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The Miocene Lacustrine Chalk from Lignite Bełchatów Deposit (Poland)—Structural and Textural Character and SO_2 Sorption Properties in the Fluid Combustion Conditions

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Abstract: The Miocene lacustrine chalk in the Bełchatów lignite deposit is one of the most important accompanying minerals. It is found in three lithological varieties: white, dark and silicified. It is selectively operated and stored on anthropogenic deposits, representing the mineral resource base. The article presents the results of research on lacustrine chalk from the Szczerców mine excavation and accumulated on the anthropogenic deposit (the Szczerców field external landfill) regarding the possibility of using SO_2 sorbent in the fluid combustion technology. It has been shown that primarily the structural and textural parameters of the rock, and to a lesser extent, the $CaCO_3$ content, are responsible for the high efficiency of SO_2 sorption. It has been proven that in this type of technology, the presence of carbonised plant matter only seemingly lowers the quality parameters of the raw material. It has a significant impact on the sorption properties, effectively influencing the expansion of porosity and specific surface during thermal decomposition. The expansion of the surface is mainly based on the pores on the border of mesopores and macropores, i.e., pores considered to be sorptive towards SO_2. These pores, because they are formed in a lower temperature range than the calcite thermal dissociation process and are connected together to form a system, act as diffusion channels of CO_2 from inside and SO_2 into the inside of the sorbent grains, intensifying the decarbonisation and SO_2 sorption processes.

Keywords: Miocene lacustrine chalk; accompanying minerals; porosity and specific surface; SO_2 sorbent; carbonate sorbent; sorption properties

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1. Introduction

The Bełchatów lignite deposit belongs to the tectonic deposits of the depression type. It is situated within the Łódź synclinorium in the Kleszczów tectonic trench (Figure 1). The frames of the trench, made of Jurassic limestones, are at the same time slopes of the mining fields: Bełchatów and Szczerców (Figure 2). Lignite is mined using the opencast method, which requires over 120 million m^3 of overburden removal per year. Among the overburdened rocks, there are many valuable raw minerals. Some of them meet the criteria of accompanying minerals and are selectively exploited and stored in the secondary deposits. They serve as a raw material base for investment projects of the mine and external recipients of mineral resources. One of the accompanying minerals in the Bełchatów deposit is lacustrine chalk. In the Bełchatów field, the chalk resources have been fully excavated. In the Szczerców field, they were estimated at approx. 29.5 million Mg, of which at least 17.5 million Mg is intended for selective extraction [1]. The article presents the results of lacustrine chalk studies in the Szczerców field, which are the result of several years of research.

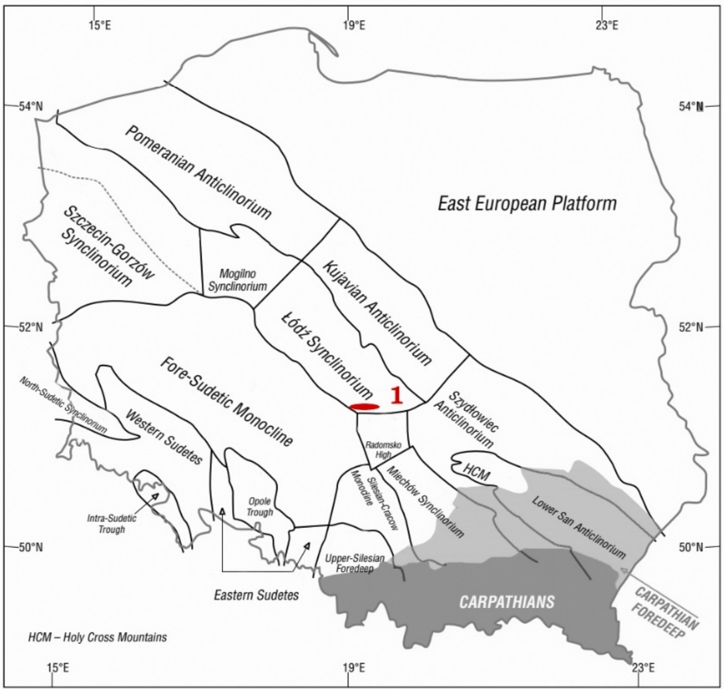


Figure 1. The locations of Bełchatów deposit on the background the main tectonic units on the sub-Cenozoic surface of the Polish [2]. Explanations: 1—Bełchatów deposit.

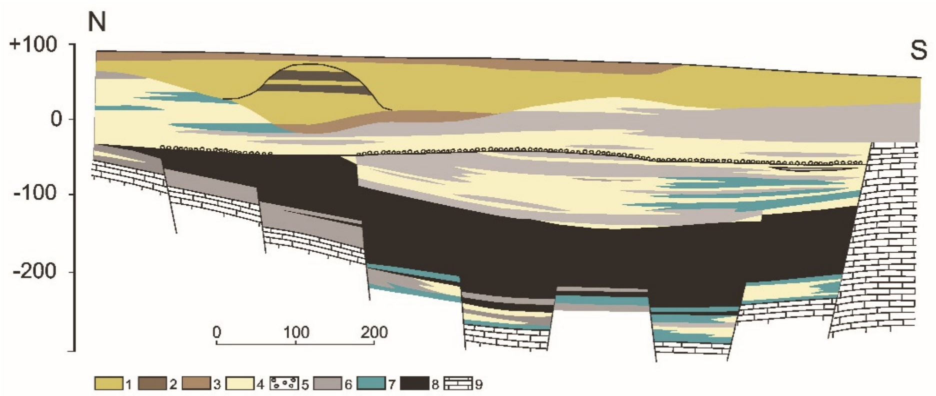


Figure 2. The geological cross-section through the Bełchatów deposit (Szczerców field) [3]. Explanations: Holocene: 1—sands, 2—silts (marginal lake-pond), 3—clay; Neogene—Paleogene: 4—fine-grained sands, 5—silts; 6—loams, 7—lignite; Jurassic: 8—limestones and marls.

In the Szczerców field, the lacustrine chalk is deposited within the Tertiary lignite complex, in several stratigraphic links: in the top and bottom part of the Lower Miocene lignite complex, where these sediments can be faced as substitutes for lignite, and also within the clay-lignite and lignite complexes (Figure 3) [4]. The analysis of the occurrence of lake carbonate sediments accompanying coal seams in the Bełchatów deposit, based on the analysis of lithological profiles of boreholes, contained in the Uniform Geological Database of the Bełchatów Mine and field observations, showed that this mineral occurs both in the form of layers with a thickness of up to over a dozen meters and takes the form of laminates with a thickness of several to several dozen centimetres. The thicker layers of lacustrine chalk are interbedded with thin layers of lignite, several to several dozen centimetres thick. Five levels (groups of layers) of lacustrine chalk can be distinguished in the vertical profile of the Szczerców field. Four of them (upper, main, middle and lower) were separated within the productive coal complex. The fifth occurs within an unproductive coal complex.

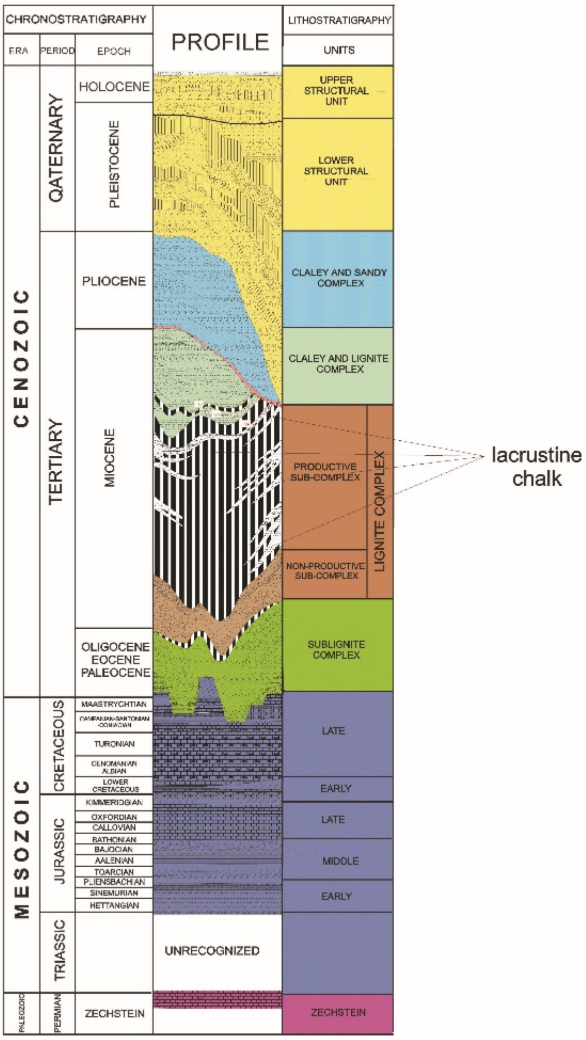


Figure 3. The lithostratigraphic profile of the over- and sub-lignite series in the Szczerców Field, (Bełchatów deposit) with marked locations of lake chalk deposits (according to the Geological Department of the Bełchatów Mine 2015) [3].

The main group of the lacustrine chalk layers is the most promising from the point of selective exploitation view. It is characterised by the largest spread (covers an area of 200 ha) and the largest thickness of up to 27 m (average 5.6 m). Currently, in the mining excavation of the Szczerców field, the lacustrine chalk is exposed on the fourth and fifth mining floors. These are sediments included in the main group of layers.

Macroscopically, lacustrine chalk is a brittle, weakly concise, highly porous rock of various colours from white, through brown, to dark brown and even black. The colour of the chalk depends on the content of coalified organic material. There are two basic lithological varieties of chalk in the deposit: white and dark. The white variety contains more than 90% wt. $CaCO_3$, up to 5% wt. of organic matter and less than 5% wt. terrigenous components. In the dark type, the $CaCO_3$ content is at a much lower level, 60–65% wt. The organic matter constitutes about 25–35% wt. It occurs mainly in the form of coal dust, i.e., fine, carbonised plant detritus. It is irregularly dispersed in the rock, creating streaked and lenticular clusters and irregular laminae. The composition of dark chalk also includes xylite fragments, up to several centimetres long, and other plant debris, such as pieces of bark, root debris, needles, etc. Depending on the content of coalified organic matter, gradual transitions from pure lake limestones through limestones with different lignite content to calcareous lignite are observed. A separate lithological variety is silicified chalk, which has a significant silica content of 30–60% wt. [5]. Macroscopically, the silicification process is recognizable mainly by the high hardness and conciseness of the rock. The increased silica content is hardly visible in the mixture with calcite.

