

## POSSIBILITIES OF UTILIZING JURASSIC LIMESTONES AND WASTE RAW MATERIALS GENERATED DURING THEIR PROCESSING – A CASE STUDY FROM CENTRAL POLAND

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### ABSTRACT

#### Aim of the study

The characteristics of the analyzed carbonate rocks in terms of their geological setting, lithological features, and quality parameters are presented.

#### Material and methods

Jurassic limestones from the Działoszyn region were subjected to characterization for lithological features and quality parameters in relation to the geological conditions of their deposits. The study also included the physicochemical characteristics of carbonate-clay flour in terms of the possibility of using it in the fertilizer industry. The samples that have been subject of analyses have been collected from Raciszyn and Raciszyn II deposits that are currently exploited.

#### Results and conclusions

The deposits are characterized by high content of  $\text{CaCO}_3$  (on average, approx. 93%). Other minerals, important in terms of the possibility of being used as fertilizers, include:  $\text{MgO}$  (0.55–1.34%), followed by  $\text{Fe}_2\text{O}_3$  (approx. 0.4%), and  $\text{Al}_2\text{O}_3$  (0.07–2.49%). In contrast, in the waste raw material, i.e. carbonate-clay flour, similarly to the limestones from the Raciszyn deposits, apart from carbonates, there is also magnesium, potassium and sulfur as well as small amounts of phosphorus and sodium, which is indicative of the possibility of using this material as a deacidifying agent. The content of microelements (Fe, Mn, Zn, Cu, Co, Mo) in carbonate-clay flour indicates that this material constitutes a potential source of these nutrients for plant mineral nutrition. The content of heavy metals and metalloid (Cd, Pb, Hg, Ni, Cr, etc.) is very low; lower than the acceptable content in liming agents and mineral fertilizers.

**Keywords:** limestones, lithology, waste raw materials, liming materials, soil improvers

## INTRODUCTION

Exploitation of limestone deposits using the open-pit method is often connected with the deposition of significant amounts of mining and processing waste. Mining waste is comprised of useless intercalations occurring within the deposit as well as earth and rock masses in its overburden (including sands, clays or clay with rock debris). By contrast, processing waste usually consists of fractions of aggregate too fine for the basic product, silt from the washing of solid rocks, or intercalations of clay rocks (Świercz et al., 2021; Blaise et al., 2022).

The growing amount of mining and processing waste generated as a result of exploitation of Jurassic limestone deposits in the Działoszyn region creates the need for its economic utilization (Nieć, 2002). In this region, numerous lithostratigraphic complexes comprising diverse share of limestones, marly limestones and marls were distinguished. Wide range of limestone varieties include: massive limestones, chalk limestones (soft, brittle, porous limestones), micritic limestones and other (Guzik et al., 2023; Kahraman, 2023). The most valuable of them are characterized by  $\text{CaCO}_3$  content above 96.5% (54% CaO) (Wierzbowski et al., 1983). The carbonate rocks exploited from deposits situated in the Raciszyn area, apart from calcium carbonate ( $\text{CaCO}_3$ ), which is their basic component, contain also other minerals. Their chemical composition and physical and mechanical properties make them suitable for the cement, lime and construction industries, as well as being useful in road construction and stabilization and levelling of post-industrial areas (Małolepszy and Gajewski, 2008; Makhlofi et al., 2015).

Waste generated during the exploitation and processing of Jurassic limestones from the Raciszyn and Raciszyn II deposits is also characterized by a high content of calcium carbonate. Additionally, in their composition other minerals occur that can be used for environmental purposes, e.g. in agriculture, reclamation of post mining areas, remediation of chemically degraded areas, and stabilization of chemical contaminants, for example in land remediation (Kęsik and Jadczyszyn, 2012; Kicińska et al., 2018, 2019; Alemu et al., 2022; Wakwoya et al., 2022; Antonkiewicz and Gworek, 2023).

The aim of the study was to indicate the possibility of utilizing carbonate-clay flour from the processing of Jurassic limestones, called the “Raciszyn” flour, after characterizing its properties. The basic physical and chemical parameters of this waste raw material are presented in the context of its suitability for the production of a new deacidifying agent or soil improver. Qualitative parameters of the analyzed flour were characterized against the geological settings and lithological features of the Jurassic carbonate rock complexes occurring in the Działoszyn region (Central Poland).

## MATERIAL AND METHODS

Jurassic limestones from the Działoszyn region were subjected to characterization for lithological features and quality parameters in relation to the geological conditions of their deposits. The study also addressed physicochemical characteristics of carbonate-clay flour in terms of the possibility of using it in the fertilizer industry. The samples that have been subject of analyses have been collected from Raciszyn and Raciszyn II deposits that are currently exploited.

