Current Issues of Processing and Industrial Utilization of Chalcedonite

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Abstract

Chalcedonite is a natural siliceous sedimentary rock. The only chalcedonite mine located in Poland is in Inowłódz, where an open cast exploitation of "Teofilów" deposits is carried out. Chalcedonite mineral from this deposit is characterized by high changeability in lithology and conciseness. [Tchórzewska D. 1997].
Chalcedonite, as an unique raw material he has been the subject of many studies. Its multiple applications include road and building industry, sanitary engineering (filtration material in wastewater treatment and drinking water purification) and cement industry. This article highlights the particularly significant problems of its processing, connected with separation of various density fraction in a jig and the most important current and new directions for its utilization as a component of concrete mix.

Keywords: chalcedonite, aggregates, mineral processing of raw materials

Introduction – characteristics of the mineral

Chalcedonite mostly consists of cryptocrystalline and microcrystalline chalcedony together with small amounts of autogenous and detrital quartz. [Tchórzewska 1997]. A characteristic feature of all chalcedonite forms are the pores (voids) which take from 5% to 25% of volume and have sizes smaller than 0.5 mm [Kosk 2008]. Depending on the origin and type of mechanical processing, chalcedonite products may be characterized by some variability in chemical composition. An average chemical composition of chalcedonite is presented in Table 1.

Directions of chalcedonite industrial utilization

Building and road industry

The basic direction of utilization of chalcedonite from "Inowlódz" mine is the production of aggregates and aggregates blends used in road and building construction. Chalcedonite aggregate can have any particle size distribution within the range of 0–100 mm, depending on the screening method. Physical and chemical properties of the chalcedonite aggregate is presented in Table 2.

Sanitary engineering

In recent years chalcedonite was utilized in sanitary engineering and environmental protection as a component of filters for purifying of drinking and waste water. Production of strictly selected aggregate size fractions for filters, used also in agriculture, is one of the most important directions of chalcedonite utilization [Kosk 2010]. The CIMB division in Cracow (formerly Institute of Mineral Building Materials – IMMB) is the originator of industrial application of chalcedonite and author of a patent for a "filter material". Chalcedonite filtration properties were investigated by IMMB in a model station of contact filters, purifying drinking water. The specific surface area of the filter grits, determined by the argon adsorption method, was within the range of 4–6 m²/g, while the total pore volume determined in the mercury porosimeter was 0.03–0.04 cm³/g [Tchórzewska 2001].

Chalcedonite shows a high usefulness for the removal of iron compounds from water, and allows for efficient removal of ammoniacal nitrogen from water in a nitrification process [Michel, 2011]. Currently, the manufactured filtration grits particle size is from 0.8 to 2.5 mm.

Cement industry

In the processing chalcedonite, considerable amounts of fine fraction are generated, which after the washing process are sent to clarifiers. Chalcedonite waste fractions collected in these clarifiers, called a chalcedonite sands, have a particle size between 0 and 2 mm. These tailings are characterized by a high SiO_2 content, and mineral composition dominated by chalcedony. It is estimated that currently about 1 million of m³ of chalcedonite waste was deposited in mine clarifiers, and their number is steadily increasing [Kosk 2010].

Fine particle size fractions of chalcedonite have been the subject of many research of possible utilization in cement industry. Some opportunities of chalcedonite utilization as a silica-bearing mineral in Portland clinker production process, were tested both in laboratory and industrial scale. Advantageous feature of this material is its high fragmentation. This fineness and the chalcedony content equally affect the improvement of sinterability and reactivity

Tab. 1. Average chemical composition of chalcedonite from „Teofilów" deposit

Tab. 1 Średni skład chemiczny chalcedonitu ze złoża „Teofilów"

Component – percentage content [%]										
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	TiO_2	P_2O_5	Calcination lost
93.0	3.5	1.7	0.3	0.3	0.17	0.03	0.03	0.10	0.02	1.1

