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# MINERALOGICAL COMPOSITION OF KAOLINITE CLAYS FROM THE "JANINA" MINE AT SUSZKI NEAR BOLESŁAWIEC (LOWER SILESIA)

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A b s t r a c t. This paper presents investigations of the mineralogical composition of Santonian clays recovered from the "Janina" mine near Bolesławiec (Lower Silesia). It was found that their characteristic feature is the presence of kaolinite showing a higher dehydroxylation temperature (DTA peak at  $670^{\circ}$ C). This kaolinite occurs in grain classes  $2-45~\mu m$ .

#### INTRODUCTION

The North-Sudetic Depression, also referred to as the Bolesławiec Trough, is filled with sedimentary rocks of considerable thickness, largely represented by continental Santonian sediments. In the southern, and particularly south-western, part of the depression these sediments attain a thickness of 400 m, becoming progressively thinner northwards.

The continental Santonian sediments are represented mainly by sandstones with kaolinite cement, containing beds and lenses of kaolinite clays with an admixture of illite. Both kaolinite sandstones and clays can be used as raw materials for the ceramic industry. The mineralogical composition of kaolinite sandstones and the technological properties of ceramic kaolin obtained from them were the subject of an earlier publication (Stoch *et al.*, 1978).

Kaolinite clays become white upon firing and have been used for centuries as a raw material for the pottery industry. Being abundant in the area of Bolesławiec, these clays were the staple raw material utilized by the potters of Bolesławiec, whose earthenware was widely known in central Europe. At present, two underground clay mines, "Bolko" (Milików) and "Janina" (Suszki), are productive near Bolesławiec. They supply potter's clay for plants manufacturing faience, semi-vitreous china-ware and stoneware throughout the country.

The Santonian kaolinite clays from Bolesławiec contain as a characteristic

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component kaolinite showing a higher than normal dehydroxylation temperature (Stoch, 1978). Neither its nature nor genesis has been satisfactorily explained yet. The interesting mineralogy of the clays, as well as their industrial importance, encouraged the authors to study their mineralogical composition. This paper presents the results of mineralogical investigations of clays from the "Janina" mine and the resulting inferences regarding the possibility of their purification and enrichment.

### GEOLOGIC STRUCTURE OF THE JANINA CLAY DEPOSIT

The Janina deposit is situated in the axial zone of the SE part of the North-Sudetic Depression. The productive series consists of sandstones with intervening clay lenses of varying thickness. The rise of this deposit is associated with the development of a delta that once was the estuary of the former Sudetic rivers. As the basin was gradually filled up, the delta shifted to NW (Milewicz, 1974).

The "Janina" mine is 30 m deep. It comprises a series of light clays underlain by dark clays with mudstones and claystones. Down to a depth of 100 m, 15 beds of potter's clay were found, dipping at  $15-10^{\circ}$  to NW. The deposit has a complex geologic structure and is disturbed by several faults. The constituent clays show both horizontal and vertical variation.

At present bed III is mined for clay. Its thickness is 40-60 cm. The clays differ from one another in colour, compactness, and the content of sand fraction. Their colour varies from light-black to grey, and from cream-yellow or beige to brown. They are interbedded in places with sandstones.

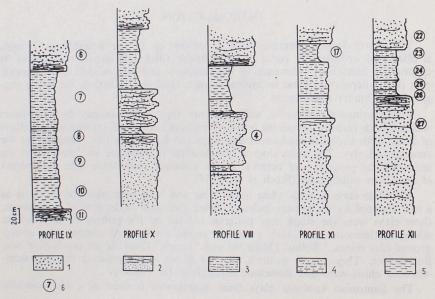


Fig. 1. Geological profiles of clay bed III from the "Janina" mine

1 - coarse-grained sandstone, 2 - fine-grained sandstone with lamination, 3 - very sand-laden clay, 4 - sandy clay, 5 - clay, 6 - sample No.

The top and bottom of the bed in question are made up of weakly compact, crumbly fine- or medium-grained sandstones of white, light-grey, or sometimes cream-yellow colour. On the contact of the top sandstones with the clay bed, higher concentration of iron was noted. Occasionally clay grades into sandstone, increasing progressively its sand content.

In the course of geologic works conducted in the mine, profiles presenting the

lithological variation of the deposit were made (Fig. 1).

#### MINERALOGICAL COMPOSITION OF CLAYS

#### Experimental material

Investigations were carried out on samples collected from two most characteristic geologic profiles of bed III (Fig. 1) and representing clays differing in macroscopic features, as well as top and bottom sandstones. Vertical variation of clays, discernible macroscopically, manifests itself in a different content of the sand fraction and in different colour, the latter being mainly due to the presence of organic matter.

Brief petrographic description of the samples studied is given in Table 1. Sandstone occurring in the deposit generally contain coarse-grained quartz. Their cement is made up of kaolinite, fine-grained quartz and, occasionally, fairly large mica flakes.

Sandstones from the top of clays contain coarse-crystalline kaolinite that forms large flakes and columnar aggregates ("worm-like" kaolinite). It is usually accompanied by coarse-grained muscovite with kaolinitized flakes (samples 4, 6, 22). Sandstones from the bottom of bed III have a cement consisting of fine-grained kaolinite and quartz.

