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Errata

	Wiersz			Danima bió	
Str.	góra	dół	Jest	Powinno być	
4		18	$n_{\gamma} - n_{\alpha} - 0.080 - 0.079$	$n_{\gamma} - n_{\alpha} = 0.080 - 0.079$	
9	13		(Ch) transformed	(Ch) partially transformed	
15	9		16.4	16.4%	
19	11		Fig. 1 12	Fig. 1, 12	
19	12		MgCc ₃	MgCO ₃	
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	plansze kredowe po str. 100		WOŁOSIŃSKI	WŁOSIŃSKI	

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BLEACHING PROPERTIES OF NON-BENTONITIC CLAY MATERIALS AND THEIR MODIFICATION

UKD 549.623.84:548.73(438.31 Rudno)

I. ACID ACTIVATION OF THE MIOCENE CLAYS FROM MACHÓW

Abstract. The mechanism and kinetics of activation of Miocene clays containing montmorillonite, chlorite, illite, kaolinite, quartz and carbonates was studied. It has been found that the montmorillonite contains more Fe in the octahedral sheet and more Al in the tetrahedral sheet than typical montmorillonites from bentonites. Sulphuric acid extracts most readily Mg, less so Fe and Al. The rate of cation extraction is the slower, the stronger the cation-oxygen or OH group bond in the octahedral sheet.

INTRODUCTION

Bleaching earths have wide application in several technologies. It has been found that bentonites with montmorillonite as the main component or fuller's earths containing palygorskite possess the best bleaching properties. Those properties are enhanced by activation in inorganic acids or other methods of chemical treatment, or by thermal activation. The materials in question are, however, scarce and not readily available whereas the demand for cheap bleaching earths is ever increasing, e.g. in connection with the environment protection.

The most common non-bentonitic material used as bleaching earth is halloysite (Ovtcharenko et al. 1967), but attempts have been also made to utilize clays containing D-kaolinite for that purpose (Horváth et al. 1973).

The present authors considered the possibility of using common clays as bleaching earths. Those clays contain montmorillonite and illite, chlorite and small amounts of kaolinite as minor components, or else mixed-layer illite (montmorillonite). This montmorillonite differ from those originating from bentonites and by weathering of tuffs in the structure of layers and

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chemical composition, viz. they contain more iron and less magnesium than the typical montmorillonites (Weaver, Pollard 1973). They also admit more isomorphous substitution of Al for Si in the tetrahedral sheet, which gives a greater electric charge to their layers. Some of them belong to the beidellite-nontronite isomorphous series. The different chemical composition and layer structure of the montmorillonite in question are due to their different genesis, as they owe their origin to the degradation of the structure of illites or chlorites (Stoch 1974).

The clays studied are difficult to activate. The reasons are presumably to be sought both in the different type of montmorillonite and in the presence of illite, which is a relatively chemical resistant mineral and

therefore not readily reacting with acids.

THE MINERALOGICAL CHARACTERISTICS OF THE CLAYS STUDIED

The investigations were carried out on the Miocene clay of marine origin derived from the overburden of the Machów sulphur deposit (Krakowiec clay). Its dominant mineral component is montmorillonite; besides, it contains illite, chlorite, and subordinate kaolinite. The clay minerals are accompanied by small amounts of quartz and carbonates (calcite, dolomite,

Table 1

Mineral composition of the clay from
Machów

(from the depth 132 m a.s.l.)

Components	Weight %		
Montmorillonite	30		
Illite	14		
Chlorite	13		
Kaolinite	6		
Quartz	29		
Calcite	4		
Dolomite	2		
Feldspar	2		

Chemical composition of the $< 0.5 \, \mu m$ fraction of the clay from Machów (from the depth 132 m a.s.l.)

Table 2

Components	Weight %
SiO ₂	47.04
Al_2O_3	19.97
TiO ₂	0.53
Fe ₂ O ₃	6.42
CaO	2.72
MgO	3.08
Na ₂ O	0.40
K ₂ O	0.51
loss on ignition	19.08
Total	99.75

siderite, Table 1). The mineralogical composition of the clays from Machów is the subject of a separate publication (Stoch et al. 1977).

The grain-size distribution of the mineral components of the clay studied is as follows. Montmorillonite is the main constituent of the fractions $< 4 \, \mu m$, its percentage increasing with the diminishing grain size. In fractions $< 0.5 \, \mu m$ its content amounts up to 87%. Illite, kaolinite and chlorite concentrate mainly in the grain fractions 1—15 μm . Carbonates and quartz are to be found mostly in the fractions 4—60 μm (Fig. 1).

Montmorillonite that occurs in the Machów clay is a dioctahedral mineral. Its chemical composition is illustrated by the chemical analysis of the $<0.5\,\mu m$ fraction (Table 2), in which its content amounts to 87 wt. %. The calculated chemical formula of montmorillonite is: $\text{Ca}_{0.19}\text{Na}_{0.05}K_{0.04}$ (Al $_{1.38}\text{Fe}_{0.31}\text{Mg}_{0.30}$) [(Si $_{3.82}\text{Al}_{0.18}\text{)O}_{10}$] (OH) $_2\cdot n$ H₂O.

