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Assessment of the potential use of limestone based on the examples of the selected deposits from southern Poland

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Abstract
The objectives of this research were to present the properties, possible directions of use and the economic potential of limestone that occurs in the deposits of southern Poland in a broader international context and also to propose a methodical algorithm, allowing for the identification of the essential uses of limestone. The Carboniferous and Middle Triassic rocks were tested. Macroscopic and microscopic description, X-ray fluorescence (XRF), qualitative and quantitative X-ray diffraction (XRD), as well as tests of physical-mechanical and sorption properties were performed. The limestones are high-purity rocks (CaO content ≥49.95 wt.%; $CaCO_3$ content ≥93.8%) with a low proportion of admixtures (mainly SiO_2 as well as Al_2O_3, Fe_2O_3, MgO and Na_2O). They have a broad scope of applications. Depending on their origin and properties, they can be used for the production of cement and lime, as a road aggregate, fertilizer, animal feed additive, mine safety dust or a sorbent for flue gas desulphurization in the iron and steel industry, as well as a component for glass production. The X-ray fluorescence (XRF) analysis can be applied as an effective principal tool for assessing the suitability of limestone for various economic purposes. On this basis, the rock varieties for further investigation, including the X-ray diffraction (XRD) analysis and tests of the physical-mechanical and sorption properties, can be selected.

Keywords
limestone properties; assessment of limestone use; economic potential of limestone; XRF; XRD

Introduction

Limestone is a sedimentary rock with many economic applications. This is due to the diversity of its mineral and chemical composition and, consequently, its physical-mechanical and technological properties. Limestone is widely used as building stone (Calvo & Regueiro, 2010; Revuelta, 2021) and for the production of lime (Jiang et al., 2019; Sandström et al., 2024), Portland cement (Lothenbach et al., 2008; Lee et al., 2024; Zhang et al., 2024), as well as mortar and concrete (Bentz et al., 2015; Souza et al., 2020; Jiang et al., 2024). In the road industry, it is applied, among others, as an aggregate (Salam et al., 2018; Trzciński et al., 2021) and as a component of mineral-asphalt mixtures (Li & Yang, 2021). In agriculture, ground limestone is commonly used as a fertilizer (Crusciol et al., 2017) and as an additive to animal feed (Gilani et al., 2022). The rock is also applied in the metallurgical industry as a flux and during smelting and refining (Sivrikaya, 2018; Gupta et al., 2024) and as a component for glass production (West, 2012) and paper production (Dölle, 2021). Environmental applications of limestone include wastewater and water treatment (Silva et al., 2012; Iakovleva et al., 2015; Turingan et al., 2022) and desulphurization of the flue gases (Lim et al., 2020; Szlugaj & Galos, 2021; Li et al., 2022). Limestone-based mineral fillers find their application in the production of plastics (Vinayagamoorthy, 2020), rubber (Zhao et al., 2021), and paints. Finely ground limestone is used in mining to mitigate the explosion potential (Huang & Honaker, 2016; Sahu & Mishra, 2024). The rock is also applied to stabilize clay soils (de Souza Batista, 2024) and has several other minor uses.

All of this makes limestone a very significant and desirable mineral resource that will remain in demand for a long time. Global limestone production in 2022 was approximately 5 Gt (Medium, 2023). The size of the global limestone market was projected to grow from USD 77.2 Billion in 2022 to USD 98.6 Billion in 2027 (Global Market Estimates, 2024).

Poland is a country rich in limestone. The deposits are mainly located in the southern belt of the country: in the Holy Cross Mountains (the vicinity of the town of Kielce), in the Silesian-Cracow (Kraków) area (between the towns of Opole, Częstochowa and Kraków), in the Lublin Upland and in central Poland (Fig. 1). Given their geological age; they represent a very wide interval. Most of them are deposits of the Jurassic (almost 60% of the resources), Cretaceous (more than 21%), Devonian (approximately 8%), and Triassic (approximately 8%) ages (Lewicka et al., 2020; Brzeziński, 2023). In addition, Cambrian, Carboniferous and Neogene deposits are also recognized. Detailed information on the occurrence and structure of these deposits was previously presented (Nieć & Tchórzewska, 2000; Stanienda, 2013; Brzeziński & Miśkiewicz, 2023).

Fig. 1. Occurrence and age of the major limestone deposit areas in Poland (after Lewicka et al., 2020; modified).

