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# ORGANIC MATTER IN KAOLIN FROM KALNO NEAR ŚWIDNICA (LOWER SILESIA)

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Abstract. Kaolin from Kalno contains up to 1.5% organic matter composed of bitumens, humic acids and fulvic acids. Humic and fulvic acids have an aromatic structure with functional groups such as hydroxyl, carboxyl, carbonyl and ester groups. Bitumens have also been found to contain large amounts of aliphatic fragments. The organic matter binds a part of iron present in the kaolin. Its removal increases significantly the whiteness of kaolin.

## INTRODUCTION

The industrial use of kaolins depends, among other things, on their colour. The colour after firing is controlled primarily by the content of colouring elements, mainly iron and titanium, but in raw state it is also significantly affected by the organic matter, which gives gray or brown colour to these materials.

Studies of the organic compounds occurring in clays are carried on mainly by pedologists and were initiated as early as in 1937 by Tiurin.

Investigations of Worrall and Green (1953) of the organic compounds present in potter's clay have shown their close similarity to lignite (brown coal) occurring in the areas where clay is recovered. According to Worrall (1956), lignite is the product of decomposition of vegetable matter, particularly of wood. This matter, consisting mainly of wax, resins, cellulose, chemicellulose and lignin, decomposes as time goes on under the influence of bacterial activity. While cellulose is decomposed rapidly and completely, wax and resins are subject only to insignificant changes, first to peat and then to lignite. Wax and resins bear a common name of bitu-

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mens whereas the products of decomposition of lignin are refrred to as humic acids.

Bojakowska (1975) proposed a division of the organic matter dispersed in clay sediments into two genetic types: sapropelic substance arising due to transformation of the organic remains of aquatic plants and animals, and humic substance forming from land plants. This author found that organic matter shows marked differentiation, depending on the physico--chemical conditions of sedimentation. In general, the matter from marine sediments has a higher content of structures of the aliphatic type while in land sediments aromatic structures are prevalent.

Humic substance, the acid character of which has been demonstrated by several investigators, consists of sparingly soluble humic acids of higher molecular mass, and of readily soluble fulvic acids. According to Łakomiec and Kozakiewicz (1970), the occurrence of pure acid forms in soils is doubtful; they tend to appear as salts and organo-mineral complexes. There is, however, a certain divergence in opinions regarding the mechanism of binding of the organic compounds by the surface of minerals. Several investigators dealing with this problem agree that, firstly, such complexes form due to the functional groups, such as alcohol, phenol and carboxyl groups, characteristic of the humic substance, and, secondly, that metallic, mainly iron and aluminium, ions take part in the formation of stable complexes clay mineral — organic matter.

The studies of Khanna and Stevenson (1962) have revealed that clay minerals containing iron or aluminium ions adsorb considerably greater amounts of humic acids than those containing calcium or hydrogen ions. The nature of such complexes has not been precisely defined. According to Pohl and Schviete (1963), they form at pH between 5 and 6, and their stability increases with time, which is characteristic of oxyhydrates. It is also feasible that multivalent cations having the character of amphions and occurring in the form of independent compounds can, as a result of hydrolysis, form gel on the surface of the mineral which, due to the electrostatic forces, helds together the negatively charged organic colloid and the grains of clay minerals.

Schnitzer (1968) investigated the reactions between metals and fulvic acids and found that the OH alcohol groups do not participate in them. He thinks that the $-COOH$ acid groups and $-OH$ phenol groups play simultaneously a significant role in these reactions whereas groups of lesser acidity are of minor importance. Kononova and Titova (1961), Dyakonova (1962) and Titova (1962) (*fide* Kauritschev *et al.* 1964) have shown experimentally that humic and fulvic acids are capable of forming chelation compounds containing iron. These authors have found that the properties of iron-humic complexes are different depending on the nature of humic substances, the degree of condensation of the aromatic nucleus, and the number of side chains containing hydrophilic groups.

Alexandrova *et al.* (1968) distinguished three groups of organo-mineral derivatives of humus acids: heteropolar salts, complex salts, and adsorption complexes. The mechanism of formation of heteropolar salts involves an exchange reaction between hydrogen of the functional groups of humus acid and corresponding cations. Pure humates and fulvates of strong bases are scarce in soils. More common are complex heteropolar salts, the most important of which are iron and aluminium complexes. Iron and aluminium ions replace hydrogen of the functional groups, giving complex salts in which metal does not behave as a cation. Iron, for example, appears in them as $Fe(OH)^{2+}$ or $Fe(OH)_{+2}$ and aluminium as $Al^{3+}$, $Al(OH)^{2+}$ or $Al(OH)_2^+$. Adsorption complexes of humus acids with clay minerals and non-siliceous forms of sesquioxides are multiform and not well known yet. The basic mechanism of their formation involves adsorption of humus substances on sesquioxide gels, giving rise to organo-mineral complexes of very variable composition which always have the ability to exchange cations. Besides adsorption, chemical bonds may form and complex compounds may rise on the film surface. Clay-humus complexes form by coalescence films on the surface of clay minerals by means of intermolecular forms of binding.

