

Leszek STOCH*, Krzysztof BAHRANOWSKI*, Zdzisława GĄTARZ**

BLEACHING PROPERTIES OF NON-BENTONITIC CLAY MATERIALS AND THEIR MODIFICATION

II. BLEACHING ABILITY OF NATURAL AND ACTIVATED KRAKOWIEC CLAYS FROM MACHÓW

UKD 553.611.35:551.782.13(438 - 35 woj. tarnobrzekskie, Machów)

Abstract. Usability of the Miocene Krakowiec clays from the sulphur mine in Machów for the production of active earths bleaching liquid sulphur and oils has been examined. These clays contain montmorillonite of the beidellite-nontronite series and their surface properties are different from those of bentonites containing typical montmorillonite. However, they are useful for the production of active earths showing selective bleaching action depending on the method of activation used. The effects of various chemical and thermal activation methods on surface properties of clays have been examined.

INTRODUCTION

Bleaching ability of clays depends on the area of their surface, the amount and diameter of pores, as well as on specific properties of the surface. Particularly important are acidic properties of the surface connected with the occurrence of acid centres of Brönsted and Lewis types. Actually we know that the former are formed due to migration of H^+ resulting from deprotonation of H_3O^+ and NH_4^+ ions in interlayer spaces of montmorillonite at elevated temperatures. These properties are also characteristic of Si-OH and Al-OH groups located along crystal edges and other discontinuity margins of the lattice. These groups are also formed by disruption of Si-O-Al bonds under the action of acids. Their formation by acid activation has been examined by numerous authors (Fripiat, 1971; Fijał *et al.*, 1976; Brückman *et al.*, 1976).

Lewis acid centres are forming in the sites occupied by unsaturated Al^{3+} and Si^{4+} cations. They are represented eg. by disrupted Si-O-Al bonds resulted from migration of protons or occurring along edges and other discontinuity margins of crystal lattice. They are formed by appropriate thermal activation.

The surface area, porosity and acidic properties of bleaching earths depend on

* Academy of Mining and Metallurgy, Institute of Geology and Mineral Deposits, Cracow (Kraków al. Mickiewicza 30).

** COBR PS „Siarkopol” Machów.

their mineral composition and can be modified using various activation methods. At the present stage of knowledge of the activation mechanism of clays, we are not able to predict exactly the results obtained by each method and its proper choice is based on experimental studies.

This paper deals with the results of studies on the influence of different activation methods on the surface properties of the Krakowiec clays from Machów and their bleaching ability with regard to liquid sulphur and rape and mineral P-3 oils. These substances are dark brown in colour due to hydrocarbons admixtures which can be removed by active earths and so decolourized. It is also supposed that active centres at the surface of clay minerals cause depolymerization of μ -sulphur. Its presence is responsible for colouration of sulphur exploited in Machów mine near Tarnobrzeg (Gařarz, 1976).

Clays from Machów consist of montmorillonite of the beidellite-nontronite type, illite and chlorite with some calcite and quartz admixture. Mineral composition of these clays as well as the mechanism and kinetics of their activation using sulphuric acid have been discussed in previous paper (Stoch *et al.*, 1977). For comparison, surface properties of typical bleaching earth Tonsil Standard (BRD product) as well as those of bentonite from Milowice (Upper Silesia) have been examined.

Determinations of specific surface area, porosity, acidity of the surface and of the heat of wetting have been carried out in the Institute of Catalysis and Physical Chemistry of the Surface of the Polish Academy of Sciences in Cracow.

METHOD OF STUDY SURFACE PROPERTIES OF CLAYS

Determination of specific surface area and porosity

Estimation of specific porosity and determination of the curves of pore distribution were performed using absorption method by applying spectrally pure argon as adsorbate. Semi-automatic volumetric apparatus has been used. The samples were preliminarily degased at 150°C for 10 hours to get the pressure as low as 10^{-4} Tr. Adsorption took place under isobaric conditions. Determination of adsorption and desorption of argon has been carried out at 77.5°K in the relative pressure range 0 – 1. Specific surface area values have been computed using BET iso-

Table 1
Specific surface estimated by BET method and heat of hydration and total acidity of clays

Sample	Specific surface area, mg ² /g	Heat of hydration cal/g	Total acidity mmol n-BA/g
Natural clay Machów 132	41.8	4.31 ± 0.05	0.50
Clay Machów 132 activated 3 hrs 16% H ₂ SO ₄	61.2	3.35 ± 0.05	0.70
Bentonite Milowice activated 3 hrs 16% H ₂ SO ₄	113.8	3.65 ± 0.05	1.00
Tonsil Standard	190.0	4.03 ± 0.05	0.90
Clay Machów < 4 μm M-1 activated 3 hrs 16% H ₂ SO ₄	74.8	6.62 ± 0.05	0.30
Clay Machów < 4 μm M-1 activated 8 hrs 16% H ₂ SO ₄	76.8	9.48 ± 0.05	0.30

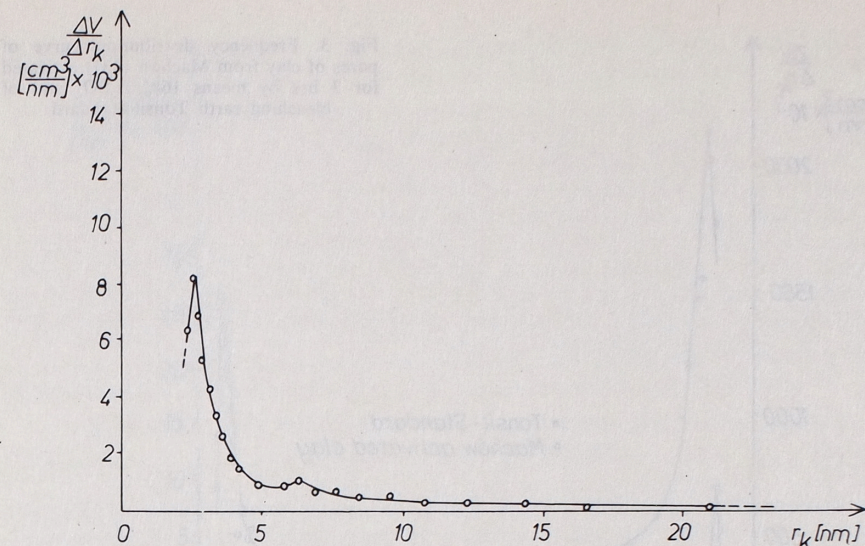


Fig. 1. Frequency distribution curve of pores of clay from Machów (M-1) activated for 3 hrs by means of 16% H₂SO₄

