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Kaolinitic clays of Turów open pit as a raw material for the production of ceramic tiles by means of fast firing

Key words

Kaolinitic clays, clays accompanying brown coal, ceramic tiles, fast firing

Abstract

Kaolinitic clays from intercoal complex B of Turów open pit are characterized by advantageous technological parameters required in industry of ceramic tiles. Technological properties of fast-fired clays are influenced, to a large extent, by time and conditions of their thermal treatment. Their fast firing in laboratory roller kiln leads to intense sintering within temperature range 1150—1200°C what results in the increase of total shrinkage and the decrease of water absorption.

Introduction

Light firing clays are important raw material for the production of ceramic tiles. They are a subject of great interest, among others in view of remarkable increase of this output in domestic industry. This growth has taken place mainly within production of floor tiles type *gres porcellanato* at the stable level of the production of wall tiles. The amount of current production of ceramic tiles in Poland is estimated at ca. 45 million m^2py wherein the share of floor tiles amounts to 50% (Pieczarowski 2003). Unfortunately, the development of production of Polish ceramic tiles factories has not corresponded with the increase of output of clays, especially light firing ones. These clays often occur together with stoneware and refractory clays. Traditionally,

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for the production of wall and floor light firing tiles the clays of Zebrzydowa, Gozdnica and Jaroszów deposits from Lower Silesia as well as of Zapniów and Żarnów deposits (the latter is also known as Paszkowice) in central Poland are being used. Their brief characteristics has been given in the last years in papers by Lewicka et al. (2001) and Pieczarowski (2003). However, domestic resources of these clays are rather poor. Because of this fact waste clays which were stored on clay dump in Zebrzydowa are met with more and more interest. According to present-day estimation this dump contains ca. 2 million t of good quality raw material. Currently, the *Ekoceramika* enterprise in Nowogrodziec (Lower Silesia) produces processed clay BB1W (5—8 thousand tpa) and light firing granulated product named *Magnat* (5—7 thousand tpa) (Lewicka et al. 2001). However, these products are characterized by disadvantageous, elevated content of colouring oxides (1.8—2.2%) and sometimes they do not show required stability of technological parameters (Pieczarowski 2003). Light firing clays also co-occur with stoneware and refractory clays in exploited deposits of brown coal (Turów, Bełchatów). The clays from Turów brown coal open pit, exploited in intercoal complex B (Fig. 1), are partly processed in SURMIN-KAOLIN enterprise in Nowogrodziec. The granulated materials, mainly in sorts TC1/W and TC1/WB, are being obtained by mixing of these clays with kaolin by-products from the process of washed kaolin production. They are characterized by high whiteness after firing (ca. 80%) and advantageous reological properties. As shortcomings one should consider the presence of fine-dispersed brown coal, share of which is estimated for ca. 0.6% (Lewicka et al. 2001) as well as relatively high price of this raw material. It is well-known that clayey raw

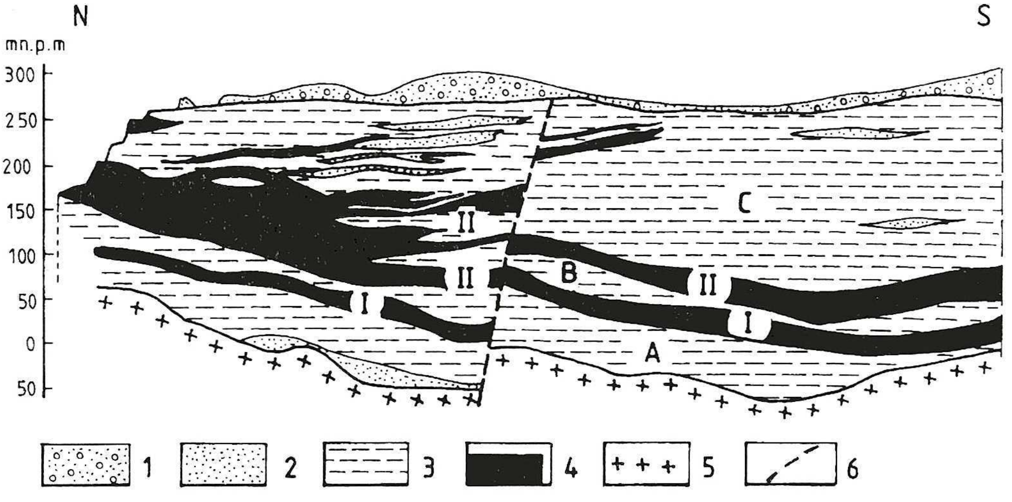

Fig. 1. Geological cross section of Turów brown coal open pit (Rippel, Pace 1979)
1 — Quaternary sediments, 2 — Tertiary sands, 3 — Tertiary clayey rocks, 4 — brown coal, 5 — Rumburk granite, 6 — fault, A — bed A, B — intercoal complex B, C — bed C, I — bed I of brown coal (lower), II — bed II of brown coal (upper)