Investigating organo-mineral complexes, Schnitzer (1968) found that the form of occurrence of iron and aluminium in these complexes depends on the molar ratio of organic matter to metal. With the ratio being 1 : 1, Fe appeared as $Fe(OH)^{2+}$ and aluminium as $Al(OH)^{2+}$; in 3 : 1 complexes — $Fe(OH)^{2+}$ and $Al(OH)_2^+$, in 6 : 1 complexes — $Fe(OH)_2^+$ and $Al(OH)_2^+$.

## EXPERIMENTAL

Investigations of the organic substance from kaolin from Kalno near Świdnica (Lower Silesia) were carried out on samples collected from the deposit and those recovered from the 35*N* borehole.

The DTA curves obtained for the kaolin studied show thermal peaks produced by the basic mineral constituents, kaolinite or halloysite, as well as a broad exothermic peak between 300 and 400°C. This exothermic peak corresponds to a slight inflexion on TG curves, due to the weight loss, and to a weak peak on the DTG curve (Fig. 1). The sample in which these effects were particularly pronounced was subjected to thermal analysis combined with the analysis of gases evolving during heating, using a Mettler thermoanalyzer. The measurements were made under vacuum, and the composition of the evolving gases was determined with a Balzers quadrupole mass spectrometer. The heating rate was 6°C/min. The results are shown in Figure 2 as curves representing the relative amounts of evolving gases of different molecular weights. It has been found that during the heating of the kaolin, gases of molecular weights of 18, 28, 29 and 44 evolve. A molecular weight of 18 corresponds to water, 44 — to carbon dioxide, 28 — to CO and $N_2$. The constituent of a molecular weight of 29 failed to be identified.

The most characteristic, however, is the water release curve. Its main extremum corresponds to dehydration of kaolinite, which coincides with an additional dehydration effect at 450°C. The latter is preceded by a weak peak at 300—350°C. The two dehydration peaks are accompanied by evolution of other gases. The first dehydration is attended by the evolution extremum of molecules of a mass of 28, and of a gaseous component of a molecular mass of 29. The second, additional, dehydration peak is attended by the evolution of $CO_2$ (molecules of a mass of 44), and it also corresponds to the second maximum on the evolution curve of a gas a molecular weight of 29 (CO, $N_2$). Both dehydration processes are to be associated with the decomposition of organic matter (pyrolysis). It is feasible that a part of $CO_2$ evolving at 400—450°C also originates from the decomposition of siderite, which is most likely present in the sample. From the analysis of gases evolving during the heating of samples it follows that the exothermic peaks appearing on DTA curves between 300 and 400°C are due to combustion of the organic matter present in the kaolin. The weight loss in this temperature range was arbitrarily assumed

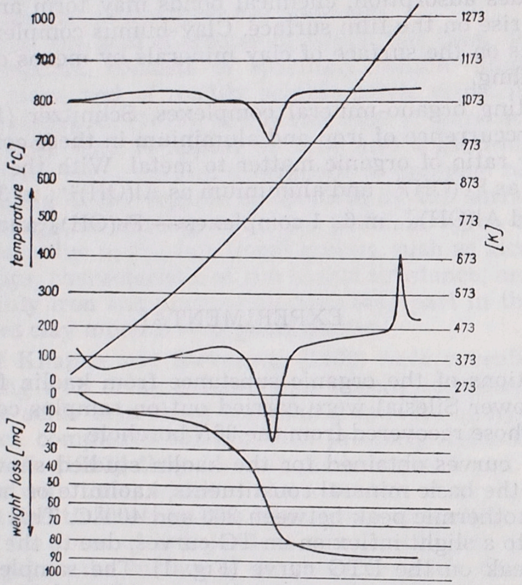

Fig. 1. Thermal curves for sample from *35N* borehole, depth 40 m

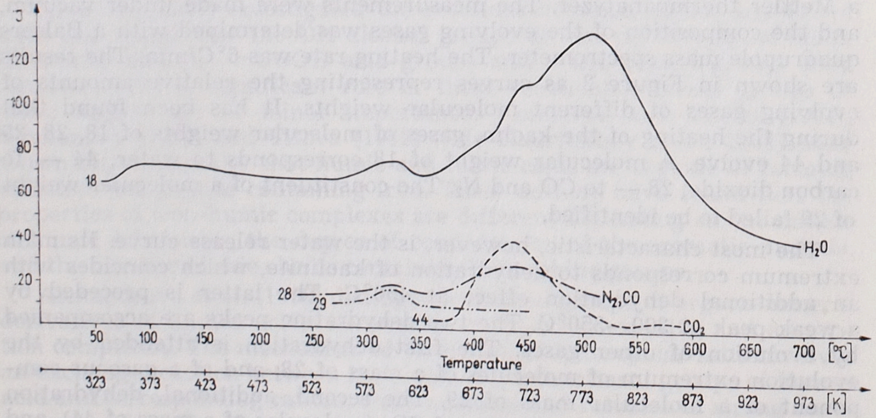

Fig. 2. Evolved gas curves, for sample from *35N* borehole, depth 40 m, during heating

as representing the content of the organic matter present in the samples. This content in the Kalno deposit varies with depth from 0.5 to 1.5% (profile 35N).