The economic resources of limestone for the lime industry in Poland amounted to ca. 5.5 billion Mg in 2023 (in 129 deposits), whereas the economic resources of limestone and marl for the cement industry were nearly 12.4 billion Mg (in 70 deposits). The annual extraction of these rocks increased steadily between 2016 and 2022 to reach approximately 50 million Mg in 2022 and decreased to 45.6 million Mg in 2023 (Brzeziński, 2023) (Fig. 2).

Fig. 2. Production of limestone and marl for the cement and lime industries in Poland in the years 2016-2022 (based on the data from PIG-PIB, 2024).

On the European scale, Poland is a significant producer of lime and cement. Lime production in our country remained at approximately 1.7-1.8 million Mg/y in 2018-2022 (Statistics Poland, 2023), while the total lime production in the European Union was estimated at 20 million Mg in 2017 (Manocha & Ponchon, 2018), and stayed at a similar level thereafter. Furthermore, cement production in Poland between 2018 and 2022 was ca. 19 million Mg/y (Statistics Poland, 2023), representing more than 10% of total cement production in the EU countries (Cembureau, 2024).

The resources of limestone used as aggregates in Poland exceeded 2 billion Mg (in more than 150 deposits) in 2023, with a stable annual production of approximately 20 million Mg (Brzeziński & Miśkiewicz, 2023).

The objectives of this research were as follows:

1. Present the economic potential of limestone that occurs in Poland based on the selected deposits.
2. Determine the properties of limestone from various deposits in southern Poland and, on this basis, identify possible directions for the use of this rock in the broader international context.
3. Propose the algorithm based on the X-ray fluorescence (XRF) analysis to assess the suitability of limestone for various economic purposes.

The algorithm concept relating to several possible ways of applying limestone has not been introduced before. The significance of the XRF and XRD analyses for the evaluation of limestone uses was discussed by Mitchell (2011). The importance of macroscopic analyses for the overall characteristics of the rock was also indicated (Mitchell, 2011). The same aspect as well as the performance of the technological tests used to assess the suitability of limestone for construction, was described, and recommendations were proposed to modify existing European regulations by Ortega-Diaz et al. (2011).

Material and Methods

Material

In total, seven samples for laboratory tests were collected from three deposits under exploitation located in southern Poland. They were obtained from the producers. For confidentiality reasons, the authors were obliged not to provide the names of the mines and details that could allow their identification. Two samples of Lower Carboniferous limestone (samples 1 and 2) come from a deposit situated in the Kraków (Cracow) area (Fig. 1). Five samples are of the Middle Triassic (Muschelkalk) age, among which three represent the Górażdże Formation (samples 3, 4 and 5), and two - the Karchowice Formation (samples 6 and 7) (Tab. 1). These rocks were collected in the vicinity of the town of Opole (Fig. 1). All the samples were dried at the room temperature before starting the analytical procedures.

Methods

The examination was performed following the methodical algorithm presented in Fig. 3. It shows the sequence of the analytical methods applied and the information obtained or the economic use of limestone, which can be identified. It includes macroscopic and microscopic description, X-ray fluorescence (XRF), qualitative and quantitative X-ray diffraction (XRD), and physical-mechanical and sorption properties tests.

The description of macroscopic and microscopic features was performed to obtain the general characteristics of the limestones studied. The results of the chemical composition analysis using X-ray fluorescence (XRF) served as a basic tool for identifying the industrial uses of the rocks. The method provides the broadest information on the chemical composition of limestone, including the content of trace elements.

Therefore, it indicates limestone suitability (or lack thereof) for most of the main uses discussed here. The results of the XRF analysis enabled sample selection for further tests. Three rock samples (1, 5 and 6), one from each deposit considered to have the highest CaO content, were chosen for the phase composition analysis by the X-ray diffraction (XRD) analysis. The results of the XRF analysis also served as a basis for selecting samples for the tests of the physical-mechanical properties of the rocks, and all samples were chosen. Based on the results of the XRD examination, two samples (1 and 5) with the highest $CaCO_3$ content were selected for the sorption properties test.