Table 1
Petrographical characteristics of the clays and sandstones from the Janina mine

| Profile | Sample<br>No | Petrographical character | Remarks  |
|---------|--------------|--------------------------|--|
| VIII    | 4            | sandstone                | fine- and medium-grained cement: coarse-grained                  |
|         | -            | the maintaine            | kaolinite with muscovite, quartz                                 |
| IX      | 6            | sandstone                | coarse-grained cement: coarse-grained kaolimite with             |
|         |              |                          | muscovite  |
|         | 7            | clay                     | coarse-grained kaolinite with muscovite                          |
|         | 8            | clay                     | fine-grained kaolinite   |
|         | 9            | clay                     | fine-grained kaolinite   |
|         | 10           | clay                     | fine-grained kaolinite   |
|         | 11           | sandstone                | coarse-grained cement: fine-grained kaolinite, quarti            |
| XI      | 17           | clay                     | very fine kaolinite  |
| XII     | 22           | . sandstone              | coarse-grained cement: coarse-grained kaolinite with mica flakes |
|         | 23           | clay                     | very sand-laden, very fine-grained kaolinite                     |
|         | 24           | clay                     | coarse-grained kaolinite, many muscovite flakes                  |
|         | 25           | clay                     | coarse-grained kaolinite, many muscovite flakes                  |
|         | 26           | clay                     | fine-grained kaolinite   |
|         | 27           | sandstone                | coarse-grained cement: fine-grained kaolinite, quart             |

The clays occurring in the deposit can be divided into two groups. One is represented by clays consisting of very fine-grained kaolinite with grains undiscernible under the microscope, forming characteristic aggregates made up of flakes showing parallel orientation. The other group consists of clays having a high content of kaolinite in the form of fairly large scales and columnar aggregates. Such clay also contains, as a rule, muscovite flakes kaolinitized to varying degrees.

Clay containing coarse-grained kaolinite commonly occur in the top and middle parts of the bed (samples 7, 24, 25). Near the bottom they grade into clays in which kaolinite is fine-grained, and which do not contain larger mica flakes.

#### Methods

The mineralogical composition of clays was determined using X-ray diffractometry and thermal analysis, X-ray diffraction patterns were obtained with a DRON—1.5 diffractometer. The content of quartz, kaolinite, minerals of the mica group (muscovite, sericite, illite), and anatase was determined quantitatively using external standards. Minerals showing the degree of crystallinity and grain-size distribution close to the minerals present in the sample were selected as standards. To check the correctness of X-ray determinations of the clay minerals content, the results were compared with the amount of water given off at  $400-700^{\circ}$ C (dehydroxylation of clay minerals), determined from TG curves, and with  $K_2$ O content (the content of minerals of the mica group). The intensity ratio of the lines  $I_{020}/I_{1\bar{1}0}$  on X-ray diffractograms of disoriented samples was assumed as the X-ray index of crystallinity (Stoch, 1974).

To detect montmorillonite and mixed-layer illite/montmorillonite minerals, fractions of grain-size  $<2~\mu m$  were separated, and X-ray diffraction patterns were taken of air-dry and glycol-treated sedimented samples of these fractions. The content of montmorillonite was determined quantitatively using a method based on the amount of water coordinating Ca²+ cations, which was obtained from TG curves for samples converted into Ca-form and treated with methylene blue to remove free water molecules from the interlayer spaces of montmorillonite (Wacławska, 1978).

Mineralogical investigations were carried out on samples from which grains larger than 45  $\mu m$  were removed by washing the samples on a sieve. The material coarser than 45  $\mu m$  consisted of quartz and single muscovite flakes. Fractions finer than 2  $\mu m$  were separated for X-ray investigations by sedimentation in a centrifuge.

A clay sample representative of the Janina deposit was separated by sedimentation into grain classes  $>\!45~\mu m,\,45-10~\mu m,\,10-2~\mu m,\,2-0.5~\mu m,\,0.5-0.3~\mu m,$  and  $<\!0.3~\mu m$ . The mineralogical composition of these classes was determined using the methods discussed earlier in this paper. Prior to separation, the suspension was stirred vigirously to achieve complete dispersion, adding ammonia as a stabilizer and adjusting the pH to 8.

# Variability of the mineralogical composition of clays in the deposit

Clays occurring in the "Janina" mine contain kaolinite as the dominant constituent. This kaolinite shows a high degree of crystallinity, and the X-ray crystallinity index  $I_{020}/I_{1\overline{10}}$  has a low value (0.7-1.0). Minerals of the mica group are another principal component of the clays. As appears from microscopic studies, these

are dioctahedral micas of the sericite (fine scales) and detrital muscovite (large flakes) type. Illite appears in grain classes finer than 2 µm. It yields a diffraction line close to 1.0 nm, markedly broadened toward low angles (Fig. 2). Its profile changes after treatment with glycol, which is indicative of the presence of mixed-layer minerals of the illite/montmorillonite type whose diffraction line overlaps that of illite. Upon glycol treatment it shifts and becomes diffuse.