Tab. 2. Characteristics of chalcedonite aggregates [Naziemiec 2014]

Tab. 2 Właściwości kruszyw chalcedonitowych [Naziemiec 2014]

Feature of aggregate	Type of norm	Unit	Type of tested aggregate	
			Grits 2/8 mm	Grits 8/16 mm
Density ρ_a	PN-EN 1097-6	Mg/m^3	2.50	2.44
Density ρ_{rd}	PN-EN 1097-6	Mg/m^3	1.78	1.80
Density ρ_{ssd}	PN-EN 1097-6	Mg/m^3	2.06	2.07
Adsorbability	PN-EN 1097-6	%	16.4	14.5
Dust content	PN-EN 933-1	%	3.3	5.8
Flatness index	PN-EN 933-3	%	12	9
Los Angeles index	PN-EN 1097-2	%	35	32
Frost resistance	PN-EN 1367-1	%	1.0	1.9

in the clinker production process [Garbacik 2005]. Fine fractions of chalcedonite collected in clarifiers are characterized by an average particle size distribution and chemical composition presented in Tables 3 and 4.

Results of investigations show improving of the sinterability for the material containing fine particles of chalcedonite, comparing with the raw material for the production of clinker with the participation of regular sand, slag and anthropogenic raw clay. The reduction of the heat consumption, required for the clinker production process, was also registered. More favorable sinterability of the raw meal containing chalcedonite, compared to the raw meal with an ordinary sand construction, was also confirmed in investigations [Garbacik 2005].

The presented chapter does not cover all industrial use of chalcedonite. There were also carried out research over utilization of chalcedonite to the production of pastes and powders to scrub in household chemicals, as the silica filler for paints and varnishes [Kosk et al. 1995], or for purifying of municipal wastewater [Jeż-Walkowiak et al. 2007]. It should be emphasized that due to the small area of occurrence of chalcedonite in Poland, this is an unique raw material and because the potential for its use in various industries, the process of extraction and enrichment of chalcedonite should be carried out in a rational manner, ensuring an optimal industrial utilization of this mineral.

Main issues of chalcedonite processing technology

The mined chalcedonite contains a significant amount of particle size fraction finer than 0.063 mm, what is undesirable in aggregate production. For this reason, the run of mine is washed prior to processing. Because of the high contents of clay minerals and mineral dust the run of mine washing process requires the use of devices with high efficiency. The process of chalcedonite washing is particularly important in the production of grit filters. In recent years, the washing of chalcedonite was carried out in drum washers. Thereafter, the sword washer of low productivity were used. There has been also attempts of utilization of pressure washer and turbo washer devices. The most favorable results were obtained for turbo washer [Naziemiec 2011]. On the bases of results of washing process tests, following conclusions can be formulated:

- Clay impurities present in chalcedonite have a very diverse susceptibility to soaking
- In static conditions, the soaking process occurs faster for dry impurities, which discloses the physical action of water, which causes swelling of clay minerals
- The shortest soaking time was obtained for dynamic conditions (mixing, attrition). Attrition results in rapid disintegration of clay which contains more of initial moisture
- For the dry clay material, a physical action of high pressure leads to breakage and hence to shorter time of the clay washout

Tab. 3 Average particle size composition of chalcedonite from clarifier (Author's investigations)

Tab. 3. Średni skład ziarnowy chalcedonitu z osadnika [badania własne]

Size fraction [mm]	Percentage content [%]
0 – 0.045	30
0.045 – 0.09	25
0.09 – 0.2	22
0.2 – 0.5	13
0.5 – 1	5
> 1	5

Tab. 4. Chemical composition of fine particle size fractions of chalcedonite from clarifier [Kosk 2008; Kosk 2010]

Tab. 4 Skład chemiczny drobnych frakcji chalcedonitu z osadnika [Kosk 2008; Kosk 2010]