Tab. 1. Lithostratigraphic Units of Muschelkalk in southern Poland (based on Szulc, 2000; Stanienda, 2013)

Lithostratigraphy				Unit Name	Type of sediment	Marine transgressive-regressive cycles
			Group Name			
TRIASSIC	Muschelkalk	*Middle*	Diplopora Formation		Post-barrier, sublitoral facies	Regression stage
		Lower	Karchowice Formation	Upper Biohermal Limestones	Barrier facies	Regression stage
				Upper Crinoidea Limestones		
				Lower Biohermal Limestones		
				Lower Crinoidea Limestones		
			Dziewkowice (Terebratula) Formation		Off-Barrier facies	The subsequent phase of transgression
			Górażdże Formation		Barrier facies	Oscillatory transgressions with elements of small-scale regressive episodes
			Gogolin Formation		Lagoonal facies Littoral facies	Initial phase of the transgression

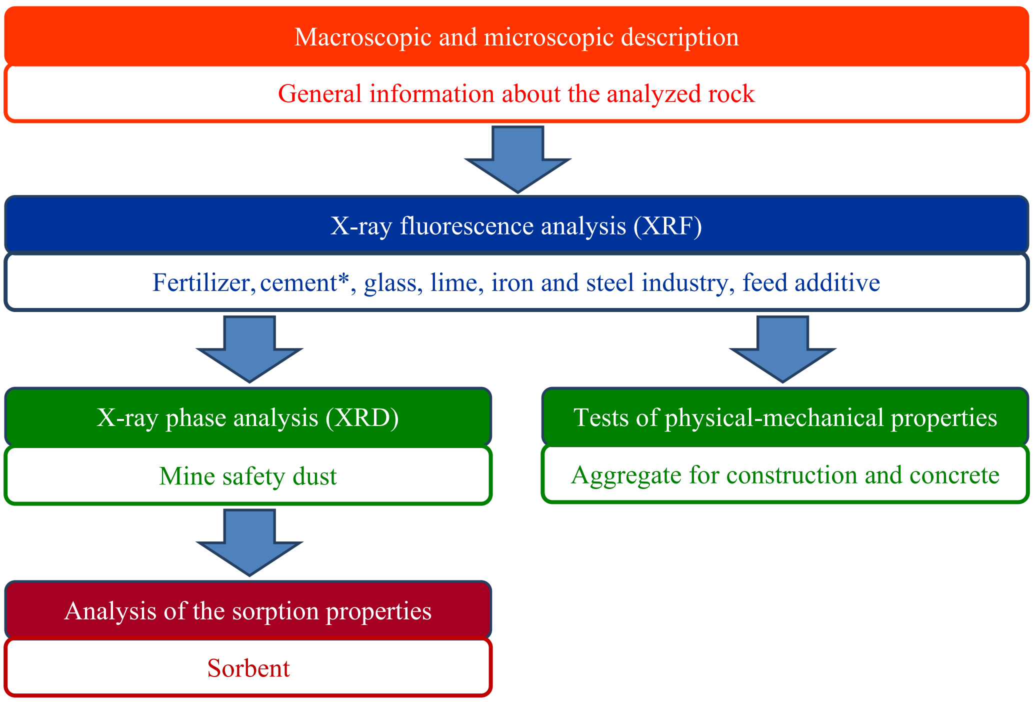

Fig. 3. Algorithm for identifying the selected economic uses of limestone (- for cement, the clay content has to be additionally determined)*

The macroscopic description comprised information on the colour of the rock, the textural and structural characteristics, and the mineral composition of the limestones.

Microscopic observations were carried out in transmitted light using the Zeiss Axioscope microscope, cooperating with the K 300 image analyzer. Observations were made at magnifications of x100 and x200.

The crushed rock samples were grinded to a fraction of <0.06 mm to perform the XRF analysis. It was carried out using the X-ray Fluorescence Spectrometer (XRF), ZSX Primus II by Rigaku, which uses wavelength dispersion for measurements. The maximum lamp voltage is 60 kV (rhodium lamp), and the measuring range is Be - U. Fundamental parameters method was used. The content of the main components and the trace elements were measured. The loss of ignition (LOI) was determined by the weight method. The XRD analysis enabled the identification of individual crystalline phases in the tested powder samples. Identification consisted of matching the obtained diffraction pattern based on the position of the peaks and their intensity to the data contained in the diffraction databases (Rietveld method). Measurements were performed using an AERIS diffractometer by PANalytical equipped with CuKα lamp; voltage 40 kV; current 8 mA; step 0.003° of angle 2theta; time 4.84 s.