The montmorillonite in question differs from the typical montmorillonite from bentonites in a higher content of iron and aluminium in the octahedral and tetrahedral sheets, respectively. Its layer charge is some-

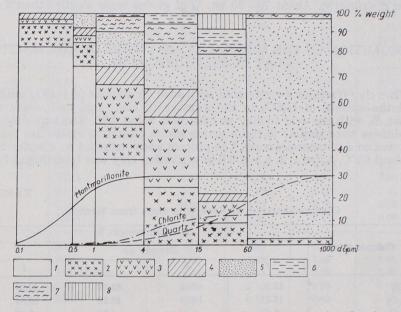


Fig. 1. The diagram of mineralogical composition of Krakowiec clay from deepness of 132 m above the sea level

1 — montmorillonite, 2 — illite, 3 — chlorite, 4 — kaolinite, 5 — quartz, 6 — dolomite,

7 — calcite, 8 — feldspar, d — substitutional diameter

what greater than that in the typical montmorillonite and is 0.47 unit charge per half unit cell, as much as 40% of the charge falling on the tetrahedral sheet.

Chlorite occurring in the clay studied is trioctahedral. As appears from X-ray analyses, it differs from the typical chlorites in a higher content of Al and Fe and a lower content of Mg.

The investigations presented in this paper were carried out on clay derived from a level of 132 m above sea level from the sulphur mine in Machów, as well as on $<4\,\mu m$ fraction separated from clays representing the bottom (sample 1), middle (sample 2) and top (sample 4) beds, rich in clay minerals. To obtain comparative data, analyses were also made on the fraction 4—40 μm (sample 3), which is characterized by a higher content of chlorite and carbonates, particularly dolomite. The following notation was used:

sample 1 — fraction $< 4 \,\mu m$ of clay from the bottom of the seam, sample 2 — fraction $< 4 \,\mu m$ of clay from the middle of the seam, sample 3 — fraction 4—40 μm of clay from the middle of the seam,

Table 3

sample 3 — fraction $4 - 40 \, \mu m$ of clay from the top of the seam.

The choice of material was determined by the fact that it makes up a fraction worth separating from the economic point of view. Moreover, it is relatively high in montmorillonite, being thus a good raw material for bleaching earths.

The clays used for analyses contained clay minerals of similar grainsize distribution. About 70—90 wt. % of grains were smaller than $2\,\mu m$.

DISSOLUTION OF THE MINERAL COMPONENTS OF THE MACHÓW CLAY IN SULPHURIC ACID

The clay fractions were treated with such an amount of $\rm H_2SO_4$ solution that the content of $\rm H_2SO_4$ in the mixture of clay, acid and water was 16 wt. %, with the acid to clay weight ratio being 0.96. The experimental conditions were similar to those under which bleaching earths are manufactures on a commercial scale. The process was conducted on a water bath at about 95°C. After 1, 3, 5 and 8 h of activation clay was centrifuged from

Chemical analyses of Krakowiec clays from Machów

	Content in weight %						
Components	Sample no						
	1	2	3	4			
SiO ₂	49.20	49.10	53.70	46.00			
Al_2O_3	15.81	16.24	12.53	16.34			
Fe ₂ O ₃	4.87	4.64	4.96	5.62			
TiO,	0.73	0.70	0.56	0.75			
CaO	8.30	9.44	9.40	9.53			
MgO	2.82	2.44	2.74	3.15			
Na ₂ O	0.69	0.69	1.15	0.66			
K ₂ O	3.67	3.59	3.28	3.65			
Loss on ignition	13.79	13.26	11.53	14.21			
Total	99.88	100.10	99.85	99.91			

the solution and the content of the characteristic chemical components determined. From the results presented in Tables 3, 4, 5 and in Figures 2a-e it follows that the dissolution of all the fraction studied proceeds at a similar rate, yet the individual chemical components of the clay go into solution in a different way. Calcium carbonate is dissolved at once, so that after 1 h the content of CaO in the solution is virtually constant. About 60% CaO present in the clay goes into solution whereas the rest remains as insoluble CaSO₄.

Aluminium and iron go readily into solution during the first hour,

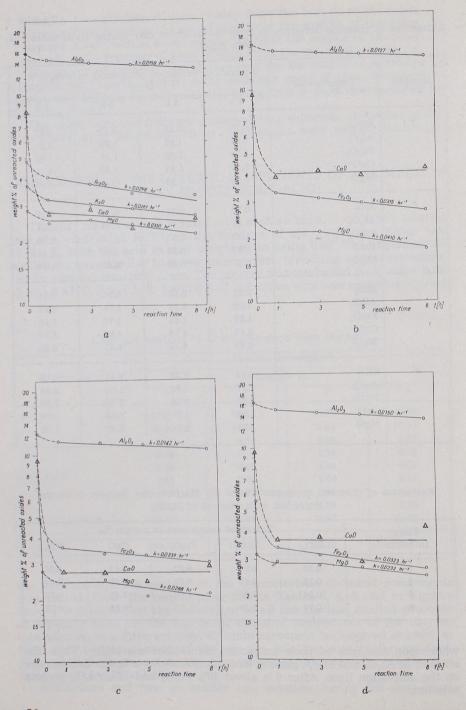
Extraction of chemical components from the Machów clay during static extraction with $\rm H_2SO_4$