Component	Percentage content [%]
SiO_2	78 – 96
Al_2O_3	1.5 – 11.6
Fe_2O_3	0.2 – 3.1
Na_2O	0.1 – 0.2
K_2O	0.2 – 1.2
TiO_2	0.1 – 0.3

- In order to maximize the washing process effectiveness, there should be applied devices in which the attrition of clay impurities takes part in the aquatic environment

Particular attention should be paid to the turbo washer devices, because they show the most effective washing process of all washing devices. These devices are very similar to sword washers, but instead of so-called swords they have a specially shaped working elements, causing not only mixing and shifting of washed aggregates, but also an intense attrition of impurities through the radial pressure exerted on washed material. The only manufacturer of these devices is a Swiss company Müller & Co. Aufbereitungstechnik. These washers have been used in washing plants in Switzerland and Germany. Figure 1 shows the general appearance of the turbo washer and a view of the shaft washer with attrition elements.

The effectiveness of the washing process significantly increases when clay impurities in the aggregate are subject to prior rubbing. Turbo washers are particularly useful when a hard-to-wash clays occur in the aggregate to be washed. Water consumption in turbo washers is similar to water use in sword washers.

New directions of investigations over industrial utilization of chalcedonite

Institute of Mineral Building Materials in Cracow has developed a recipe of perlite-like material on the basis of chalcedonite. Based on the results of laboratory and pilot-scale tests, a material with properties similar to the natural perlite was obtained, which was patented under "material perlite" (No. PL 346448) [Kosk I. 2000]. In the experimental lab of IMMB it was tested the production perlite-like material in industrial scale. Another way of utilization of chalcedonite for artificial aggregate production is to make a lightweight aggregate from sewage sludge and mineral waste. Pilot plant production of lightweight aggregate carried out in OSiMB in Cracow and it was preceded by a research work carried out in IMBiGS in Warsaw [Góralczyk et al. 2009]. Aggregate for pilot-scale firing was prepared according to the recipe:

– 10% of glass dust from disposal of kinescopes
– 40% of the waste of chalcedonite from "Inowłódz" mine
– 50% of the sludge from the wastewater treatment plant "Płaszow"

Chalcedonite waste from sludge tanks in "Inowłódz" mine was within the particle size 0 to 1 mm and the sample for tests was app. 80% of moisture . The sludge sample used in the moist form having a water content approx. 80%. The materials used to form the aggregate material have first undergone mixing processes. At the first stage the glass dust and chalcedonite were mixed, and then there were mixed sludge from pre-mixed mineral waste. The obtained product was subjected to the process of granulation on disc pelletizer. The obtained granules, after drying process, are presented in Figure 2.

The dried pellets were subjected to firing in the rotary furnace fuel oil. The firing of aggregate was carried