In X-ray diffraction patterns of the fractions  $<45\,\mu m$ , the 1.0 nm line is a superposition of the sharp muscovite and sericite line and the diffuse illite line. Due to this, broadening of the 1.0 nm line and a reduction in its intensity indicate that the content of illite has increased and that of muscovite and sericite decreased (Table 2).

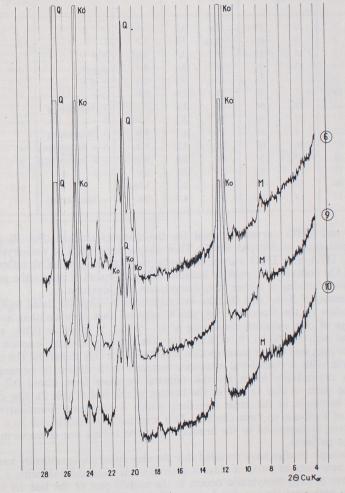


Fig. 2. Fragments of X-ray diffraction patterns of the grain class < 45 µm separated from clays (samples 9, and 10) and sandstone cement (sample 6)

Table 2 Mineralogical characteristics of the  $<45~\mu m$  fraction of clays and sandstones from the profiles of the Janina mine

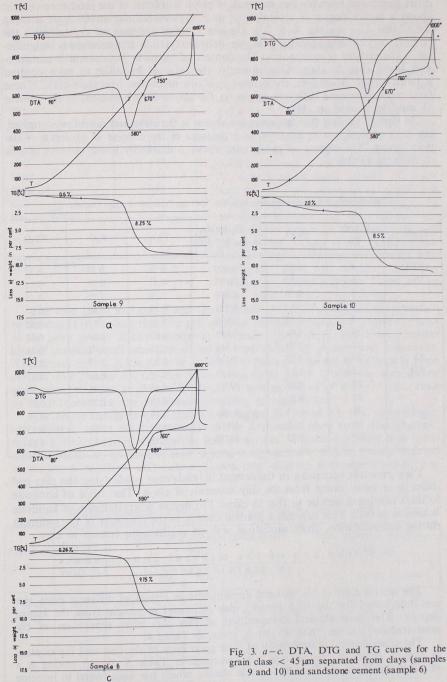
|         |              |       | ral compo      |        | Kao-                       | X-ray index                                  |   | De-<br>flexion<br>on the             | Weight                             |
|---------|--------------|-------|----------------|--------|----------------------------|--|---|--------------------------------------|------------------------------------|
| Profile | Sample<br>No | micas | kao-<br>linite | quartz | linite/<br>illite<br>ratio | of cry-<br>stallinity<br>of the<br>kaolinite | Intensity of the<br>mica (1 nm)<br>X-ray line | DTA<br>and<br>DTG<br>curves<br>670°C | loss<br>weight %<br>20 –<br>–160°C |
| VIII    | 4            | 9     | 74             | 17     | 8.2                        | 0.66   | +   |                                      | 0.75                               |
| IX      | . 6          | 9     | 66             | 25     | 7.3                        | 0.7  |   |                                      | 0.25                               |
|         | 7            | 16    | 55             | 29     | 3.4                        | 0.87   | ++  | + -                                  | 1.00                               |
|         | 8            | 18    | 58             | 24     | 3.2                        | 0.87   | +++   | ++                                   | 1.00                               |
|         | • 9          | 17    | 53             | 30     | 3.1                        | 0.9  | +++   | ++                                   | 0.50                               |
|         | 10           | 21    | 54             | 25     | 2.6                        | 0.9  | ++  | +                                    | 2.00                               |
|         | 11           | 18    | 64             | . 18   | 3.6                        | 0.7  | + broadening                                  |                                      | 1.25                               |
| XI      | 17           | . 23  | 50             | 28     | 2.2                        | 1.0  | +++   | ++                                   | 0.50                               |
| XII     | 22           | 8     | 54             | 38     | 6.7                        | 0.6  | + broadening                                  |                                      | 0.01                               |
|         | 23           | 16    | 61             | 23     | 3.8                        | 0.8  | ++ broadening                                 | +                                    | 1.50                               |
|         | 24           | 15    | 54             | 31     | 3.6                        | 0.76   | ++ broadening                                 | ++                                   | 1.25                               |
|         | 25           | 19    | 56             | · 25   | 2.9                        | 0.9  | .++   | ++                                   | 1.00                               |
|         | 26           | 24    | 54             | 22     | 2.2                        | 0.9  | North Rich                                    | ++                                   | 0.01                               |
|         | 27           | 14    | 56             | 30     | 4.0                        | 0.6  | + broadening                                  | +                                    | 0.00                               |

DTA and DTG curves obtained for the samples studied (Fig. 3) display pronounced peaks at 580 and 980°C. Their shapes are typical of well-crystallized kaolinite. DTA and DTG curves for some clays show a marked inflexion at 670°C on the endothermic peak of kaolinite. This inflexion is due to the presence of kaolinite showing a higher dehydroxylation temperature.