Sample	Components	Amount of extracted component in weight % after				
		1 h	3 h	5 h	8 h	
1	SiO ₂	0.20	0.31	0.17	0.17	
	Al_2O_3	0.95	1.56	1.93	2.54	
	Fe ₂ O ₃	0.78	1.08	1.45	1.52	
	CaO	5.57	5.43	5.99	5.75	
	MgO	0.34	0.27	0.40	0.65	
2	SiO ₂	0.28	0.31	0.16	0.16	
	Al_2O_3	1.11	1.53	1.86	2.41	
	Fe ₂ O ₃	1.33	1.57	1.74	1.99	
	CaO	5.57	5.29	5.57	5.24	
	MgO	0.27	0.30	0.40	0.69	
3	SiO ₂	0.22	0.38	0.24	0.19	
	Al_2O_3	1.00	1.27	1.54	2.08	
	Fe ₂ O ₃	1.37	1.62	1.70	1.95	
	CaO	6.68	6.73	6.96	6.50	
	MgO	0.40	0.23	0.67	0.60	
4	SiO ₂	0.17	0.28	0.19	0.16	
	Al ₂ O ₃	1.17	1.62	1.99	2.68	
	Fe ₂ O ₃	2.20	2.49	2.70	2.90	
	CaO	5.85	5.75	6.59	5.24	
	MgO	0.24	0.34	0.40	0.64	

 $$\rm T\,a\,b\,l\,e\,\,5$$ Extraction of chemical components from the Machów clay (sample 1) during activation with renewal of $\rm H_2SO_4$

Time	Extracted component in weight %					
in hours	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	
1	0.18	0.92	0.62	3.02	0.56	
3	0.33	1.48	0.89	5.57	0.64	
5	0.54	1.92	1.06	6.45	0.73	
8	0.74	2.39	1.25	6.85	0 73	

whereupon the rate of their extraction diminishes markedly. Then the amount of Al_2O_3 and Fe_2O_3 passing into solution shows a linear dependence on the activation time. After 8 h, about 40% Fe_2O_3 and 16% Al_2O_3 go into solution.



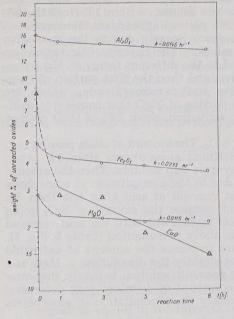


Fig. 2. Dissolution rate of selected fractions of Krakowiec clays from Machów, activated by H₂SO₄

a — sample 1, b — sample 2, c — sample 3, d — sample 4, e — sample 1 activated by H_2SO_4 in 8 h with reneval of acid after 1, 3, 5 and 8 h

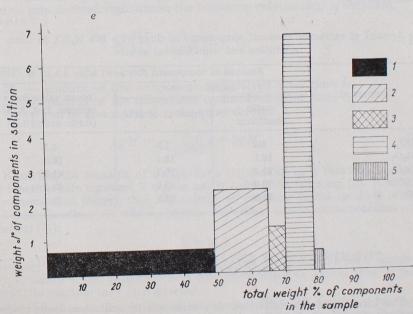


Fig. 3. Content of main chemical components of Krakowiec clay (sample 1) in solution after 8 h by H₂SO₄ activation with renewal after 1, 3, 5 and 8 h

 $1 - SiO_2$, $2 - Al_2O_3$ $3 - Fe_2O_3$, 4 - CaO, 5 - MgO

Extraction of magnesium proceeds in a very characteristic way. About 10% of MgO present in the clay goes into solution within 1 h from the beginning of activation. After that time a plateau appears on the dissolution curve, whereupon the curve slopes down linearly due to the successive portion of magnesium passing into solution. The characteristic regions on the clay dissolution curve correspond to the different forms of Mg occurrence. Dolomite is the first to dissolve, and then the first portion of magnesium goes into solution. Chlorite and montmorillonite, which are sparingly soluble, supply the second portion of MgO that passes into solution at a much slower rate. After 8 h activation, about 23% of MgO present

in the clay goes into solution.

Worth noting is the extraction of SiO₂. The amount of silica passing into solution increases systematically, attaining a maximum after 3 h, when about 0.6% of SiO₂ present in the clay goes into solution. Then the amount of extracted SiO₂ decreases rapidly due to the precipitation of amorphous silica gel. It has been presumed that renewal of acid after less than 3 h will stop the precipitation of gel and increase the amount of SiO₂ going into solution. Experimental extraction carried out with the acid renewed after 1, 3, 5 and 8 h has confirmed the above presumption (Table 5, Fig. 3). It has been found that this procedure increases the amount of extracted SiO₂ to 1.5 wt. %, as well as enhances slightly the dissolution of MgO and CaO. The amount of aluminium that goes into solution is nearly the same as during static extraction, while the amount of dissolved iron decreases. The renewal of acid eliminates definitely the precipitation of amorphous silica (Table 6).

 $$\rm T\,a\,b\,l\,e\,\,6$$ Amount of extracted chemical components of clays with 16% $\rm H_2SO_4$ in static conditions and with renewal of acid

	Amount of component dissolved after 8 h in %					
Component	sar	mean value for samples 1, 2, 3, 4 (static activation)				
Component	static conditions renewal of acid					
SiO ₂	0.4	1.5	0.5			
Al ₂ O ₃	16.1	15.1	16.0			
Fe ₂ O ₃	31.2	25.7	41.3			
CaO	70.0	82.5	63.0			
MgO	23.0	25.9	23.4			

THE KINETICS OF EXTRACTION OF THE CHEMICAL COMPONENTS OF CLAYS

The kinetics of dissolution of clay minerals in acids has been studied by several authors. Initially, the investigations aimed to determine the cations making up to the tetrahedral and octahedral sheets of the layers (Brindley, Youell 1951; Gastuche, Fripiat 1962). Later studies focussed on the mechanism of dissolution of montmorillonites (Osthaus 1954, 1956), palygorskite and sepiolite (Abdul-Latif, Weaver 1969) and chlorites (Ross 1967, 1968, 1969) in acids, as well as on the distribution of iron in the kaolinite layers (Petzold 1972, Horváth 1976).