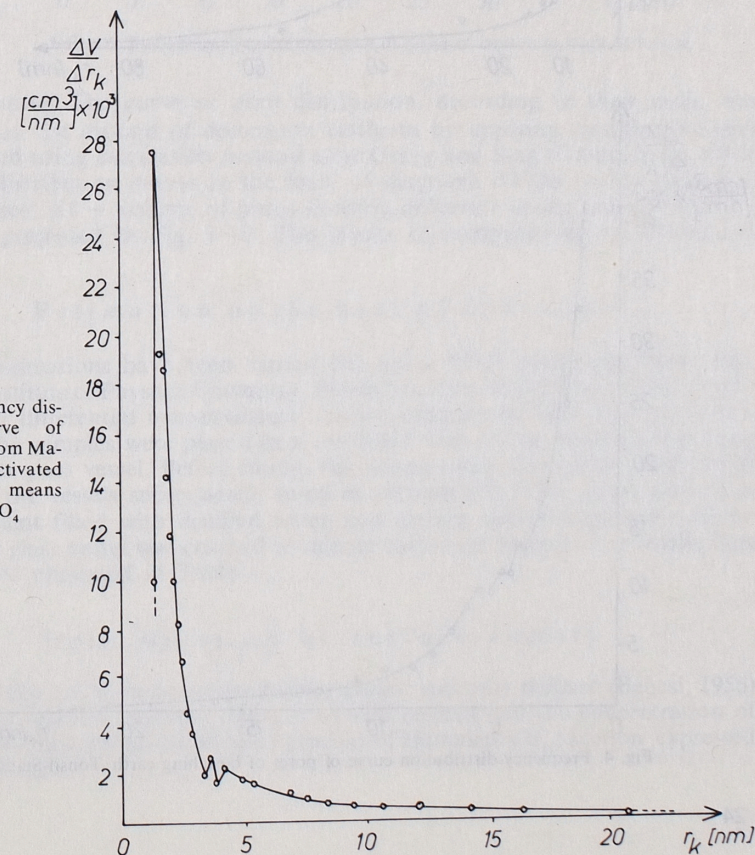


Fig. 2. Frequency distribution curve of pores of clay from Machów (M-1) activated for 8 hrs by means of 16% H₂SO₄

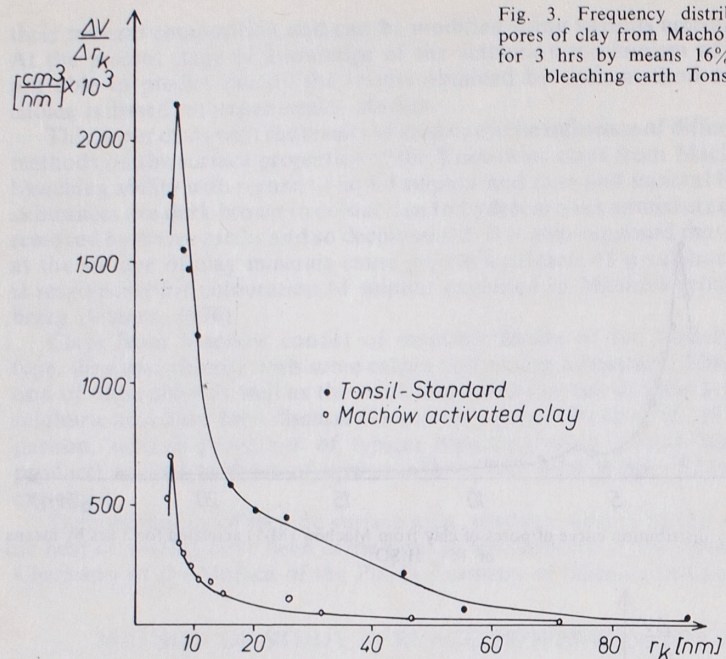


Fig. 3. Frequency distribution curve of pores of clay from Machów (132) activated for 3 hrs by means 16% H_2SO_4 and of bleaching earth Tonsil-Standard