The results of X-ray and thermal investigations of clays are listed in Table 2. From studies of the fractions <45 µm it appears that they contain a similar assemblage of clay minerals consisting of 16-20 wt. % of micas (illite, sericite, muscovite) and 50-60 wt. % of kaolinite. The content of sand fraction in the clays is varying, and so are some specific features of the clay minerals. The content of kaolinite with a disordered structure increases with depth. In consequence, the X-ray crystallinity index for this mineral increases from about 0.7 or 0.9 for the top parts of clay to 0.9 for the bottom of the bed (Table 2). The content of micas increases in the same direction, which is expressed quantitatively by the ratio of kaolinite to mica content. This increase is primarily due to a higher illite content, as suggested by the broadening of the 1.0 nm line of micas in X-ray diffraction patterns.

Microscopic studies have revealed that the clay minerals, specifically kaolinite, from the near-bottom parts of clays is finer-grained. Kaolinite showing a higher temperature of dehydroxylation occurs in the middle part of the bed, its content decreasing both near the top and bottom. The clay samples in which it is present contain large muscovite flakes as well.

Clay minerals present in the cement of sandstones overlying the clay bed



differ somewhat from the clay minerals of clays. Kaolinite of the sandstone cement shows a higher degree of crystallinity, its X-ray crystallinity index  $I_{020}/I_{1\overline{10}}$  being 0.6 (Table 2 — samples 4, 6, 22). Despite so high a degree of crystallinity, the content of kaolinite showing a higher dehydroxylation temperature is insignificant in the cement of sandstones. The content of micas in the cement is considerably lower than in clays. Consequently, the ratio of kaolinite to mica content is twice higher. Moreover, the cement contains much less iron than clays. These facts seem to suggest different origins of the clay minerals present in the cement of sandstones and in clays.

In view of the fact that feldspars are absent in the clays and sandstones studied, the K<sub>2</sub>O content can be assumed as a measure of the content of minerals of the mica group. The cement of sandstones shows a markedly lower content of this constituent (Table 3).

\$T\$ a ble  $\,3$  Characteristic chemical components in the  $\,<\!45~\mu m$  fraction of clays (weight  $\,\%\!)$ 

| Profile | Sample<br>No | Fe <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> soluble in the 9% HCl | TiO <sub>2</sub> | K <sub>2</sub> O | Na <sub>2</sub> O |
|---------|--------------|--------------------------------|--|------------------|------------------|-------------------|
| VIII    | 4            | 0.17                           | 0.020  | 0.76             | 0.77             | 0.35              |
| IX      | 6            | 0.53                           | 0.095  | 0.51             | 0.71             | 0.25              |
|         | 7            | 0.58                           | 0.016  | 0.70             | 1.29             | 0.15              |
|         | 8            | 0.64                           | 0.011  | 0.78             | 1.46             | 0.07              |
|         | 9            | 0.63                           | 0.021  | 0.80             | 1.35             | 0.15              |
|         | 10           | 0.81                           | 0.019  | 0.87             | 1.69             | 0.08              |
|         | 11           | 2.70                           | 1.310  | 0.73             | 1.41             | 0.23              |
| XI      | 17           | 0.27                           | 0.020  | 0.53             | 1.87             | 0.24              |
| XII     | 22           | 0.57                           | 0.019  | 0.45             | 0.66             | 0.17              |
|         | 23           | 0.65                           | 0.013  | 0.86             | 1.31             | 0.08              |
|         | 24           | 0.53                           | 0.014  | 0.68             | 1.22             | 0.07              |
|         | 25           | 0.55                           | 0.060  | 0.78             | 1.52             | 0.10              |
|         | 26           | 0.55                           | 0.012  | 0.84             | 1.89             | 0.12              |
|         | 27           | 0.72                           | 0.270  | 0.59             | 1.15             | 0.12              |

Clay minerals occurring in the cement of sandstones underlying the clay bed differ to a lesser extent from the clay minerals of clays. The ratio of kaolinite to mica content is similar to that in clays. The degree of crystallinity of kaolinite is similar as well. This suggests a gradual change in the character of the sediment during sedimentation, from sandstone with an argillaceous cement to clay.

## Distribution of the mineral constituents in grain classes

The distribution of the mineral constituents in classes of different grain size was determined for the JC potter's clay recovered at present from the Janina deposit. The mineralogical composition of this clay after separation of the sand fraction coarser than 45  $\mu m$  is given in Table 4.

The mineralogical composition of each grain class of the clay and the content of typical chemical components are presented in Table 5. Worth noting is a relatively low content of micas in these classes, which has been found to increase

 $$\rm T~a~b~l~e~4$$  Chemical composition of the  $<\!45~\mu m$  fraction of  $\rm JC_1S$  potter's clay from the "Janina" mine (weight %)

| Content<br>weight % |
|---------------------|
| 59.03               |
| 27.23               |
| 0.74                |
| 0.65                |
| 1.07                |
| 1.14                |
| 0.09                |
| 1.51                |
| 9.16                |
| 100.62              |
|                     |

Analyst: L. Budek.

significantly only in the classes finer than 0.3 µm and 0.5 – 0.3 µm (Fig. 4). A feature deserving note is the high degree of crystallinity of kaolinite in all the grain classes. It is somewhat lower in the class 0.3 – 0.5 µm, while poorly ordered kaolinite occurs only in the grain class < 0.3 µm, its percentage, however, being very small (12.4 wt. %). Kaolinite showing a higher temperature of dehydroxylation was found in the grain class 2 – 45 µm, and DTA and DTG curves for these fractions display an additional peak at 670°C (Fig. 5).