The white and dark varieties dominate the deposit. The silicified variety occurs sporadically. The drilling profiles show both gradual and sharp transitions between different varieties of lacustrine chalk, which indicates variability in sedimentation conditions. The lacustrine chalk in the Bełchatów mining field was the subject of lithostratigraphic, petrographic-mineralogical and technological studies. These studies detailed the lithological formation of the rock, defined as freshwater limestones, limestone gyttja, calcareous clays and silts, and even limestone lignite, which was initially determined when documenting the deposit. The researches have also become the basis for making the initial characterisation of raw materials. Based on the contents of $CaCO_3$, three technological varieties of lacustrine chalk were distinguished, (1) the so-called very pure, with a content of 90–98% by weight. $CaCO_3$, (2) containing 80–90% and (3) less than 80% by weight. $CaCO_3$. Its usefulness was determined, among others, for the production of painting, technical and fodder chalk, in the reclamation of land contaminated with heavy metals, as well as a calcium fertilizer. The subsequent experimental studies proved the possibility of its use in the lime industry (for the production of burnt and hydrated lime), cement (for the production of white cement), building materials, glass, ceramics, cellulose and confectionery. The usefulness of lacustrine chalk for the production of synthesized calcium silicified—wollastonite was also demonstrated [6]. Currently, the demand for this mineral is practically non-existent. Chalk is used only to a negligible degree by agriculture. The lake varieties are jointly mined and stored in an anthropogenic deposit, which serves as a resource base for this mineral. This significantly limits the demonstrated possibilities of its economic use.

Considering the resources of lacustrine chalk intended for extraction in the Szczerców Field, research was undertaken on the possibilities of its economic use.

The article presents the results of the research on lacustrine chalk deposited in the Szczerców field and accumulated in an anthropogenic deposit (the external disposal site of accompanying minerals in the Szczerców field) as SO_2 sorbent in the fluidized bed combustion technology. The accumulated resources of the lacustrine chalk on this disposal site amount to approx. 18,000 m^3 (as of 31 December 2020).

2. Materials for Research and Methodology

The research materials were 86 samples of lacustrine chalk taken from 36 exploratory drilling cores ahead of the exploitation front in the Szczerców mining field and 12 samples taken from the anthropogenic deposit (the Szczerców field external landfill). The samples taken from the drill cores represented all types of chalk present in the deposit: white (20 samples), dark (53 samples) and silicified (13 samples). The varieties of chalk are together exploited and accumulated; the material taken from the anthropogenic deposit was mixed. They take into account their colour, and the content of organic matter has been described as dark chalk.

The research was aimed at recognizing the mineralogical and petrographic character and physicochemical properties in order to determine the efficiency of SO_2 sorption in the fluidized bed combustion technology. For the purpose of comparative research, an industrial sorbent made of Jurassic limestone was also included.

The test methodology covered:

1. Determining the mineral composition, petrographic nature and structural and textural characteristics of the examined lacustrine chalk. For this purpose, X-ray diffraction (MiniFlex 600, Rigaku, Tokyo, Japan), optical (BX51, Olympus, Tokyo, Japan) and scanning microscopy (Quanta 200 FEG, FEI, Hillsboro, OR, USA) were applied.

2. Chemical composition. Apart from the quantitative determination of $CaCO_3$ and $MgCO_3$ by complexometric titration, the content of SiO_2, Al_2O_3, K_2O, Na_2O, Fe_2O_3, Mn_2O_3 and TiO_2 was also tested. The research was performed with atomic emission spectroscopy (ICP-OES Plasma 40, PerkinElmer, Waltham, MA, USA). The samples were

mineralized using a high-pressure microwave mineralizer (Speedwave Xpert, Berghof, Eningen, Germany). Mineralisation was carried out in a closed system. Additionally, the content of organic carbon (C_{org}) as well as deposit moisture (W_t^r) and analytical moisture (W^a) was examined. The multiphase analysis apparatus for carbon and water determination was used for the tests (RC612C, LECO, Benton Harbor, MI, USA).

3. The study of the specific surface area and porosity was carried out using the low-temperature nitrogen sorption method. The ASAP 2020 device for precise sorption measurements (Micromeritics, Norcross, GA, USA) was used for the analysis. Immediately before measurement, the samples were dried at 105° C for 1 h and then annealed under vacuum at 150 °C for 12 h. The specific surface area (S_{BET}) was determined based on low-temperature nitrogen adsorption isotherms at −196 °C according to the Brunauer–Emmet–Teller (BET) method. [7]. The total pore volume (V_{tot}) was also calculated for the relative pressure p/p0 = 0.99. In addition, specified:

- The micropores volume ($V_{mik}{}^{DR}$), pores with a width of less than 2 nm, according to the Dubinin-Radushkevich method, and their share in the total pore volume $V_{mik}{}^{DR}/V_{tot}{}^{0.99}$;

- The mesopores volume ($V_{mez}{}^{BJH}$), pores with a diameter above 2 nm and below 50 nm, according to the Barrett-Joyner-Halenda (BJH) method, and their share in the total pore volume ($V_{mez}{}^{BJH}/V_{tot}{}^{0.99}$);

- The macropores volume (V_{mak}), pores with a diameter above 50 nm, are calculated by subtracting the volume of micropores and mesopores from the total pore volume: $V_{mak} = V_{tot}{}^{0.99} - (V_{mik}{}^{DR} + V_{mez}{}^{BJH})$ and their share in the total pore volume $V_{mak}/V_{tot}{}^{0.99}$.

The analyses were performed in accordance with standards: ISO 9277:2010 [8], ISO 15901-2:2006 [9], ISO 15901-3:2007 [10].

Porous texture analysis was performed using mercury porosimetry. The following porous texture parameters were determined:

- The coefficient of effective porosity, which is the ratio of pore volume to the total volume of the sample [11–14]:

$$\phi = \frac{V_{tot}}{V_b} \cdot 100\% = \frac{V_b - V_s}{V_b} \cdot 100\% = \left(1 - \frac{\rho_b}{\rho_s}\right) \cdot 100\% \tag{1}$$

Explanations: ϕ—the coefficient of effective porosity (%); V_{tot}—the total volume of mercury in the pores (mL); V_b—external volume (mL); V_s—skeleton volume (mL); ρ_b—bulk density (g/mL); ρ_s—skeletal density (g/mL).

- The specific surface area of porous space, that is, the pore area in relation to the sample unit mass. This parameter characterises the flow resistance of reservoir media in the porous medium. The specific surface area, assuming the reversibility of the injection process, is determined based on the obtained pore volume according to the following equation [11,14]:

$$A = -\frac{1}{\gamma \cos\theta} \int_0^V PdV \tag{2}$$

Explanations: A—the total surface area of porous space (m^2/g); dV—partial pore volume corresponding to the given capillary pressure (m^3); P—capillary pressure (psi); γ—surface tension of mercury (dyna/cm); θ—contact angle (°).

- The average pore diameter (D_{av}) is expressed with the weight of the pore size for the entire pore diameter range in the sample and is calculated using the following equation [11,13]:

$$D_{av} = \frac{4 \cdot V_{tot}}{A} \tag{3}$$

Explanations: D_{av}—the average pore diameter (μm); V_{tot}—the total volume of mercury in the pores (mL); A—total specific surface area of the pore space (m^2/g).

4. The sulphation experiment was carried out based on the guidelines developed by the Ahlstrom Development Laboratory [15]. This method is based on determining

two indicators: the reactivity (RI index) and absolute sorption (CI—capacity index). The reactivity index determines the ratio of the calcium content in the sample to the amount of sulphur after the sorption process (Ca/S moles). The absolute sorption index CI, in turn, determines the amount of sulphur adsorbed by 1000 g of the sorbent (g S/1000 g of the sorbent). The SO_2 sorption studies were carried out using a material with a particle size of 0.125–0.250 mm. The sulphation experiment was carried out on the basis of an instance designed on the basis of a gas-tight retort furnace acting as a fixed bed. The sulphation process was carried out in two ways. In the first, the samples were decarbonated at 850 °C for 30 min before the sulphation process. In the second, the samples were directly subjected to the sulphation process without prior decarbonation. A sample of the sorbent mass of 150 mg was placed inside the combustion chamber, on a perforated ceramic plate, in such a way that the individual grains of the sorbent were not in contact with each other. In this way, free access of gases to individual sorbent grains was ensured during the experiment. First, synthetic air, containing 80% N_2 and 20% O_2, was passed through it. Then, a gas containing 1780 ppm of SO_2, 3% of O_2, 16% of CO_2 and N_2 making up the rest was passed through the samples with a speed of 950 mL/s for another 30 min. In the next stage, the content of absorbed sulphur was determined using an elemental analysis apparatus for carbon, hydrogen, nitrogen and sulphur (Series 628) by LECO. The results of the research became the basis for calculating the values of reactivity (RI) and absolute sorption (CI) indicators according to the formula:

$$\mathrm{RI} = \frac{\frac{x_{\mathrm{Ca}}}{100}\cdot\frac{M_{\mathrm{S}}}{M_{\mathrm{Ca}}}\cdot\left(1-\frac{M_{\mathrm{CO_2}}}{M_{\mathrm{C}}}\cdot\frac{x_{\mathrm{C_p}}}{100}-\frac{M_{\mathrm{SO_3}}}{M_{\mathrm{S}}}\cdot\frac{x_{\mathrm{S_p}}}{100}\right)}{\frac{x_{\mathrm{S_p}}-x_{\mathrm{S_b}}}{100}+\frac{M_{\mathrm{CO_2}}}{M_C}\cdot\left(\frac{x_{\mathrm{C_p}}\cdot x_{\mathrm{S}_p}-x_{\mathrm{C}_p}\cdot x_{\mathrm{S_p}}}{10000}\right)} \tag{4}$$

$$\mathrm{CI} = \frac{1000\cdot\left[\frac{x_{\mathrm{S_p}}-x_{\mathrm{S_b}}}{100}+\frac{M_{\mathrm{CO_2}}}{M_{\mathrm{C}}}\cdot\left(\frac{x_{\mathrm{C_p}}\cdot x_{\mathrm{S_b}}-x_{\mathrm{C}_p}\cdot x_{\mathrm{S_p}}}{10000}\right)\right]}{1-\frac{M_{\mathrm{CO_2}}}{M_{\mathrm{C}}}\cdot\frac{x_{\mathrm{C_p}}}{100}-\frac{M_{\mathrm{SO_3}}}{M_{\mathrm{S}}}\cdot\frac{x_{\mathrm{S_p}}}{100}} \tag{5}$$

Explanations: x_{Ca}, $x_{\mathrm{C_p}}$, $x_{\mathrm{S_p}}$, $x_{\mathrm{C_p}}$ and $x_{\mathrm{S_p}}$ —percentages of calcium in the sorbent, carbon in the sorbent after the sulphating process, sulphur after the sulphating process, carbon before the sulphating process and sulphur before the sulphating process, respectively (%); M_{S}, M_{Ca}, M_{C}, $M_{\mathrm{CO_2}}$ and $M_{\mathrm{SO_3}}$—molar masses of sulphur, calcium, carbon, carbon dioxide and sulphur trioxide, respectively (kg/kmol).

To evaluate the sorption capacity, the five-level scale proposed by the Ahlstrom Development Laboratory was used (Table 1).