### Carbonate-clay flour

Carbonate-clay flour is obtained during the production of aggregates in the WKG Raciszyn mine and consists of carbonate and clay minerals.

The following analytical methods were applied to characterize the physicochemical properties of carbonate-clay flour:

- XRD phase composition analysis – a qualitative method of phase composition testing using PXRD (powder X-ray diffractometry) using a Smartlab SE (Rigaku) diffractometer;
- the analysis was performed within the angle range of 5–60° 2 $\theta$ , using reflection geometry mode with CuK $\beta$  filter. Step width was set at 0.01°, and scan speed was equal to 10°/min.;
- loss on ignition using thermogravimetric method (EN 196-2:2013-11);
- dry matter by weight method (ISO 11465:1993);
- reaction – pH in H<sub>2</sub>O (flour : solution = 1:5) by potentiometric method (EN ISO 10390:2022);
- CEC (cation exchange capacity) was determined using NH<sub>4</sub>Cl (Pansu and Gautheyrou, 2006);

- total (close to general) content of elements in the flour was determined after wet mineralization in a mixture of concentrated  $\text{HClO}_4$ (70%) and  $\text{HNO}_3$ (65%) acids, (3:2 v/v), (Jones and Case, 1990);
- the content of elements in the obtained flour filtrates was determined using a PerkinElmer Optima 7300 DV atomic emission spectrometer (Jones and Case, 1990); spectrally pure reagents and Aldrich standard solutions were used in chemical analyzes.

### Quality control of analyzes

Determinations in each of the analyzed samples were carried out in three replications. Accuracy of the analytical methods was verified based on certified reference materials and standard solutions: CRM023-050 – Trace Metals – Sandy Loam 7 (RT Corporation).

## RESULTS AND DISCUSSION

### Geological setting of occurrence of the analyzed limestone deposits in the Działoszyn region in Poland

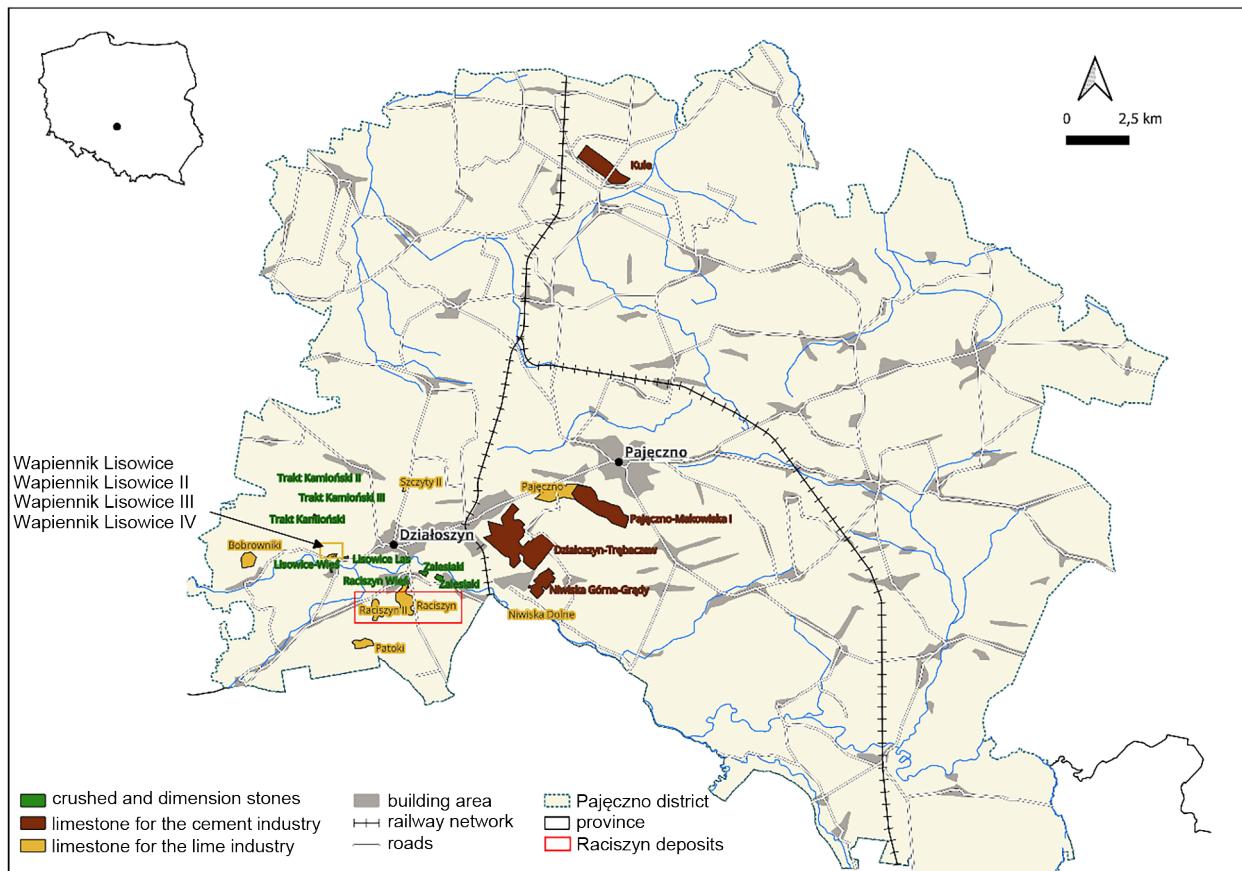
The outcrops of Jurassic limestones in the area of the Silesian-Cracovian monocline occur from the vicinity of Kraków in the south to the vicinity of Wieluń and Działoszyn in the north (Matyszkiewicz et al., 2006). In this region, three basic varieties of limestone are distinguished, showing variability in terms of lithological features, degree of lithification, and quality parameters. These include platy, bedded and massive limestones, which were formed in different parts of the Upper Jurassic sedimentary basin. The considerable lithological diversity of carbonate sediments building the Silesian-Cracovian monocline is a reflection of the facial variability associated with the strong development of biohermal complexes (mainly affected by silicious sponges and cyanobacterial structures) and dividing them basins (Matyja and Wierzbowski, 2004; Bukowska and Bukowski, 2023). In the area of Działoszyn, the presence of an over a biohermal complex was found, dozen-kilometer-long and several-kilometer-wide, showing a latitudinal extent, like most of this type of structures within the Silesian-Cracovian monocline (Matyja and Wierzbowski, 2004).