The above-cited authors were concerned with the kinetics of dissolution of pure minerals in HCl. In this paper, on the other hand, the mechanism of dissolution of a polymineral montmorillonite clay (the Machów clay) was studied. Moreover, sulphuric acid was used as having wider application in the technology of clay activation.

If we assume that clay dissolution is a first-order, or pseudo-first-order, reaction, then the process can be described by the equation:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = kM \ [1]$$
or
$$\frac{\mathrm{d}(M_0 - x)}{\mathrm{d}t} = -kM \ [2],$$
hence
$$\frac{\mathrm{d}M}{\mathrm{d}t} = -kM \ [3]$$

where:

 M_0 — initial amount of the component,

M — amount of undissolved component after time,

t. x — amount of dissolved component.

Integrating eq. [3] in the interval between t_1 and t_2 and converting the natural into decimal logarithms, the following relationship is obtained:

$$\lg \frac{M_1}{M_2} = \frac{k}{2.303} (t_2 - t_1)$$
 [4]

where:

 M_1 — amount of the component undissolved after time t_1 , M_2 — amount of the component undissolved after time t_2 .

Eq. [4] can be also restated in the general form:

$$\lg M = -\frac{k}{2.303} t + \lg M_0$$
 [5]

Knowing the amount of undissolved component as a function of time, the reaction rate constant k can be easily calculated from eq. [5]. It should be remembered though that the calculated constant is the product of the acid concentration (A), which changes with time, and the true reaction rate constant (k_1) :

$$k = k_1 A$$

However, the kinetics of clay dissolution can be described with satisfactory accuracy if the sulphuric acid used is so much in excess that its loss due to the reaction may be neglected.

The kinetics of dissolution of the montmorillonite clay from Machów in $\rm H_2SO_4$ was studied by a method similar to that adopted by Osthaus (1954) and Abdul-Latif and Weaver (1969). Accordingly, plots were constructed in such a way that the weight % of undissolved metal oxide was plotted in logarithmic scale on the abscissa and the time of reaction be-

tween clay and sulphuric acid on the ordinate. The reaction rate constants were calculated from formula [5].

The solubility curves obtained for clay both under static conditions and when the acid was changed are very similar, consisting essentially of two parts: a steep region corresponding to rapid extraction of cations, and a straight line part, slightly inclined to the abscissa, reflecting slow extraction of Al, Fe and Mg. In the case of Mg, the curve has additionally a horizontal segment which indicates that extraction of that element is inhibited between the first and third hour of the process (Fig. 2a—d).

The steep part of the curve corresponds to the extraction of carbonates $CaCO_3$, $CaCO_3 \cdot MgCO_3$, free iron oxides and amorphous substance, which make the surface of clay minerals practically unavailable for acid. The straight line region of the plot corresponds to the removal of metal cations from the structure of clay minerals. The cations in question are extracted at different rates. Aluminium, which has the highest ionic potential of all the cations occupying the octahedral sheet and which forms in consequence the strongest bonds with oxygen, is extracted at the slowest rate. The larger cations Fe and Mg, which substitute for aluminium in the octahedral sheet, are weakly bonded (lower ionic potential) and, due to this, more readily removed from the structure of clay minerals.

In the interval between 1st and 8th hour of dissolution in H_2SO_4 the extraction rate constant can be determined for each cation from the inclination of that part of the curve (Table 7). It is evident from the results

 $$\operatorname{\mathtt{Table}}$$ 7 Extraction rate constants for clay minerals occurring in the Machow clay

	Extraction rate constants k (hr ⁻¹)					
Component	sample				sample 1 activated	
	1	2	3	4	with acid renewal after 1, 3, 5 and 8 h	
Al_2O_3	0.0158	0.0127	0.0142	0.0150	0.0146	
Fe ₂ O ₈	0.0296	0.0315	0.0239	0.0323	0.0223	
MgO*	0.0330	0.0410	0.0288	0.0232	0.0115	

^{*} Value calculated on the basis of 3 results (after 3, 5 and 8 h of extraction)

that the rate of extraction of magnesium during acid activation of the Machów clay is the most rapid, that of iron less so, and the rate of aluminium dissolution the slowest. This sequence corresponds to that observed by Abdul-Latif and Weaver (loc. cit.) in palygorskite, although these authors used HCl solution for activation.

The dissolution of a polymineral substance, i.e. the clay from Machów, in sulphuric acid is a complex process. X-ray analyses of the insoluble residue have revealed that, when the acid is not renewed during the process, it contains gypsum and hydrated magnesium sulphate. It appears that dissolution of the constituent minerals is accompanied by crystallization of sulphates. Upon their precipitation, the amount of cations of a given element in the solution is determined by the solubility of its sulphate. This statement is borne out by the dissolution curve obtained for Mg (Fig.

2a-d). After rapid dissolution of dolomite (steep region of the curve), crystallization of magnesium sulphate takes place and the magnesium concentration in the solution becomes stabilized (horizontal part of the curve). As the dissolution proceeds, clay minerals are decomposed and the constituent $\mathrm{Mg^{2+}}$ goes partly into solution. Simultaneously, the sulphuric acid is partly used up and, consequently, the concentration of $\mathrm{SO_4^{2-}}$ ions in the solution decreases, causing the already precipitated sulphates to pass into solution at such a rate that the product of $\mathrm{Mg^{2+}}$ and $\mathrm{SO_4^{2-}}$ concentrations remains the same. This process determines the inclination of the straight line region of the solubility curve. Similar considerations hold for $\mathrm{Ca^{2+}}$, the concentration of which is determined by the solubility of $\mathrm{CaSO_4 \cdot 2H_2O}$ in sulphuric acid solution.