Table 1. The reference values of the reactivity (RI) (Ca moles/S moles) and the absolute sorption (CI) (g S/1000 g of the sorbent) [15].

The Sorption Capacity of the Sorbent	RI (kmol Ca/kmol S)	CI (g S/1 kg of Sorbent)
Excellent	<2.5	>120
Very good	2.5–3.0	100–120
Good	3.0–4.0	80–00
Sufficient	4.0–5.0	60–80
Low quality	>5.0	<60

5. The temperature and decomposition degree and the thermal dissociation course of lacustrine chalk process (TGA/DSC 3+, Mettler Toledo, Greifensee, Switzerland). The research was carried out using thermogravimetry (TG) and differential scanning calorimetry (DSC). The samples were analysed in the temperature range of 20–1000 °C. The heating rate was 20 °C/min. The measurements were made in the air atmosphere to clearly separate the decompositions of $MgCO_3$ and $CaCO_3$.

In order to characterise the decarbonation and SO_2 sorption processes, the mentioned texture parameters were determined for both the decarbonised and sulphated samples, phase composition and textural nature of the resulting desulphurisation products. A scanning microscope (FEI Quanta 200 FEG), the low-temperature nitrogen sorption method (ASAP 2020, Micromeritics) and mercury porosimetry (AutoPore IV 9500, Micromeritics) were used for the testes.

The research was carried out with the use of research equipment of the AGH University of Science and Technology in Cracow with the support of the Energy Centre AGH.

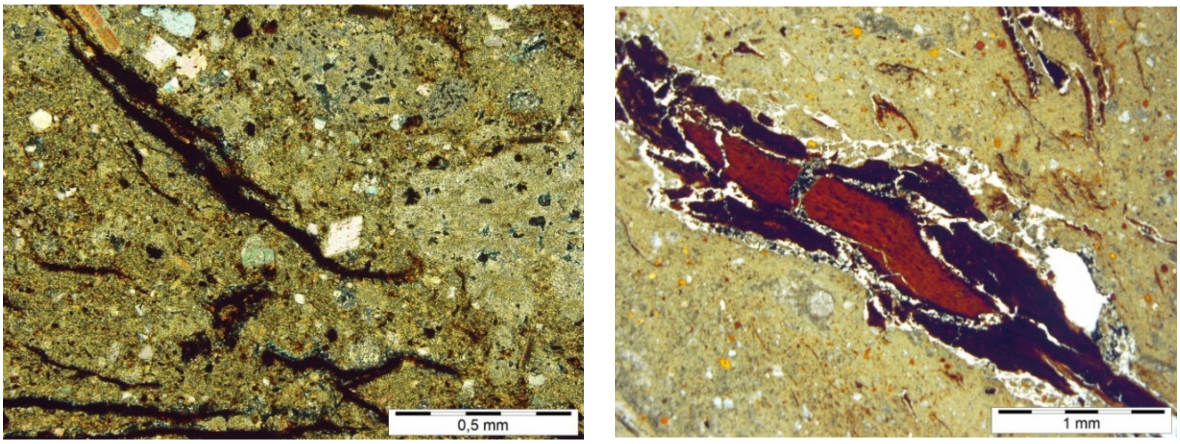
3. Results and Discussion

3.1. Mineral and Chemical Composition of the Lancustrine Chalk Tested

Calcite ($CaCO_3$) is the main mineral component of lacustrine chalk, including white, dark and silicified. In addition to calcite, the presence of quartz was found in the mineral composition of the dark and silicified chalk using the X-ray diffraction method. In the dark chalk samples, clay minerals represented mainly by kaolinite, illite and pyrite were also identified.

In microscopic observations, it was found that calcite occurs in the form of a microcrystalline rock background with a crystal size from 2 to 5 µm. It is a typical orthochemical component of rock, formed as a result of precipitation from lake water rich in calcium acid carbonate, due to the decrease in CO_2 content, as a result of waves, temperature changes and the development of organic life. Additionally, it plays the role of cement. A small part of the calcite micrite may exist in the form of the so-called pseudo micrite, which has clear cement features but is formed during diagenesis or may come from abrasion of limestone rocks from the edge of the Kleszczów tectonic graben [16]. In the dark variety, the microcrystalline rock background is tinted with lignite dust, and in the silicified type, it is impregnated with silica, mainly opal and chalcedony, less often microcrystalline quartz. Within the microcrystalline rock background, there are the sparite calcite crystals, usually forming aggregates, in each variety of the lacustrine chalk. Moreover, a group of allochemical components performed function a skeleton in the rock. In addition, a number of allochemical components have been identified as a skeleton in the rock. These are mainly crushed carbonate shells of molluscs and calcitized algae remains, as well as intraclasts, oncoids and peloids. The fragments of Jurassic limestones were also identified, originating from the eroded slopes of the tectonic trench. The allochemical components are usually in a dispersed form, which allows them to be classified according to Dunham's classification [17] to Floatstone (>10% of allochemical components are larger than 2 mm) and Wackstone (<10% of allochemical components is greater than 2 mm). At the same time, these are the types of limestone most frequently represented by the lacustrine chalk in the Szczerców field. The Grainstone and Rudstone were rare among the tested lake chalk samples. The Bindstone, an autochthonous variety of limestone, formed by calcified algae mats, has been very rarely identified. This type of limestone was difficult to identify due to its poor state of preservation and recrystallization.

Among the noncarbonate components, mainly quartz grains, fewer feldspars were distinguished. They are poorly rounded and have different sizes, from pelitic through aleurite to psamite. A permanent allochemical component of lacrustine chalk is also organic material, represented by fragments of mainly brittle (Figure 4a) and gelled xylites (Figure 4b), carbonised plant detritus and components resistant to oxidation and destructive action of bacteria, such as waxes and resins, characterised by a high content of organic carbon. Among the noncarbonate components of orthochemical origin, clay minerals and pyrite, mainly framboidal, were identified.

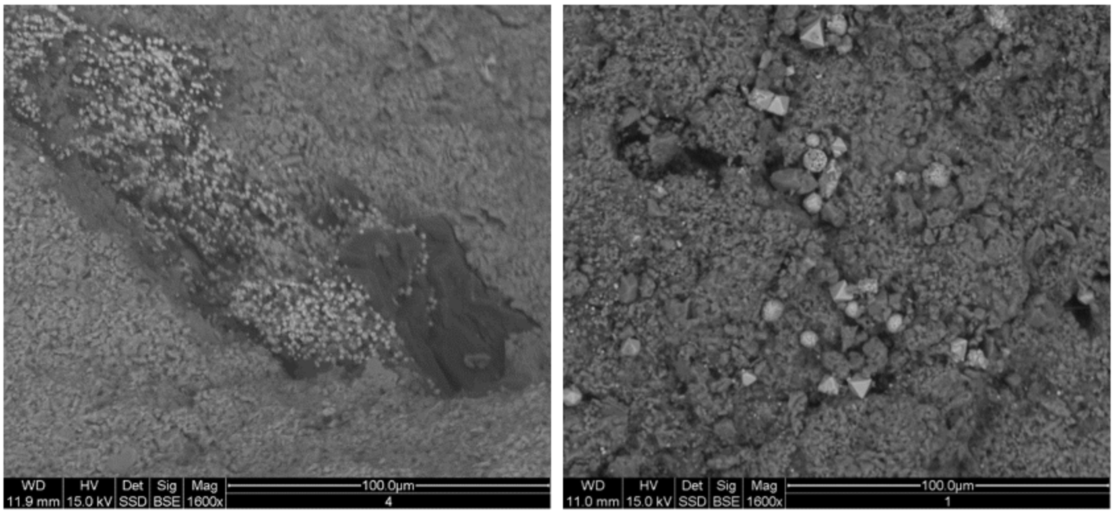


(**a**) (**b**)

Figure 4. The lacustrine chalk of the dark variety in the Szczerców field. (**a**) Visible detritus of a carbonised organic substance and (**b**) visible partially gelled xylite. Polarizing microscope Xp.

The content of noncarbonate components in the lacustrine chalk individual lithological varieties is strongly diversified. In the white chalk, it is usually at the level of a few percent of the rock's volume, and in the dark variety, it reaches even 45% by volume. In addition, white chalk is characterised by a very low variability of the mineral composition, while dark and silicified chalk show significant differences both in the content of calcite and noncarbonate components. The noncarbonate components are unevenly distributed in the rock. The clay substance occurs in the streaks and laminas form, where it is usually heavily masked with lignite dust.

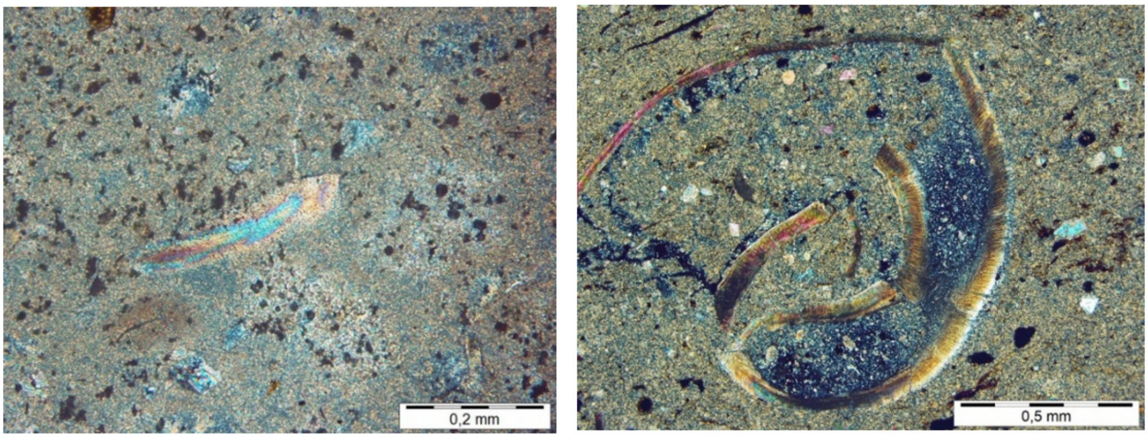
This type of clay minerals and organic material occurrence is accompanied by pyrite, often framboidal (Figure 5a,b), and iron compounds of oxide nature (their identification was difficult due to the presence of lignite matter). Quartz grains, in turn, are responsible for the presence of sanded chalk inserts.



(**a**) (**b**)

Figure 5. The SEM image of dark lacustrine chalk. Visible carbonised organic matter pyrite impregnated (**a**) and idiomorphic and framboidal pyrite crystals (**b**) in the light of backscattered electrons.