Further investigations aimed to explain the nature of the organic matter, its role in binding iron, as well as the effect of its extraction on whiteness of the kaolin and on iron removability from kaolin.

Investigations were carried out on < 45 μm fraction of four kaolin samples differing in colour but having a similar mineralogical composition, grain-size distribution and colouring oxides content. They contained about 90% kaolinite, 4—6% micas and 4—7% quartz (Table 1). The content of $Fe_2O_3$ varied from 1.01 to 1.07% (Table 4). The carbon content, determined by Tiurin's method (1951) modified by Oleksynowa, was 0.1—0.14% (Table 2), which corresponds to 0.16—0.24% of organic matter. Samples of lower whiteness (Table 3) contained a greater amount of organic matter.

Table 1

Content of main mineral constituents in material < 45 μm [weight %]

| Sample | Kaolinite | Micas | Quartz | Index of crystallinity of kaolinite $I_{010} : I_{1\bar{1}0}$ |
|---|---|---|---|---|
| *Ko — I* | 91 | 5 | 4 | 0.84 |
| *Ko — II* | 91 | 5 | 4 | 0.84 |
| *Ko — III* | 89 | 5 | 6 | 0.86 |
| *Ko — IV* | 89 | 6 | 7 | 0.84 |

Table 2

Carbon content in the organic matter extracts [weight %]

| Sample | Raw material | After extraction of bitumens | After extraction with $Na_4P_2O_7$ | After first extraction with NaOH | After second extraction with NaOH | Sample after complete extraction |
|---|---|---|---|---|---|---|
| *Ko — I* | 0.11 | 0.10 | 0.069 | 0.028 | 0.038 | 0.067 |
| *Ko — II* | 0.10 | 0.09 | 0.043 | 0.033 | 0.030 | 0.057 |
| *Ko — III* | 0.11 | 0.11 | n.d. * | 0.037 | 0.041 | 0.068 |
| *Ko — IV* | 0.14 | 0.12 | 0.056 | 0.038 | 0.028 | 0.069 |

* Not determined

To explain the nature of the organic matter, an attempt at its extraction was made, using a method devised by Boratyński and Wilk (1963). This method is widely used by pedologists.

The extraction involved the following procedures:

1. Extraction of bitumens with a 1 : 1 mixture of ethyl alcohol and benzene in the Soxhlet apparatus for 20 h.

Table 3

Whiteness of kaolin samples after extraction of organic matter

| Sample | Whiteness [%], λ = 459 nm | | | | | |
|---|---|---|---|---|---|---|
| | Raw material | After extraction of bitumens | After extraction with $Na_4P_2O_7$ | After first extraction with NaOH | After hydrolysis with $H_2SO_4$ | After second extraction with NaOH |
| *Ko — I* | 77.5 | 76.6 | 78.4 | 78.3 | 80.6 | 82.2 |
| *Ko — II* | 75.8 | 74.8 | 77.2 | 78.0 | 79.4 | 80.3 |
| *Ko — III* | 66.3 | 65.0 | 72.1 | 72.0 | 76.1 | 76.2 |
| *Ko — IV* | 62.9 | 61.9 | 67.3 | 69.6 | 70.7 | 73.2 |

Table 4

Iron content in the organic matter extracts

| Sample | $Fe_2O_3$ [weight %] | | | | | | |
|---|---|---|---|---|---|---|---|
| | Raw material | Extracts in benzene/ethyl alcohol | Extract in $Na_4P_2O_7$ | First extract in NaOH | Extract in $H_2SO_4$ | Second extract in NaOH | Material after extraction |
| *Ko — I* | 1.01 | n.d.* | 0.05 | 0.01 | 0.09 | — | 0.86 |
| *Ko — II* | 1.07 | n.d. | 0.06 | 0.01 | 0.20 | — | 0.85 |
| *Ko — III* | 1.07 | n.d. | 0.19 | 0.01 | 0.39 | — | 0.72 |
| *Ko — IV* | 1.05 | n.d.* | 0.21 | 0.01 | 0.15 | — | 0.90 |

* Not determined.

2. Extraction with 0.1 n $Na_4P_2O_7$ solution at a pH of 7. The kaolin sample was shaken with a pyrophosphate solution for 1 h whereupon the suspension was left for 23 h. Then the sediment was separated from the solution by centrifuging and coagulated with sodium sulphate. The whole procedure was repeated seven times. The solutions obtained from each extraction were put together for further investigations.

3. Extraction with 0.1 n NaOH solution. The same procedure was adopted as for extraction with sodium pyrophosphate, and it was repeated seven times.

4. Hydrolysis of organic matter. The kaolin sample was treated with 0.5 n $H_2SO_4$ solution and left for 24 h. Then it was centrifuged to separate the solution from solids.