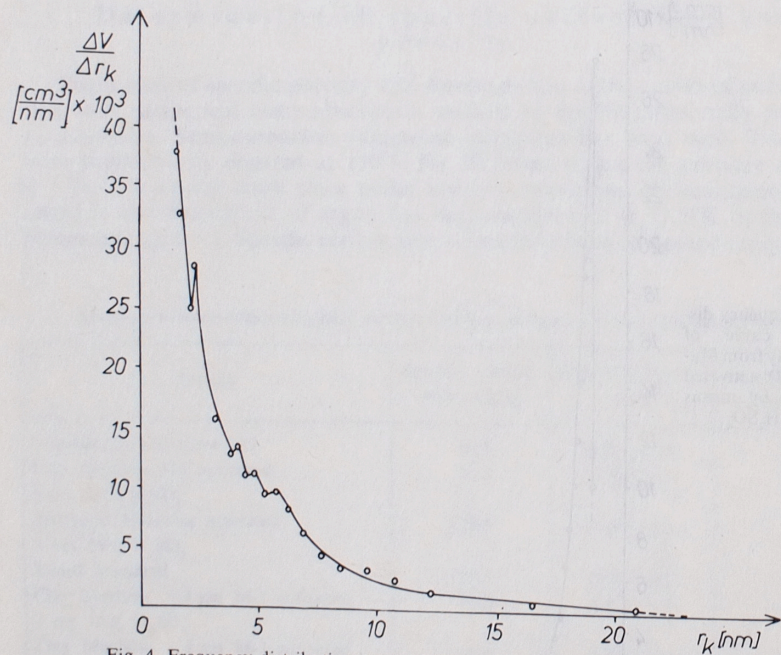


Fig. 4. Frequency distribution curve of pores of bleaching earth Tonsil-Standard

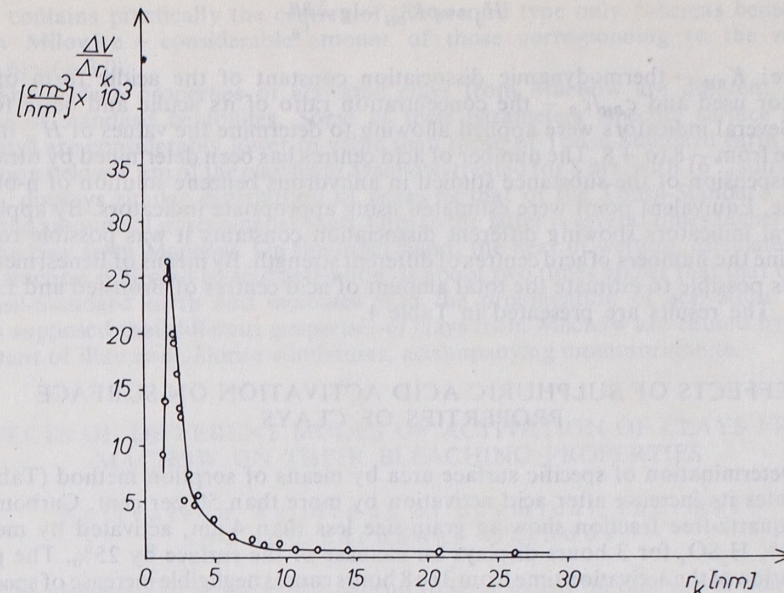


Fig. 5. Frequency distribution curve of pores of bentonite from Milowice

therm equation. The curve of pore distribution, according to their radii, was estimated on the ground of desorption isotherm by applying modified Kelvin's equation and using calculation method after Gregg and Sing (Gregg, Sing, 1967). The pore distribution curves in the form of diagrams $\Delta V/\Delta r = f/r$ (where r - radii of pores, ΔV - volume of pores showing definite r in the range $r + \Delta r$, $r - \Delta r$) are presented in Fig. 1-5. The results of computations are detailed in Table 1.

Estimation of the heat of hydration

These estimations have been carried out using BMR microcalorimeter, produced by Institute of Physical Chemistry, Polish Academy of Sciences in Warsaw and adapted for differential measurements. All the estimations have been performed at 22°C. The samples were placed in a cell filled with 15 c.c. distilled water and fused within glass vessel. Before fusing, the samples were heated for 10 hours at 120°C and the vessels subsequently fused at vacuum (10^{-4} Tr). After placing in the instrument filled with distilled water and getting stable temperature of the system, the glass vessel was crushed to initiate hydration process. The results thus obtained are presented in Table 1.

Determination of surface acidity

The acidity has been determined using Benesi indicator method (Benesi, 1956) allowing to estimate both the strength of acid centres and the concentration of them. The former can be determined by means of Hammett's H_0 function expressed by the formula:

$$H_0 = pK_{BH} - \lg \frac{c_{BH}}{c_B}$$

where: K_{BH} – thermodynamic dissociation constant of the acidic form of indicator used and c_{BH}/c_B – the concentration ratio of its acidic and basic form.

Several indicators were applied allowing to determine the values of H_0 in the range from -8 to $+8$. The number of acid centres has been determined by titration of suspension of the substance studied in anhydrous benzene solution of *n*-butylamine. Equivalent point were estimated using appropriate indicators. By applying several indicators showing different dissociation constants it was possible to determine the numbers of acid centres of different strength. By means of Benesi method it was possible to estimate the total amount of acid centres of Brönsted and Lewis type. The results are presented in Table 1.

EFFECTS OF SULPHURIC ACID ACTIVATION ON SURFACE PROPERTIES OF CLAYS

Determination of specific surface area by means of sorption method (Tab. 1) indicates its increase after acid activation by more than 50 per cent. Carbonate- and quartz-free fraction showing grain-size less than $4 \mu\text{m}$, activated by means of 16% H_2SO_4 for 3 hours displays an increase of the surface by 25%. The prolongation of the activation time from 3 to 8 hours causes negligible increase of specific surface area of this fraction – from 74.8 to $76.8 \text{ m}^2/\text{g}$. These values are much lower than those of Tonsil Standard bleaching earth which amounts to $190 \text{ m}^2/\text{g}$, whilst that of bentonite activated by 16% H_2SO_4 for 3 hours – to $114 \text{ m}^2/\text{g}$.

Interesting data result from the frequency distributions of pores examined by means of sorption method (Fig. 1–5). The curve for Tonsil Standard earth (Fig. 4) indicates this absorbent to have pores of very variable dimensions. Though smaller than 2 nm predominate, those larger, from 3 to 10 nm in size, are also abundant. When comparing with Tonsil Standard Earth, the activated clay from Machów (sample 132) displays considerably lower porosity, whereby the range of pore sizes is small (Fig. 3).

An increase of activation time of below $4 \mu\text{m}$ clay fraction to 8 hours causes a change of the frequency distribution curve of pores (Fig. 2). When compared with the sample activated for 3 hours, the amount of small pores (2 nm) increases more than three times, whilst that of larger ones (3 – 10 nm) – approximately 2 times (Fig. 1). The number of pores ca. 2 nm in size approaches that shown by Tonsil Standard earth. Bentonite from Milowice (Fig. 5) displays similar frequency distribution of pore sizes as the fraction below $4 \mu\text{m}$ of the clay from Machów, activated for 8 hours by means of sulphuric acid.

The heat of hydration (Tab. 1) is the measure of wettability of clays by water, as well as of their hydrophylic properties. Both natural and activated clays from Machów and their finer fractions treated for 3 and 8 hours, show high heat of wetting, whereas that of the latter fractions exceed this heat of the Tonsil Standard bleaching earth.

The acidity of clays from Machów depends on the mode of chemical treatment (Tab. 1). The activated clay (sample 132) displays acidity very close to that of Tonsil-Standard earth but different distribution of acid centres. Tonsil-Standard earth is characterized by high amount of centres showing acidity from -3 to $+1.5$ and from $+3.3$ to $+4.8$. On the other hand, the activated clay sample 132 contains low amount of centres of the first type and high – of the second one. Natural

clay contains practically the centres of the second type only, whereas bentonite from Milowice – considerable amount of those corresponding to the range (-5.6) – (-3.0) .

The surface properties of activated clays from Machów are different from those of standard bentonites. Some of their parameters (specific surface area, acidity) are considerably lower in value than those of Tonsil-Standard earth. The fraction below $4 \mu\text{m}$ of the clay from Machów, treated for 8 hrs. with 16% sulphuric acid, displays similar distribution of pores as that of the Tonsil-Standard earth but the amount of pores smaller than 2 nm in the latter is several times higher than in the clay from Machów. On the other hand, the heat of wetting, calculated for this fraction subjected to acid activation, is about two times higher than that of the Tonsil-Standard earth and increases with the prolongation of activation time. It is supposed that different properties of clays from Machów are caused by high content of illite and chlorite admixtures, accompanying montmorillonite.

EFFECTS OF DIFFERENT MODES OF ACTIVATION OF CLAYS FROM MACHÓW ON THEIR BLEACHING PROPERTIES

Activation by means of chemical, thermal and ion exchange methods

The properties of active earths depend to large extent on the type of exchange cations (Popiel, Żyła, 1976). Clays of Machów, activated using sulphuric acid, contain Ca^{2+} as exchangeable cations. This is indicated e.g. by X-ray study, since activation results in the formation of fine-grained Ca sulphate (gypsum) which, being relatively easily soluble in water, causes excess of Ca^{2+} cations in clay suspension. Consequently, just these cations occupy interlayer positions in montmorillonite.