Since the solubility of calcium sulphate is considerably less than that of magnesium and iron sulphates, a change in the concentration of sulphate ions affects insignificantly the concentration of ${\rm Ca^{2+}}$ in the solution, which remains virtually constant (Fig. 2a-d — horizontal part of the curve). When the acid is renewed during dissolution, calcium from ${\rm CaSO_4 \cdot 2H_2O}$ is extracted more slowly than magnesium and iron, precipitated at the beginning of activation as sulphates (Fig. 2e). Due to this, the renewal of acid after 1 h results in the extraction of nearly all iron and magnesium combined in the form of sulphates, whereas only a part of calcium is dissolved under those conditions. In the successive stages of dissolution with the renewal of acid, magnesium, iron and aluminium present in the layer silicates go into solution, and simultaneously the remaining calcium sulphate is still being extracted. This behaviour of calcium is reflected in the shape of its solubility curve, differing from those obtained for the other elements (Fig. 2e).

CHANGES IN THE STRUCTURE OF CLAY MINERALS DURING DISSOLUTION IN SULPHURIC ACID

Changes occurring in clay minerals as a result of dissolution in sulphuric acid were investigated using X-ray diffraction, thermal analysis and infrared absorption spectroscopy.

X-Ray Diffraction Analysis

The structural changes produced in clay minerals by sulphuric acid involve mainly the exchange of interlayer cations and selective dissolution of components of the octahedral and tetrahedral sheets. These changes are pronounced in X-ray diffraction patterns, 001 reflections being particularly sensitive to them. After 1 h activation, carbonates are dissolved and gypsum and hydrated magnesium sulphate precipitate at their cost, while the structure of illite or kaolinite is not affected by the acid. The 001 montmorillonite line becomes diffuse in the range of 17.5—10 Å, showing a faint maximum at 14.5 Å. Prolonged activation results in a gradual decrease in the intensity of the clay mineral reflections, and in the case of montmorillonite, a displacement of the peak towards 10 Å has been addi-

tionally recorded. All this becomes pronounced when the acid is renewed

at each stage of activation (Fig. 4f).

Diminished intensity of the clay mineral lines is due to partial breakdown of their structure, proceeding in the sequence: chlorite > montmorillonite > illite > kaolinite.

Thermal Analysis

Sample 1 as the most representative of the material studied and the richest in montmorillonite was selected for the analyses (Fig. 5).

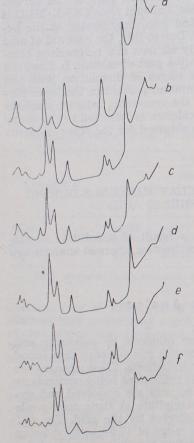
The DTA curve for sample 1 activated in sulphuric acid for 8 h is presented in Figure 6. It shows an endothermic peak at 120°C, corresponding

to dehydration and a weight loss of 4%, and an exothermic peak in the range 300-460°C, due to combustion of the organic substance attended by a weight loss which is difficult to determine. The dehydroxylation peak at 560°C is accompanied by a weight loss of 4%, and the endothermic peak at 900°C by a weight loss of 1.4%.

The activated clay shows a smaller weight loss at 120°C and a less pronounced endothermic peak. It has been found that acid activation does not affect the number of hydroxyl groups given off at 560°C but increases the amount of water released at about 900°C. This water appears presumably in the form of OH groups which act as active acid centres.

The clay activated by stages, with the acid renewed after 1, 3, 5 and 8 h, contains more interlayer water released both at 120°C (6 wt. %) and at higher temperatures (6.3 wt. % at 560°C and 1.4 wt. % at about 800°C). A DTA curve for the clay activated in this way is presented in Figure 7.

Acid-activated samples show a slight shift of the thermal peaks towards



26. 54. 55. 50. 18. 18. 14. 15. 10. 8. 6. 4.

42

Fig. 4. X-ray diffraction patterns of sample 1 a - raw, b - activated by H2SO4 for 1 h, c - activated by H2SO4 for 3 h, d - activated by H2SO4 for 5 h, e - activated by H2SO4 for 8 h, f - activated by H2SO4 for 8 h with renewal of acid after 1, 3, 5 and 8 h

lower temperatures, which is most likely due to a general deterioration in the degree of crystallinity of clay minerals.

Infrared Absorption Spectroscopy

The analyses were made in the UR-10 spectrophotometer, using KBr disks.

Infrared spectroscopic investigations have yielded some interesting data concerning the structural changes occurring in clay minerals dissolved in

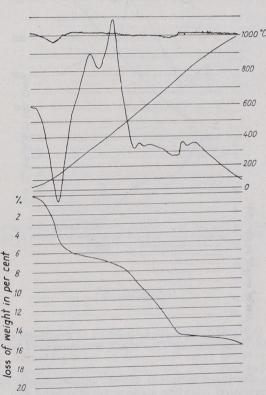


Fig. 5. Thermal curve of sample 1 of Krakowiec clay from Machów

sulphuric acid (Fig. 8). In the range of valence vibrations of hydroxyl groups, the band 3625 cm⁻¹, which arises due to the coincidence of bands produced by vibrations of OH groups in the crystal lattice of montmorillonite, illite and kaolinite, shows a systematic decrease in its intensity with the time of activation. Similar variability has been recorded for the band 920 cm⁻¹, corresponding to Al-OH deformation vibrations. The relative intensity of the band 525 cm⁻¹ produced by Al-O valence vibrations diminishes as well. These observations suggest that the ions are removed selectively from the octahedral lattice sites of montmorillonite and illite. The Si-O-Al oxygen bridges are disrupted, giving rise to SiOH groups which become strong acid centres of the Brönsted type (Fijał *et al.* 1975, 1976). Kaolinite is considerably less subject to transformation; its bands corresponding to vibrations of OH groups (3700 cm⁻¹) do not virtually change