5. Second extraction with NaOH solution. It was carried out as in (3), and the procedure was repeated seven times.

In the extracts obtained with pyrophosphate and NaOH solutions fulvic acids were separated from humic acids by acidification with $H_2SO_4$ to a pH = 1. After acidification, humic acids precipitated in all the extracts. They were filtered off, washed to remove excess reagents, and dried at 50°C. The remaining solution containing fulvic acids was evaporated at the same temperature, and fulvic acids were extracted from the dry residue with acetone.

The fulvic and humic acids obtained in this way were subjected to infrared absorption analysis in an *UR-10* spectrophotometer.

After each stage of extraction the amount of carbon and iron going into solution was determined, and the whiteness of samples was measured. Moreover, the content of $Fe_2O_3$ soluble in 9% HCl was determined and the whiteness was measured again after this form of iron had been removed.

After extraction with the method of Boratyński and Wilk, a certain amount of organic matter (about 0.07% C) still remained in the samples. In order to separate it, the samples were shaken with 40% HCl, and during this treatment the mineral constituents were dissolved. The residue, *i.e.* the organic matter that failed to be extracted before, was washed to remove HF, dried at 50°C, and subjected to infrared absorption spectroscopik analysis.

The amount of carbon passing into solution was assumed as a measure of the organic substance separated in each stage of extraction; only when bitumens were extracted witha mixture of alcohol and benzene, their amount was estimated from the difference in carbon content in the sample before and after the extraction.

Using the method of Boratyński and Wilk, not more than half the organic matter is removed from kaolins (Table 2). The smallest amount, corresponding to about 0.01% C, is extracted with a mixture of alcohol and benzene. More carbon is removed by the other procedures: about 0.05% by treatment with sodium pyrophosphate, about 0.04% by the first and about 0.04% by the second extraction with NaOH solution. It must be stressed, however, that the numerical data obtained are only approximate because for a carbon content so low as in the kaolins studied, the accuracy of Tiurin's method is low as well.

Extraction of the organic matter from the kaolin affects its whiteness (Table 3). While the extraction of bitumens has no effect on the whiteness, the subsequent treatment increase it progressively. The total increase in whiteness due to the removal of the organic matter varies from 5 to 10%.

Because of the small amount of the organic matter available for investigations, infrared spectroscopic analysis had to be confined to the bituminous substance and the fractions of humic and fulvic acids separated with sodium hydroxide solution, as well as to the residue left after dissolution of the mineral constituents in hydrofluoric acid.

On evaporation of the solvent, bitumens are a brown oily liquid. Classical qualitative analysis has shown that they do not contain nitrogen or sulphur. Infrared absorption spectra have revealed the presence of a great number of aliphatic fragments, which is evidenced by very intense bands at 2930 and 2860 $cm^{-1}$ caused by C-H stretching vibrations (Fig. 3). Aromatic nuclei are present in the bitumens as well. They display characteristic absorptions arising from C-H bending vibrations at 670, 710, 800 and 810 $cm^{-1}$, $C = C$ stretching vibrations of skeletal aromatic nuclei (1460, 1570, 1610 $cm^{-1}$), and from C-H stretching vibrations in the form of a multiplet centered close to 3070 $cm^{-1}$.

The bitumens also contain $C = O$ carbonyl groups (acid, ester or

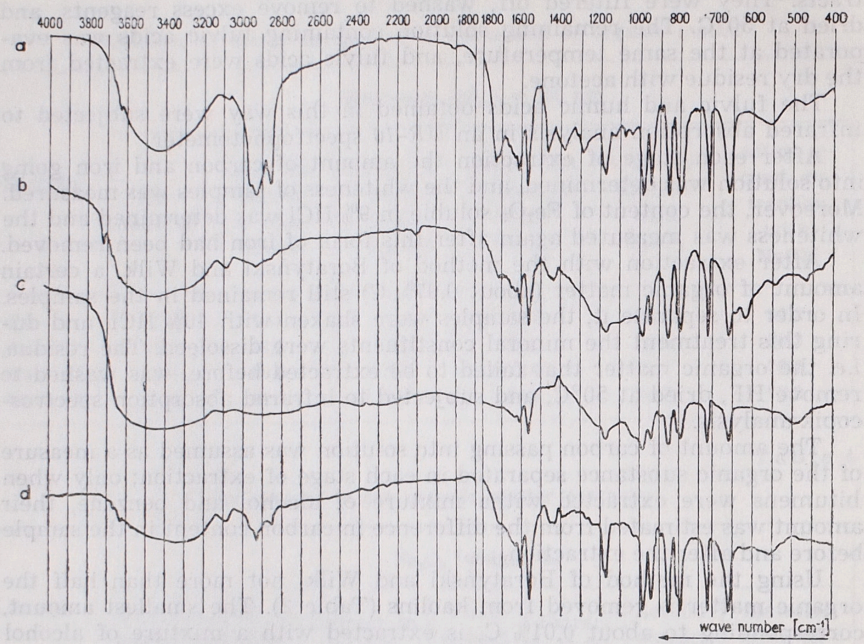

Fig. 3. IR absorption spectra of organic matter from sample $K_0$ — *III*: *a* — bitumens, *b* — humic acids, *c* — fulvic acids, *d* — HF-insoluble matter