Sodium, ammonium and chromium were chosen as cations substituting calcium. The first two univalent ions are able to disperse and to disintegrate clay aggregates into single flakes, causing distinct increase of specific surface. Chromium is a coagulative agent. Its ability to change easily the valency is of essential importance in some catalytic processes.

Ion exchange procedure was carried out by treating clay samples with 1 N solutions of sodium, ammonium and chromium chlorides on water bath at ca. 95°C and successive repeated washings with the same solution. The excess of salts was removed until no eluting Cl ions were detected. In this study natural clay samples (132) were used as well as its – $4 \mu\text{m}$ fraction, preliminarily activated with 16% H_2SO_4 for 3 hrs.

Another mode of activation used consisted in heating natural (132) samples at 300°C to remove hygroscopic water and the substances blocking the active centres. Heating at higher temperatures (500 – 600°C) increases porosity and specific surface. Thermally activated samples were successively treated for 3 hrs. with 16% sulphuric acid solution. It was attempted to correlate these studies with those on ability to bind organic molecules (methylene blue) by clay surface.

The values of specific surface areas, computed using Hang and Brindley's method, are the measure of their sorptive properties relative to methylene blue. The effects of thermal activation of the natural sample (132) at 200 , 300 , 350 and 500°C for 2 hrs. are presented in Table 2. As follows from these data, heating at 500°C distinctly increases the ability of bleaching of liquid sulphur but not of oils. It is supposed that these two processes are connected with different active centres and mechanisms.

Heating at 500°C causes complete removal of sorbed water from clay minerals

Table 2
Bleaching of sulphur and oils by thermally activated clay from Machów

Temperature °C	Degree of bleaching in %		
	sulphur	P-3 oil	rape oil
200	79	22	16
300	77	20	13
350	80	22	16
500	93.2	20	16

Table 3
Bleaching of sulphur and oils by clay from Machów saturated with: Na⁺, NH₄⁺, Cr³⁺

Sample	Degree of bleaching in %		
	sulphur	P-4 oil	rape oil
Na ⁺ - satur. clay	66.7	42	12
NH ₄ ⁺ - satur. clay	64.3	46	14
Cr ³⁺ - sat. clay	58.4	34	12

and their partial dehydroxylation. Organic matter and sulphides present are also removed at this temperature. The exchange of Ca²⁺ ions by Na⁺, NH₄⁺ or Cr³⁺ caused no distinct increase of bleaching ability of sulphur and oils by this clay (Tab. 3).

The aim of another series of experiments was to determine the influence of complex activation methods on bleaching ability of oils by clays. The < 4 μm fraction of the Machów clay was activated by means of: 1) chemical, 2) combined chemical and thermal, and 3) repeated chemical treatments. The results are presented

Table 4
Bleaching properties of the < 4 μm fraction differently activated clay from Machów (sample M-1)

Activation method	Rape oil		P-3 oil	
	consumption of earth in %	bleaching degree in %	consumption of earth in %	bleaching degree in %
16% H ₂ SO ₄ for 3 hrs	1.0	43.7	4.0	64.3
16% H ₂ SO ₄ for 3 hrs and thermal at 300°C for 1 hrs	1.0	36.2	4.0	71.4
16% H ₂ SO ₄ for 3 hrs and thermal at 600°C for 1 hrs	1.0	27.9	4.0	71.4
thermal at 300°C for 1 hrs and 16% H ₂ SO ₄ for 3 hrs	1.0	51.1	4.0	72.2
thermal at 600°C for 1 hrs and 16% H ₂ SO ₄ for 3 hrs	1.0	32.8	4.0	72.2
16% H ₂ SO ₄ for 3 hrs and ion exchange for:				
Na ⁺	1.5	34.7	4.0	72.2
NH ₄ ⁺	1.5	42.9	4.0	77.8
Cr ³⁺	1.0	21.9	4.0	77.8
Cr ³⁺	1.5	27.4	4.0	72.2
Cr ³⁺	1.0	32.8	4.0	61.1
Cr ³⁺	1.5	45.6	4.0	61.1
16% H ₂ SO ₄ for 8 hrs with acid change after 1, 2, 2, 3 hrs	1.0	73.0	4.0	61.1
	1.5	87.6		

Table 5
Specific surface determined by Hang and Brindley's method (1970)

Sample	Specific surface area m ² /g
M-1 < 4 μm Na ⁺ - saturated	169.3
M-1 < 4 μm NH ₄ ⁺ - saturated	156.0
M-1 < 4 μm Cr ³⁺ - saturated	62.4
Tonsil Standard	163.8

in Table 4. As follows from these data, combined chemical and thermal activation results in a decrease of ability of the clay in question to bleach rape oil but increases that of bleaching P-3 oil when compared with the sample activated with sulphuric acid only. Heating at 600°C does not cause any change of bleaching properties relative to the sample subjected to thermal activation at 300°C. However, if the sample was preliminarily heated and afterwards treated with sulphuric acid, bleaching properties relative to both oils are improved, whereby the tendency to act selectively on different oils does not change. The best properties are obtained after heating the sample for 1 hour at 300°C and subsequent activation with 16% H₂SO₄ for 3 hours.

Introduction of exchange cations after chemical activation of clay results in an increase of bleaching ability relative to mineral oils (P-3) whilst that of monovalent NH₄⁺ and Na⁺ - improves bleaching properties in general. Contrarily to other

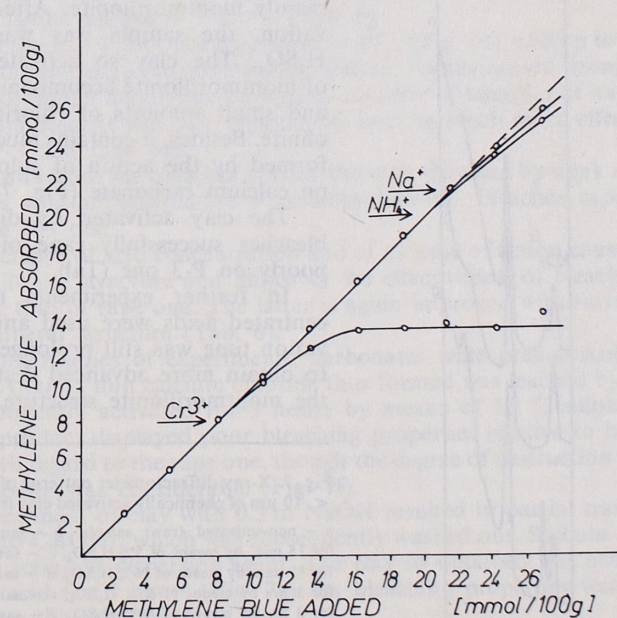


Fig. 6. Relation between adsorbed and added amounts of methylene blue for the fraction < 4 μm of the Machów clay (M-1) saturated with Na⁺, NH₄⁺, Cr³⁺

methods, chemical activation, consisting in repeated change of acid, causes very distinct increase of bleaching properties relative to rape oil. This confirms earlier observations on different bleaching mechanism of liquid sulphur and oils and on another type of active centres or diverse distribution of pores defining bleaching of rape oil and mineral P-3 one respectively.