Within the Upper Jurassic sediments occurring in the area of Działoszyn, Wierzbowski et al. (1983) distinguished a number of lithostratigraphic complexes with a varied share of limestones, marly limestones and marls, with a total thickness of over 200 m (Pinkosz et al., 2004). Within their outcrops, deposits of carbonate and carbonate-clay rocks were documented, constituting the raw material base for the cement and lime industry as well as for the production of dimension stone and crushed aggregates (Fig. 1). They belong to various lithostratigraphic levels of the lowest stage of the Upper Jura (Oxfordian). The highest content of  $\text{CaCO}_3$  (even above 96.5%) can be found in Zawodzie bedded limestones, Miedzna chalky limestones, Zalesiaki massive limestones, Niwiska chalky limestones, micritic limestones and chalky limestones from Pajęczno (Table 1) (Wierzbowski et al., 1983; Pinkosz et al., 2004).

Zalesiaki limestones, currently mined in the Raciszyn and Raciszyn II deposit, belonging to the WKG Raciszyn mine (own name: WKG – Wapiennik Kamienna Góra), are of particular importance among the distinguished varieties of limestone. These rocks occur in the form of two lithological varieties – chalky and massive. The former is represented by a poorly solid, brittle pelitic limestones of white color. The latter, on the other hand, is a strongly lithified limestone of white to yellow to rusty color, associated with the occurrence of iron compounds (Łapucha, 2019).

Due to the presence of irregularly distributed caverns up to several centimeters in size, they are referred to as “Polish travertine” (Fig. 2).

In these caverns, iron and manganese compounds as well as calcite crystals are found, sometimes filling their entire interior. A characteristic feature of massive limestones is also the presence of numerous stylolites (Smoleńska, 1983). Due to the decorative properties and generally thick (sometimes not clearly visible) bedding, rocks of this variety were used in the past as a dimension stone (Nieć, 2002). The total thickness of the Zalesiaki limestone complex in the Działoszyn region is estimated at about 30 m. The limestones of the chalky and massive varieties are irregularly distributed in the profiles of the analyzed deposits of Raciszyn and Raciszyn II (Smoleńska, 1983; Bromowicz and Figarska-Warchał, 2012).