ketone), with the corresponding bands at 1710, 1720, 1740 $cm^{-1}$. Ester groupings are responsible for C-O absorptions bands close to 1170, 1180 and 1280 $cm^{-1}$. Intense absorption in the region between 3200 and 3600 $cm^{-1}$ testifies to the presence of free and associated carboxyl groups, as well as alcohol and phenol groups. A comparison of infrared absorption spectra shows that the bitumen extracts from respective samples differ in the content of functional carboxyl, ester, ketone, alcohol and phenol groups. Infrared spectra of fulvic and humic acids show no differences (Fig. 3*b* and *c*), except that the absorption bands of fulvic acids are somewhat broadened and have lower intensity.

Both fractions display aromatic absorption (C = C skeletal at 1450, 1560, 1610 $cm^{-1}$; C-H bending at 660, 800, 860 $cm^{-1}$; C-H stretching between 3050 and 3100 $cm^{-1}$). In the region between 1600 and 1800 $cm^{-1}$ fulvic acids display slightly weaker absorption than humic acids. The absorption bands appearing in this region are to be attributed to C = O carboxyl (acid, ketone, ester) groups and to C = C double bonds.

At 1200 and 1000 $cm^{-1}$ both organic fractions display absorption caused by C-O stretching vibrations. The bands assigned to O-H vibrations of carboxyl, phenol and alcohol groups, both free and associated (3200—3600 $cm^{-1}$), are weaker for fulvic and humic acids than for bitumens. In contrast to bitumens, the spectra of humic and fulvic acids failed to show the presence of absorption bands characteristic of C-H stretching vibrations of aliphatic groupings.

Infrared absorption investigations of the organic matter remaining in the sample after extraction by the method of Boratyński and Wilk, and obtained by dissolution of the mineral constituents in hydrofluoric acid have shown that it yields absorption bands similar to those produced by humic and fulvic acids. Moreover, it displays C-H stretching absorptions from aliphatic groupings (2800—2950 $cm^{-1}$) like those recorded for bitumens but of much lower intensity.

It has been found that during the extraction of organic matter also iron passed into solution (Table 5). After complete extraction, $Fe_2O_3$ content in the kaolin samples decreased from 1.01—1.07% to 0.7—0.9%. In the extract of pyrophosphate solution the content of $Fe_2O_3$ was 0.05—0.21% in relation to the mass of untreated sample, and in the sulphuric acid extract — 0.09—0.39%.

Table 5

Content of iron soluble in 9% HCl after extraction of organic matter

| Sample | $Fe_2O_3$ [weight %] | | | | | |
|---|---|---|---|---|---|---|
| | Raw material | After extraction with benzene/ethyl alcohol | After extraction with $Na_4P_2O_7$ | After first extraction with NaOH | After hydrolysis with $H_2SO_4$ | After second extraction with NaOH |
| *Ko — I* | 0.17 | 0.18 | 0.08 | 0.09 | 0.06 | 0.06 |
| *Ko — II* | 0.22 | 0.18 | 0.16 | 0.16 | 0.07 | 0.10 |
| *Ko — III* | 0.38 | 0.32 | 0.24 | 0.24 | 0.09 | 0.12 |
| *Ko — IV* | 0.17 | 0.11 | 0.12 | 0.11 | 0.08 | 0.09 |

When assessing the quality of kaolins, one of the criteria applied is the content of iron soluble in acid solutions, most commonly in 9% HCl. Accordingly, an attempt was made to establish a relation between the amount of iron dissolved by this acid and that going into the extracts during the separation of organic matter. To this end, the amount of iron that could be dissolved from the sample using 9% HCl was checked after each stage of extraction of the organic matter (Table 6). It appeared that after extraction with sodium pyrophosphate the amount of iron going into HCl solution is less than that passing from the untreated sample because iron has partly passed into the pyrophosphate extract, and the subsequent stages of extraction with NaOH solution did not change the amount of iron going into HCl solution. The total amount of iron that was removed from the kaolins during complete extraction of the organic matter with the method of Boratyński and Wilk and subsequent treatment with hydrochloric acid is somewhat greater than the amount of iron dissolved from the untreated sample. While in the untreated sample about 0.2—0.4% $Fe_2O_3$ was dissolved in hydrochloric acid, the combined extraction of the organic matter and HCl treatment removed 0.3—0.5% $Fe_2O_3$ from the kaolin samples.