Determination of specific surface area using sorption of methylene blue by chemically activated samples, subsequently altered into mono-ionic forms (Na^+ , NH_4^+ , Cr^{3+} - Tab. 5, Fig. 6) indicated positive correlation between the value of this surface and bleaching ability of mineral oil. Clay containing montmorillonite with Na^+ or NH_4^+ in exchangeable positions displays higher specific surface than that with Cr^{3+} in interlayer spaces and thus shows better bleaching ability of mineral oils (P-3).

Chemical activation of clays using various acids and sodium hydroxide solutions

The experiments have been carried out with fractions finer than $10 \mu\text{m}$ which are easy to obtain under industrial conditions, being separated from the bottom and middle part of the overburden of sulphur deposit (cross-section II) which were found to be the richest in clay minerals (Fig. 7a).

The first mode of activation consisted in the action of weak (5%) sulphuric acid for a possibly short period of time (15 min) as to dissolve carbonate minerals (calcite, dolomite) but not to change the structure of clay minerals, mainly montmorillonite. After this activation, the sample was washed from H_2SO_4 . The clay so activated consists of montmorillonite accompanied by illite and small amounts of chlorite and kaolinite. Besides, it contains much gypsum, formed by the action of sulphuric acid on calcium carbonate (Fig. 7b).

The clay activated by diluted acid bleaches successfully rape oil but acts poorly on P-3 one (Tab. 6).

In further experiments more concentrated acids were used and the activation time was still prolonged in order to obtain more advanced destruction of the montmorillonite structure.

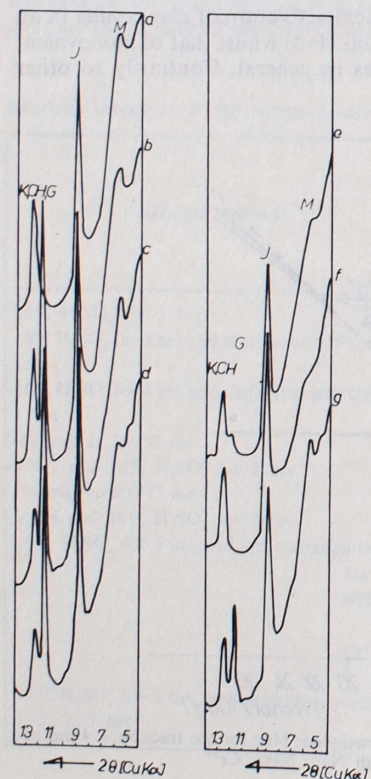


Fig. 7. X-ray diffractometer patterns of the fraction $< 10 \mu\text{m}$ of chemically activated clay from Machów
a - non-activated (raw) sample, *b* - sample activated for 15 min. by means of 5% H_2SO_4 , *c* - sample activated for 15 min. by means of 16% H_2SO_4 , *d* - sample activated for 3 hrs by means of 30% H_2SO_4 , *e* - sample activated for 3 hrs by means of 50% H_2SO_4 , *f* - sample activated for 15 min. by means 5% HCl and for 3 hrs by means 16% H_2SO_4 , *g* - sample activated for 0.5 hrs by means 0.5 n NaOH and for 3 hrs by means 16% H_2SO_4 .

Table 6

Bleaching properties and mineral composition of the $< 10 \mu\text{m}$ fraction of clay from Machów obtained by different activation methods

Activation method	Degree of bleaching of oil		Mineral composition
	rape oil	P-3 oil	
5% H_2SO_4 for 15 min.	76.0	36.4	montmorillonite, illite, very abundant gypsum
16% H_2SO_4 for 15 min.	64.0	45.5	montmorillonite, illite, very abundant gypsum
30% H_2SO_4 for 3 hrs	72.0	56.9	defected montmorillonite, illite, gypsum
50% H_2SO_4 for 3 hrs	76.0	59.0	strongly, defected montmorillonite, illite
5% HCl for 15 min.	32.0	43.0	defected montmorillonite, illite
and 16% H_2SO_4 for 3 hrs 0.5 NaOH for 15 min. and 16% H_2SO_4 for 3 hrs	56.0	50.0	montmorillonite, illite, a little gypsum

Activation by means of 16% sulphuric acid for 15 min resulted in partial destruction of this structure, manifested by some decrease of intensity of its X-ray reflections (Fig. 7c). The content of gypsum was also found to be lower than before. The clay thus obtained displayed worse bleaching properties relative to rape oil but much better relative to P-3 one (Tab. 6).

The increase of H_2SO_4 concentration to 30% (Fig. 7d), and up to 50% (Fig. 7e), as well as the prolongation of activation time to 3 hours caused stronger destruction of montmorillonite manifested by further decrease of intensity of its 001 reflection. The gypsum content was also diminished, causing much more effective bleaching of both P-3 and rape oils.

As follows from the obtained results, the clay activated by weak acid, dissolving carbonates without destruction of montmorillonite, bleaches rape oil but only poorly the P-3 one.

The increase of acid concentration and of its time of action causes alteration of montmorillonite structure and improves the effectiveness of bleaching of P-3 oil, decreasing that of rape one. The latter is again improved with further destruction of clay mineral structure (Tab. 6).

In another series of experiments, carbonates were preliminarily removed by 5% HCl. After 15 min calcium chloride thus formed was leached by water and the clay subsequently activated for 3 hours by means of 16% sulphuric acid. The obtained product displayed poor bleaching properties relative to both oils, particularly with regard to the rape one, though the degree of destruction of montmorillonite structure was considerable (Fig. 7f).

The treatment of clay with 0.5 n NaOH resulted in partial transformation of CaCO_3 into Ca(OH)_2 which was subsequently washed out. Sodium carbonate thus formed is acting as dispersing agent. The clay so obtained was activated by 16% sulphuric acid for 3 hours (Fig. 7g). Its bleaching properties were much better than before this treatment.