**Fig. 1.** Deposits of Upper Jurassic carbonate rocks in the Działoszyn area recognized as a resource base for the cement, lime and construction industry as of the end of 2022 (source: Szuflicki et al., 2024; own compilation)

**Table 1.** Upper Jurassic carbonate rock complexes distinguished in the Raciszyn area and the possibility of their application (source: Wierzbowski et al., 1983; Pinkosz et al., 2004)

Lithostratigraphic complex	Main varieties of rocks	Thickness [m]	Possibility of application
Middle plate limestones	I <sup>1)</sup> : 90–96.5% CaCO <sub>3</sub> , ml <sup>2)</sup> m <sup>3)</sup>	na <sup>4)</sup>	
Chalky limestones from Pajęczno	I: > 96.5% CaCO <sub>3</sub> , I: 90–96.5% CaCO <sub>3</sub>	na	limestones and marls for cement industry; limestone for industrial applications; strongly lithified limestone locally for construction purposes
Lower marly complex	m	na	
Lower plate limestones	I: 90–96.5% CaCO <sub>3</sub> , ml	na	
Micritic limestones	I: > 96.5% CaCO <sub>3</sub> , I: 90–96.5% CaCO <sub>3</sub>	0–144	cement and lime industry
Niwiska chalky limestones	I: > 96.5% CaCO <sub>3</sub> ; I: 90–96.5% CaCO <sub>3</sub>	30–130	cement industry (high-quality raw material)

Lithostratigraphic complex	Main varieties of rocks	Thickness [m]	Possibility of application
Plate limestones with tuberoids	l: > 96.5% CaCO <sub>3</sub> ; l: 90–96.5% CaCO <sub>3</sub>	0–40	— (low thickness)
Zalesiaki massive limestones <sup>5)</sup>	l: > 96.5% CaCO <sub>3</sub> ; l: 90–96.5% CaCO <sub>3</sub>	approx. 100	lime industry; production of crushed-aggregates and dimension stones
Miedzno chalky limestones	l: > 96.5% CaCO <sub>3</sub> ; l: 90–96.5% CaCO <sub>3</sub>		cement and lime industry
Zawodzie bedded limestones	l: > 96.5% CaCO <sub>3</sub> ; l: 90–96.5% CaCO <sub>3</sub>	>100 m	cement and lime industry
Jasna Góra limestones	ml, m	8.5–14	— (considerable depth of occurrence)

<sup>1)</sup> 1 – limestones, <sup>2)</sup> ml – marly limestones, <sup>3)</sup> m – marls, <sup>4)</sup> na – data not available, <sup>5)</sup> Raciszyn and Raciszyn II deposits belong to this unit



**Fig. 2.** Polish travertine from Raciszyn, Raciszyn II deposit. Dimension of block no. 974: 240 × 140 × 225 cm. (Photo by: Ireneusz Skuta, July 15, 2024)

In the analyzed limestone deposits, manifestations of karst phenomena were observed, including, among others, karst funnels, chimneys and fissures. The share of karst limestones in the Raciszyn deposit is relatively low and accounts for approx. 7%, while in recent years, exploitation in the Raciszyn II deposit has been carried out in the part of deposit in which its share is approx. 40% (Łapucha, 2019, 2020). Karst phenomena are developed both along joints surface and in accordance with the limestone bedding (Będkowski et al., 2013). In addition, karst limestones occurring in the upper part of the deposit were incorporated into the overburden (Będkowski et al., 2013). Taking into account that the total volume of extraction of limestone from the analyzed deposits has recently exceeded one million tons annually, significant amounts of rock material that is currently not used economically are generated during the mining and processing operations.

### **Qualitative parameters of limestones from the analyzed deposits**

Micrite limestones documented in the deposits of Raciszyn and Raciszyn II are characterized by a high content of  $\text{CaCO}_3$  (on average about 93%, and maximum even 98.40%). Other components, important from the point of view of the possibility of their environmental use, include:  $\text{MgO}$  from 0.21 to 4.06% (on average 0.55–1.34%),  $\text{Fe}_2\text{O}_3$  from 0.03 to 1.78% (on average approx. 0.4%), and  $\text{Al}_2\text{O}_3$  from 0.07 to 2.49%. A considerable diversity is noted in the case of  $\text{SiO}_2$  content, which in the Raciszyn deposit varies from 0.34 to 8.70% (an average of 2.38%) and in the

Raciszyn II deposit from 0.12 to 22.17% (on average 2.65%) (Table 2). Locally, a larger share of  $\text{SiO}_2$  is associated with the occurrence of karstified rocks. The voids present in the rocks, resulting from the dissolution of calcium carbonate, are filled with sandy clay deposits containing, among others, silica and aluminosilicates (Łapucha, 2019, 2020).