Illite from the grain classes  $< 0.3 \mu m$  and  $0.3-0.5 \mu m$  contains an admixture of mixed-layer illite/montmorillonite. Its content, however, is insignificant because glycol treatment does not cause any pronounced changes of the profile of the 1.0 nm line of micas. Treatment with methylene blue has revealed that the content of montmorillonite layers in the grain class  $< 0.3 \mu m$  is 17 wt. %

The data listed in Table 5 and the diagram of the mineralogical composition of the clay (Fig. 6) show that fine-grained illite prevails quantitatively over minerals of the mica group. It concentrates in the grain classes finer than 2  $\mu m$ . Coarser classes contain small amounts of micas represented by sericite and muscovite. Also worth noting is the ratio of kaolinite to mica percentage in respective grain classes. For classes  $<2~\mu m$  this ratio varies from 3.3 to 1 with the diminishing grain size, whereas in classes  $2-45~\mu m$  it attains values of 0.6-0.9, i.e. close to those noted for the argillaceous cement of sandstones.

The above results provide evidence to suggest that there are two, mineralogically distinct, types of clay material in the Santonian clays from the "Janina" mine: 1. fine material of grain-size less than 2  $\mu$ m, consisting of illite with interstratifications of montmorillonite layers, and kaolinite with a poorly ordered structure; 2. medium- and coarse-grained clay of grain-size more than 0.5  $\mu$ m,

Table 5

Mineral composition of the fractions of clay from the "Janina" mine

| Fractions | Content<br>of fraction | Characteristic chemical components weight % |                  |                   |                  |                  | Main mineral components weight % |           |        |
|-----------|------------------------|---|------------------|-------------------|------------------|------------------|----------------------------------|-----------|--------|
| μm        | weight %               | Fe <sub>2</sub> O <sub>3</sub>              | TiO <sub>2</sub> | Na <sub>2</sub> O | K <sub>2</sub> O | H <sub>2</sub> O | micas                            | kaolinite | quartz |
| >45       | 18.1                   | 0.09  | 0.21             | 0.17              | 0.14             | _                | 1                                | -         | 99     |
| 45 – 10   | 17.8                   | 0.30  | 0.75             | 0.18              | 0.52             | 7.0              | 5                                | 48        | 47     |
| 10 - 2    | 27.1                   | 0.38  | 0.78             | 0.15              | 0.91             | 8.5              | 9                                | 58        | 33     |
| 2 - 0.5   | 19.0                   | 0.94  | 0.92             | 0.27              | 2.03             | 10.25            | 20                               | 67        | 13     |
| 0.5 - 0.3 | 5.5                    | 0.66  | 0.78             | 0.15              | 1.74             | 11.25            | 21                               | 74        | 5      |
| <0.3      | 12.4                   | 1.55  | 0.92             | 0.23              | 3.82             | 8.75             | 48                               | . 48      | 4      |

made up of well-ordered kaolinite (including kaolinite showing a higher dehydroxylation temperature) and small amounts of micas occurring as sericite and detrital muscovite.

From the above considerations it seems feasible that the origin of these two types of material was different. The coarser material could have owed its origin to the washing-out of the pre-existing sandstones with a kaolinite cement. The clays formed, therefore, by simultaneous deposition of these two materials, as well as of quartz sand. The rate of supply of these materials changed with time. This is reflected in the vertical variation of the mineralogical composition observed in the profile, as well as is the cause of horizontal variability of the clays. The content of coarser material increased progressively toward the top of the bed. At a certain point, the nature of the deposited sediment changed completely, and sandy-clay sediment began to form, giving rise to the sandstone layer.

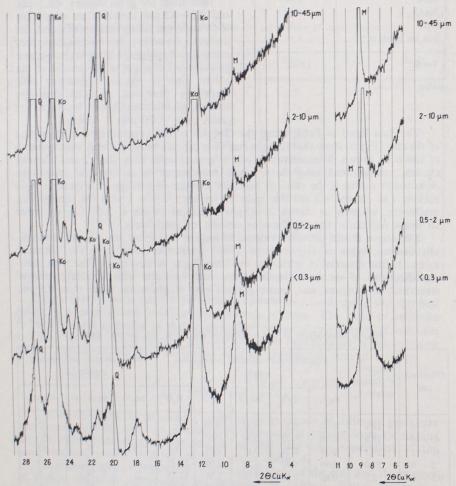


Fig. 4. Fragments of X-ray diffraction patterns of grain classes separated from the JC<sub>1</sub>S clay

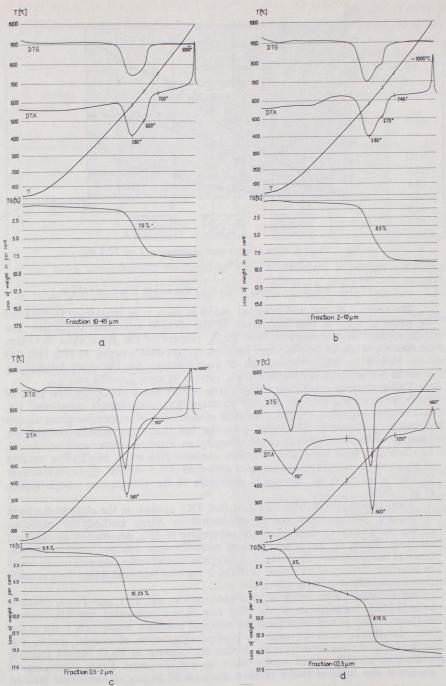


Fig. 5. a-d DTA, DTG and TG curves for grain classes separated from the JC<sub>1</sub>S clay