The action of HCl solution caused, most probably, an aggregation of clay grains. This process could not proceed during hydroxide treatment which caused

Table 7

Specific surface and volume of pores of the $< 10 \mu\text{m}$ fraction of clay from Machów (estimated by means of BET method) activated using different methods

Activation method	Specific surface area m^2/g	Volume of pores $\text{N cm}^3(\text{Ar})/\text{g}$
5% H_2SO_4 for 15 min.	139.0	38
30% H_2SO_4 for 3 hrs	261.4	55
5% HCl for 15 min. and 16% H_2SO_4 for 3 hrs	231.2	66
0.5 N NaOH for 15 min. and 16% H_2SO_4 for 3 hrs	206.0	64

dissolution of amorphous component of clays. Sodium carbonates thus formed exerted dispersing action on clay particles, increasing specific surface area and facilitating acid activation and structural destruction.

As follows from these experiments, the bleaching ability of P-3 oil increases with progressing destruction of montmorillonite, reaching maximal value of 59%. On the other hand, rape oil is effectively bleached (by 76%) using not destructed montmorillonite clay after removal of carbonates. The latter process is probably conditioned by interlayer spaces of montmorillonite or by the presence of porous clay aggregates cemented by gypsum.

Destruction of montmorillonite causes a decrease of bleaching properties with regard to this oil which are improved after the action of concentrated acid causing strong alteration of its structure.

The results of measurements of specific surface area and porosity of selected activated clays, using spectrally pure argon as adsorbate, are presented in Tab. 7. As follows from these data, the clay activated with 5% H_2SO_4 for 15 min shows relatively small specific surface area ($138 \text{ m}^2 \text{ per g}$). After treatment with 30% or 16% acid (following preliminary activation with HCl or NaOH to remove carbonates) higher specific surfaces (up to $206 - 261 \text{ m}^2 \text{ per g}$) were obtained. This increase is accompanied by that of total volume of pores.

No distinct correlation between specific surface area and bleaching ability of active earths relative to rape oil is observed. Clays showing specific surfaces area in the range $206 - 261 \text{ m}^2/\text{g}$ display bleaching ability 32 to 72%, whilst those slightly activated of specific surface area $139 \text{ m}^2/\text{g} - 76\%$. Better pronounced interrelation of these features is observed in the case of P-3 mineral oil.

Effect of aqueous extraction on mineral composition and bleaching properties of active earths from Machów

Calcite and dolomite contained in clays are dissolved during activation using sulphuric acid. The resulting Ca and Mg sulphates may influence the bleaching properties of clays but are easily removed by prolonged aqueous leaching, causing positive change in sorptive properties.

The experiments were carried out with a mixture consisting of 1 part of Krakowiec clay from Machów (fraction below $10 \mu\text{m}$) and 1 part of bentonite from Milowice (the same fraction). This mixture was activated for 5 hours with 16% sulphuric acid which was consumed in 25% relative to the mass of the pulp. Activation and bleaching tests of oils have been carried out in OBR PS "Siarkopol" in Machów.

After activation, the samples were washed with water at ca. 60°C . Each decantation was followed by sampling the pulp. The samples were dried and disintegrated,

sieved through the 0.064 mesh sieve and its bleaching ability regarding to rape and P-3 oils was examined. Washing distinctly influenced the bleaching ability in question. The increase of bleaching degree with washing is presented in Tab. 8.

X-ray diffractometric studies using DRON-1 apparatus have been carried out to determine the differences in mineral composition of clay caused by water extraction. It was found that the sample washed only once contains considerable amounts of calcium sulphates – mainly gypsum and some anhydrite. Besides, tetra-, hexa- and hepta-hydrated magnesium sulphates have been identified. Montmorillonite $d = 15.0$ basal reflection is poorly visible and hardly identifiable narrow 13.2 line appears. Successive decantations resulted in a decrease of sulphates contents and after fourth leaching they disappeared nearly completely. This process is accompanied by distinct decrease of bleaching properties relative to rape oil and simultaneous increase of that of mineral P-3 one.

After disappearance of sulphates we observe distinct changes in the shape and intensity of montmorillonite 001 (15.4) reflection. It is hardly visible till the third washing and after removal of sulphates – distinctly increases in intensity. This phenomenon can be explained by coagulation of montmorillonite in the presence of sulphates. The resulted flocculae consist of differently oriented flakes cemented with aggregated gypsum grains. Microporosity of these aggregates results not only from interlayer spaces but also from intergranular pores of larger sizes. These pores can also participate in sorption. Initially, washing causes dissolving of some sulphate particles increasing the accessibility of the interiors of aggregates and of interlayer montmorillonite spaces. Initial increase of bleaching ability of clays relative to rape oil can be attributed just to this process.

Simultaneous crystallization of fine-grained calcium and magnesium sulphates on the surface of clay minerals (mainly montmorillonite) can block some active centres, particularly these responsible for the sorption of substances colouring the P-3 oil. Removal of sulphates makes these centres accessible to dye particles. Gradual increase of bleaching ability of the clay in question in regard to mineral oil P-3 with progressing washing is explained by this process (Tab. 8).

The increase of intensity of 001 montmorillonite line indicates that progressing removal of sulphates causes disaggregation of clay mineral flakes which tend to

Table 8

Effect of water washing on bleaching properties of clays from Machów activated using 16% H_2SO_4 for 5 hrs

No of subsequent decantation	pH of aqueous extract of dry earth	Acidity recalculated into H_2SO_4 in %	Degree of bleaching in %	
			rape oil	P-3 oil
1	—	—	74.2	21.4
2	1.20	22.21	82.3	29.6
3	1.45	8.47	84.2	35.7
4	1.80	3.09	70.8	42.8
5	2.00	0.87	63.0	42.8
6	2.50	0.22	56.9	50.0
7	3.00	0.06	57.7	50.0
8	6.20	—	49.2	60.0
9	7.20	—	36.0	50.0
10	8.35	—	32.0	42.6

form parallel arrangements. This process causes closer packing of flakes resulting in a decrease of intergranular porosity of aggregates. Distinct decrease of bleaching ability of active earths from Machów relative to rape oil can be partly due to this phenomenon.

Consequently, washing process diminishes bleaching ability relative to rape oil but slightly increases this property in regard to mineral oil P-3. The obtained results confirmed the earlier reported observation on different mechanism of bleaching of mineral and edible oils by activated clay from Machów.

CONCLUSIONS

Studies on sulphuric acid activation of non-bentonitic materials of the Krakowiec clay type, consisting of montmorillonite of the beidellite-nontronite series, illite and chlorite as the main components, have shown them to be suitable for obtaining bleaching earths. The usefulness of these activated clays in refining sulphur as well as rape and P-3 oils was examined. These substances contain hydrocarbons colouring them yellow-brownish. The active earths in question when introduced in the amount of 1% are sorbing and removing these colouring components. It is supposed that in the case of sulphur depolymerization of μ -modification of this element (being one of colourizing agents) takes place at the surface of clay minerals.

