,85	360—450	10,28
410 endoth.	530	51,71	450—530	4,86
	580	53,71	530—580	2,00
450 endoth.	740	55,43	580—740	1,72
540 endoth.				
690 endoth.				
820 endoth.				

* The quantitative evaluation of the derivatogram of urea is recently impossible. While reactions, connected to the thermal decomposition of the urea take place simultaneously and in function of the thermal gradient, they are differently evaluated by different authors. Only the presumable explanation of the urea's derivatogram could be given.

The derivatogram of the urea-containing *HM* (Fig. 10. and Table V.), however differs considerably from the curves of both the pure urea and the pure *HM*. The peak characteristic of the melting of urea decreased to 115 °C. It is conspicuous that the strong endothermic peak, characteristic of the thermal decomposition of urea at 420 °C, disappeared and instead of it small endothermic peak maximum occurs at

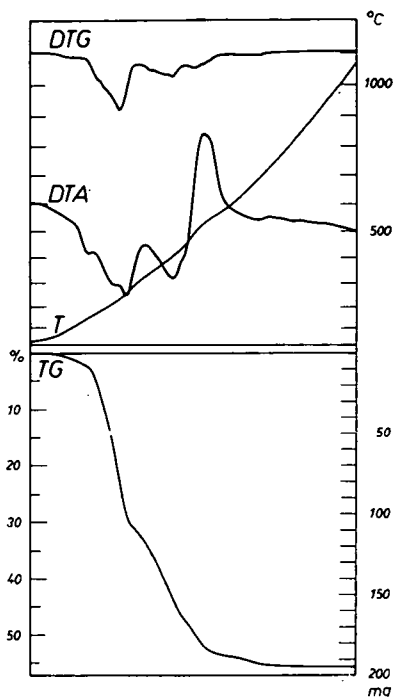


Fig. 9. Derivatogram of urea containing *NaM*. Sample: 350 mg. DTA 1/15, DTG 1/15, TG 200 mg, T 1200° C.

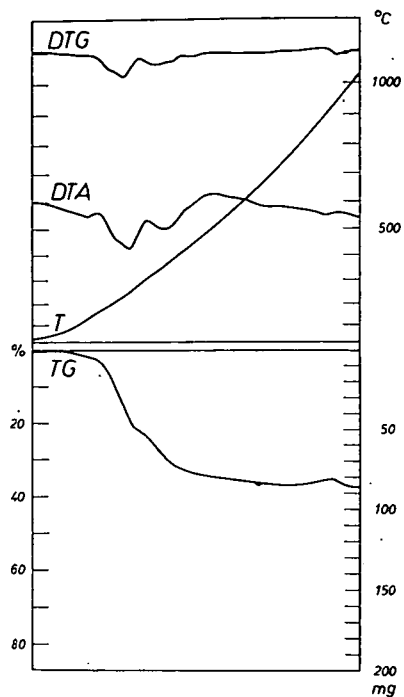


Fig. 10. Derivatogram of urea containing *HM*. Sample: 230 mg. DTA 1/15, DTG 1/15, TG 200 mg, T 1200° C.

360 °C which may presumably derive from different processes. The exothermic peak, characteristic of the urea's thermal decomposition at 520 °C, also disappeared which can be registered in case of urea-containing *NaM*.

The dissimilar behaviour of the *NaM*-, resp., *HM*-urea observed in the course of their thermal decomposition, shows the different urea-bond of the two clay minerals. Both montmorillonites fixed the certain part of urea on their surfaces (endothermic peaks at low temperatures). The endothermic peaks of the two substances at low temperature are dissimilar and this fact shows different urea quantities bound by the two different cation-montmorillonites on their surface.

The *HM* of acidic behaviour [GLAESER, MANTIN, MERING, 1963; POMMER and CARRELL, 1960; SAWHNEY and FRINK, 1966] reacts to urea, showing slightly basic behaviour [SABALITSCHKA and KUBISCH, 1924], presumably according to acid-base reaction. (This is also justified by the structure investigation of MORTLAND, 1966 and HARTER, 1967, done by IR-method.) The formed *HM*-urea molecule-compound

[WERNER, 1923] presumably hinders the entering of water, resp. urea molecules the lattice of the clay mineral. Therefore, in the course of the thermal decomposition of the *HM*-urea the selectivity cannot be observed, the two substances have a mutual influence on their thermal decomposition, and the *HM* brought into contact with diluted urea solution swells only in a small degree [LIBOR and GRABER, 1969].