To assess limestone suitability as an aggregate for construction applications, the following determinations were made: grain size, fines content, resistance to fragmentation, bulk density, water absorption, resistance to freezing, load-bearing capacity index (CBR), specific surface area, clay content, and cation exchange capacity (CEC). Testing methods specified in European standards (PN-EN 932; PN-EN 933; PN-EN 1097)[1] were used, including the way of sample preparation required for each parameter. The geometrical properties of aggregates were not determined as they concern specific aggregate fractions obtained during processing.

Samples for the test of sorption properties were chosen based on the results of the XRD analysis. Two samples (1 and 5) were used. The test was conducted on the limestone powder obtained by grinding the initial limestone samples. Each sample had a mass of 1.5 g and a grain size of 0.125-0.25 mm. The samples were initially calcined at 850 °C in the electrically heated laboratory furnace under synthetic flue gas composed of 16% CO_2, 3% O_2 and 81% N_2. Subsequently, the samples were sulfated for 60 minutes by adding 1,870 ppm of SO_2 to the flue gas mixture. The flow rate of the flue gas was 5 l/min. The sulfur content in the samples was determined by a Leco TruSpec analyzer. The values of the RI and CI coefficients, which indicate the efficiency of the desulfurization process and, therefore, the quality of the sorbent, were determined (Hycnar, 2018). The reactivity index (RI) is defined as the number of moles of calcium needed to bind a mole of sulfur, while the absolute sorption index (CI) is the amount of sulfur bound by 1000g of the sorbent (Wichliński & Włodarczyk, 2021). The values of the coefficients were calculated as described by Wichliński & Włodarczyk (2021). The analysis results were then compared with the Ahlstrom sorbent classification (Hycnar, 2018) (Tab. 2).

Tab. 2. The Ahlstrom Pyropower reference values of the reactivity index (RI) and the absolute sorption index (CI) (Hycnar, 2018)

Sorbent quality	RI [Ca/S moles]	CI [g S/1000g of a sorbent]
Excellent	<2.5	>120
Very good	2.5-3.0	100-120
Good	3.0-4.0	80-100
Sufficient	4.0-5.0	60-80
Low	>5.0	<60

Results

Macroscopic description

The analyzed rocks differ in colour and textural-structural properties. The intense reaction with HCl confirms that they are abundant in calcium carbonate.

Carboniferous micritic limestone (samples 1 and 2) is dark grey in colour (Figs. 4a, b), which is related to the admixtures of bituminous substance.

Middle Triassic limestone of the Górażdże Formation (samples 3-5) is grey-yellow (Figs. 4c, e) or brown-yellow (Fig. 4d). The yellow and brown tint indicates the presence of iron compounds. The rock is micritic, rarely sparitic (Fig. 4d). In some parts, the texture is organodetrital (visible fossils detritus). The limestone is usually massive and partly porous. The reduced hardness of sample 3 is related to the presence of clay minerals and iron compounds. Middle Triassic rock of the Karchowice Formation (samples 6 and 7) is grey-beige and grey-yellow, in some places brownish in colour (Figs. 4f, g), reflecting the occurrence of iron compounds. In places, sample 7 shows dark grey manganese dendrites. The texture is micritic, partly (sample 7) organodetrital (daily trochites are visible). The limestone is massive, rarely porous or cavernous.

[1] All of the standards referred to here are complex standards. Each of them consists of several parts, which were published in different years. Therefore, the year can not be given. Consequently, only the main number and the main title, without the year of publishing, are given in the list of the references.

a) Sample 1 b) Sample 2 c) Sample 3 d) Sample 4

e) Sample 5 f) Sample 6 g) Sample 7

Fig. 4. Photographs of the limestone samples

Microscopic description

Carboniferous limestone (samples 1 and 2) in the microscopic images has an organodetritic texture and, in some areas, a sparitic or microsparitic texture (Fig. 5a). Bioclasts (allochems - organic debris) and single or multiple larger sparitic calcite crystals are usually scattered chaotically in the microsparitic or, in some places, sparitic rock mass. Bioclasts vary in size and shape. Larger, sparitic calcite crystals fill the veins or sockets. Calcite is a predominant component of the rocks studied. In some crystals, cleavage is visible (Fig. 5b). In sample 2 (Fig. 5c), twinning of calcite crystals can be observed. Additionally, iron compounds are present, forming concentrations or filling stylolites (Fig. 5d).