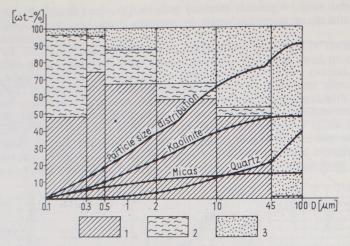


Fig. 6. Diagram of the mineralogical composition of the  $JC_1S$  clay I - kaolinite, 2 - micas, 3 - quartz and remaining

#### Iron and titanium oxides in the clays

The content of iron and titanium oxides is clays is an important factor from the point of view of their utilization by the ceramic and other industries. The clays studied have a relatively low  $Fe_2O_3$  content in the grain class <45  $\mu$ m, amounting to about 0.55 wt. % This class corresponds roughly to clay that has been washed to reduce the amount of sand fraction. On the other hand,  $TiO_2$  content in the clays is relatively high, varying from 0.7 to 0.8 wt. %

The amount of chemically soluble iron is very small (Table 3). The bulk of  $Fe_2O_3$  is structural iron of the clay minerals. This statement is supported, e.g. by the data regarding the mineralogical composition of respective grain classes of the clays (Table 5). Classes of grain-size less than 2  $\mu$ m contain the greatest amount of  $Fe_2O_3$ , showing simultaneously an increased illite content. It can be calculated from these data that illite contains 3.16 wt. %  $Fe_2O_3$ . The content of structural iron in kaolinite has been estimated at 0.2-0.3 wt. % i.e. it is similar to that noted in other clay-sandy sediments of the Bolesławiec trough (Stoch et al., 1978).

X-ray investigations have revelated that TiO<sub>2</sub> appears in the clays in the form of anatase. The anatase content determined by X-ray methods in respective classes of the clay corresponds to the percentage of TiO<sub>2</sub> determined by chemical methods (Table 5). No other titanium minerals were detected, and to correlation was noted between the content of TiO<sub>2</sub> and that of other minerals which could be titanium carriers, as e.g. micas or illites. It has also been found that TiO<sub>2</sub> content varies insignificantly with the grain size.

On the basis of the mineralogical composition and TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> contents in individual grain classes of the JC<sub>1</sub>S clay, it was calculated how the content of these oxides, as well as of the three principal minerals, would very it the grainsize distribution were changed by gradual elimination of coarser grains, e.g. by washing. It was found (Table 6) that the content of Fe<sub>2</sub>O<sub>3</sub> would increase while that of TiO<sub>2</sub> would remain more or less the same. From mineralogical studies it also appears that a division diameter of 10 µm, or somewhat greater,

| di seletation de la constanta della constanta de la constanta de la constanta de la constanta | Content                | Mi    | neral composi | Iron and titanium oxides content weight % |                                |                  |
|---|------------------------|-------|---------------|---|--------------------------------|------------------|
| Grain-class<br>μm   | of grain<br>class<br>% | micas | kaolinite     | quartz<br>and<br>remaining                | Fe <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> |
| <63   | 100.0                  | 14    | 47            | 39  | 0.60                           | 0.71             |
| <45   | 81.8                   | 17    | 58            | 25  | 0.70                           | 0.84             |
| <10   | 64.0                   | 21    | 60            | 19  | 0.80                           | 0.86             |
| <2  | 36.9                   | 30    | 61            | 9   | 1.08                           | 0.89             |
| < 0.5   | 17.9                   | 44    | 55            | 5   | 1.22                           | 0.84             |
| < 0.3   | 12.4                   | 48    | 48            | 4   | 1.53                           | 0.92             |

is the most advantageous for washing processes because it permits obtaining a material with the highest possible kaolinite content, a relatively low content of micas and quartz (Table 6), and the content of Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> less than 0.8 wt. %.

Owing to a relatively low  $Fe_2O_3$  content, the clays show good whiteness (Table 7). The whiteness was determined on powdered samples of fractions <45  $\mu$ m

 $\begin{array}{c} & \text{T a b le 7} \\ \text{Technological properites of the } \text{JC}_{1}\text{S} \text{ potter's} \\ \text{clay from the "Janina" mine} \end{array}$ 

| Technological properties          | Values                |
|-----------------------------------|-----------------------|
| Drying shrinkage                  | 5%                    |
| Bending strenght after drying     | 24 kG/cm <sup>2</sup> |
| Refractoriness                    | 165/171 sP            |
| Firing shrinkage:                 |                       |
| 1473°K (1200°C)                   | 9.8%                  |
| 1523°K (1250°C)                   | 11.4%                 |
| 1573°K (1300°C)                   | 13.4%                 |
| Water absorption after firing at: | pel basicos           |
| 1473°K (1200°C)                   | 11.2%                 |
| 1523°K (1250°C)                   | 7.2%                  |
| 1573°K (1300°C)                   | 2.7%                  |
| Whiteness after firing at:        |                       |
| 1473°K (1200°C)                   | 78%                   |
| 1523°K (1250°C)                   | 76%                   |
| 1573°K (1300°C)                   | 68%                   |

fired at 1300°C, as measurements on clays in the natural state appeared to be unreliable due to the presence of varying amounts of organic matter and quartz. Chemical treatment with hydrochloric acid to remove free Fe<sub>2</sub>O<sub>3</sub> fails to increase the whiteness of clay because of the low content of chemically soluble (free) Fe<sub>2</sub>O<sub>3</sub>.