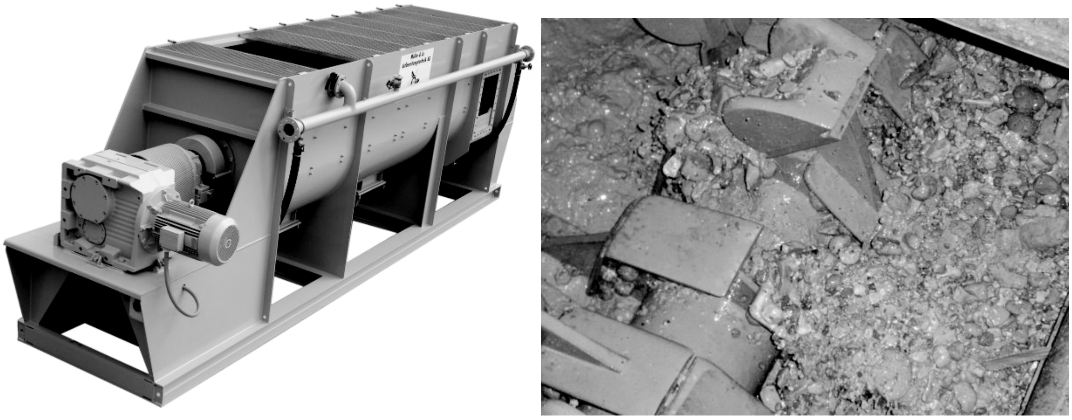

Fig. 1. Turbo washer manufactured by Müller & Co Aufbereitungstechnik AG

Rys. 1 Turbo płuczka produkcji Müller & Co Aufbereitungstechnik AG

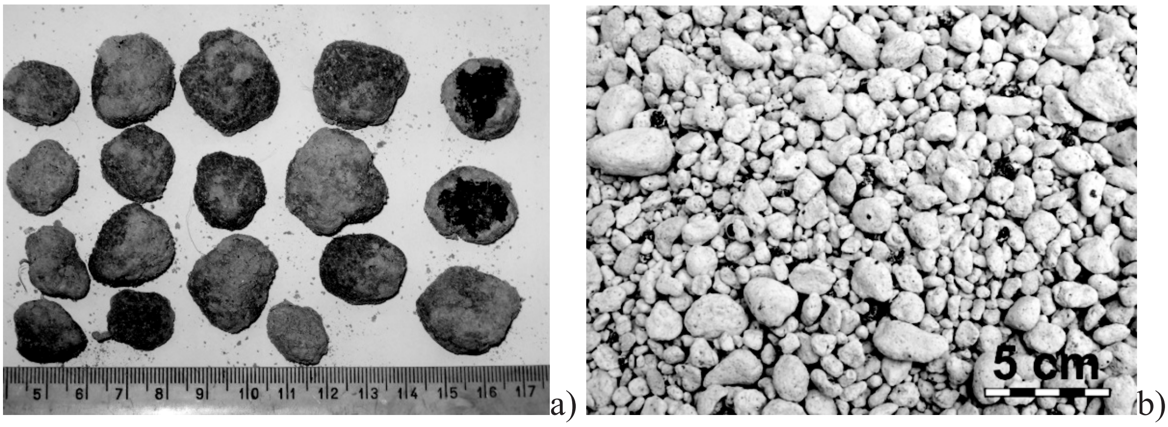

Fig. 2. Wet pellets of artificial light aggregates unaltered (a) and after drying process (b)

Rys. 2 Granule kruszywa sztucznego w stanie wilgotnym (a) i po procesie wypalania (b)

out in a rotary furnace (Fig 3), with no external heat exchanger, in a short cooling zone, with dimensions 0.39/0.54 x 7 m. An energy intensity in production of artificial lightweight aggregates is a very important issue, due to the firing processes at high temperatures. The water content in sewage sludge, which must be evaporated, equals approximately 80%. After mixing of all components the material with moisture of 45% is being obtained and it is requires about 2500 kJ of heat per 1 kg of dry aggregate. It is the largest heat consumption in entire heat balance of the process. Sewage sludge contains a significant amount of organic substances, and thus, in the process of firing the heat obtained from their combustion significantly improves the energetic balance of the process.

The calorific value of the tested sludge was 11 MJ/kg for dry material. The conducted material and heat balance shows that that the unit heat consumption for producing an artificial lightweight aggregate (after taking into account the heat obtained from the combustion of organic materials) is approximately 4500 kJ/kg of aggregate. The unit electricity consumption is about of 30 kWh/Mg of aggregate, with a productivity of 15 Mg/h.

The aggregate were tested for determination the following physical and mechanical properties: bulk density in a loose state, the density of particles, frost resistance, water absorption, resistance to crushing, in accordance with PS-EN 13055-1: 2003 There were also marked contents of heavy metal compounds in aqueous extracts according to PN-EN 1744-3: 2004.