Surface properties of the Krakowiec clays are different from those of typical bentonites but they can be used for the production of bleaching earths.

By applying different methods of thermal, chemical and ion exchange activation, it is possible to improve the bleaching properties of earths produced from the Machów clays relative to the three substances examined. Bleaching action of the earths thus obtained is very selective in character. Bleaching ability of sulphur can be improved by heating the raw clay for 2 hours within temperature range 200–500°C. The best bleaching properties are obtained by heating at 500°C. It is supposed that this process causes an increase of the number of acid centres of Lewis type.

Rape oil is best bleached by earths containing montmorillonite of considerably damaged structure by the action of strong (30–50%) sulphuric acid or by repeated activation using renewed portions of this acid. This method of activation results in the formation of increased amount of acid centres of Brönsted type, responsible for bleaching of rape oil.

Mineral P-3 oil is the most resistant to bleaching using the clays studied. The best bleaching ability of it is characteristic of clays which before chemical activation by means of 16% H_2SO_4 were preliminarily heated for 2 hours at 300°C. The oil in question is best bleached by clays activated with 16% H_2SO_4 and containing NH_4^+ as exchange cation.

Aggregate structure of active earths is of considerable importance in bleaching ability of oils. The existence of aggregates showing appropriate sizes of pores distinctly improves eg. bleaching ability of rape oil.

By applying proper chemical and thermal treatment and by selecting definite exchange cations it is possible to control *a priori* the surface properties of clays. This can be the basis for producing active earths showing differentiated bleaching properties, suitable for refining definite types of substances.

REFERENCES

- BENESI H.A., 1956: Acidity of catalyst surfaces. I. Acid strength from colors of adsorbed indicators. *J. Am. Chem. Soc.* 78, 21, 5490–5494.
- BRÜCKMAN K., FIJAŁ J., HABER J., KLAPYTA Z., WILTOWSKI T., ŻABIŃSKI W., 1976: Influence of different activation methods on the catalytic properties of montmorillonite. *Miner. Polon.* 7, 2, 5–14.
- FIJAŁ J., KLAPYTA Z., ZIETKIEWICZ J., ŻYŁA M., 1976: Studies on the fluoroderivatives of layer silicates. Part II. The effect of fluoride solutions on the structural and surface properties of montmorillonite. *Miner. Polon.* 7, 2.
- FRIPIAT J.J., 1971: Some applications of nuclear magnetic resonance to surface chemistry. *Catalysis Rev.* 5, 2, 269–282.
- GĄTARZ Z., 1976: Przydatność ilów krakowieckich z kopalni w Machowie do produkcji ziem odbarwiających. Praca doktorska AGH. Kraków.
- GREGG S.J., SING K.S.W., 1967: Adsorption, surface area and porosity. Academic Press, London-New York.
- PHAM THI HANG, BRINDLEY G.H., 1970: Methylene blue absorption by clay minerals. Determination of surface areas and cation exchange capacities (clay-organic studies XVIII) *Clays and Clay Minerals* 18, 203–212.
- POPIEL B., ŻYŁA M., 1976: Sorption of non-polar substances by transition metal cations modified montmorillonite. *Miner. Polon.* 7, 1, 13–25.
- STOCH L., BAHRANOWSKI K., BUDEK L., FIJAŁ J., 1977: Bleaching properties of non-bentonitic clay materials and their modification. I. Acid activation of the Miocene clays from Machów. *Miner. Polon.* 8, 1, 31–51.

Leszek STOCH, Krzysztof BAHRANOWSKI, Zdzisława GĄTARZ

WŁASNOŚCI ODBARWIAJĄCE ILASTYCH SUROWCÓW NIEBENTONITOWYCH I ICH MODYFIKOWANIE

II. WŁASNOŚCI ODBARWIAJĄCE ILÓW KRAKOWIECKICH Z MACHOWA I ICH MODYFIKOWANIE

Streszczenie

Przeprowadzono badania nad możliwością otrzymywania ziem bielących z ilów krakowieckich z nadkładu złoża siarki w Machowie koło Tarnobrzega. Iły te składają się z montmorillonitu, illitu i chlorytu. Przez odpowiednią aktywację kwasową, obróbkę termiczną i wymianę jonową można otrzymywać z nich ziemie aktywne o zróżnicowanych właściwościach. Sprawdzono przydatność tych ziem do rafinacji siarki, oleju rzepakowego oraz oleju mineralnego P-3. Substancje te zawierają węglowodory barwiące je na kolor żółtobrunatny. Otrzymane ziemie aktywne wprowadzone w ilości około 1% sorbują i usuwają składniki barwiące. W przypadku siarki, jak się przypuszcza, na powierzchni minerałów ilastych zachodzi również depolimeryzacja pierścieni siarki μ , która również jest składnikiem barwiącym siarkę.

Stosując różne metody obróbki termicznej, chemicznej i wymianę jonową można zwiększyć właściwości odbarwiającej ziem wytwarzanych z ilów z Machowa względem trzech badanych substancji. Działanie odbarwiającej tak przygotowanych ziem jest bardzo selektywne.

Zdolność odbarwania siarki można zwiększyć przez ogrzewanie iltu przez 2 h w zakresie temperatur 200–500°C. Najsilniejsze właściwości odbarwiającej uzyskuje

się przez ogrzewanie w 500°C. Jak się przypuszcza ogrzewanie powoduje wzrost ilości centrów kwasowych typu Lewisa.

Олеј rzepakowy odbarwiany jest najlepiej przez ziemie, w których struktura montmorillonitu została silnie naruszona przez działanie kwasem siarkowym o dużym stężeniu (30–50%) lub powtarzaną kilkakrotnie aktywacją z wymianą użytego kwasu. Ten sposób aktywacji wywołuje powstanie znacznej ilości centrów kwasowych typu Brönsteda, którym przypisać można obserwowany wzrost zdolności odbarwiania oleju rzepakowego.

Олеј mineralny P-3 odbarwia się najtrudniej za pomocą badanych ilów. Najlepsze właściwości odbarwiania tego oleju mają iły, które przed aktywacją chemiczną 16-procentowym H_2SO_4 ogrzewane były przez 2 h w temperaturze 300°C. Dobre właściwości odbarwiania tego oleju mają iły aktywowane 16-procentowym H_2SO_4 zawierające jako kation wymienny NH_4^+ .