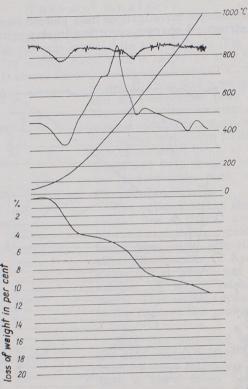


Fig. 6. Thermal curve of sample 1 of Krakowiec clay from Machów after $\rm H_2SO_4$ activation for 8 h

their intensity. During dissolution of calcium carbonate, sparingly soluble gypsum is precipitated, yielding a characteristic band 675 cm⁻¹.

A slightly different spectrum has been recorded for sample 1 subjected to dissolution with the change of the acid after 1, 3, 5 and 8 h (Fig. 9). During acid activation the structure of clay minerals undergroes profound degradation due to the extraction of a large number of cations from the octahedral sites. This process is reflected by the changes in both the intensity ratio of the bands corresponding to OH valence vibrations of kaolinite (3600—3700 cm⁻¹) and in the shape of the spectrum in the range 900—950 cm⁻¹. From the above observations it is evident that multi-stage acid activation results in a higher degree of degradation of the structure of clay minerals.

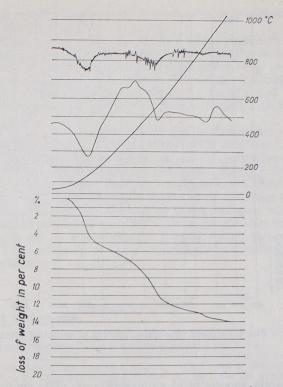


Fig. 7. Thermal curve of sample 1 of Krakowiec clay from Machów activated for 8 h with renewal of acid after 1, 3, 5 and 8 h

DISCUSSION

The present studies have revealed that acid activation of polymineral clays, represented by the Miocene clay from Machów, with sulphuric acid proceeds in the following way: In the initial stage (shorter than 1 h), carbonate minerals (calcite, dolomite, siderite), free iron oxides and presumably amorphous components of the allophane type are dissolved. Then the rate of extraction of the chemical components of clay is less rapid, and the cations from the structure of clay minerals go into solution.

In the first phase of dissolution calcium, magnesium and presumably also iron sulphates are precipitated. Their solubility determines the number of cations extracted by $\rm H_2SO_4$ from the structure of clay minerals during subsequent activation. After 3 h activation, amorphous silica is precipitated from the solution.

Precipitation of sulphates and silica can be prevented if the acid is renewed in the course of activation. Then, after a time longer than 1 h, the amount of components passing into solution is controlled by the solubility

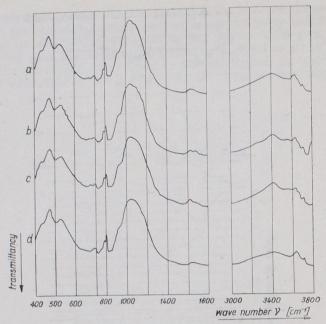


Fig. 8. Infrared absorption spectra of sample 1 after: a = 1 h, b = 3 h, c = 5 h, d = 8 h by activation H_2SO_4

of clay minerals, especially of montmorillonite. The amount of dissolved aluminium and magnesium increases as well.

The dissolution rate constants of cations of the crystal lattice of clay minerals show that magnesium is extracted most readily whereas iron and aluminium less so. This fact can be accounted for in the following way: The aluminium cation, having the highest ionic potential, forms the strongest bonds with oxygen and OH groups in the structure of montmorillonite; iron and magnesium cations, on the other hand, have a lower ionic poten-

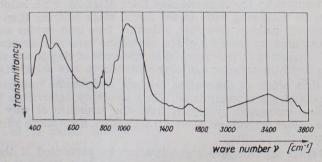


Fig. 9. Infrared absorption spectrum of sample 1 activated by ${\rm H_2SO_4}$ for 8 h with renewal of acid after 1, 3, 5 and 8 h

tial and, forming weaker bonds in the structure of clay minerals, are removed faster than aluminium.

Besides montmorillonite, the clay studied contains chlorite, illite and kaolinite as minor constituents. As appears from X-ray powder analyses, acid activation affects in the highest degree the structure of montmorillonite and chlorite, to a lesser extent that of illite, while kaolinite virtually fails to be transformed. Partial breakdown of the structure of clay minerals manifests itself in the diffusion of 001 lines recorded in their X-ray diffraction patterns.

Acid activation of clay minerals results in the diminished intensity of the absorption bands of OH groups in the range of 3625 cm⁻¹, as well as of Al-OH deformation vibrations and Al-O valence vibrations. This evidences that cations are removed from the octahedral sheet. Activation with the renewal of acid causes more profound degradation of the structure of clay minerals than activation conducted under static conditions.

Sulphuric acid increases the amount of water released when heating the activated clay at about 560 and 800°C. It is presumably the water of OH groups, which act as active centres formed under the influence of sulphuric acid. The formation of those centres gives bleaching properties to the activated clays.