The kaolinite cement of sandstones overlying the clays has a much lower Fe<sub>2</sub>O<sub>3</sub> content. The cement of sandstones occurring in the bottom of the clay bed contains a little more Fe<sub>2</sub>O<sub>3</sub>, but it is mostly "free" iron. After its removal, the amount of iron is similar to that present in clays.

After separation of sand fraction, the cement of the weakly compact sandstones from the top of the clay bed has a mineralogical composition similar to kaolin, and a low content of Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. Since it also shows very good whiteness, it can find application as kaolin in the ceramic industry.

Santonian kaolinite clays from bed III of the "Janina" mine are characterized by the presence of kaolinite showing a high degree of crystallinity. In the upper part of the clay bed, the degree of structural ordering of kaolinite is higher than found in residual kaolins  $(I_{020}:I_{11\overline{1}}]$  about 0.6). A part of this kaolinite shows a higher dehydroxylation temperature than ordinary kaolinite (DTA peak at 670°C). Higher concentration of such kaolinite was noted in the middle part of the bed, where detrital muscovite was also found. It is feasible that kaolinite showing a higher dehydroxylation temperature owes its origin to kaolinitization of muscovite flakes. Besides coarse-grained kaolinite showing a high degree of crystallinity and muscovite, the clays studied contain fine-grained illite with interstratifications of montmorillonite layers in the ratio of 3:1, as well as fine--grained kaolinite displaying a disordered structure. These minerals concentrate in the grain class < 0.5 µm.

The quantitative ratio of these two types of mineral constituents (coarseand fine-grained) varies in the vertical profile. The content of illite and fine--grained kaolinite increases towards the bottom of the bed, and the ceramic properties of the clays vary accordingly.

From the above studies it seems feasible that coarse-grained kaolinite originates from the cement of the Santonian sandstones in which the clays occur.

The clays under study contain a relatively small amount of Fe<sub>2</sub>O<sub>3</sub>. It is mainly iron entering into the structure of illite. The clays show very good whiteness when fired. The gretaer part of quartz can be removed by washing, and washed clay can be obtained with properties close to kaolins used in the whiteware industry.

The clays contain relatively much TiO<sub>2</sub> (about 0.8 wt. %), which occurs as fine-grained anatase. The ceramic industry requires raw materials with the smallest possible content of this oxide. Therefore, taking into account the advantageous properties of these clays, it is advisable to devise a method of reducing TiO, content.

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#### CHARAKTERYSTYKA MINERALOGICZNA IŁÓW KAOLINITOWYCH Z KOPALNI JANINA W SUSZKACH KOŁO BOLESŁAWCA DOLNY ŚLASK

#### Streszczenie

Wśród piaskowców santońskich występujących na obszarze niecki północnosudeckiej występują pokłady biało wypalających sie iłów kaolinitowych. Niektóre z nich stanowia cenny surowiec ceramiczny. Zbadano skład mineralny takich iłów wydobywanych w kopalni Janina w Suszkach koło Bolesławca (tab. 2 i 5, fig. 6). Specyficzną cechą tych iłów jest duża zawartość kaolinitu, który charakteryzuje się bardzo wysokim stopniem krystaliczności, nie spotykanym normalnie w glinach. Stopień uporządkowania struktury kaolinitu z górnej cześci warstwy iłów jest większy nawet niż kaolinitu z kaolinów rezydualnych (tab. 2). Cześć tego kaolinitu wykazuje wyższą niż normalny kaolinit temperature dehydroksylacji (pik DTA w 670°C, fig. 3 i 5). Ily te zawierają ponadto detrytyczny muskowit, a w klasie ziarnowej drobniejszej od 0,5 µm stwierdza się znaczna koncentracje illitu zawierającego przerosty pakietów montmorillonitowych w stosunku ilościowym 3:1. Towarzyszy mu kaolinit o niskim stopniu krystaliczności.

W iłach z kopalni Janina da się wyróżnić dwa odrębne mineralogicznie typy materiału ilastego: 1) drobny o ziarnach mniejszych od 2 μm składający się z illitu z przewarstwieniami pakietów montmorillonitu i illitu o słabo uporządkowanej strukturze, 2) średnio i gruboziarnisty o ziarnach większych od 0,5 μm, złożony z kaolinitu o wysokim stopniu krystaliczności (z udziałem kaolinitu o podwyższonej temperaturze dehydroksylacji) oraz niewielkich ilości mik typu serycytu i detrytycznego muskowitu. Pochodzenie tych dwu rodzajów materiału było przypuszczalnie różne. Udział materiału grubszego wzrasta od spagu do

stropu warstwy iłów.