Extraction of the organic matter from kaolins causes a systematic increase in their whiteness after each stage of extraction (Table 3). The total increase in whiteness was 5—16%. The additional extraction of iron with

Table 6

Whiteness of kaolin samples after extraction of organic matter and of iron soluble in 9% HCl

| Sample | Whiteness [%], λ = 659 nm | | | | | |
|---|---|---|---|---|---|---|
| | Raw material | After extraction with benzene/ethyl alcohol | After extraction with $Na_4P_2O_7$ | After first extraction with NaOH | After hydrolysis with $H_2SO_4$ | After second extraction with NaOH |
| *Ko — I* | 77.5 | 77.1 | 78.1 | 81.5 | 81.3 | 83.5 |
| *Ko — II* | 75.8 | 74.8 | 77.2 | 80.6 | 80.8 | 83.6 |
| *Ko — III* | 66.3 | 70.0 | 72.7 | 77.0 | 77.0 | 80.2 |
| *Ko — IV* | 62.9 | 65.7 | 68.2 | 73.7 | 72.9 | 76.5 |

HCl increases the whiteness by another 1—3%. The removal of iron with HCl from untreated samples increases their whiteness by 1—4%.

Extraction of organic matter by the method of Boratyński and Wilk is a time-consuming procedure. Therefore, a simpler method was adopted, involving extraction with glacial acetic acid and acetone in Soxhlet apparatus. The extraction was carried out on sample *Ko-III*.

When dry, the extract obtained with acetic acid is a brown-reddish powder containing no nitrogen or sulphur. Its infrared absorption spectrum (Fig. 4*b*) shows intense, broad bands in the region 1400—1500 $cm^{-1}$, corresponding respectively to symmetric and asymmetric vibrations of the $COO^{-1}$ carboxylanium ion. Simultaneously, a very weak absorption occurs above 1700 $cm^{-1}$, arising from C = O carboxyl groups, both ketone and ester. The intense absorption bands produced by C = O stretching vibrations of carboxyl groups fail to appear in the acetic acid extract spectrum. This fact is indicative of formation of salts and chelation of the carbonyl and ketone groups, which phenomena are responsible for the displacement of the bands associated with the latter to lower frequencies. Assuming that acids, alcohols and phenols of the organic fraction were entirely converted into salts and chelates, the intense absorption band in the region 3200—3600 $cm^{-1}$ is to be attributed to stretching vibrations of water molecules. The 2850 and 2930 $cm^{-1}$ bands correspond to C-H stretching vibrations in alkyl groups. There also occur bands caused by skeletal stretching vibrations in the aromatic nuclei. Moreover, the aromatic nuclei are responsible for absorptions at 660, 720, 800 and 3060—3100 $cm^{-1}$.

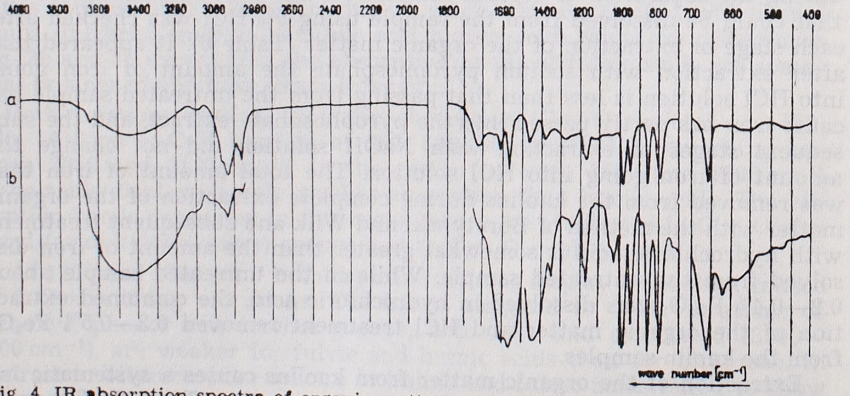

Fig. 4. IR absorption spectra of organic matter extracted from sample $K_o$ — *III* with: *a* — acetone, *b* — acetic acid

Due to extraction with acetic acid, the sample whiteness increased from 66.3 to 72.2%.

The infrared absorption spectrum of the organic matter extracted with acetone is identical with the spectra of bitumens extracted using the method of Boratyński and Wilk (Fig. 4*a*). This extraction increased the whiteness to 68.5%.

## CONCLUSIONS

The kaolin from Kalno contains up to 1.5% organic matter which is composed of both bitumens and humic and fulvic acids. A characteristic feature of bitumens is the presence of a large number of aliphatic fragments. It is feasible that a part of mobile humic compounds goes into the mixture of alcohol and benzene, which is evidenced by absorption bands from functional groups similar to those recorded for humic and fulvic acids.

It has been found that the humic and fulvic acids in the kaolin from Kalno have a similar aromatic skeleton with the functional groups such as hydroxyl, carboxyl, carbonyl and ester groups.

The organic matter binds iron, and its extraction increases markedly the whiteness of kaolin.

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## SUBSTANCJA ORGANICZNA W KAOLINIE Z KALNA KOŁO ŚWIDNICY (DOLNY ŚLĄSK)

### Streszczenie

Badania termiczne kaolinu z Kalna wykazały, że na krzywych DTA oprócz efektów termicznych związanych z podstawowymi składnikami mineralnymi w zakresie 300—400°C występuje szeroki efekt egzotermiczny. Na krzywych TG odpowiada mu słabe przegięcie związane z ubytkiem masy a na krzywej DTG — słaby pik. Efekt ten przypisano spalaniu substancji organicznej obecnej w kaolinie. Jej zawartość, oceniona na podstawie ubytku masy, wynosiła co najwyżej 1,5%. Badania termiczne połączone z analizą gazów wydzielających się w trakcie ogrzewania wykazały, że w zakresie 300—350°C występują maksima na krzywych wydzielania się gazów o ciężarach drobinowych 18 ($H_2O$), 28 ($CO$, $N_2$) i 29 (?).