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WŁASNOŚCI ODBARWIAJĄCE ILASTYCH SUROWCÓW NIEBENTONITOWYCH I ICH MODYFIKOWANIE

I. AKTYWACJA KWASOWA IŁÓW MIOCEŃSKICH Z MACHOWA

Streszczenie

Przeprowadzono badania nad aktywacją kwasową iłów mioceńskich z Machowa koło Tarnobrzega, które zawierają montmorillonit, illit, chloryt i niewielkie ilości kaolinitu, kwarc oraz węglany (kalcyt, dolomit, syderyt). Montmorillonit iłu z Machowa różni się od montmorillonitu z bentonitów większą zawartością Fe w warstwie oktaedrycznej i glinu w warstwie tetraedrycznej. Aktywację wykonano przy pomocy 16% roztworu kwasu siarkowego w temperaturze 96°C.

W pierwszym etapie aktywacji (krótszym od jednej godziny) rozpuszczeniu ulegają minerały węglanowe (kalcyt, dolomit, syderyt) oraz wolne tlenki żelaza, a także przypuszczalnie bezpostaciowe składniki typu alofanu. Dalej proces ekstrakcji składników chemicznych iłu przebiega z mniejszą szybkością, a do roztworu przechodzą kationy ze struktury minerałów ilastych.

W trakcie pierwszego etapu rozpuszczania następuje wytrącenie się siarczanów wapnia, magnezu, a przypuszczalnie i żelaza. Ich rozpuszczalność wpływa na ilość kationów ekstrahowanych ze struktury minerałów ilastych przez roztwór kwasu siarkowego w dalszej aktywacji.

Po trzygodzinnej aktywacji obserwuje się wytrącanie się bezpostaciowej krzemionki z roztworu.

Zjawisko wytrącania się siarczanów oraz krzemionki można wyeliminować stosując aktywację z wymianą kwasu siarkowego. Wówczas po czasie dłuższym od 1 godziny ilość składników przechodzących do roztworu determinowania jest rozpuszczaniem się minerałów ilastych, a głównie montmorillonitu. Zwiększa się też wówczas ilość rozpuszczonego glinu i magnezu.

Stałe szybkości rozpuszczania kationów z sieci przestrzennej minerałów ilastych wykazują, że najszybciej ekstrahowany jest magnez, wolniej żelazo i glin.

Tłumaczyć to można tym, że kation glinu mający największy potencjał jonowy tworzy najsilniejsze wiązania z tlenem i grupami OH w strukturze montmorillonitu, natomiast kationy żelaza i magnezu o mniejszym poten-

cjale jonowym jako słabiej związane w strukturze minerałów ilastych usuwane sa szybciej od glinu.

Jak wynika z badań rentgenograficznych w czasie aktywacji iłu najsilniej naruszona zostaje struktura montmorillonitu i chlorytu, w mniejszym stopniu illitu, a kaolinit praktycznie nie ulega zmianie.

W widmie absorpcyjnym w podczerwieni iłu aktywowanego następuje osłabienie intensywności pasm grup OH w zakresie 3625 cm⁻¹ oraz drgań deformacyjnych Al-OH i walencyjnych Al-O wskazujące na usuwanie kationów z warstw oktaedrycznych minerałów ilastych.

Aktýwacja z wymianą kwasu powoduje przy tym dalej idące naruszenie struktury minerałów ilastych w porównaniu z aktywacją w warunkach statycznych.

Działanie kwasu siarkowego wywołuje zwiększenie ilości wody oddawanej w czasie ogrzewania iłu aktywowanego w temperaturze około 560° oraz 800°C. Jest to przypuszczalnie woda grup OH spełniających rolę centrów aktywnych powstałych pod wpływem kwasu siarkowego. Ich postawanie nadaje aktywowanym iłom własności odbarwiające.

OBJAŚNIENIE FIGUR

- Fig. 1. Diagram składu mineralnego iłu krakowieckiego z głębokości 132 m n.p.m.

 1 montmorillonit, 2 illit, 3 chloryt, 4 kaolinit, 5 kwarc, 6 dolomit, 7 kalcyt, 8 skaleń, d średnica zastępcza
- Fig. 2. Postęp rozpuszczania wybranych frakcji iłów krakowieckich z Machowa, aktywowanych kwasem siarkowym a próbka 1, b próbka 2, c próbka 3, d próbka 4, e próbka 1 aktywowana kwasem siarkowym 8 h z wymianą kwasu po 1, 3, 5 i 8 h
- Fig. 3. Zawartość głównych składników chemicznych iłu krakowieckiego (próbka 1) w roztworze po 8 h aktywacji kwasem siarkowym z wymianą kwasu po 1, 3, 5 i 8 h $1 \mathrm{SiO}_2$, $2 \mathrm{Al}_2\mathrm{O}_3$, $3 \mathrm{Fe}_2\mathrm{O}_3$, $4 \mathrm{CaO}$, $5 \mathrm{MgO}$
- Fig. 4. Rentgenogramy próbki I a surowej, b aktywowanej kwasem siarkowym 1 h, c aktywowanej kwasem siarkowym 3 h, d aktywowanej kwasem siarkowym 5 h, e aktywowanej kwasem siarkowym 8 h, f aktywowanej kwasem siarkowym 8 h z wymianą kwasu po 1, 3, 5 i 8 h
- Fig. 5. Termogram próbki 1 ilu krakowieckiego z Machowa
- Fig. 6. Termogram próbki 1 iłu krakowieckiego z Machowa aktywowanego kwasem siarkowym 8 h
- Fig. 7. Termogram próbki I iłu krakowieckiego z Machowa aktywowanego 8 h z wymianą kwasu po 1, 3, 5 i 8 h
- Fig. 8. Widma absorpcyjne w podczerwieni próbki 1 po: a-1 h, b-3 h, c-5 h, d-8 h aktywacji kwasem siarkowym
- Fig. 9. Widmo absorpcyjne w podczerwieni próbki 1 aktywowanej kwasem siarkowym 8 h z wymianą kwasu po 1, 3, 5 i 8 h