The Triassic limestone of the Górażdże Formation (samples 3-5) shows a microsparitic (Figs. 5e-g) or biomorphic (Figs. 5h-l) texture. Sample 3 is built of a microsparitic rock mass, while samples 4 and 5 are composed of bioclasts cemented by a microsparitic binder. Veins and sockets filled with sparitic calcite can be seen (Fig. 5f). In some crystals, bidirectional cleavage can be observed (Fig. 5g). The bioclasts, varying in size and shape, are scattered chaotically in the rock mass (Figs. 5h-j). Foraminifera, Bivalvia, and Gastropoda were identified (Figs. 5h, i, k). The bioclasts are mainly surrounded by iron compounds (Figs. 5k, l). The interiors are filled with microsparite, sparite calcite, or iron compounds.

The rocks of the Karchowice Formation (samples 6 and 7) have a sparitic and organodetritic texture (sample 6) or a biomorphic texture (sample 7) (Figs. 5m, o). They are massive and porous in places (Fig. 5m, o). Bioclasts have varied sizes and shapes. In sample 6, they are more elongated and have a fibrous structure (Fig. 5m). Some bigger calcite crystals with clearly visible cleavage systems can be observed (Fig. 5n). The interior of the bioclasts in sample 7 is filled with micritic or microsparitic calcite, and some bioclasts are filled with sparitic calcite crystals.

X-Ray Fluorescence (XRF) results

The CaO content varies between 49.95 wt.% (sample 3) and 54.94 wt.% (sample 6) (Tab. 3). The proportion of MgO is not greater than 0.60 wt.%, and that of Fe_2O_3 does not exceed 0.40 wt.%. Sample 3 contains the highest amount of silica and clay (SiO_2 = 8.10 wt.%, Al_2O_3 = 1.99 wt.%, respectively) among the samples studied. This indicates the presence of silicates and aluminosilicates such as quartz, clay minerals, and feldspars. The latter is also associated with sodium and potassium oxides. In samples 4 and 5, also representing the Górażdże Formation of the Middle Triassic, the content of SiO_2 and Al_2O_3 is much lower (1.57 wt% and 0.21 wt.%, as well as 1.60 wt.% and 0.23 wt.%, respectively).