### **Phase composition of carbonate-clay flour**

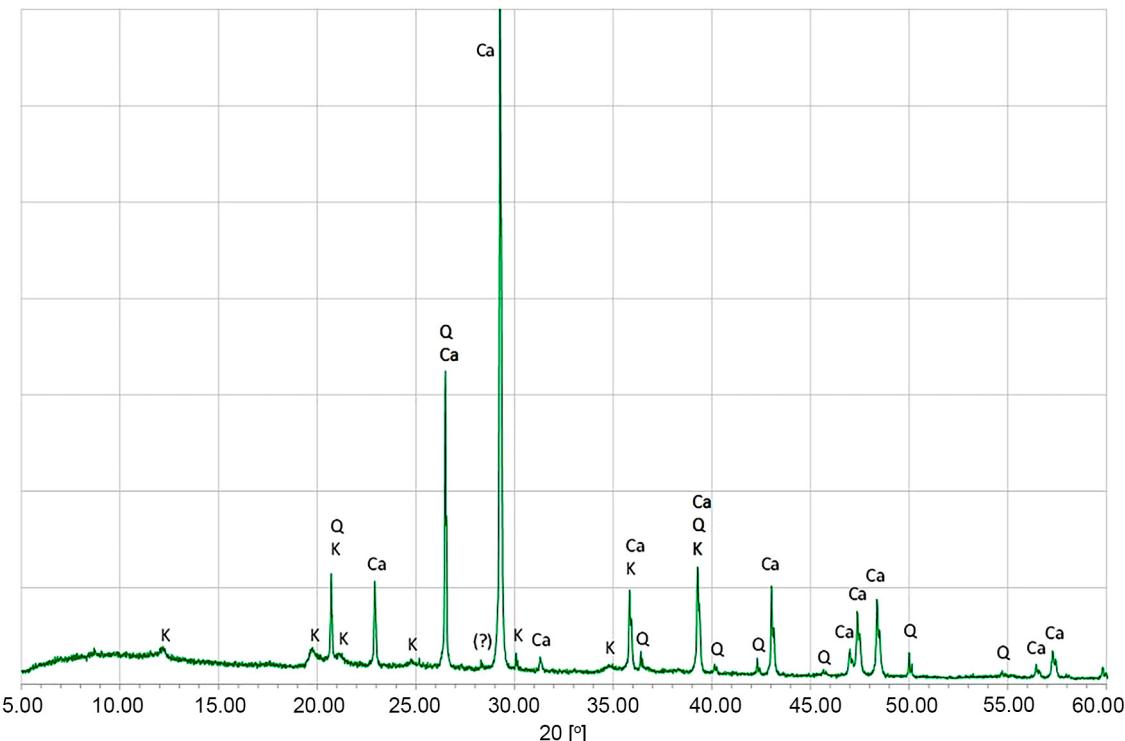
The paper determines the possible environmental use of processing material from the extraction of limestone deposits from the Działoszyn region. The diffractogram of the sample of carbonate-clay flour indicates that the main crystalline phases identified in the sample are calcite ( $\text{CaCO}_3$ ), quartz ( $\text{SiO}_2$ ) and kaolinite (aluminosilicate, Fig. 3).

The X-ray diffractogram of the tested carbonate-clay flour (Fig. 3) indicates that, in addition to the deacidifying substance (calcite), there are clay minerals, represented by kaolinite, which play an essential role in shaping soil fertility (Johnston et al., 2022). Kaolinite, an alkaline aluminum silicate, unlike other clay materials, has a compact structure and thereby is characterized by low plasticity as well as low cation exchange sorption capacity (Johnston et al., 2022).

The crystalline phases of the analyzed carbonate-clay flour indicate that this material is extremely valuable in terms of being used in fertilizers, especially of a deacidifying and sorbing nature. By contrast, the beneficial physicomechanical properties of the tested flour mean that it can also be used to increase water retention in the soil (Wang et al., 2024).

**Table 2.** Chemical composition and physicomechanical properties of limestones from Raciszyn and Raciszyn II deposit (source: MIDAS database of the Polish Geological Institute – National Research Institute; Będkowski et al., 2013; Łapucha 2019, 2020)

Deposit	Content [%]				
	$\text{CaCO}_3$	$\text{MgO}$	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$
Raciszyn	78.50–98.40 mean 93.13	0.30–1.22 mean 0.55	0.35–8.70 mean 2.38	0.07–2.20 mean 0.44	0.03–1.50 mean 0.36
Raciszyn II	74.96–97.77 mean 92.70	0.21–4.06 mean 1.34	0.12–22.17 mean 2.65	0.12–2.49 mean 0.94	0.04–1.78 mean 0.40



**Fig. 3.** X-ray pattern of carbonate-clay flour (source: Authors' own elaboration)

Abbreviations: *Q* – quartz, *Ca* – calcite, *K* – kaolinite, (?) – unidentified

The phase (chemical) composition of carbonate-clay flour suggests that, apart from the main components of calcium and silicon, this material contains significant amounts of aluminum, iron, followed by magnesium, potassium, titanium, manganese, and phosphorus, as well as small amounts of sulfur, sodium, zinc and strontium (Table 3). After prior physicochemical transformations, the above elements, occurring in various chemical forms (e.g. oxide, carbonate), may constitute a potential source of these substances for plants (Kicińska, 2021; Yahaya et al., 2023). Coloring oxides, especially Fe, Mn, Ti, present in the carbonate-clay flour, give it a greyer, ashy colour rather than white.