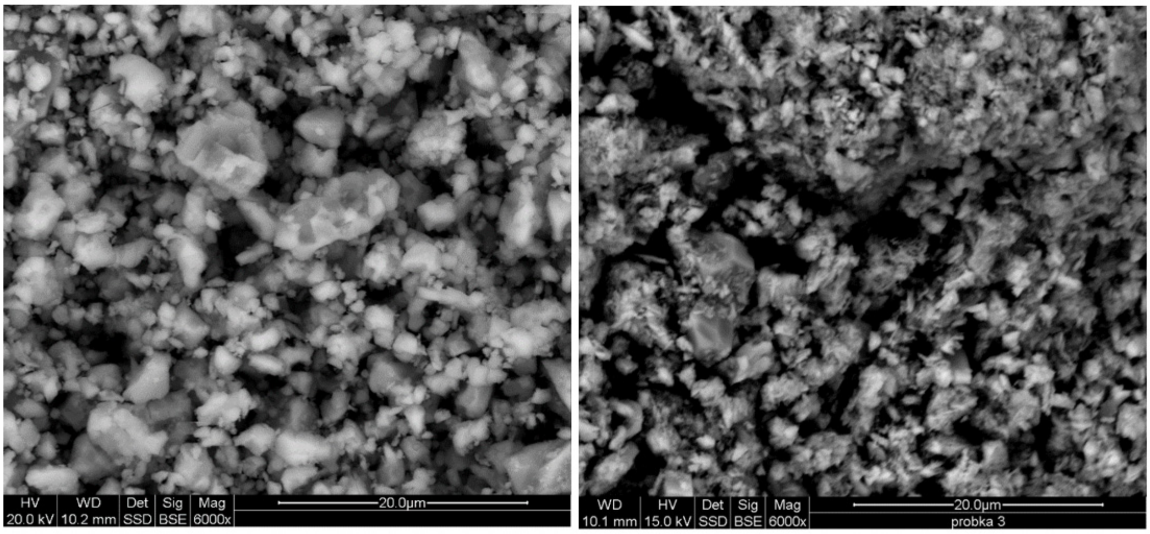
The silification process is associated with the presence of opal and chalcedony and less frequently autogenous quartz. The most often manifested in the replacement of the calcite in bioclasts, impregnating the pores of the rock opal and chalcedony and rarely autogenic quartz (Figure 6a,b). The forms of silica occurrence indicate that the process took place at the stage of diagenesis and was cement-like, but the biogenic structure of the rock did not change. The source of silica could be formation water, squeezed out of neogeneous clay sediments under the influence of mechanical compaction. The sources of silica can also be searched for in the process of calcification of volcanic glass and feldspars, which are present in the pyroclastic material from which the tonsteins were formed [18].



(a) (b)

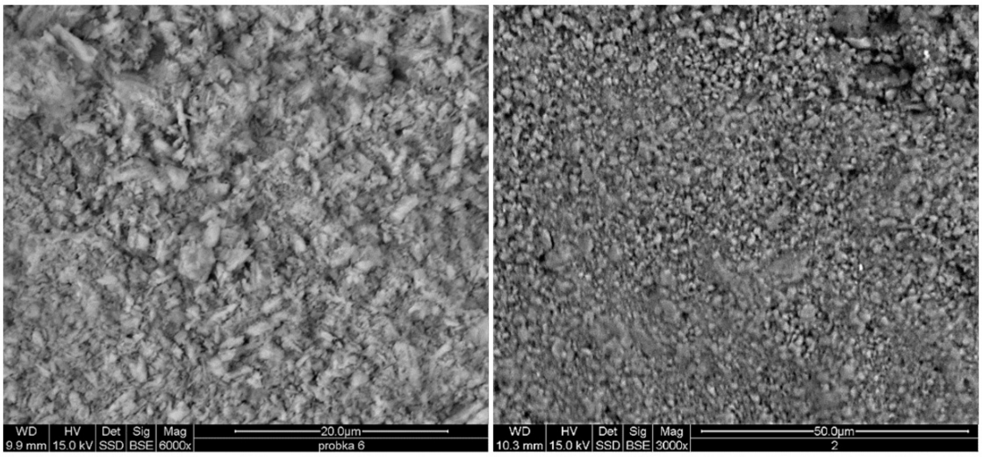
Figure 6. The silicified lacustrine chalk. The visible chalcedony-filled rock pores (**a**) and the calcite replacement process by opal CT (**b**). Polarizing microscope, Xp.

The content of noncarbonate components has a decisive influence on the structural and textural diversity of the rock. The only carbonate varieties are characterised by a microcrystalline structure and a disordered and porous texture (Figure 7). The increased content of both organic and terrigenous material makes the structure become detrital in nature, and textures are streaking, even layering. The dark and siliceous substances also reduce the porosity of the rock (Figure 8a,b) while increasing its compactness and hardness.



(a) (b)

Figure 7. The SEM image of white lacustrine chalk. The visible microcrystalline structure and porous texture of the rock in the light of backscattered electrons (**a**,**b**).



(a) **(b)**

Figure 8. The SEM image of the lacustrine chalk: dark (**a**) and silicified (**b**) varieties. The visible microcrystalline structure and compactness texture in the light of backscattered electrons.

The mineral composition of lacustrine chalk identified by microscopy was detailed by the X-ray examinations. In the phase composition of the clay substance, illite and kaolinite were distinguished. The presence of aragonite was found in the samples of lacustrine chalk, which was rich in calcareous shells of molluscs. The iron oxide compounds of hematite nature and trace amounts of gypsum were additionally identified in the material from the anthropogenic deposit. Hematite is an effect of pyrite oxidation under atmospheric conditions. Gypsum was formed as a result of the CaO reaction (coming from the dissolution of calcite under the influence of atmospheric factors), with SO_2 resulting from the oxidation of pyrite.

Table 2 shows the chemical composition of individual lithological varieties of lacustrine chalk collected from drilling cores and the anthropogenic deposit. The content of moisture (W_t^r, W^a) and organic carbon (C_{org}) is also included.

Table 2. The chemical composition of individual lithological varieties of lacustrine chalk occurring in the Bełchatów deposit (Szczerców field) and in the secondary deposit [% wt.].

Component	**The Lithological Varieties of Lacustrine Chalk**			**The Lacustrine Chalk from Secondary Deposit**	**Industrial Sorbent [19]**
	White	**Dark**	**Silicified**		
SiO_2	0.08–0.92 0.45	1.02–8.11 3.45	19.23–42.11 30.08	0.52–7.52 2.48	0.17
TiO_2	0.01–0.03 0.02	0.02–0.06 0.05	0.01–0.05 0.03	0.01–0.05 0.04	-
Al_2O_3	0.08–0.42 0.37	1.05–5.12 3.12	0.11–4.12 1.60	0.96–4.21 2.56	0.11
Fe_2O_3	0.05–0.14 0,08	0.69–3.55 1.23	0.27–2.15 0.68	0.14–2.01 1.09	0.03
CaO	52.20–55.71 53.89	29.28–43.90 38.26	12.89–27.36 19.00	36.11–51.09 43.32	55.57
MgO	0.11–0.18 0.15	0.08–0.20 0.12	0.10–0.14 0.12	0.09–0.19 0.13	0.08
MnO	0.01–0.02 0.01	0.01–0.04 0.03	0.01–0.04 0.02	0.01–0.04 0.03	-
K_2O	0.02–0.09 0.03	0.06–0.19 0.12	0.02–0.07 0.04	0.05–0.16 0.10	0.002
Na_2O	0.01–0.04 0.02	0.03–0.08 0.06	0.01v0.06 0.03	0.01–0.06 0.05	0.003
$CaCO_3$	92.94–99.26 95.42	52.21–78.04 68.10	22.94–48.80 33,82	64.37–89.90 76.25	98.92

Table 2. *Cont.*

Component	The Lithological Varieties of Lacustrine Chalk			The Lacustrine Chalk from Secondary Deposit	Industrial Sorbent [19]
	White	Dark	Silicified		
$MgCO_3$	0.24–0.38 0.31	0.12–0.44 0.25	0.23–0.27 0,25	0.17–0.36 0.27	0.17
Corg.	0.05–0.52 0.14	9.25–24.12 16.13	0.08–1.11 0,35	4.11–19.32 9.41	n.t.
W_t^r	19.89–28.36 24.11	29.69–38.74 34.27	5.85–9.48 6.12	11.11–42.78 27.36	n.t.
W^a	0.84–1.2 0.95	3.11–6.9 4.48	0.5–1.85 1.07	2.39–6.89 4.01	0.20

Explanations: The $CaCO_3$ and $MgCO_3$ content was determined by titration; C_{org}—organic carbon content as a component of lignite matter; W_t^r—total (deposit) moisture content in the lacustrine chalk, determined immediately after drilling the core or collecting it from the anthropogenic deposit; W^a—hygroscopic (analytical) moisture content;—that content is less than 0.001% wt.; n.t.—not tested.

The chemical composition is different between the lithological varieties of chalk and the carbonised chalk samples taken from the drilling cores and the anthropogenic deposit. The differences concern mainly the content of CaO ($CaCO_3$) as well as C_{org} and SiO_2. The white variety is characterised by the highest (on average 53.89% wt.), and the silicified has the lowest (on average 19% wt.) content of CaO. In the dark variety, the CaO content is on average 38.26% wt. in samples taken from drill cores and 48.46% wt. is taken from an anthropogenic deposit. The organic carbon content in the white and silicified form is low and amounts to 0.14% wt. and 0.35% wt., respectively. In the dark chalk, the average C_{org} content is 16.13% wt. in samples taken from drill cores and 9.41% wt. in samples taken from the anthropogenic deposit. The SiO_2 content is an indicator of the advancement of the silification process. It may also be evidence of the sandiness of the lacustrine chalk. In the silicified variety, the SiO_2 content ranges from 19.23% to 42.11% wt. and averages 30.08% wt. The contents of the remaining chemical components are less differentiated. MgO present in the samples is in the $MgCO_3$ form. It should be combined with the presence of magnesium calcite, as evidenced by the higher $MgCO_3$ content in the white variety (on average 0.31% wt.) compared to other varieties of lacustrine chalk (on average 0.25%–0.27% wt.). The content of K_2O and Na_2O should be associated with the presence of clay substance, hence slightly higher contents in the dark chalk. In the carbonised version, higher Fe_2O_3 contents were also found, confirming its relationship with pyrite and iron oxide compounds, formed as a result of oxidation of this mineral, as well as TiO_2 and MnO, which should be combined with both clay and terrigenous material that could transport these elements.