Rys. 1. Przekrój geologiczny złoża węgla brunatnego Turów (Rippel, Pace 1979)
1 — osady czwartorzędowe, 2 — piaski trzeciorzędowe, 3 — trzeciorzędowe skały ilaste, 4 — węgiel brunatny, 5 — granit rumburski, 6 — uskok, A — pokład A, B — kompleks międzywęglowy B, C — pokład C, I — pokład I węgla brunatnego (dolny), II — pokład II węgla brunatnego (górny)

materials applied in the ceramic tile industry should be characterized, among others, by the low content of the carbon (below 0.3% C) (Pieczarowski 2003).

On account of the low price, the producers of ceramic tiles are interested in raw clays being obtained casually during the exploitation of brown coal, among others in Turów open pit. The shortcoming of such a raw material is its changeability and — particularly — contamination by brown coal as well as by pyrite and siderite concretions. These difficulties can be solved, to some extent, in brown coal open pits by means of selected storing of exploited raw materials on secondary heaps. In a paper by Pytliński and Strempski (1994) performed on the example of clays of Turów brown coal deposit which were being stored for a long period of time (thirteen years to be exact) it was shown that such chemical processes as oxidation of organic matter and pyrite decomposition occurred. They lead to the improvement of properties, especially of these clays which are impured by organic matter. It allows for their utility both in raw state and after benefication. However, this improvement is not possible in all the cases. So, in clays being impured by pyrite the improvement of properties takes place which allows for their utilization only in a raw state. They cannot be used as a raw material for benefication. Finally — according to paper by Pytliński and Strempski (1994) — clays impured by spherosiderites are not suitable for ceramics in the raw state as well as after benefication. So, one of the essence factors having an effect on the possibility of utilization of Turów clays accumulated on a secondary storage is their mineral composition.

Clays of Turów deposit for many years have been a subject of technological interest, particularly of ceramic industry. This can be confirmed by a great number of publications on this topic, both of basic character and applied one. As it follows from the paper by Ratajczak and Wiśniewski (1999) the amount of these papers is more than fifty. Ceramic properties of Turów clays have been determined so far after their traditional firing. The changes in technology of ceramic tiles production and common use of fast firing require hence raw material characterization of Turów clays for such a purpose. That is why this problem is the subject of the present paper.

1. Sample material and its mineralogical characteristics

In the complex B of Turów open pit clays useful for ceramic industry are present. They are situated between the first and second bed of brown coal. However, the possibilities of their industrial utilization are limited, what is caused by such factors as: coal content (brown coal inserts sometimes reach thickness ca. 300—500 mm), considerable variety of sand content, contamination by pyrite and siderite concretions as well as high K_2O content exceeding even 2% (Simiczyjew, Jasiński 1995). The scheme of structure of intercoal complex B has been presented in Fig. 2. Its total thickness usually does not exceed 20 m in this part of complex which is suitable for industrial utilization. In the upper part of this profile the coal-contact layer of thickness 1—4 m occurs which is impured by inserts of brown coal. Below it, there is a layer of clayey rock of similar thickness which is commonly determined as *pure clay*. The samples used for studies performed in this paper came also from there. The third layer of clay, 4—6 m thick, is to a large extent contaminated by pyrite, markasite, siderite and also by brown coal inserts. At last,