Iły zawierają stosunkowo niewiele żelaza przy znacznej zawartości tytanu występującego w formie anatazu (tab. 3 i 5). Wykazują też bardzo dużą białość po wypaleniu. Przez zmniejszenie zawartości TiO, droga wzbogacania można byłoby uzyskać z nich surowiec zbliżony białością w masie ceramicznej do kaolinów, o znacznie większej od nich plastyczności i wytrzymałości na złamanie.

#### OBJAŚNIENIA DO FIGUR

Fig. 1. Profile geologiczne pokładu III iłów kopalni Janina

1 - piaskowiec gruboziarnisty, 2 - piaskowiec drobnoziarnisty z laminacją, 3 - ił silnie zapiaszczony, 4 - ił zapiaszczony, 5 - il, 6 - nr próbki

Fig. 2. Fragmenty rentgenogramów klasy <45 µm wydzielonej z iłów (próbki 9 i 10) oraz lepiszcza piaskowców (próbka 6) Q - kwarc, Ko - kaolinit, M - mika

Fig. 3. a-c. Krzywe DTA, DTG, TG klasy <45 μm wydzielonej z iłów (próbki 9 i 10) oraz lepiszcza piaskowców (próbka 6)

Fig. 4. Fragmenty rentgenogramów klas ziarnowych wydzielonych z ilu gatunku JC,S

Fig. 5. a-d. Krzywe DTA, DTG, TG klas ziarnowych wydzielonych z iłu gatunku J $C_1$ S

Fig. 6. Diagram składu mineralnego iłu JC, S 1 - kaolinit, 2 - mika, 3 - kwarc i pozostałe

### МИНЕРАЛОГИЧЕСКАЯ ХАРАКТЕРИСТИКА КАОЛИНИТНЫХ ГЛИН ИЗ ШАХТЫ ЯНИНА В СУШКАХ ВБЛИЗИ БОЛЕСЛАВЦА — НИЖНЯЯ СИЛЕЗИЯ

#### Резюме

Среди сантонских песчаников, которые залегают на территории северо--судетской впадины, присутствуют залежи каолинитовых глин белых после обжига. Некоторые являются ценным сырьём керамической промышленности. Был исследован минеральный состав таких глин добываемых в шахте Янина в Сушках вблизи Болеславца (табл. 2 и 5, фиг. 6). Характеристической чертой этих глин является большое содержание каолинита, которому свойственна высокая степень кристаллизации, обычно необнаруживаемая в глинах. Степень упорядоченности структуры каолинита в верхней части пласта глин больше, чем даже в каолините из резидуальных каолинов (табл. 2). Для части этого каолинита свойственна температура дегидроксилации выше, чем для обычного каолинита (пик DTA при температуре в 670°C, фиг. 3 и 5). Кроме этого, в глинах содержится детритический мусковит, а в зерновом классе меньше 0,5 µм была обнаружена большая концентрация иллита, содержащего прослойки монтмориллонитных пакетов в количественном соотношении 3:1. Этому минералу сопутствует каолинит с низкой степенью совершенства структуры.

В глинах из шахты Янина можно выделить два разных минералогических типа глинистого материала: 1. мелкий с зернами меньше 2 дм, состоящий из иллита с прослойками пакетов монтмориллонита и иллита с мало упорядоченной структурой, 2. средний и крупный с зернами больше 0,5 дм, состоящий из каолинита с большой степенью совершенства структуры (с присутствием каолинита, характеризирующегося повышенной температурой дегидроксилации) и небольшого количества слюд типа серицита и детритического мусковита Происхождение этих двух типов материала было, кажется, разное. Содержание более крупного материала возрастает от подошвы до кровли пласта

глин.

Глины содержат относительно небольшое количество железа при большом содержании титана, который присутствует в форме анатаза (табл. 3 и 5). Этим глинам свойственна большая белизна после обжига. Из-за уменьшения содержания ТіО, путём обогащения из этих глин было получено сырьё, которые по белизне в керамической массе близко каолинам более пластичное и с большим сопротивлением излому.

#### ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Геологические профили III яруса шахты Янина 1- крупнозернистый песчаник, 2- мелкозернистый песчаник с ламинацией, 3- глина с большой примесью песка, 4 — песчанистая глина, 5 — глина, 6 — номер образца

Фиг. 2. Фрагменты рентгенограмм класса < 45 дм, выделенного из глин (образцы 9 и 10) и цемента песчаников (образец 6)

Q - кварц, Ко - каолинит, М - слюда

- Фиг. 3. а—с. Кривые DTA, DTG и TG класса < 45 µм, выделенного из глин (образцы 9 и 10) и цемента песчаников (образец 6)
- Фиг. 4. Фрагменты рентгенограмм зерновых классов выделенных из глин типа JC,S
- Фиг. 5. a-d. Кривые DTA, DTG и TG зерновых классов выделенных из глин типа JC,S
- Фиг. 6. Диаграмма минерального состава глин [С.5] 1 — каолинит, 2 — слюда, 3 — кварц и другие