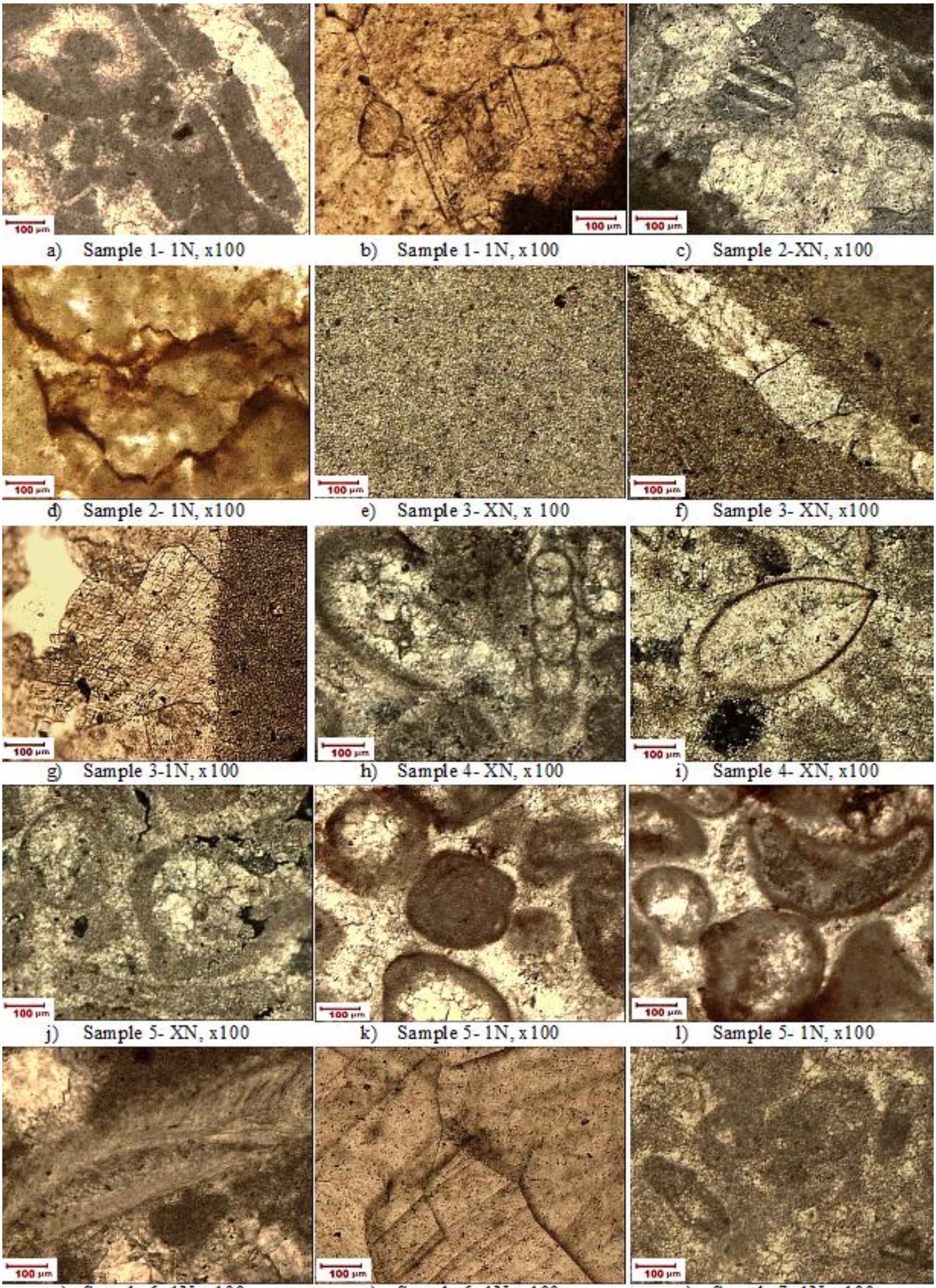

Fig. 5. Microscopic photographs of limestone samples

When considering the Carboniferous limestone (samples 1 and 2) and Triassic limestone from the Karchowice Formation (samples 6 and 7), the SiO_2 content is approximately 5 wt.% and 3-4 wt.%, respectively, and the Al_2O_3 content ≤0.20 wt.% and ≤0.55 wt.%, respectively. Sample 3 is also characterized by the highest content of F and Ti (Tabs. 3 and 4). In samples 4 and 5, a very high Cl content (643 and 1444 ppm) (Tab. 4) was observed. The results indicate the high purity of the tested rocks.

Data on Carboniferous limestone are similar to those obtained by Lech (2011) and Haoran et al. (2018). The limestone of the Górażdże Formation studied here is poorer in CaO but more abundant in SiO_2, Al_2O_3, and Na_2O, with similar content of trace elements, compared to the rocks previously examined by Szulc (2000) and Stanienda (2013). The Karchowice Formation limestone is characterized by the comparable values of CaO, SiO_2, and Al_2O_3 as well as the content of trace elements to those presented in references (Szulc, 2000; Stanienda, 2013) but higher values of Na_2O.

Tab. 3. The main components of the rocks studied [wt.%]

Chemical component	Sample 1	2	3	4	5	6	7
SiO_2	5.06	5.44	8.10	1.57	1.60	3.83	3.19
TiO_2	0.00	0.01	0.06	0.01	0.01	0.02	0.02
Al_2O_3	0.14	0.20	1.99	0.21	0.23	0.53	0.51
Fe_2O_3	0.03	0.04	0.39	0.28	0.29	0.25	0.32
MnO	0.00	0.01	0.00	0.01	0.02	0.01	0.01
MgO	0.39	0.49	0.60	0.20	0.23	0.46	0.36
CaO	50.38	50.32	49.95	53.27	53.48	54.94	51.57
Na_2O	0.57	0.54	0.38	0.42	0.83	0.37	0.26
K_2O	0.01	0.03	0.17	0.02	0.03	0.05	0.05
SO_3	0.09	0.09	0.16	0.21	0.21	0.40	0.33
BaO	0.00	0.00	0.00	0.00	0.00	0.05	0.00
SrO	0.02	0.03	0.10	0.02	0.02	0.08	0.06
ZnO	0.00	0.00	0.01	0.01	0.01	0.01	0.02
F	0.00	0.00	0.07	0.00	0.00	0.00	0.00
Cl	0.01	0.01	0.01	0.06	0.14	0.01	0.01
LOI	43.30	42.80	38.00	43.70	42.90	39.00	43.30
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Tab. 4. Trace elements of the rocks studied [ppm]