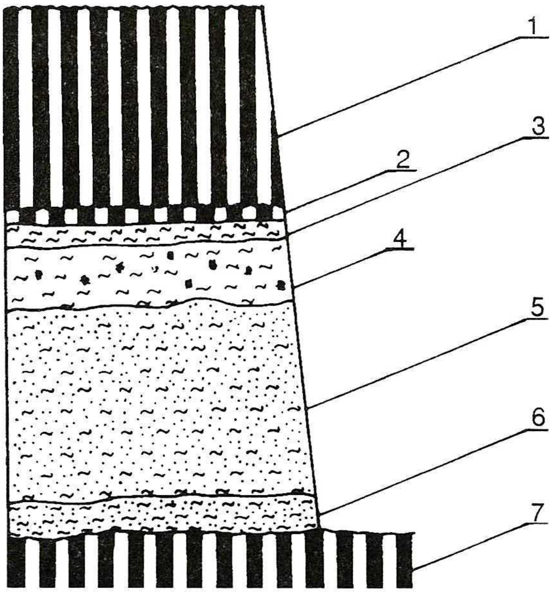

Fig. 2. Variability of occurrence of clayey and clastic rocks in intercoal complex B of Turów open pit (Kaczarewski, Strempski 1995)

1 — bed II of brown coal (upper), 2 — coal-contact layer, 3 — layer of useful clays (*pure clays*), 4 — layer of clay with pyrite, markasite, siderite and brown coal inserts., 5 — layer of clayey rocks with elevated content of clastic material (sands, gravels), 6 — layer of clayey sands and gravels, 7 — bed I of brown coal (lower)

Rys. 2. Zmienność zalegania skał ilastych i okruchowych w kompleksie międzywęglowym B w kopalni Turów (Kaczarewski, Strempski 1995)

1 — pokład II węgla brunatnego (górny), 2 — przywęglowa warstwa kontaktowa, 3 — warstwa iłów użytecznych (czystych), 4 — warstwa iłów z wtrąceniami pirytu, markasytu, syderytu i węgla brunatnego, 5 — warstwa iłów z podwyższonym udziałem materiału klastycznego (piaski, żwiry), 6 — warstwa zailonych piasków i żwirów, 7 — pokład I węgla brunatnego (dolny)

the clayey rocks of the fourth layer (10—20 m) have the composition similar to the previous layer; however, they are characterized by elevated content of clastic material (sands, gravels). Industrial usebility of clayey rocks of the third and fourth layers, as well as the deepest layer of clayey sands and gravels at thickness of 4—8 m is very limited.

As it was stated earlier, the samples used for technological studies originated from the second layer being distinguished in the intercoal complex B. They were sampled at the beginning 2002. In the samples studied kaolinite is the dominant clay mineral. Apart from it, illite occurs in lesser amount. Non-clay minerals are represented by quartz and relics of K-feldspar. In these samples the occurrence of pyrite and siderite in amounts exceeding the X-ray detection limit was not stated. A representative X-ray pattern is given in Fig. 3.

Chemical analyses of the samples studied performed with reference to main elements (Table 1) shows a high Al_2O_3 content in them. It reaches almost 30 wt.%, which takes place in case of kaolinitic clay sampled in February 2002. The characteristic feature of the clays studied is relatively high content of K_2O in them which exceeds even 2 wt.%. Among colouring oxides

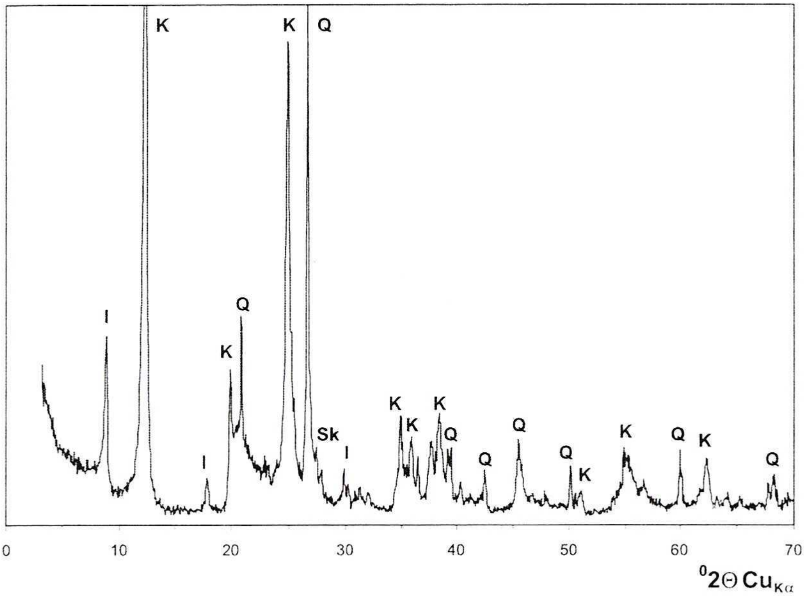

Fig. 3. X-ray pattern of kaolinitic clay from Turów open pit (intercoal complex B, layer of pure clays) sampled in April 2002
K — kaolinite, I — illite, Q — quartz, Sk — K-feldspar