Test results determination of basic physico-mechanical and chemical properties of artificial lightweight aggregate, obtained from a pilot plant test, are shown in Table 5 and 6. Analogous results for aggregates obtained from sewage sludge and mineral waste in pilot scale, are fully compliant with the requirements of that declare leading manufacturers of lightweight aggregates from natural raw materials. The lightweight aggregate obtained from waste in pilot-scale is safe for the environment and shows even slightly higher resistance to crushing and frost than an expanded clay mineral.

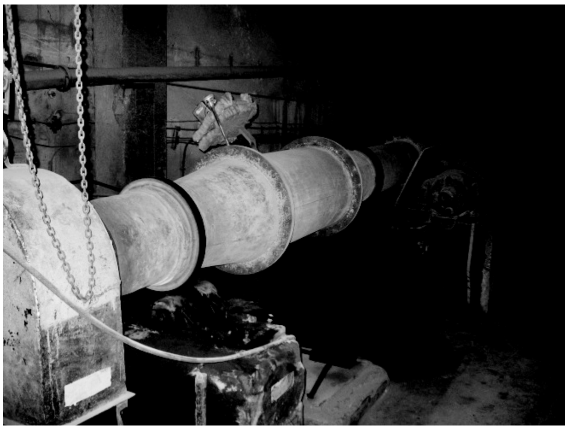

Fig. 3. Rotary furnace for sintering of light aggregates

Rys. 3 Piec obrotowy do wypalanie kruszywa sztucznego

Tab. 5. Investigations over chosen physico-mechanical properties of lightweight aggregate

Tab. 5 Badania wybranych właściwości fizyko-mechanicznych sztucznego kruszywa lekkiego

Type of test	Norm applied in test	Results for:		Nominal values for expanded clay
		Aggregate produced in 1170°C	Aggregate produced in 1200°C	
Absorptivity	PN-EN 1097-6	33.0 [%]	28.6 [%]	≤ 37.0 [%]
Bulk density in loose state	PN-EN 1097-3	550 [Mg/m^3]	560 [Mg/m^3]	400-550 [Mg/m^3]
Frost resistance	PN-EN 13055-1	≤ 1.06 [%]	≤ 0.20 [%]	≤ 2 [%]
Resistence to crushing	PN EN 13055-1	3.1 [MPa]	3.3 [MPa]	≥ 0.8[MPa]

Methods of improvement the quality of chalcedonite enrichment products

Some investigations were conducted in ICiMB on aggregate from "Inowłódz" mine as well as on concretes made with the participation of chalcedonite grits. The characteristics is shown in Table 7.

The test results showed that chalcedonite aggregate allows for obtaining the concrete class C25/30 at an average cement content in concrete about 350 kg/m³. It should be emphasized a high frost resistance of concrete with chalcedonite aggregate (the reduction in its compressive strength was not registered even after 150 cycles of freezing-defrosting). In contrast, an undesirable feature of the concrete produced from this aggregate is its high absorbability of over 14% by weight.

Analyzing the results of density and water absorption and absorption of chalcedonite grits and concrete, it was highlighted the purposefulness of the aggregate separation based on its variable density. Suitable tests were performed in the laboratory jig at AGH University of Science and Technology. The test was performed on a size particle size class 4/8 mm and 8/16 mm. Four samples from four different layers of the jig were taken in order to determine the water absorption and density. The results are shown in Table 8.

The obtained results indicate the purposefulness of densimetric separation of chalcedonite products from "Inowłódz" mine. The jig products in the form of grits to concrete have far less water absorption while filtration grits have increased surface area. Both of these features are very important in the case of application of grits to concrete and filter components. Grits with a lower absorption guarantee obtaining of concrete with more favorable quality parameters. High water absorption increases the ratio of water/chalcedonite (w/c) in the concrete mix, which is disadvantageous. The ratio of the w/c in concretes should not exceed 0.6. Using chalcedonite with a water absorption of 14%, water in amount corresponding to the ratio of w/c value 0.76 should be added in order to obtain the proper consistency of concrete. At the water absorption aggregate about 10% the w/c ratio should be less than 0.6.