TABLE V

Data of loss of weight of urea-containing H-montmorillonite on the basis of its derivatogram

Temperature and character of peak maximums °C	Loss of weight pertaining to a given temperature °C per cent	Loss of weight pertaining to the temperature interval °C per cent
130 endoth.	120 1,15	
160 endoth.	160 1,34	0—160 1,34
210 endoth.	220 12,04	160—195 5,18
250 endoth.	300 22,60	220—300 10,56
310 endoth.		
360 endoth.	420 23,17	300—420 9,57
440 endoth.		
500 exoth.	495 34,34	420—495 2,17
610 exoth.		
670 endoth.	740 36,52	495—740 2,18
890 endoth.		

TABLE VI

Data on the changes of the weight of urea and clay-minerals containing urea on the basis of the TG curves of the derivatogram and of the material balance

Materials examined	Decrease of weight % of the total urea present			Evaporated moisture, per cent of the initial material
	420—600 °C	300—460 °C	0—300 °C	
Urea	8,0	42,7	49,3	—
H-montmorillonit-urea	9,6	30,2	60,4	3,5
Na-montmorillonit-urea	23,7	53,0	23,3	24,5

The *NaM* bound the urea in two different ways. The urea was partly connected to the surface of the clay mineral's lattice, but dissimilarly to the chemical bond characteristic of the *HM*-urea. On the DTA curve of the derivatogram the peaks characteristic of both the urea and the *NaM* can be separately registered. Certain part of urea enters the clay mineral's lattice. This is proved by the fact that the characteristic peaks of both the *NaM* and urea appear (though they mutually influence their thermal decomposition), and the endothermal peak indicating the final decomposition of urea occurs, as well. In the temperature interval of 420 to 600 °C the losses of weight, related to the total urea quantity of the system, are nearly of the same value in case of *HM*-urea, while in case of *NaM*-urea the loss of weight is nearly three times greater than those of the values given below (Table VI; columns

2 and 4). In case of urea and urea-containing *HM* the loss of weight observed at low temperatures (0 to 300 °C) proved to be considerably greater than in case of urea-containing *NaM*. The decompositions of medium temperatures (300 to 420 °C) do not show differences of this measure. These data prove that the H- and *NaM* bind the urea in different ways and that *NaM* binds it in its crystal structure.

As a summary the following facts were stated: the urea molecule enters the lattice of *NaM*; the quality of the exchangeable cations influences this entering; the bond of H-, resp. *NaM* is different; it can be proved by derivatograph that *HM* bound chemically the considerable part of urea on its lattice-surface; the *NaM* partially bound the urea presumably not in chemical way, while the other part of urea was bound in the lattice of the clay mineral [LIBOR, GRABER, DONÁTH, 1970].

TABLE VII

Thermal investigation of Na-, H-, NH₄M-urea melting systems

Number of investigation	Sign of Montmorillonite	Montmorillonite: urea ratio	Heating velocity °C/min.	Length of time of heating min.	Note
Karbamid I.	—	—	1200/100 600/100 600/150 600/100+ } 600/400 }	720	
A 1. B 1. II. 2.	NaM NaM HM HM	1:0,35 1:0,35 1:0,35 1:0,35	600/100 600/100+ } 600/400 } 600/100 600/100+ } 600/400 }	90 360	Keeping the mixture at 132° C for 4 hours
C 1. III. A 1. B 2.	NH ₄ M NaM HM	1:0,35 1:0,35 1:0,35	1200/100 300/100 300/100		At 130 and 200° C temperature was kept for 15—15 minutes
A 1. B 1. IV. 2. 3. 4. B 1. 2.	NaM NaM NaM NaM NH ₄ M NH ₄ M	1:0,25 1:0,50 1:0,75 1:1 1:0,30 1:0,30	1000/100 1000/100 1000/100 1000/100 1000/100 1200° C/100	100 100 100 100 100 100	10 minutes at 130° C and further heating by the given temperature gradient

On the basis of our investigations the specially formed *NaM* and *HM* seems to be able for utilizing as chemical fertilizer, first of all due to the urea-retaining capacity.