Dla wyjaśnienia charakteru substancji organicznej przeprowadzono jej ekstrakcję metodą Boratyńskiego i Wilka z czterech próbek kaolinu (frakcji $< 45$ µm) różniących się barwą, a nie wykazujących istotnych różnic w składzie mineralnym, ziarnowym i zawartości tlenków barwiących. Zawierały one około 90% kaolinitu, 4—6% mik i 4—7% kwarcu. Ilość $Fe_2O_3$ mieściła się w granicach 1,01—1,07%. W próbkach tych stwierdzono 0,10—0,14% C, co odpowiada 0,16—0,24% substancji organicznej, przy czym próbki o niższej białości zawierały większą ilość tej substancji.

Metodą Boratyńskiego i Wilka udało się usunąć z kaolinów tylko około połowy zawartej w nich substancji organicznej. Najmniejszą ilość, odpowiadającą ok. 0,01% C, usunięto mieszaniną benzenu i alkoholu etylowego; do roztworu pirofosforanu sodu przeszło około 0,05% C; ługiem sodowym wyekstrahowano około 0,04% C, a powtórne działanie tym odczynnikiem, po przeprowadzeniu hydrolizy kwasem siarkowym, pozwoliło usunąć dalsze 0,04% C. Po pełnym cyklu ekstrakcyjnym w próbkach pozostało jeszcze ok. 0,07% C. W skład substancji organicznej zawartej w kaolinie z Kalna wchodzą zarówno bituminy jak i kwasy fulwowe oraz huminowe. Metodą spektroskopii absorpcyjnej w podczerwieni stwierdzono, że cechą charakterystyczną bituminów jest obecność dużej ilości fragmentów alifatycznych. Kwasy huminowe i fulwowe mają szkielet węglowodorowy alifatyczny i aromatyczny z grupami funkcyjnymi, wśród których wyróżniono: grupy hydroksylowe, karboksylowe, karbonylowe i estrowe. Substancja organiczna pozostająca w próbkach po ekstrakcji ma charakter analogiczny jak wydzielone kwasy huminowe i fulwowe.

W trakcie ekstrakcji substancji organicznej do roztworów ekstrakcyjnych przeszła również pewna ilość żelaza. Po pełnej ekstrakcji zawartość $Fe_2O_3$ w próbkach zmniejszyła się z pierwotnej ilości około 1,0% do ok. 0,7—0,9%. W ekstrakcie pirofosforanowym stwierdzono 0,05—0,20% $Fe_2O_3$ w stosunku do masy próbki wyjściowej a w ekstrakcie kwasu siarkowego 0,09—0,4%.

Ekstrakcja substancji organicznej pirofosforanem sodowym wpłynęła także na ilość żelaza usuwalnego z kaolinu 9% HCl. Okazało się, że po tej ekstrakcji do roztworu HCl przeszła mniejsza ilość żelaza niż z próbki wyjściowej, część bowiem żelaza przeszła uprzednio do ekstraktu pirofosforanowego. Dalsze etapy ekstrakcji substancji organicznej — ługiem sodowym — nie wpłynęły na ilość żelaza rozpuszczalnego w HCl. Sumaryczna ilość żelaza, jaką można było usunąć z badanych kaolinów stosując ekstrakcję substancji organicznej a następnie działanie kwasu solnego, jest nieco większa niż ilość żelaza usuwalnego tym kwasem wprost z próbki pierwotnej. HCl rozpuszczał z próbki pierwotnej około 0,2—0,4% $Fe_2O_3$ a dzięki połączonej ekstrakcji substancji organicznej i obróbki HCl usunięto 0,3—0,5% $Fe_2O_3$.

Usunięcie substancji organicznej z kaolinu Kalno spowodowało wzrost ich białości. Następował on systematycznie po każdym etapie ekstrakcji. Całkowity przyrost białości wyniósł 6—10%. Dodatkowe usunięcie żelaza HCl zwiększyło białość o dalsze 1—3%. Usunięcie żelaza HCl z próbek wyjściowych zwiększało ich białość o około 1—4%.