Determination of loss on ignition in the carbonate-clay flour was used to measure the content of unburned carbon. This parameter is related to the direction of utilization of the tested material (Fan and Brown, 2001). If the value of loss on ignition is less than 5% of the mass, then such material can be used

in the construction industry, among others for the production of concrete (Straka et al., 2014). Analysis of the carbonate-clay flour loss on ignition indicates that this material is rich in unburned coal, which is of great importance to the possible environmental use (Table 3) (Mu et al., 2017). In addition, the high value of the loss on ignition warrants a conclusion that after introduction to soil, this material will be able to retain moisture, sequestrate carbon dioxide, which is important in the circular economy (CE) (COM, 2015; Wang et al., 2024).

#### Physicochemical properties of carbonate-clay flour

The dry matter content in the carbonate-clay flour does not exceed 21%, indicating that this material has a fairly high moisture content (Table 4). Adequate moisture content of fertilizing raw materials is necessary for bonding with other mineral, mineral-organic materials in order to create durable fertilizer granules or soil improvers in the form of granules

**Table 3.** Phase (chemical) composition of carbonate-clay flour (source: Authors' own elaboration)

Property	Content [%]	Property	Content [%]
Loss on ignition at 1025°C	32.21 ± 0.17 <sup>1</sup>	Mn <sub>3</sub> O <sub>4</sub>	0.23 ± 0.05
CaO	38.80 ± 0.16	TiO <sub>2</sub>	0.23 ± 0.05
SiO <sub>2</sub>	20.30 ± 0.52	P <sub>2</sub> O <sub>5</sub>	0.20 ± 0.05
Al <sub>2</sub> O <sub>3</sub>	4.49 ± 0.11	SO <sub>3</sub>	0.03 ± 0.05
Fe <sub>2</sub> O <sub>3</sub>	2.72 ± 0.05	Na <sub>2</sub> O	0.01 ± 0.24
MgO	0.40 ± 0.11	ZnO	0.01 ± 0.05
K <sub>2</sub> O	0.33 ± 0.13	SrO	0.01 ± 0.05

<sup>1</sup> ± standard deviation

or pellets (Malinowski et al., 2016). The determined cation exchange capacity (CEC) of carbonate-clay flour points to a fairly large ion-exchange and sorption capacity, which significantly exceeds the parameters for heavy soils (Enang et al., 2022). The CEC value allows this material to be used to improve soil valuation properties, increase water retention in light soils, for land reclamation and for the production of sorbent fertilizers (Ratajczak and Hycnar, 2017).

The analysis of macroelements content (Ca, Mg, K, S, P, Na) shows that carbonate-clay flour contains the most calcium (351.6 g Ca · kg<sup>-1</sup> DM of flour), whereas in terms of calcium oxide it is 49.2% CaO, and in terms of calcium carbonate it is 87.9% CaCO<sub>3</sub>. The content of this nutrient indicates the possibility of using the flour as a liming agent in agriculture and an agent for immobilization of chemical pollutants (trace elements) in soil (Kęsik and Jadczyszyn, 2012; Li et al., 2024a).

Owing to the high reactivity and solubility of the analyzed carbonate-clay flour, it can be classified among high-quality materials that show suitability for the production of soil deacidifying agents, soil improvers, or other fertilizing products (Antonkiewicz et al., 2023; Kęsik and Jadczyszyn, 2012).