Chemical component	Sample 1	2	3	4	5	6	7
P	29	36	90	30	65	45	47
Ti	21	61	373	69	44	94	133
Mn	30	45	35	119	127	81	62
Ni	15	20	16	16	24	19	24
Cu	23	19	17	13	22	20	14
Zn	30	28	40	73	82	98	148
Rb	bdl	bdl	6	bdl	bdl	bdl	bdl
Cr	bdl	bdl	bdl	bdl	bdl	6	bdl
Pb	bdl	bdl	bdl	bdl	62	bdl	bdl
Cl	81	85	139	643	1444	92	103
As	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Hg	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Cd	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Sb	bdl	bdl	bdl	bdl	bdl	bdl	bdl

Explanation: bdl- below detection limit

X-Ray Diffraction (XRD) results

Figure 6 shows an example of the diffractogram obtained from the Carboniferous limestone (Sample 1), while the results are given in Tab. 5.

Samples tested are high-purity limestones that contain between 93.8 wt.% and 99.5 wt.% calcium (Tab. 5). Sample 1 reveals a small dolomite admixture (Fig. 6, Tab. 5), which was not detected in other samples. Quartz occurs in a much-varied amount (0.3 – 5.3 wt.%); in sample 5 (the Górażdże Formation) is the most abundant. Clay minerals are represented by kaolinite, a small admixture (0.6 wt.%) of which was found in sample 6 (the Karchowice Formation) (Tab. 5).

The results of the X-Ray Diffraction analysis of Carboniferous limestone (sample 1) and the Triassic limestone from the Górażdże Formation (sample 5) are similar to those previously published by Stanienda (2013). More distinct differences are observed for the limestone of the Karchowice Formation (sample 6), which was previously found to contain larger admixtures of high magnesium calcite, dolomite, siderite, muscovite, and albite (Stanienda, 2013).

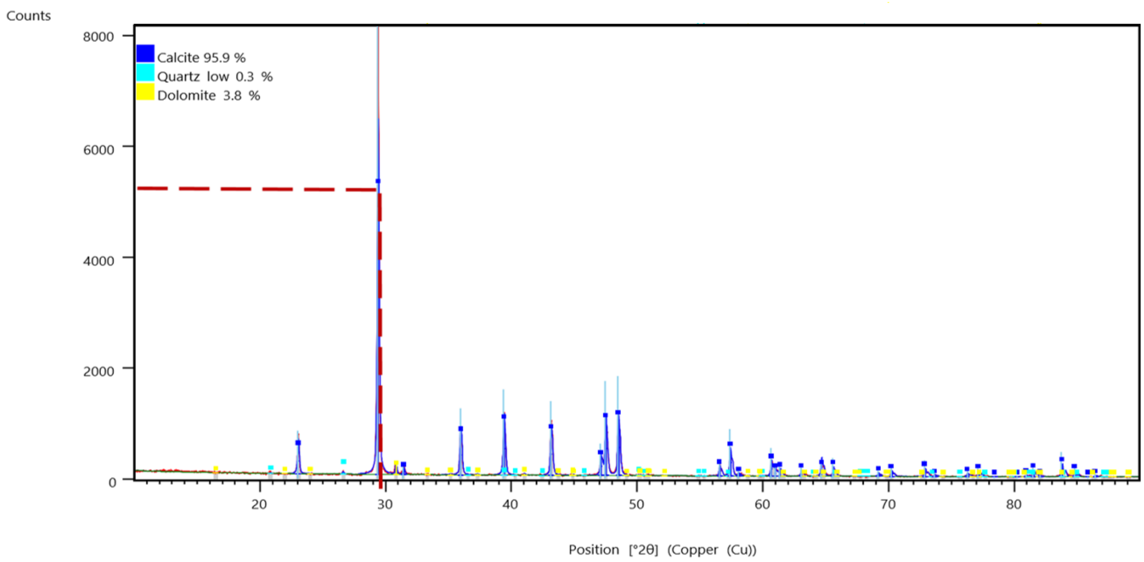

Fig. 6. Example of a diffractogram obtained (sample 1 – Carboniferous limestone)

Tab. 5. Results of the X-Ray Diffraction analysis [wt.%]

Mineral phase	Sample 1	Sample 5	Sample 6
Calcite [$CaCO_3$]	95.9	99.5	93.8
Dolomite [$CaMg(CO_3)_2$]	3.8	bdl	bdl
Quartz [SiO_2]	0.3	0.5	5.3
Kaolinite [$Al_2(Si_2O_5)(OH)_4$]	bdl	0.0	0.9

Explanation: bdl- below detection limit

Results of the physical-mechanical properties tests

The grain composition is the basic characteristic of aggregates that determines their suitability for applications in the construction industry. For the aggregate samples analyzed, the grain size results from the types of commercial products offered by the mining plant. The grain size can be modified, but this requires a change in the production process.