Rys. 3. Dyfraktogram rentgenowski iłu kaolinitowego z kopalni Turów (kompleks międzywęglowy B, warstwa czystych iłów) pobranego w kwietniu 2002
K — kaolinit, I — illit, Q — kwarc, Sk — K-skaleń

TABLE 1

Chemical composition of kaolinitic clays from intercoal complex B of Turów brown coal open pit

TABELA 1

Skład chemiczny iłów kaolinitowych z kompleksu międzywęglowego B z kopalni węgla brunatnego Turów

Content [wt.%] / Compound	Sample collected in		
	February 2002	March 2002	April 2002
SiO_2	52.9	55.0	53.4
Al_2O_3	28.6	27.1	26.7
Fe_2O_3	1.48	1.59	1.34
TiO_2	1.46	1.02	0.99
CaO	0.14	0.10	0.06
MgO	0.52	0.59	0.50
K_2O	1.98	2.02	2.10
Na_2O	0.24	0.26	0.21
LOI	12.7	11.9	15.6
Total	100.02	99.58	100.90

content of TiO_2 is elevated (ca. 1 wt.%) and almost the same as Fe_2O_3. Taking trace elements into account, the increased amount of Sr (70—110 ppm) and especially Ba (310—460 ppm) is noticeable.

TABLE 2

The main technological parameters of kaolinitic clays from intercoal complex B of Turów brown coal open pit

TABELA 2

Podstawowe parametry technologiczne iłu kaolinitowego z kompleksu międzywęglowego B z kopalni węgla brunatnego Turów

Parameter		Sample collected in		
		February 2002	March 2002	April 2002
Humidity (BN-71/6714-16)	%	22.8	21.6	20.7
Make-up water (BN-83/7011-31)				
Relative	%	25.8	25.1	24.7
Absolute	%	34.8	33.4	32.9
Shrinkage on drying (BN-85/7011-11)	%	6.4	6.0	5.9
Bending strength after drying (BN-83/7011-22)	MPa	2.92	2.75	2.87
Firing shrinkage (BN-85/7011-11)				
1100°C*	%	6.9	7.0	7.2
1150°C*	%	9.8	9.3	9.3
1200°C*	%	10.5	9.8	9.9
1200°C**	%	8.9	9.6	9.2
Total shrinkage (BN-85/7011-11)				
1100°C*	%	13.3	13.0	13.1
1150°C*	%	16.2	15.3	15.5
1200°C*	%	16.9	15.8	15.8
1200°C**	%	15.3	15.6	15.1
Bending strength after firing (BN-83/7011-22)				
1200°C*	MPa	28.95	24.68	27.22
1200°C**	MPa	22.45	19.71	23.14
Water absorption after firing (determined by boiling method according to BN-82/7001-08)				
1100°C*	%	10.7	11.1	12.1
1150°C*	%	5.0	5.2	5.9
1200°C*	%	2.5	2.4	2.7
1200°C**	%	3.3	3.5	4.4

* Firing in laboratory roller kiln.
** Firing in industrial roller kiln.

2. The technological parameters of clays studied and their discussion

The determination of the main technological parameters of clays — both in raw state and particularly after their firing — is important from the viewpoint of designing the composition of ceramic bodies in order to obtain products with expected properties, i.e. the low water absorption and porosity required for ceramic tiles of *gres porcellanato* type. The clays studied were fast fired in roller kilns which are the modern technological solution in ceramic tiles industry. Currently, these kilns are already commonly applied in this technology. In comparison with traditional firing of stoneware floor tiles, which was being performed mainly in tunnel kilns that lasted for a long period of time (ca. 60 hours), firing in roller kilns leads, among others, to the significant diminishing of fuel consumption as well as of reduction of flue gases emission evolving during firing of ceramic tiles.