According to the regulation by the Polish Minister of Economy (Regulation 2010), the minimum CaO content in materials from limestone rock processing is 40% (Table 1 attached to the Regulation of the Minister of Economy 2010). The analyzed carbonate-clay flour meets the requirements for varieties of fertilizer lime type 05 (Calcium carbonate. Processing of limestone rocks). High moisture con-

**Table 4.** Physicochemical properties of carbonate-clay flour (source: Authors' own elaboration)

Parameter	Unit	Content
Dry matter	%	20.3 ± 0.6
pH <sub>(H<sub>2</sub>O)</sub>	—	10.2 ± 0.3
CEC*	mmol(+) · kg <sup>-1</sup> DM	184.8 ± 7.8
Total macroelements		
Phosphorus (P)		0.11 ± 0.01
Potassium (K)		1.62 ± 0.14
Sodium (Na)		0.11 ± 0.01
Magnesium (Mg)	g · kg <sup>-1</sup> DM	2.42 ± 0.06
Calcium (Ca)		351.6 ± 13.3
Sulfur (S)		0.53 ± 0.06
Total microelements		
Iron (Fe)		540.4 ± 17.0
Manganese (Mn)		249.1 ± 11.5
Cobalt (Co)		1.13 ± 0.08
Molybdenum (Mo)	mg · kg <sup>-1</sup> DM	0.04 ± 0.00
Zinc (Zn)		12.06 ± 0.81
Copper (Cu)		1.28 ± 0.09
Trace elements		
Cadmium (Cd)		0.14 ± 0.02
Lead (Pb)		2.70 ± 0.17
Mercury (Hg)		0.008 ± 0.001
Nickel (Ni)	mg · kg <sup>-1</sup> DM	1.49 ± 0.18
Chromium (Cr)		1.69 ± 0.19
Arsenic (As)		1.34 ± 0.08

CEC – cation exchange capacity

tent (reaching almost 80%), which may hinder the even distribution of flour, especially on light soils, will be a problem limiting the use of this material as a liming agent. To reduce the moisture level of the tested carbonate-clay flour, it should be dried using energy from renewable sources (RES). For example, it is recommended to dry the flour using solar tunnels or other energy sources that reduce the drying costs of this material.

The analyzed material also contains magnesium, potassium and sulfur, and small amounts of phosphorus and sodium. The content of the above-mentioned macroelements indicates that it is a valuable raw material for the production of a soil improver (Li et al., 2024b). Nitrogen was not recorded in the analyzed carbonate-clay flour, which stems from the alkalinity of this material and its mineral composition (Świercz et al., 2021).

The content of microelements (Fe, Mn, Zn, Cu, Co, Mo) in carbonate-clay flour indicates that this material, being a natural mineral substance, constitutes a potential source of these nutrients for plant mineral nutrition (Wakwoya et al., 2022).

The content of heavy metals and metalloid (Cd, Pb, Hg, Ni, Cr, As) in carbonate-clay flour is at a very low level and remains below the permissible content in agriculturally used soils (Regulation, 2016).

The chemical analysis shows that carbonate-clay flour has a diverse mineral composition, so it can be recommended in fertilization systems, in the form of a soil improver, and will be a source of nutrients for plants. From the point of view of crop fertilization, the tested carbonate-clay flour contains almost all the necessary nutrients, albeit in concentrations lower than in mineral fertilizers (Zhang et al., 2024). A large part of

these components occurs in carbonate form, and due to their low solubility, they are not so directly available to plants (Buni, 2014; Kibet et al., 2023). That is why, the action of carbonate-clay flour is slow and depends on physicochemical properties of the soil to which this material will be applied (Buni, 2014; Garbowksi et al., 2023).

#### Evaluation of the usefulness of carbonate-clay flour in view of legal regulations

To authorize carbonate-clay flour for marketing, in the form of a liming (deacidifying) agent, the content of heavy metals in this material needs to be checked. The permissible content of pollutants in mineral fertilizers and plant growth enhancers of mineral origin must not exceed the limits specified in the regulations of the Minister of Agriculture and Rural Development (Regulation MARD 2008, 2009) (Table 5).

The chemical composition of carbonate-clay flour (Table 4) shows that the content of metalloids in this material was very low and did not exceed the permissible content for fertilizer lime and other mineral fertilizers and plant growth enhancers of mineral origin (Table 5) (Regulation, 2008, 2009).

The analysis of the chemical composition shows that carbonate-clay flour does not constitute a potential source of metalloids for the soil, which indicates that this material is safe for the environment and, after a positive opinion issued by Institute of Soil Science and Plant Cultivation National Research Institute in Pulawy, it may lose the status of processing material and may be marketed in the form of liming agent or soil improver (Act on Fertilizers and Fertilization, 2007; Regulation 2008, 2009; Kęsik and Jadczyszyn, 2012).