### OBJAŚNIENIA FIGUR

Fig. 1. Krzywe analizy termicznej próbki z otworu *35N*, głębokość 40 m

Fig. 2. Krzywe wydzielania się gazów w czasie ogrzewania, z próbki z otworu *35N*, głębokość 40 m

Fig. 3. Widma absorpcyjne w podczerwieni substancji organicznej z próbki *Ko-III*
*a* — bituminy, *b* — kwasy huminowe, *c* — kwasy fulwowe, *d* — substancja nierozpuszczalna w HF

Fig. 4. Widma absorpcyjne w podczerwieni substancji organicznej wyekstrahowanej z próbki *Ko-III*:
*a* — acetonem, *b* — kwasem octowym

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## ОРГАНИЧЕСКОЕ ВЕЩЕСТВО В КАОЛИНЕ ИЗ КАЛЬНА ВБЛИЗИ СВИДНИЦЫ (НИЖНЯЯ СИЛЕЗИЯ)

### Резюме

Термические исследования каолина из Кальна показали, что на кривых термического дифференциального анализа (DTA) кроме термических эффектов связанных с основными минеральными компонентами присутствует в диапазоне 300—400°C широкий эгзотермический эффект. На кривых TG ему соответствует малозаметный прогиб, связанный с убытком массы, а на кривой DTG малозаметный пик. Этот эффект был приписан сгоранию органического вещества, которое присутствует в каолине. Его количество, оцененное по убытку массы, составило, как самое большое, 1,5%. Термические исследования совмещённые с анализом выделяющихся во время нагревания газов показали, что в диапазоне 300—350°C на кривых выделения газов с молекулярным весом 18($H_2O$), 28($CO$, $N_2$) и 29 (?) присутствуют максимумы.

Для того, чтобы выяснить характер органического вещества, была проведена его экстракция, по методу Боратынского и Вилка, из четырёх образцов каолина (размеры частиц $< 45$ μm), различающихся цветом, но без существенных различий в минеральном и зерновом составах и по составу окрашивающих окислов. Образцы содержали около 90% каолинита, 4—6% слюд и 4—7% кварца. Количество $Fe_2O_3$ содержалось в границах от 1,01% до 1,07%. В образцах обнаружено 0,10—0,14% C, что соответствует 0,16—0,24% органического вещества, при чём образцы менее белые содержали большее количество этого вещества.

По методу Боратынского и Вилка было возможно удаление около половины органического вещества содержащегося в каолинах. Самое низкое количество, соответствующее около 0,01% C, было удалено при помощи промывания смесью бензена и этилового алкоголя; в раствор пирофосфата натрия перешло около 0,05% C; при помощи натрового щелка удалено около 0,04% C, а вторичное воздействие этого реактива, после гидролиза серной кислотой, сделало возможым удаление следующих 0,04% C. После полного экстракционного цикла в образцах осталось ещё около 0,07% C. В состав органического вещества, содержащегося в каолине из Кальна, входят так битумы, как и фульвокислоты и гуминокислоты. По методу ИК спектроскопии было обнаружено, что характерным свойством битумов является присутствие больших алифатических фрагментов. У гуминокислоты и фульвокислоты скелет из углеводородных соединений алифатических и ароматических с функциональными группами, среди которых были выделены: гидроксильная, карбоксильная, карбонильная и сложноэфирная группы. Органическое вещество, которое осталось в образцах после экстракции, по характеру аналогично выделенным гуминокислотам и фульвокислотам.

Во время экстракции органического вещества в экстракционные растворы перешло тоже некоторое количество железа. После полной экстракции количество $Fe_2O_3$ в образцах уменьшилось от исходного количества на около 0,5% до около 0,7—0,9%. В пирофосфатном экстракте было обнаружено 0,05—0,20% $Fe_2O_3$ по отношению к массе исходного образца, а в вытяжке серной кислоты — 0,09—0,4%.

Экстракция органического вещества пирофосфатом натрия повлияла тоже на количество железа, которое можно удалить из каолина при помощи 9% HCl. Оказалось, что после этой экстракции в раствор HCl перешло меньшее количество железа, чем из исходного образца, так как часть железа уже прежде перешла в пирофосфатный экстракт. Следующие этапы экстрагирования органического вещества натровым щелком не повлияли на количество железа растворимого в HCl. Суммарное количество железа, которое было возможным извлечь из изучаемых каолинов при помощи извлечения органического вещества, а в дальнейшем воздействием соляной кислоты, немного больше, чем количество железа удаляемого этой кислотой непосредственно из исходного образца. HCl растворял в исходном образце около 0,2—0,4% $Fe_2O_3$, а благодаря совместной экстракции органического вещества и обработке соляной кислотой удалось удалить 0,3—0,5% $Fe_2O_3$.

Удаление органического вещества из каолина Кально привело к увеличению его белизны. Увеличение это систематически наблюдалось после каждой этаппы экстракции. В целом увеличение белизны составило 6—10%. Добавочное извлечение железа при помощи HCl увеличило белизну на дальших 1—3%. Удаление железа при помощи HCl из исходных образцов увеличивало их белизну на около 1—4%.

## ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Кривые термического анализа образца из скважины *35 N*, глубина 40 м.

Фиг. 2. Кривые выделения газов во время нагревания, образец из скважины *35 N*, глубина 40 м.

Фиг. 3. ИК-спектр поглощения диапазоне органического вещества из образца *Ko-III*
*a* — битумы, *b* — гуминокислоты, *c* — фульвокислоты, *d* — вещество нерастворимое в HF

Фиг. 4. ИК-спектр поглощения диапазоне органического вещества извлечённого из образца *Ko-III*
*a* — при помощи ацетона, *b* — при помощи уксусной кислоты