Na zdolność odbarwiania olei istotny wpływ wywiera również budowa agregatowa ziemi aktywnej. Istnienie agregatów o odpowiedniej wielkości por poprawia m.in. zdolność odbarwiania oleju rzepakowego.

Przez obróbkę chemiczną, termiczną i dobór kationów wymiennych można w sposób zamierzony sterować właściwościami powierzchniowymi ilów. Możliwe jest to drogą m.in. wytwarzania ziem aktywnych o zróżnicowanych właściwościach odbarwiających nadających się do rafinacji określonych rodzajów substancji.

OBJAŚNIENIA FIGUR

- Fig. 1. Krzywa rozkładu por ilu z Machowa (M-1) aktywowanego 3 h 16-procentowym H_2SO_4 ,
Fig. 2. Krzywa rozkładu por ilu z Machowa (M-1) aktywowanego 8 h 16-procentowym H_2SO_4 ,
Fig. 3. Krzywa rozkładu por ilu z Machowa (132) aktywowanego 3 h 16-procentowym H_2SO_4 oraz ziemi odbarwiającej Tonsil-Standard
Fig. 4. Krzywa rozkładu por ziemi odbarwiającej Tonsil-Standard
Fig. 5. Krzywa rozkładu por bentonitu z Milowic
Fig. 6. Zależność zaadsorbowanego od dodanego błękitu metylenu dla frakcji $< 4 \mu m$ ilu z Machowa (M-1) nasyconych: Na^+ , NH_4^+ , Cr^{3+}
Fig. 7. Rentgenogramy frakcji $< 10 \mu m$ ilu z Machowa aktywowanych chemicznie
a – próbka nieaktywowana, b – próbka aktywowana 15 min – 5-procentowym H_2SO_4 , c – próbka aktywowana 15 min 16-procentowym H_2SO_4 , d – próbka aktywowana 3 h 30-procentowym H_2SO_4 , e – próbka aktywowana 3 h 50-procentowym H_2SO_4 , f – próbka aktywowana 15 min 5-procentowym HCl oraz 3 h 16-procentowym H_2SO_4 , g – próbka aktywowana 0,5 h 0,5 n NaOH oraz 3 h 16-procentowym H_2SO_4

Лешек СТОХ, Кишицкоф БАХРАНОВСКИ, Здислава ГОНТАЖ

OBESWCZEWIAJĄCE SWOJSTWA GLINISTOGO NEBENTONITOWEGO SYR'JA I IХ МОДИФИЦИРОВАНИЕ

II. OBESWCZEWIAJĄCE SWOJSTWA KRAKOWECKICH GLIN S MAHOVA I IХ МОДИФИЦИРОВАНИЕ

Резюме

Были проведены исследования возможности получения отбеливающих земель из краковецких глин с кровли месторождения серы в Махове возле Тарнобжега. Эти глины состоят из монтмориллонита, иллита и хлорита.

Путём соответствующей кислотной активации, термообработки и ионного обмена можно из них получить активные земли с разнородными свойствами. Была проверена пригодность этих земель к рафинированию серы, суперного масла а также минерального масла П-3. Эти вещества содержат углеводороды, окрашивающие их в жёлтокоричневый цвет. Полученные активные земли, введенные в количестве 1%, сорбируют и удаляют красящие компоненты. В случае серы, как предполагается, на поверхности глинистых минералов имеет место также деполимеризация серных колец μ , которая является также составной красящей серу.

Применяя разные методы термической, химической обработки и ионного обмена можно увеличить отбеливающие свойства земель, полученных из глин с Махова относительно трёх исследуемых веществ. Отбеливающее действие земель, приготовленных таким путём, является очень селективным.

Способность отбеливания серы можно увеличить посредством подогревания глины в течение 2 часов в пределах температур 200–500°C. Самые сильные отбеливающие свойства достигаются посредством подогревания в температуре 500°C. Как предполагается, подогрев вызывает возрастание количества кислотных центров типа Левиса.

Суперное масло лучше всего отбеливается землями, в которых структура монтмориллонита сильно нарушена действием серной кислоты большой концентрации (30–50%) или многократно повторяемой активацией с заменой использованной кислоты. Такой способ активации вызывает образование значительного количества кислотных центров типа Бренштедта, которым можно присвоить наблюдаемый взрост способности отбеливания суперного масла.

Хуже всего с помощью исследуемых глин отбеливается минеральное масло П-3. Наилучшие свойства отбеливания этого масла имеют глины, которые перед химической активацией 16 процентным раствором H_2SO_4 подогревались в течение 2-ух часов в температуре 300°C. Хорошие способности отбеливания этого масла имеют глины активированные 16 процентным раствором H_2SO_4 , содержащие в качестве обменного катиона NH_4^+ .

На способность отбеливания масел существенное влияние имеет также внутреннее строение активной земли. Существование агрегатов с соответствующей величиной пор улучшает кроме прочего, способность отбеливания суперного масла.

Путём химической, термической обработок и подбора обменных катионов можно планомерно управлять поверхностными свойствами глин. Возможно таким путём создание активных земель с разнородными свойствами отбеливания, пригодными для рафинирования определённых видов веществ.

ОБЪЯСНЕНИЕ К ФИГУРАМ

- Фиг. 1. Кривая распределения пор глины с Махова (M-1) активированной в течение 3 час. 16-процентным H_2SO_4
Фиг. 2. Кривая распределения пор в глине с Махова (M-1) активированных 8 час 16-процентным H_2SO_4
Фиг. 3. Кривая распределения пор в глине с Махова (132) активированной 3 час. 16-процентным H_2SO_4 и отбеливающих земель Тонсил-Стандард
Фиг. 4. Кривая распределения пор отбеливающей земли Тонсил-Стандард
Фиг. 5. Кривая распределения пор bentонита с Мильовиц

Фиг. 6. Зависимость адсорбированной от добавленной метиленовой сини для фракций < 4 мкм глины с Махова (М-1) насыщенной Na^+ , NH_4^+ , Ca^{2+} .

Фиг. 7. Рентгенограммы фракций < 10 мкм глины с Махова, активированной химически
а — неактивированная проба, в — проба активированная 15 мин. 5-процентным раствором H_2SO_4 ,
с — проба активированная 15 мин. 16-процентным H_2SO_4 , d — проба активированная 3 час. 30-
процентным H_2SO_4 , e — проба активированная 3 час. 50-процентным H_2SO_4 , f — проба активи-
рованная 15 мин. 5-процентным HCl и 3 час. 16-процентным H_2SO_4 , g — проба активированная 0,5 час.
0,5 л NaOH и 3 час. 16-процентным H_2SO_4