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ОБЕСЦВЕЧИВАЮЩИЕ СВОЙСТВА ГЛИНИСТОГО НЕБЕНТОНИТНОГО СЫРЬЯ И ИХ ВИДОИЗМЕНЕНИЯ

І. КИСЛОТНАЯ АКТИВАЦИЯ МИОЦЕНОВЫХ ГЛИН ИЗ МАХОВА

Резюме

Проводились исследования кислотной активации миоценовых глин из Махова вблизи Тарнобжега, в состав которых входит монтмориллонит, иллит, хлорит и незначительное количество каолинита, кварца и бикарбонаты (кальцит, доломит, сидерит). Монтмориллонит в глинах из Махова отличается от монтмориллонита в бентонитах большим содержанием Fe в октаэдрических слоях и аллюминия в тетраэдрическом слое. Активация проводилась 16% раствором серной кислоты при температуре 96°C.

На первой этапе активации (которая короче 1 часа) растворяются бикарбонатные минералы (кальцит, доломит, сидерит) и свободные окислы железа, а также, вероятно, аморфные вещества типа аллофана. Дальнейший процесс экстракции химических компонентов глины протекает с меньшей скоростью, а в раствор переходят катионы из структуры глинистых минералов.

На первой этапе растворения происходит выпадание из раствора сульфатов кальция, магния и, вероятно, железа. Их растворимость влияет на количество катионов удаляемых из структуры глинистых минералов из-за воздействия серной кислоты в дальнейшей активации.

После трёхчасовой активации отмечается выпадание из раствора аморфоного кремнезёма.

Существует возможность исключить явление выпадания сульфатов и кремнезёма путём активации с обменом серной кислоты. Тогда после периода большего, чем 1 час, количество элементов переходящих в раствор определяется растворением глинистых минералов, главным образом монтмориллонита. Увеличивается тогда тоже количество растворов аллюминия и магния.

Постоянные окорости растворения катионов из пространственной решётки глинистых минералов показывают, что с найбольшей скоростью происходит удаление магния, медленнее железа и аллюминия.

Это объясняется тем, что катион аллюминия, обладающий найбольшим ионным потенциалом, дает в структуре самые сильные связи с кислородом и гидратными группами монтмориллонита, а катионы железа и магния с меньшим ионным потенциалом, слабее связанные в структуре глинистых минералов, подлежат более быстрому удалению.

По результатам рентгенографических исследований видно, что во время активации глин в самой большой степени нарушается структура монтмориллонита и хлорита, в меньшей степени иллита, а каолинит практически не изменяется.

В инфракрасном спектре поглощения активированной глины происходит ослабление интенсивности полосы гидроксильных групп в области

3625 см⁻¹, а также деформационных колебаний Al-OH и валентных Al-O показывающее, что происходит удаление катионов из октаэдрических слоёв в глинистых минералах.

Активация с обменом кислоты является за одно причиной больших нарушений структуры глинистых минералов по сравнении с активацией

в статических условиях.

Действие серной кислоты вызывает увеличение количества воды, которая уволяется во время подогрева активированной глины при температуре около 560°С и 800°С. Это, по всей вероятности, вода групп ОН, которые играют роль активных центров образованных воздействием серной кислоты. Их образование придаёт активированным глинам обесцвечивающие свойства.

ОБЪЯСНЕНИЯ К ФИГУРАМ

- Фиг. 1. Днаграмма минерального состава краковецких глин добытых из глубины 132 м выше уровнени моря
 - 1 монтмориллонит, 2 иллит, 3 хлорит, 4 каолинит, 5 кварц, 6 доломит,
 - 7 кальцит, 8 полевой шпат, d приведённый диаметр
- Фиг. 2. Степень растворения избранных фракций краковецких глин из Махова активированных серной кислотой a образец l, b образец l, e образец e0 образец e1 образец e3 образец e4 образец e8 час. e6 обменом кислоты после e1, e8 час.
- Фиг. 3. Количество главных химических компонентов краковецких глин (образец 1) в растворе после 8 часов активации серной кислотой с обменом кислоты после 1, 3, 5 и 8 час. $1-\mathrm{SiO}_2, 2-\mathrm{Al}_2\mathrm{O}_3, 3-\mathrm{Fe}_2\mathrm{O}_3, 4-\mathrm{CaO}, 5-\mathrm{MgO}$
- Фиг. 4. Рентгенограммы образца I a сырого, b активированного серной кислотой в течение 1 часа, e активированного серной кислотой в течение 3 час., d активированного серной кислотой в течение 5 час., e активированного серной кислотой в течение 8 час., f активированного серной кислотой в течение 8 час. e собменом кислоты после 1, 3, 5 и 8 час.
- Фиг. 5. Термограмма образца 1 краковецких глин из Махова.
- Фиг. 6. Термограмма образца 1 краковецких глин из Махова активированного серной кислотой в течение 8 часов
- Фиг. 7. Термограмма образца *I* краковецких глин из Махова активированного в течение 8 часов с обменом кислоты после 1, 3, 5 и 8 час.
- Фиг. 8. ИК-спектр поглощения образца 1 a после 1 часа, b после 3 часов, c после 5 часов, d после 8 часов активации серной кислотой
- Фиг. 9. ИК-спектр поглощения образца 1 активированного серной кислотой в течение 8 час., с обменом кислоты после $1,\ 3,\ 5$ и 8 часов