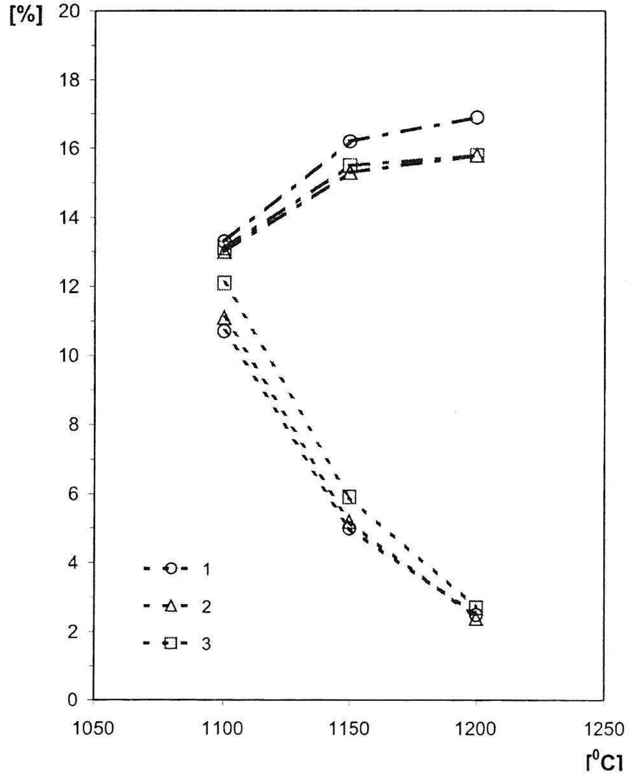

Fig. 4. Total shrinkage (upper part of figure) and water absorption (lower part of figure) of kaolinitic clay from Turów open pit (intercoal complex B, layer of pure clays) after its fast firing in laboratory roller kiln in temperatures 1100°, 1150° and 1200°C

1 — sample collected in February 2002, 2 — sample collected in March 2002, 3 — sample collected in April 2002

Rys. 4. Skurczliwość całkowita (górna część rysunku) i nasiąkliwość (dolna część rysunku) iłu kaolinitowego z kopalni Turów (kompleks międzywęglowy B, warstwa czystych iłów) po jego szybkościowym wypaleniu w laboratoryjnym piecu rolkowym w temperaturach 1100°, 1150° i 1200°C

1 — próbka pobrana w lutym 2002, 2 — próbka pobrana w marcu 2002, 3 — próbka pobrana w kwietniu 2002

The time of firing samples of Turów clays studied was differentiated and amounted to:

— 2 hours & 22 minutes — in laboratory roller kiln,

— 65 minutes — in industrial roller kiln.

As follows from industrial experience, the above-mentioned period of time of thermal treatment leads to the obtaining of comparable results of technological studies. Consequently, the investigations in laboratory roller kiln can give information on the behaviour of clay fired in industrial conditions.

The determination of the main technological parameters of clays studied were performed according to the obligatory Polish standards. The results of these studies together with standard numbers are shown in Table 2.

On the basis of the studies performed the following remarks can be mentioned:

— the high bending strength after drying — which is only a little less than 3 MPa — confirms the considerable plasticity of the clay studied. It results from high content of clay minerals (kaolinite, also illite) which is confirmed by significant amount of Al_2O_3 (almost 30 wt.%),

— technological properties of fast-fired clays are influenced to a large extent by time and conditions of their thermal treatment,

— the clays studied undergo intense sintering within temperature range 1150—1200°C what is accompanied by the increase of total shrinkage and the decrease of water absorption after their firing (Table 2, Fig. 4).

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IŁY KAOLINITOWE Z KOPALNI TURÓW JAKO SUROWIEC DO PRODUKCJI PŁYTEK CERAMICZNYCH METODĄ SZYBKOŚCIOWEGO WYPALANIA

Słowa kluczowe

Ił kaolinitowy, kopaliny towarzyszące, płytki ceramiczne, szybkościowe wypalanie

Streszczenie

Badane iły kaolinitowe pochodzące z kompleksu międzywęglowego B kopalni Turów wyróżniają się korzystnymi parametrami technologicznymi wymaganymi w przemyśle ceramicznym. Na ich właściwości technologiczne po wypaleniu metodą szybkościową w znacznym stopniu wpływają czas i warunki obróbki termicznej. Wypalanie badanych iłów tą metodą w laboratoryjnym piecu rolkowym prowadzi do intensywnego spiekania w zakresie temperatur 1150—1200°C, co zaznacza się m.in. wzrostem skurczliwości całkowitej i spadkiem nasiąkliwości.