The moisture is an important utility feature of the lacustrine chalk, especially in the case of energetic use. Introduced into the combustion chamber, due to the high heat of water evaporation, it can reduce the calorific value of the fuel. It also has a negative effect on the temperature of the so-called exhaust gas "dew point" (exhaust gas temperature at which the process of condensation of water vapor or its sublimation at a set pressure) can begin. It is responsible for the economics of transporting this mineral and thus the territorial range of profitability of its use. In Polish climatic conditions, especially in the winter, the moisture can cause serious problems related to freezing during transport and storage. The content of deposit moisture (W_t^r) and analytical moisture (W^a) is presented in Table 2. The deposited (total) moisture is understood as the moisture that the chalk samples contain at the moment and shortly after being extracted from the deposit (drilling a hole in this case). It is the sum of transient (unstable) and hygroscopic (permanent) moisture. The analytical moisture (W^a) is close to the hygroscopic moisture content and determines the moisture content at 105 °C, in the sample in equilibrium with the environment (air-dried for 72 h). The lacustrine chalk in the deposit, similarly to lignite, is dehydrated and dried up due to the removal of the overburden. Despite this, the deposit moisture content (W_t^r) is at a high level and amounts on average to: 34.27% wt. in the carbonised variety, 24.11% wt. in the white and 27.36% wt. from the anthropogenic deposit. Only in the silicified variety, it is clearly lower (6.12% wt). The analytical moisture content (W^a) is, on average: 4.48% wt. in the dark chalk, 0.95% wt. in white and 4.01% wt. in the variety from an anthropogenic deposit. In the silicified variety, it is at the level of 1.07% wt. The results of the research show that lacustrine chalk easily gives back and absorbs surface moisture in atmospheric conditions. This exchange is very clearly visible in the chalk samples taken from the anthropogenic deposit, where the total moisture content is the most diversified and is in the range of 11.11–42.78% wt. The atmospheric conditions during sampling are responsible for this diversity. The high moisture content is undoubtedly associated with the addition of carbonised organic matter (lignite) and with the structural and textural character of the rock, especially with significant porosity.

The chemical composition of the industrial sorbent is characterised by a high CaO content (55.57 wt.%) with a negligible content of other chemical components. The analytical moisture content does not exceed 0.20% wt.

3.2. Parameters of the Porous Texture Lacustrine Chalk

The parameters of the porous texture, determined by the low-temperature nitrogen sorption method, indicate the differentiation of both the specific surface area and porosity (Table 3). It should be noted that the white 4.68 m^2/g and the silicified 3.11 m^2/g varieties are clearly lower in the surface compared value to the dark variety, both in the case of samples taken from drill cores (8.28 m^2/g) and from the anthropogenic deposit (8.01 m^2/g). The specific surface area of white chalk is expanded mainly by macropores and mesopores, whose share in the total pore volume is 56.3% and 40.6%, respectively. In the case of the silicified and dark variety, both in the case of samples from the drilling cores and the anthropogenic deposit, the specific surface area was shaped mainly by mesopores (46.2%, 45.7% and 47.4%) and micropores (30.8%, 30.4% and 44.7%). The content of macropores is clearly lower, especially in the case of dark chalk from an anthropogenic deposit (7.9%). This is confirmed by the average pore diameter. In the case of white chalk, it is characterised by a significantly higher value compared to other types of chalk. The industrial sorbent, made of Jurassic limestone, compared to chalk varieties, has a much smaller specific surface (1.22 m^2/g). In turn, the total volume of pores, as well as the share of micropores, mesopores and macropores, correspond to the sifted variety.

Table 3. The porous texture parameters as determined by low-temperature nitrogen sorption of the lacustrine chalk individual lithological varieties and industrial sorbent.

Parameter	**Symbol**	**Unit**	**The Lithological Varieties of Lacustrine Chalk**			**The Lacustrine Chalk from Secondary Deposit**	**Industrial Sorbent**
			White	**Dark**	**Silicified**		
Specific area	S_{BET}	[m^2/g]	4.68	8.28	3.11	8.01	1.22
Total pore volume	$V_{tot}^{0.99}$	[cm^3/g]	0.032	0.046	0.013	0.038	0.011
Micropores volume	V_{mik}^{DR}	[cm^3/g]	0.001	0.014	0.004	0.017	0.003
Share of micropores in the total pore volume	$V_{mik}^{DR}/V_{tot}^{0.99}$	-	0.031 (3.1%)	0.304 (30.4%)	0.308 (30.8%)	0.447 (44.7%)	0.29
Mesopores volume	V_{mez}^{BJH}	[cm^3/g]	0.013	0.021	0.006	0.018	0.005
Share of mesopores in the total pore volume	$V_{mez}^{BJH}/V_{tot}^{0.99}$	-	0.406 (40.6%)	0.457 (45.7%)	0.462 (46.2%)	0.474 (47.4%)	0.45
Macropores volume	V_{mak}	[cm^3/g]	0.018	0.011	0.003	0.003	0.003
Share of macropores in the total pore volume	$V_{mak}/V_{tot}^{0.99}$	-	0.563 (56.3%)	0.239 (23.9%)	0.231 (23.1%)	0.079 (7.9%)	0.250 (25.0%)
Average pore diameter	$D_{śr}$	nm	17.4	9.5	4.2	8.3	10.3
Average pore diameter	$D_{śr}$	µm	0.0174	0.0095	0.0042	0.0083	0.0103

Explanations: the pore size ranges are given according to the pore classification introduced by the International Union of Pure and Applied Chemistry (IUPAC)—micropores: <2 nm; mesopores: 2–50 nm; macropores: >50 nm.

The other values represent the parameters of the porous texture, determined by mercury porosimetry (Table 4). It is associated with a measuring range of pore diameters of both research methods. The mercury porosimetry method does not cover the micropore measuring range, i.e., pores below 2 nm in diameter. Additionally, in this case, the highest value of the specific surface area is a characteristic of dark chalk: 6.85 m^2/g (taken from the drill cores) and 6.36 m^2/g (coming from an anthropogenic deposit). However, the differences between the white and dark variety are much smaller. In the case of the other pore space parameters, such as the total pore volume, average pore diameter and the effective porosity, larger values are assigned white chalk (Table 4).

Table 4. The porous texture parameters as determined by mercury porosimetry of the individual lithological varieties of lacustrine chalk and industrial sorbent.

The Lacustrine Chalk Variety	Specific Area S_{POR} [m^2/g]	Total Pore Volume V_{POR} [cm^3/g]	Average Pore Diameter D_{POR} [µm]	Effective Porosity P_{POR} [% vol.]	
White	4.43	0.89	0.24	40.91 *	38.02 **
Dark	6.85	0.54	0.18	28.85 *	12.11 **
Silicified	2.12	0.29	0.07	12.74 *	8.22 **
Dark from the anthropogenic deposit	6.36	0.41	0.12	27.45 *	11.56 **
industrial sorbent					
Limestone	1.12	0.32	0.14	22.02 *	5.20 **

Explanations: * for the full range of pore diameters: 0.0005–1000 µm; ** for pore diameter range: 0.01–10 µm.

The parameters of the industrial sorbent porous texture determined by the mercury porosimetry method, in particular the specific surface area and effective porosity, compared to lacustrine chalk, especially of the white and dark varieties, achieve significantly lower values (Table 4).

3.3. SO_2 Sorption Efficiency

The values of the CI and RI indices presented in Table 5, determined by two sulphation methods, allowed the evaluation of the sorption properties of lacustrine chalk and industrial sorbent. In the case of white and dark varieties, they were assessed as excellent ($RI < 2.5$; $CI > 120$). The silicified chalk was considered to be a low-quality sorbent, which is related to the low $CaCO_3$ content (33.83% wt.). The industrial sorbent efficiency, although rated as excellent, is lower compared to lacustrine chalk. The differences are especially visible in the case of the simultaneous decarbonation and sulphation method. The RI and CI values of white and carbon chalk are at this level, while the industrial sorbent is lower. Comparing the RI and CI values of white and dark lacustrine chalk with the industrial sorbent, which is one of the best products of this type on the domestic market, it should be assumed that this mineral can be successfully used as a highly effective SO_2 sorbent, characterised by higher desulphurisation efficiency compared to limestone-milling products.

From analyzing the $CaCO_3$ content in individual lithological varieties of lacustrine chalk and in the industrial sorbent in relation to the RI and CI values, it can be seen that the efficiency of SO_2 sorption, independently from the $CaCO_3$ content in the sorbent, is also influenced by other sorbent parameters. The $CaCO_3$ content in the white chalk is much higher than in the dark chalk (Table 2), yet the RI and CI values determined for the white variety are more favourable (Table 5).

Table 5. The values of reactivity indexes (RI) [mol Ca/mol S] and absolute sorption (CI) [gS/1000g sorbent] of the individual lithological varieties of lacustrine chalk and the industrial sorbent.

Reactivity Indexes	**The Lacustrine Chalk Variety (Samples Taken from Drilling Cores)**			**The Dark Lacustrine Chalk from Anthropogenic Deposit**	**Industrial Sorbent**
	White	**Dark**	**Silicified**		
by the method of decarbonation and then sulphation					
RI	1.38	1.35	8.52	1.33	2.24
CI	173	176	49	180	143
Assessment of reactivity	Excellent	Excellent	Low quality	Excellent	Excellent
by the method of simultaneous calcination and sulphation					
RI	1.40	1.35	10.80	1.33	2.48
CI	171	175	19	180	128
Assessment of reactivity	Excellent	Excellent	Low quality	Excellent	Excellent

Explanations: the reactivity index (RI) was calculated according to the formula (4); the sorption index (CI) was calculated according to the formula (5).

3.4. The Lacustrine Chalk Parameters Responsible for the Efficiency of SO_2 Sorption

The decisive influence on the efficiency of SO_2 capture in fluidized bed boilers, apart from the phase and chemical composition, is:

- the structural and textural nature of the sorbent, and above all its porosity, which shapes the course of the sulphation process, both in the laboratory and industrial conditions. The process of binding SO_2 takes place on the inner surface of the pores formed during the decarbonation of the sorbent;

- the course and temperature of calcite thermal dissociation [19,20].

An attempt was made to define the parameters of lacustrine chalk affecting its reactivity. The analysis of the rock texture parameters presented in Tables 3 and 4 showed that the sorption properties of chalk could not be explained by a simple relationship related to the size of the pores in the sorbent and the size of the specific surface area. The white chalk, even though it has a smaller specific surface (S_{BET}—4.43 m^2/g; S_{POR}—4.68 m^2/g) compared to dark chalk, coming from both drilling cores (S_{BET}—12.28 m^2/g; S_{POR}—6.85 m^2/g) and the anthropogenic deposit (S_{BET}—11.89 m^2/g; S_{POR}—6.11 m^2/g), characterised by comparable RI and CI values. The porosity is also essentially unaffected by the efficiency of SO_2 sorption. The white chalk is characterised by a clearly higher effective porosity compared to the dark one (Table 4). The observed differences should be related to the size of the rock pores. The specific surface of the white chalk was developed mainly based on mesopores and macropores, with an insignificant share of micropores. This is confirmed by the value of the average pore diameter, which is 17.4 nm and is clearly higher compared to the average pore diameter of the dark chalk—9.5 nm and 8.3 nm (Table 4). The specific surface of dark chalk, both taken from boreholes and from the associated minerals storage site, is developed mainly by micropores and mesopores with a smaller share of macropores (Table 3). In the light of the research [18,20], the texture parameters of the porous dark chalk should be considered unfavourable for SO_2 sorption, while the chalky texture parameters are highly favourable. Despite this, the efficiency of SO_2 capture in both varieties is very similar.