IV. INVESTIGATION OF Na-, H- AND NH₄M — UREA MELTS

I. Heating the pure urea up to its melting point by different thermal gradients and keeping it at this temperature (130 °C) for various length of time, we observed that urea reaching its melting point does not decompose. Keeping the

system at the melting point in different times, slow and continuous thermal decomposition commenced. This decomposition depended on the heating gradient and time, but after 12 hours heating we could not observe the equilibrium (Table VII/I).

2. The following step was to heat the mixtures of Na-, H- and NH_4M — urea of 1:0,35 ratio in the same way and the systems were kept at the melting point of urea for various length of time. Our aim was to investigate that the temporal thermal decomposition of urea is influenced or not by the presence of different cation-containing clay minerals (Table VII/II).

The results demonstrated in every case that, independently of the cation's quality bound to montmorillonite, endothermal reaction resulted parallel with considerable loss of weight. On the one hand the measure of this loss of weight depended on the cation's quality, and was connected to the endothermal reaction, on the other. Further it was also observed that in contrary of the thermal decomposition of pure urea the equilibrium resulted in case of heatings of shorter times. The time of the attainment of equilibrium depended on the cation's quality bound to the montmorillonite. This time proved to be 4 hours in case of *NaM*-urea and 6 hours in case *HM*-urea system. This experience proved that one part of urea enters the *NaM* in such cases too, when urea contacts it as a melt. It is also conspicuous that urea being in contact with the surface of montmorillonite shows more difficult decomposition in case of *HM* than in case of *NaM*-urea system. It is therefore presumable that urea reacts chemically to *HM* also in the melt.

These statements are justified by the experiments in the course of which the mixture of 1:0,35 ratio of the *Na*- and *HM* - urea was heated by 300 °C/100 min. heating velocity and the system was kept at 130 and 200 °C for 15—15 minutes in the course of heating (Table VII/II).

Results show that in the *HM*-urea system, in contrary of the *NaM*-urea system, an endothermal peak occurs at 95 °C which is followed by an exothermal peak at 125 °C (Table VII/III). The further thermal decomposition takes place similarly to that of the *NaM*-urea system. This energetic change may indicate the chemical bond forming between the *HM* and the urea.

The experiments of the fourth group of Table VII/IV were performed to establish the minimal clay mineral/urea ratio, in which case the presence of urea has some influence on the thermal decomposition of the clay mineral. On the basis of the experiments' results this phenomenon occurred at a clay mineral/urea ratio of 1:0.35.

SUMMARY

H-, *Na*- and *HN₄M* brought into contact with urea were investigated. Investigations included clay minerals brought into contact with urea in solution and melt.

Authors stated that the bound of urea to montmorillonite was dependent on the cation's quality.

1. Two molecule layer of urea was bound in the lattice of *NaM*. After the desiccation of the gel urea crystallized in the lattice of the clay mineral which lies in an elementar cell layer between the d_{001} basal spaces of the *NaM*. The "c" axis of urea crystal is perpendicular to that of the montmorillonite lattice.

The investigated cation-montmorillonites swelled in a slight degree in ethanolic urea solution and this was hardly influenced by the quality of

the exchangeable cations. These data also prove the significance of water in the swelling of montmorillonite.

2. Regarding the thermal behaviour of H^- , and NaM brought into contact with diluted urea solution the fact could be also stated that the urea-bond of the two cation-montmorillonites is different.

HM bound chemically the considerable part of urea on the surface its lattice. NaM bound the one part of urea on its surface presumably not by chemical bond, the other part of urea was bound in the lattice of the clay mineral. This statement agrees with the results of the preliminary performed X-ray diffractometric investigations.

3. The H^- , Na^- and NH_4M being in contact with urea melt showed dissimilar thermal behaviour. These results also showed that urea in solution may bind to these montmorillonites in the same way as in watery agent.

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