Tab. 6. Investigations over washing out of Cr, Cd, Cu, Ni, Pb, Zn from the lightweight

Tab. 6 Badanie wymywalności Cr, Cd, Cu, Ni, Pb, Zn ze sztucznego kruszywa lekkiego

Type of test	Norm applied in test	Tests results [mg/l]	Nominal values [mg/l]
Determination of hazardous substances in aqueous extracts according to: PN-EN 1744-3:2004	PN-EN 1233: 2000	Cr < 0,05	0.2
	PN-EN ISO8288: 2002	Cd- < 0,02 Cu < 0,05 Ni- < 0,1 Pb- < 0,2	0.2 0.5 0.5 0.5

Tab. 7. Properties of hardened concrete based on chalcedonite aggregate [Kosk et. Al, 2005]

Tab. 7 Właściwości stwardniałego betonu na bazie kruszywa chalcedonitowego [Kosk i inni, 2005]

Feature of concrete	Norm applied in test	Unit	Value
Frost resistence after 150 cycles of freezing/defrosting (weight loss)	PN-85/B-04500	%	1,0
Frost resistence after 150 cycles of freezing/defrosting (decrease in compressive strenght)	PN-85/B-04500	%	0,0
The density of the hardened concrete saturated with water	PN-EN 12390-7	Mg/m^3	2,08
Absorptivity	PN-88/B-06250	%	14,0
Compression resistence after 28 days	PN-EN 12390-3	MPa	34,6
The depth of water penetration under a pressure 0,5 MPa	PN-EN 12390-8	mm	32

Tab. 8. Density and water absorption of chalcedonite fractions

Tab.8 Gęstość i nasiąkliwość wydzielonych frakcji chalcedonitu

Density and water absorption of aggregate according to norm PN-EN 1097-6	Units	Particle size fraction			
		4/8 [mm]		8/16 [mm]	
		Lower layer	Upper layer	Lower layer	Upper layer
Volumetric density of particles ρ_a	Mg/m^3	2.42	2.36	2.38	2.28
Density of dry particles ρ_{rd}	Mg/m^3	1.89	1.62	1.94	1.60
Density of particles ρ_{ssd}	Mg/m^3	2.11	1.93	2.13	1.90
Water absorption WA_{24}	%	11.6	19.4	9.6	18.8

In the process of filtration grits production the high porosity and surface area of the grits are features of a major importance. The filter grits with a particle size of 0.8/2.5 mm, used so far, had a surface area of $5m^2/g$. After separation of chalcedonite in a jig, the grits with a specific surface area of 6.98 m^2/g and a porosity of 29.8% were obtained. The porosity of the product at the bottom of the jig was 20.0%. Obtaining of grits with higher porosity is also advantageous if they are utilized in gardening.

Summary and Conclusions

Chalcedonite is a unique silica rock, with wide applications in production of building materials and environmental protection. It is particularly suitable for the production of filtration grits and as a component of sets being the feed to the firing processes (production of cristobalite, perlite-like material, lightweight aggregates and cement clinker). High fragmentation of fine size fractions and the mineral composition, which is dominated by amorphous silica (microcrystalline) causes that the temperature of the firing process can be carried out at lower temperatures, what reduces the process energy consumption.

The mechanical processing of chalcedonite, one of the most important operations is the washing process. Due to the high content of clay minerals and mineral dusts, devices with high washing efficiency are required to this process. This task best meet turbo washers and sword washers. Chalcedonite is one of the few rocks characterized by high variation of density and water absorption. Application of densimetric separation allows to obtain products with different physical characteristics. For the production of concretes there may be used grits with a lower water absorption, while in the production of filtration grits the product with a higher surface area can be obtained.