The recorded thermal effects of the individual varieties of lacustrine chalk thermal decomposition in the temperature range of 25–1000 °C have the same course in all tested samples (Table 6 and Figure 9). They differ only in weight loss (Table 7), which is determined by the content of moisture, organic matter of plant origin and calcite. All recorded thermograms are dominated by a wide endothermic effect, starting at approx. 620 °C and ending at approx. 830 °C with a maximum between 800.0–807.9 °C and with a sharp collapse (almost at right angles) from the side of higher temperatures responsible for the course of the process thermal dissociation of calcite (decarbonation) (Figure 9). In addition, there are exothermic effects associated with the decomposition of organic matter of plant origin. Four reactions of this type were recorded in each variety of the chalk. The reactions maximum in the white and silicified varieties are in the temperature ranges: 323 °C—1st maximum; 385–386 °C—2nd maximum; 408 °C—3rd maximum; 525–526 °C—4th maximum. In the dark chalk, the distribution of maximum temperatures of exothermic effects is slightly different. The first maximum was recorded in a temperature range similar to that of the white and silicified variety; 2nd—404.5–407 °C; 3rd—493–495 °C; 4th—526.1–529.0 °C. This shows the different nature of the lignite substance and its carbonisation state, which is confirmed by microscopic observations. The reactions should be associated with the oxidation of organic compounds [21]. Moreover, in low-temperature ranges, thermal effects related to the loss of residual moisture were recorded: surface—23–31 °C (in all varieties of chalk) and 50–72 °C—hygroscopic (except for white chalk). The thermal decomposition of lacustrine chalk ends at a temperature of 825–827 °C with a total weight loss from 39.06% wt. (silicified chalk) to 50.03% wt. (dark chalk). Raising the temperature to 1000 °C does not cause any additional weight loss or thermal reactions. The decomposition temperature of calcite in lacustrine chalk is lower compared to the decomposition temperature of this mineral in limestone. In the case of industrial sorbent, the calcite decarbonization temperature begins at approx. 680 °C and ends at 921.6 °C. The calcite decomposition is accompanied by a weight loss, which at the temperature of 850 °C amounts to 49.32% wt. The decarbonation degree of the industrial sorbent at 850 °C is 85% wt.

Table 6. The thermal effects occurring during heating of the tested samples of lacustrine chalk in temperatures up to 1000 °C.

Number Sample	The Lacustrine Chalk Variety (Samples Taken from Drilling Cores)			The Dark Lacustrine Chalk from Anthropogenic Deposit	Industrial Sorbent
	WHITE	Dark	Silicified		
Range 25–110 °C	29.0 end.	27.0 end. 72.0 end.	23.0 end. 50.0 end.	31.0 end. 62.6 end.	71.0 end.
Range 110–600 °C	323.1 exo. 385.0 exo. 408.8 exo. 525.1 exo.	323.4 exo. 404.5 exo. 493.0 exo. 529.0 exo.	329.1 exo. 386.0 exo. 408.0 exo 527.0 exo.	323.1 exo. 407.0 exo. 495.0 exo. 526.1 exo.	- - - -
Range 600–850 °C	807.9 end.	800.0 end.	804.3 end.	801.6 end.	-
Range 850–1000 °C	-	-	-	-	921.0

Explanations: exo.—exothermic reaction; end.—endothermic reaction.

Table 7. Weight loss during heating of the tested samples of lacustrine chalk [% wt.].

Number Sample	The Lacustrine Chalk Variety (Samples Taken from Drilling Cores)			The Dark Lacustrine Chalk from Anthropogenic Deposit	Industrial Sorbent
	White	Dark	Silicified		
Range 25–110 °C	3.31	7.55	1.75	6.38	0.08
Range 25–600 °C	19.00	15.00	7.04	19.98	0.30
Range 25–850 °C	43.52	50.03	39.06	50.0	49.32
Range 25–1000 °C	43.52	50.03	39.06	50.0	58.32

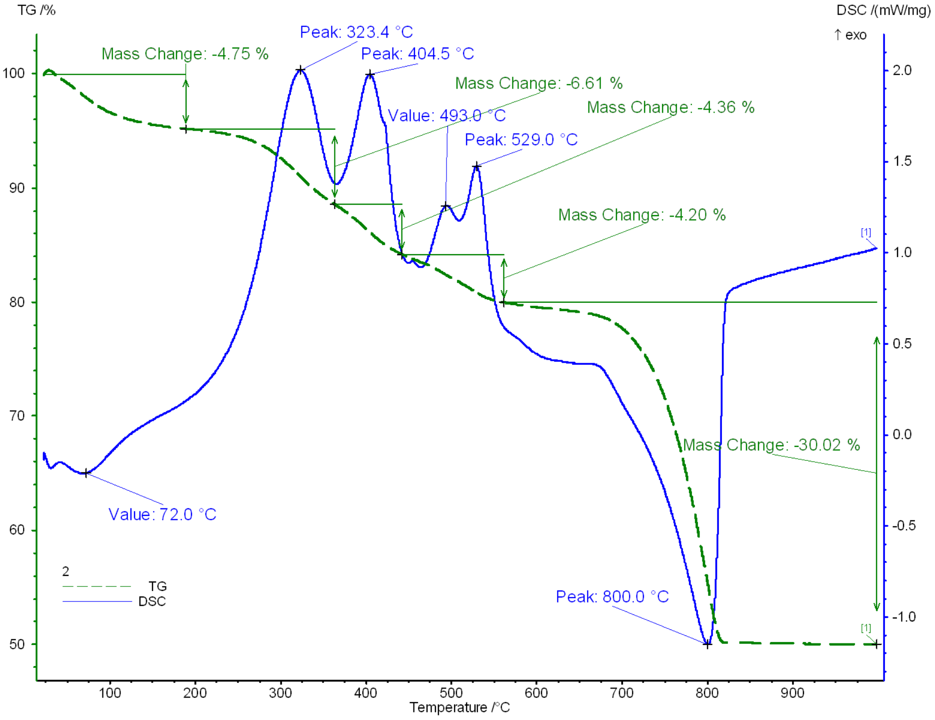


Figure 9. The thermal curves TG and DSC of the dark lacustrine chalk from the drilling cores, showing the course of the thermal dissociation process.

The course of thermal decomposition of individual varieties of lacustrine chalk has a decisive influence on the development of the porosity and specific surface of the sorbent. Tables 8 and 9 present the parameters of the porous texture after the decarbonation process at the temperature of 850 °C (combustion temperature in fluidized bed boilers) of individual lithological varieties of lacustrine chalk, taken from drilling cores and from an anthropogenic deposit, in relation to industrial sorbent made of limestone, determined using low-temperature sorption nitrogen (Table 8) and mercury porosimetry (Table 9).

Table 8. The porous texture parameters as determined by low-temperature nitrogen sorption of individual lithological varieties of lacustrine chalk and industrial sorbent after the decarbonation process.

Parameter	Symbol	Unit	The Lacustrine Chalk Variety (Samples Taken from Drilling Cores)			The Dark Lacustrine Chalk from Anthropogenic Deposit	Industrial Sorbent
			White	Dark	Silicified		
Specific area	S_{BET}	[m^2/g]	9.12	8.78	4.51	8.01	5.33
Total pore volume	$V_{tot}^{0.99}$	[cm^3/g]	0.062	0.086	0.036	0.088	0.081
Micropores volume	V_{mik}^{DR}	[cm^3/g]	0.001	0.004	0.007	0.003	0.021
Share of micropores in the total pore volume	$V_{mik}^{DR}/V_{tot}^{0.99}$	-	0.016	0.047	0.194	0.034	0.259
Mesopores volume	V_{mez}^{BJH}	[cm^3/g]	0.023	0.051	0.011	0.062	0.055
Share of mesopores in the total pore volume	$V_{mez}^{BJH}/V_{tot}^{0.99}$	-	0.371	0.593	0.306	0.705	0.679
Macropores volume	V_{mak}	[cm^3/g]	0.038	0.031	0.018	0.023	0.005
Share of macropores in the total pore volume	$V_{mak}/V_{tot}^{0.99}$	-	0.613	0.360	0.500	0.261	0.062
Average pore diameter	$D_{śr}$	nm	16.4	14.2	8.05	13.9	8.11
Average pore diameter	$D_{śr}$	µm	0.0164	0.0142	0.0081	0.0139	0.0081

Explanations: the pore size ranges are given according to the pore classification introduced by the International Union of Pure and Applied Chemistry (IUPAC)—micropores: <2 nm; mesopores: 2–50 nm; macropores: >50 nm.

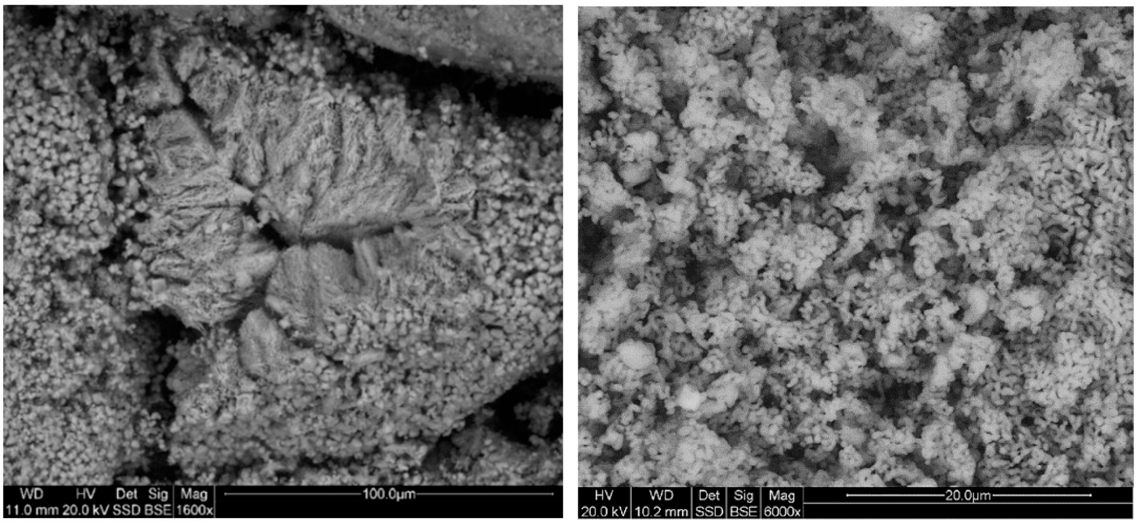
Table 9. The porous texture parameters as determined by mercury porosimetry of individual lithological varieties of lacustrine chalk and the industrial sorbent after the decarbonation process.

The Lacustrine Chalk Variety	**Specific Area S_{POR} [m^2/g]**	**Total Pore Volume V_{POR} [cm^3/g]**	**Average Pore Diameter D_{POR} [µm]**	**Effective Porosity P_{POR} [% vol.]**	
white	8.72	1.16	0.22	58.78 *	52.11 **
dark	6.98	1.46	0.64	68.12 *	66.22 **
silicified	3.10	0.59	0.35	12.74 *	10.12 **
dark from anthropogenic deposit	6.41	1.42	0.56	64.87 *	63.52 **
Industrial sorbent					
Jurassic limestone	2.93	0.85	0.17	52.17*	38.21**

Explanations: * for the full range of pore diameters: 0.0005–1000 µm; ** for the range of pore diameters: 0.01–10 µm.