**Table 5.** Permissible limits of pollutants in liming agents and mineral fertilizers (source: Regulation, 2008, 2009)

Metal(lloid)	Fertilizer lime	Lime fertilizer with magnesium	Other mineral fertilizers and agents
	mg · kg <sup>-1</sup> CaO	mg · kg <sup>-1</sup> CaO + MgO	mg · kg <sup>-1</sup> fertilizer
Cadmium (Cd)	8	15	50
Lead (Pb)	200	600	140
Arsenic (As)	—	—	50
Mercury (Hg)	—	—	2

## CONCLUSIONS

1. In the deposits of Zalesiaki limestones in Raciszyn, two varieties of Upper Jurassic limestones were documented, characterized by a varied lithologic features and degree of lithification. These include chalky (soft) limestones and massive (hard) limestones occurring irregularly in the profiles of the analyzed deposits.
2. In the analyzed limestone deposits, numerous manifestations of karst processes were recorded. Clay-silica deposits, which, during the exploitation of the deposit, must be removed and constitute mining waste that is currently not used economically, constitute the filling of karst voids. At the same time, in the course of aggregate production processes, processing waste in the form of carbonate-clay flour is generated.
3. The main crystalline phases identified in the tested carbonate-clay flour include calcite ( $\text{CaCO}_3$ ), quartz ( $\text{SiO}_2$ ) and clay minerals (kaolinite) playing an essential role in shaping soil fertility.
4. Carbonate-clay flour contains large amounts of calcium carbonate, reaching almost 96.5%, which can be used in agriculture as a liming (deacidifying) agent or a soil improver.
5. The content of metalloids in carbonate-clay flour was extremely low and did not exceed the permissible content for fertilizer lime or other mineral fertilizers and plant growth enhancers of mineral origin.

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## MOŻLIWOŚCI ZAGOSPODAROWANIA WAPIENI RACISZYŃSKICH ORAZ SUROWCÓW ODPADOWYCH POWSTAŁYCH PODCZAS PRZERÓBKI WAPIENI JURAJSKICH

### ABSTRAKT

#### Cel pracy

W artykule zaprezentowano możliwości zagospodarowania wapieni jurajskich pochodzących z rejonu Działoszyna oraz surowców odpadowych powstających w trakcie ich wydobycia i przeróbki. Przedstawiono charakterystykę analizowanych skał węglanowych ze względu na ich pozycję geologiczną, wykształcenie litologiczne oraz parametry jakościowe. Następnie przedstawiono skład chemiczny surowca odpadowego pod kątem zagospodarowania nawozowego.

#### Materiał i metody

Wapienie jurajskie z rejonu Działoszyna zostały poddane charakterystyce pod względem wykształcenia litologicznego oraz podstawowych parametrów jakościowych w odniesieniu do uwarunkowań geologicznych występowania ich złóż. Badania obejmowały także charakterystykę fizykochemiczną mączki węglanowo-ilastnej pod kątem możliwości jej zastosowania w przemyśle nawozowym. Analizowane próbki pobrano ze złóż Raciszyn i Raciszyn II, które są obecnie eksploatowane.

#### Wyniki i wnioski

Badane złoża z rejonu Działoszyna charakteryzują się wysoką zawartością  $\text{CaCO}_3$  (średnio ok. 93%). Spośród innych minerałów, ważnych ze względu na możliwość ich nawozowego zagospodarowania, występują:

MgO (średnio 0,55–1,34%), Fe<sub>2</sub>O<sub>3</sub> (średnio ok. 0,4%) oraz Al<sub>2</sub>O<sub>3</sub> (średnio 0,07–2,49%). Natomiast w surowcu odpadowym, tj. w mączce węglanowo-ilastej, podobnie jak w wapieniach ze złóż Raciszyna, oprócz węglanów znajdują się także magnez, potas i siarka oraz niewielkie ilości fosforu i sodu. Pozwala to na wykorzystanie tego materiału jako środka odkwaszającego. Zawartość mikroelementów (Fe, Mn, Zn, Cu, Co, Mo) w mączce węglanowo-ilastej wskazuje, że materiał ten, będąc naturalną kopaliną, stanowi potencjalne źródło tych składników do mineralnego odżywiania roślin. Metale ciężkie i metaloid (Cd, Pb, Hg, Ni, Cr, As) występują na bardzo niskim poziomie, mniejszym niż dopuszczalne zawartości w środkach wapniających i nawozach mineralnych. Na podstawie badań nad składem mineralnym mączki węglanowo-ilastej stwierdza się, że zawartość wyżej wymienionych składników (makro-, mikroelementów i metali ciężkich) jest na poziomie optymalnym dla nawozów, dlatego materiał ten stanowi wartościowy surowiec do produkcji środka wapniającego i/lub poprawiającego właściwości gleby.

**Słowa kluczowe:** wapienie, litologia, surowce odpadowe, środki wapniające, polepszacz gleby, zagospodarowanie