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Literatura – References

1. Garbacik A. Określenie przydatności chalcedonitu „Mikrosil" jako surowca krzemonośnego do produkcji klinkieru portlandzkiego. Praca IMMB. Kraków 2005.
2. Góralczyk i in. Próba półtechniczna wytworzenia sztucznego kruszywa lekkiego z osadów ściekowych i odpadów mineralnych. Prace Naukowe Instytutu Górnictwa Politechniki Wrocławskiej nr 125. Seria Studia i Materiały 35. Górnictwo i Geologia XI. Wrocław 2009.
3. Jeż-Walkowiak J., Dymaczewski Z., Weber Ł., 2007 – Filtracja przez złoże chalcedonitowe, ścieków biologicznie oczyszczonych. XIII Konferencja Naukowo-Techniczna, Białowieża 2007; Komitet Inżynierii Środowiska PAN-Lublin
4. Kosk I. Kompleksowe zagospodarowanie odpadowych surowców chalcedonitowych. Gospodarka Surowcami Mineralnymi. PAN. Tom 26 – zeszyt 1. Kraków 2010.
5. Kosk I. Wpływ zróżnicowania chalcedonitów ze złoża „Teofilów nad Pilicą na ich walory surowcowe. Rozprawa doktorska. Uniwersytet Śląski 2008.
6. Kosk I., Pabis J., Tchórzewska D., 1995 – Ocena jakościowo-ilościowa poszczególnych odmian surowców krzemionkowych występujących w złożu „Teofilów" i produktów jego przeróbki. Projekt celowy Nr 7 7668 94 C/1969, IMMB Kraków
7. Michel M. Charakterystyka chalcedonitu ze złoża Teofilów pod katem możliwości wykorzystania w technologii uzdatniania wody i oczyswzczania ścieków. Gospodarka Surowcami Mineralnymi. PAN. Tom 27- zeszyt 1. Kraków 2011.
8. Naziemiec Z. Turbopłukanie. Surowce i Maszyny Budowlane. Nr 5/2011.
9. Naziemiec Z. Badania kruszyw chalcedonitowych. Opracowanie ICiMB. Kraków 2014.
10. Raport końcowy – projekt celowy nr 7 76689 C/1969. Kompleksowe zagospodarowanie i racjonalne wykorzystanie surowca ze złoża „Teofilów". IMMB Kraków 1997.
11. Ratajczak T. Wyszomirski P. Charakterystyka mineralogiczno - surowcowa chalcedonitów spongiolitowych z Teofilowa nad Pilicą. Gospodarka Surowcami Mineralnymi. Tom 7 – zeszyt 1. Kraków 1991.
12. Tchórzewska D. i in. Dodatek nr 2 do dokumentacji geologicznej złoża chalcedonitu „Teofilów w kat B+C1+C2 IMMB Kraków 1997.
13. Tchórzewska D. i in. Nowe zastosowania chalcedonitu jako sorbentu w procesie oczyszczania wód. Przegląd Geologiczny. Vol 49. Kraków 2001.

Problemy przetwarzania i przemysłowego wykorzystania chalcedonitu

Chalcedonit jest naturalną krzemionkową skałą osadową. Jedyna w Polsce kopalnia chalcedonitu znajduje się w Inowłodzu, gdzie sposobem odkrywkowym prowadzona jest eksploatacja ze złoża „Teofilów". Chalcedonit z tego złoża charakteryzuje się dużą zmiennością litologiczną i zwięzłością. [Tchórzewska D. 1997].

Chalcedonit jako unikatowy surowiec był przedmiotem wielu badań i wdrożeń. Szeroki wachlarz jego potencjalnych zastosowań obejmuje przemysł budowlany i drogowy, inżynierię sanitarną (materiał filtracyjny w oczyszczaniu ścieków komunalnych i uzdatnianiu wód) oraz przemysł cementowy. W niniejszym artykule zwrócono uwagę na szczególnie istotne problemy jego przeróbki związane głównie z wydzielaniem w osadzarkach frakcji surowca o różnych gęstośc

Słowa kluczowe: chalcedonit, kruszywa mineralne, przeróbka surowców mineralnych