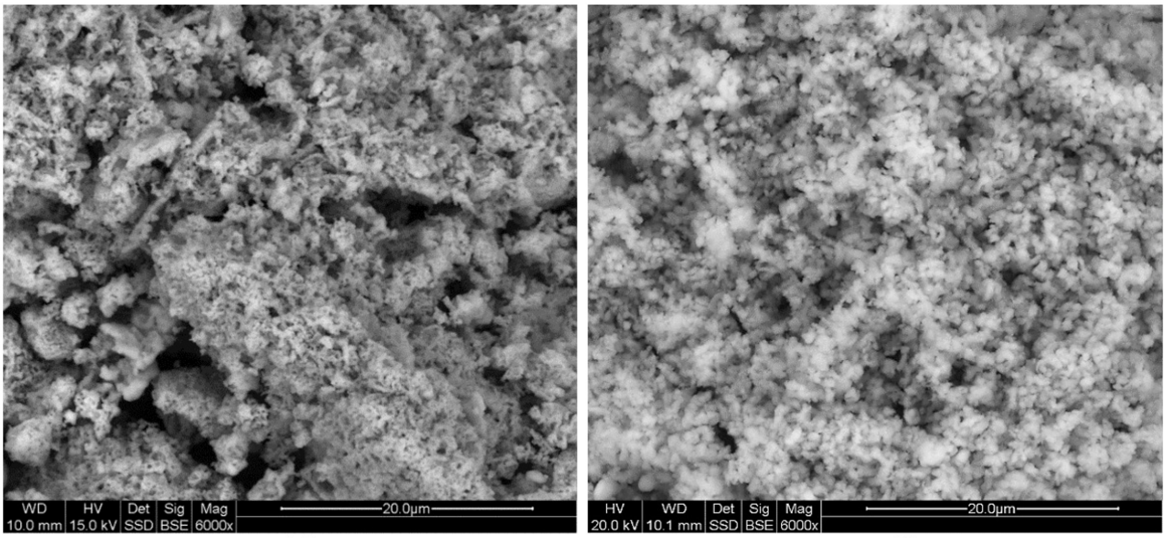
The thermal decomposition process of lacustrine chalk causes the expansion of the porous texture parameters. However, the specific surface area of individual varieties of the chalk after the decarbonation process at 850 °C is diverse. According to measurements, white chalk expanded the area to the greatest extent: S_{BE}T—9.12 m^2/g (before the S_{BET} decarbonation process—4.68 m^2/g); S_{POR}—8.72 m^2/g (before the S_{POR} decarbonation process—4.43 m^2/g). The chalk surface area values were determined before (S_{BET}—8.28 m^2/g and 8.01 m^2/g; S_{POR}—6.85 m^2/g and 6.36 m^2/g) and after the decarbonation process (S_{BET}—8.78 m^2/g and 8.01 m^2/g; S_{POR}—6.98 m^2/g and 6.41 m^2/g) are on the same level. This may suggest that the surface has not been developed with secondary pores. However, other texture parameters such as effective porosity (before—28.85% and 27.45%; after—68.12% and 64.87%) and the average pore diameter (before—0.18 µm and 0.12 µm; after—0.64 µm and 0.56 µm) (Table 9), as well as observations of the surface morphology made with the use of a scanning microscope (Figure 10a,b), indicate the expansion of porosity and thus the development of the surface area. The differences are visible mainly in the case of the effective porosity determined for the pore diameter range: 0.01–10 µm, considered as sorptive [19,20]. In the case of the tested dark chalk samples, they are 12.11% and 11.56% before the decarbonation process and 66.22% and 63.52% after the decarbonation process. These values are much higher, both than white and silicified chalk, as well as industrial sorbent. The industrial sorbent, in comparison with white and dark chalk, has the lowest effective porosity value both for the full range of pore diameters (0.0005–1000 µm)—52.17% and the range of sorption pore diameters (0.01–10 µm)—38,21%. The differences in the surface formation of the white (Figure 10a,b), dark (Figure 11a) and silicified (Figure 11b) chalk and industrial sorbent (Figure 12b) are visible in microscopic observations (SEM).

The parameters of the sorbent porous texture after the decarbonation process, such as the pore diameter and the effective porosity, have a decisive influence on the structural and textural character of the calcium sulphate formed on the sorbent grains surface. The grains of the white and dark lacustrine chalk were covered in sulphate with an extremely porous texture (Figure 13a,b). The sulphate crusts were formed on the surfaces of the silicified chalk and industrial sorbent grains, with less numerous open pores and a much smaller diameter (Figure 13c,d). The porous texture of the calcium sulphates formed on the sorbent grains surface (Figure 13a,b) guarantees the free flow of SO_2, ensuring uniform sulphation of the grains [22]. If a sulphate with a limited porosity texture forms on the sorbent grains surface (Figure 13c,d), the diffusion of SO_2 in the initial desulphurisation stage will be stopped, which will result in a low degree of sorbent utilisation, manifested by the presence of unreacted, and under industrial conditions, undissociated sorbent grain cores [19,23,24]. It should be concluded that the porosity of the sorbent, and not the $CaCO_3$ content in the sorbent, determines the efficiency of SO_2 sorption under the fluidized bed combustion technology. The SO_2 sorption process takes place on the inner surface of the pores formed during thermal dissociation. The reactivity and the ability to bind SO_2 increase with the expansion of porosity and an increase in the specific surface area [25]. Due to the fact that the molar volume of the resulting desulphurisation products ($CaSO_4$) is greater than that of $CaCO_3$, the reactivity of the sorbent will be determined by the size of the specific surface area capable of reacting with SO_2. The surface capable of reacting with SO_2 should be considered one that has been developed through pores of sufficiently large diameters on the border of the mesopores and macropores (division according to IUPAC) [19,20].



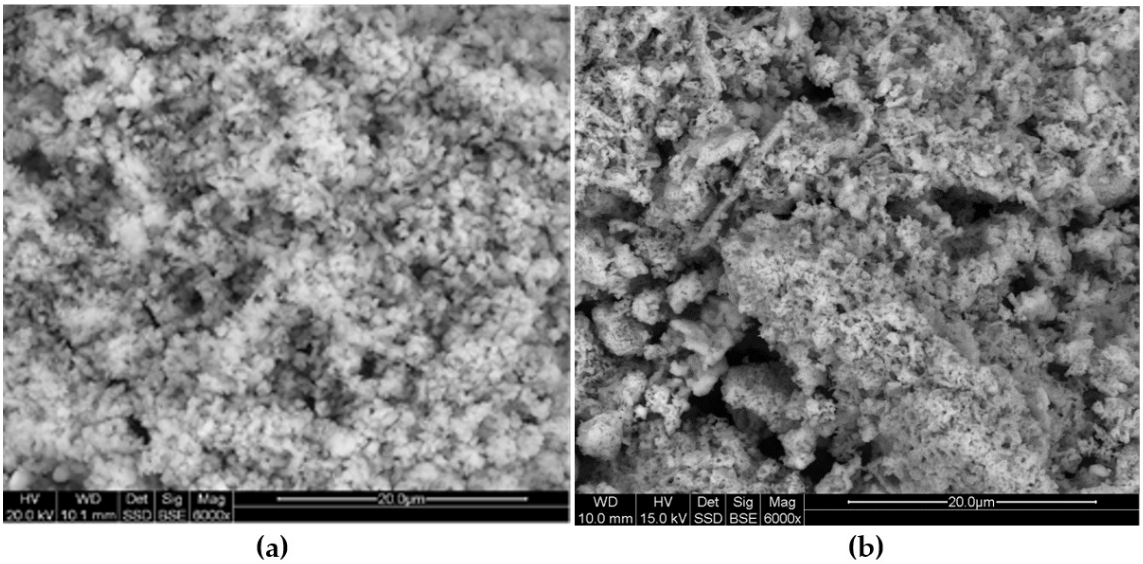
(a) **(b)**

Figure 10. The SEM image of the white lacustrine chalk grains morphology (fraction 0.125–0.250 mm) after the decarbonation process (**a**,**b**). The visible calcified algal structures after the decarbonation process (**a**).



(a) **(b)**

Figure 11. The SEM image of the lacustrine chalk grains morphology (fraction 0.125–0.250 mm) after the decarbonation process: dark (**a**) and silicified (**b**).



(a) **(b)**

Figure 12. The SEM image of the industrial sorbent grain morphology (fraction 0.125–0.250 mm) before (**a**) and after (**b**) the decarbonation process.

Typically, in the case of calcareous sorbents, secondary porosity is formed during the calcite thermal dissociation process. In the case of lacustrine chalk containing carbonised plant matter, the specific surface is additionally expanded by its complete oxidation (burning). Due to the fact that the combustion of organic matter takes place at much lower temperatures (approx. 320–530 °C) than the decomposition of calcite (approx. 800 °C), the pores formed to intensify the CO_2 removal process from the calcite structure and SO_2 migration into the sorbent grains, fulfilling the function of diffusion channels. It will be important in the real conditions, where the processes of decarbonation and SO_2 sorption occur almost simultaneously. An attempt to reflect this type of condition is the simultaneous sulphation and decarbonation method (sorbent grains are sulphated without prior decarbonisation). The RI and CI indexes, determined by this method for the dark lacustrine chalk samples, correspond to the values obtained by the sulphation method, preceded by the decarbonation process. In the case of white chalk, the differences are barely noticeable. They differ significantly in the case of silicified chalk and the industrial sorbent (Table 5).

The analysis of the pore size after the decarbonation process leads to interesting conclusions. The pore volume distributions as a function of their diameter presented in Figure 14 show that the specific surface of white and carbonised chalk after the decarbonation process, compared to the industrial sorbent, was much more developed based on pores, on the mesopore and macropore border, the so-called sorption pores. In the lacustrine chalk, they cover a wide range of diameters, from approx. 0.05–3 µm. In the industrial sorbent, the range of diameters is narrower; it is in the range from approx. 0.2–3 µm. In both cases, the pores formed during decarbonation are built up with $CaSO_4$. In the case of white and dark chalk, the pores are completely covered with sulphate, and in the case of sorbent, some of the pores remain unfilled (Figure 14). In the phase composition of the samples after the sulphation process by the simultaneous calcination and sulphation method, no unreacted portions of CaO and undissociated $CaCO_3$ were identified by X-ray diffraction. The efficiency of SO_2 sorption of lacustrine chalk, white and dark varieties, compared to the industrial sorbent, is higher. The micropores and smaller mesopores are responsible for the lower degree of sulphate filling the industrial sorbent pore space. At the initial stage of sulphation, their inlets are blocked sulphate particles, making it difficult to diffuse SO_2 inside the grains' sorbent. On the sorbent grains surface, the massive sulphate crusts are formed, as shown in Figure 13d. The SO_2 sorption process is stopped, resulting in the presence of unreacted portions of CaO and even undissociated $CaCO_3$, visible on the X-ray diffraction patterns of samples sulphated by simultaneous calcination and sulphation method. The sorption process is similar in the case of the silicified chalk. The pores considered to be sorptive were formed in the smallest amount, and the specific surface to a large extent was expanded based on micropores and smaller mesopores that do not participate in the binding of SO_2. Additionally, given the low $CaCO_3$ content, the silicified chalk cannot be used as an SO_2 sorbent.

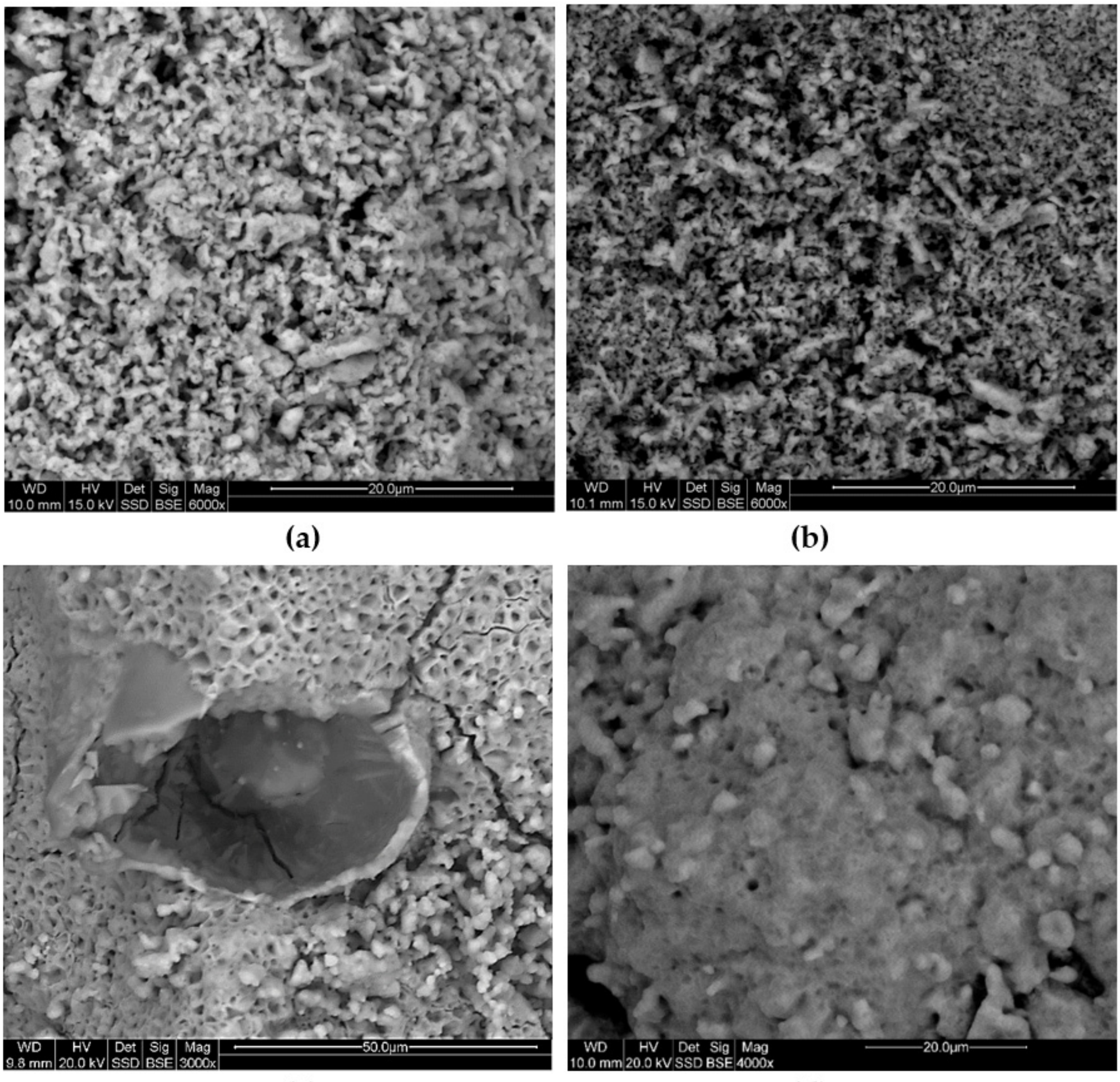


Figure 13. The SEM image of the white (**a**), dark (**b**), silicified (**c**) lacustrine chalk and industrial sorbent (**d**) morphology grains after the sulphation process.

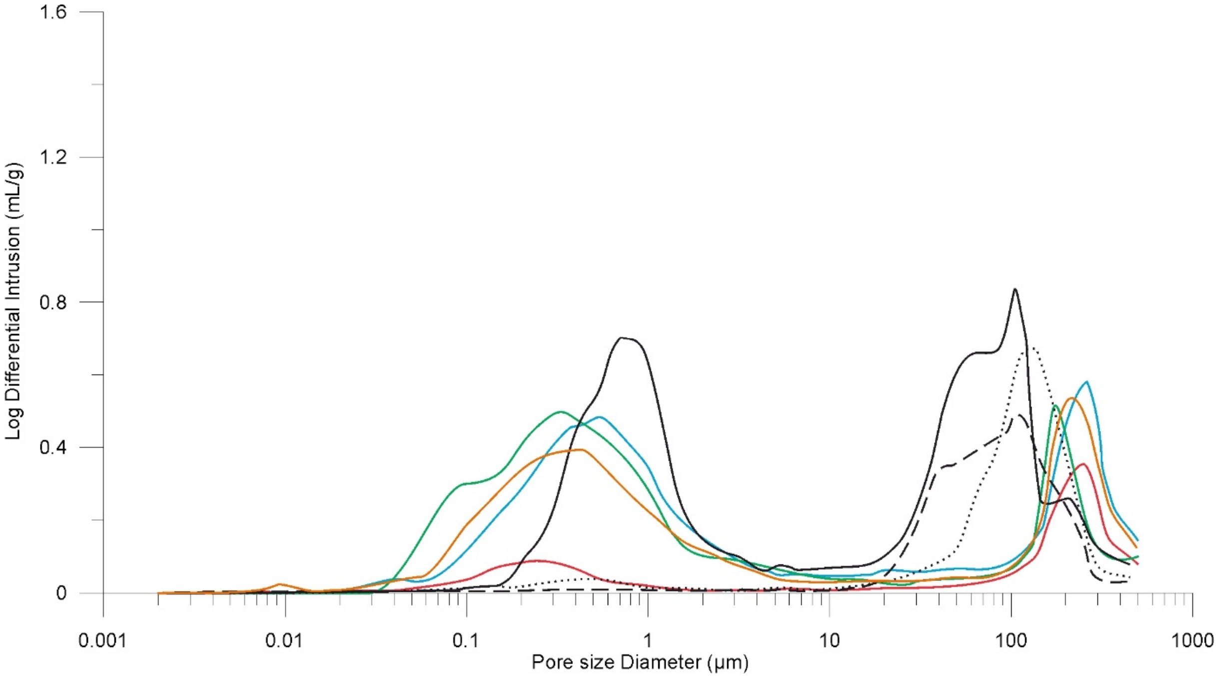


Figure 14. The pore volume distributions as a function of their diameter: the industrial sorbent (···· sample natural; – after decarbonation; — after sulphation) and individual lacustrine chalk varieties (dark: – taken from the drill core, – taken from the anthropogenic deposit; – white; – silicified) after the decarbonation process.

4. Conclusions

1. The lacustrine chalk in the Bełchatów deposit comes in three lithological varieties: white, dark and silicified. The deposit is dominated by white and dark varieties, while the silicified variety is an accessory component. The varieties differ in the content of $CaCO_3$. In addition, the dark chalk contains carbonised organic material and the silicified silica, mainly in opal and chalcedony forms. The varieties are together exploited. As a result, the chalk collected in the anthropogenic deposit represents the dark variety. When analysing the possibilities of economic use of the lacustrine chalk deposited in the Bełchatów deposit, the material collected in the landfill should be considered.

2. The determined values of the reactivity (RI) and sorption (CI) indices, as well as other physicochemical parameters of the lacustrine chalk, indicate the possibility of using the white and dark varieties in the form of sorbent to reduce SO_2 emissions in the fluidal combustion technology. The silicified chalk cannot be regarded as a potential SO_2 sorbent. Collection from the landfill, along with other chalk varieties, does not adversely affect the quality parameters of the raw material.

3. The lacustrine chalk of the white variety represents a material with high chemical activity due to the high content of $CaCO_3$, microcrystalline structure and texture parameters such as high porosity and specific surface developed mainly by mesopores and macropores. It can be successfully used as a raw material to produce SO_2 sorbent. The organic matter added in the dark variety significantly reduces the $CaCO_3$ content. The presence of carbonised organic matter only seemingly lowers the quality of dark chalk as a raw material for sorbent production. It contributes to the expansion of porosity and specific surface during the process of thermal dissociation of calcite. The expansion is based on a wide range of pore diameters on the border of meso and macropores. The pores formed are interconnected into a system, thanks to which they are able to function as CO_2 diffusion channels from the inside and SO_2 to the inside of the sorbent grains, intensifying the decarbonation and sulphation processes. After the sulphation process, these pores disappear, which indicates that their inner surface is built up by the formation of $CaSO_4$.

The outer surface of the chalk grains after the sulphation process becomes porous, which contributes to the high degree of sorbent utilisation.

4. The dark lacustrine chalk compared to the industrial limestone sorbent, even though it is characterised by a significantly lower $CaCO_3$ content, shows a much higher efficiency of SO_2 sorption expressed by the values of the RI and CI indexes. The efficiency of SO_2 sorption is determined by the parameters of the porous texture. The difference in the efficiency of SO_2 capture between lacustrine chalk and industrial sorbent is significantly influenced by the thermal dissociation temperature of calcite and the related degree of decarbonation at 850 °C. Calcite decomposition in the case of lake chalk ends in temperature from 825 °C to 827 °C. In the case of sorbent, it ends only after exceeding 920 °C, and the degree of calcite decomposition at 850 °C is 85%. The analysing the course process of thermal decomposition lacustrine chalk should be noted series of exothermic reactions in the temperature range of 320–530 °C, which are associated with oxidation of organic material. The pores formed as a result of this oxidation will intensify the processes of decarbonation and sulphation, acting as CO_2 and SO_2 diffusion channels.

5. The presence of carbonised organic material in the lacustrine chalk will have another positive aspect. It will increase the rate of heating of the sorbent grains (heat exchange between the outer surface of the grain and its interior), accelerating the release of CO_2 from the calcite structure and the binding of SO_2 on the decarbonised inner surface of the pores formed. This will be important in the case of desulphurisation technology, where the contact time of the sorbent with the flue gas in the combustion chamber is short.

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