Of the seven analyzed aggregate samples, these obtained from the Triassic limestones (samples 3-7) are characterized by the continuous grain size (Fig. 7), while those produced from the Carboniferous limestone are single-fraction coarse aggregates (Fig. 7). Continuous-grained aggregates are preferred for use in construction.

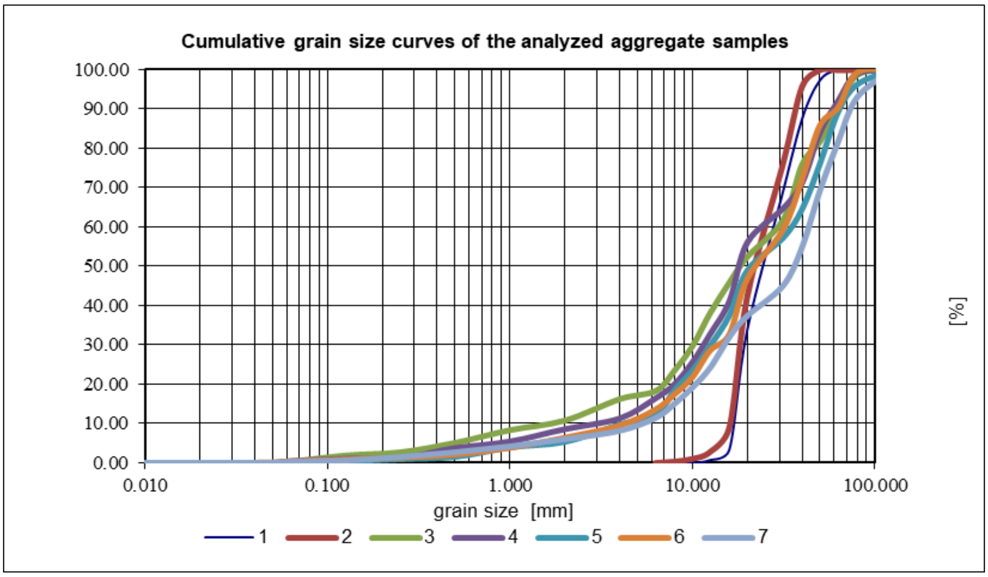

Fig. 7. Cumulative grain size curves of the analyzed aggregate samples

The aggregates do not contain the oversize particles. They are characterized by a much-varied fines content (0 – 11.02%) (Tab. 6). In the Carboniferous limestone (samples 1 and 2), it is <2%, which classifies this rock into the f2 aggregate category, according to the PN-EN 13242+A1 standard (2010). Aggregates 6 and 7, representing the Karchowice Formation, are classified in the f4 category. The Góraždže Formation aggregates (samples 3-5) contain >8% fines (Tab. 6), which limits the possibility of their use for construction purposes, and according to the PN-EN 13242+A1 standard (2010), they are out of class. Resistance to fragmentation (LA coefficient) ranges from 25 to 52 (Tab. 6), being high when the Carboniferous limestone and the limestone of the Karchowice Formation are considered (classes LA_{35} and LA_{30}, respectively) (PN-EN-13242+A1, 2010). Aggregates 3-5 show very low resistance (LA_{60} category).

The bulk density of the aggregates tested is typical for rocks of this type and ranges from 2.65 to 2.71 g/cm^3 (Tab. 6). The aggregates obtained from limestone belonging to the Karchowice Formation have the highest resistance to freezing, which does not exceed 1.1% (Tab. 6), while the several times lower resistance is a characteristic of the aggregates from the Góraždže Formation (18-26%). The water absorption results (4.56-8.33%) correspond to this relationship, although the differences observed are not as significant. The aggregates produced from the Carboniferous limestone and those from the Karchowice Formation limestone have a high load-bearing capacity index (CBR) (46-54), while the aggregates 3-5 obtained from limestone representing the Góraždže Formation have much poorer properties (Tab. 6). The aggregates studied vary significantly in terms of their specific surface area (51-154 m^2/g) (Tab. 6), with the highest values recorded for the limestone of the Góraždže Formation (samples 3-5). The cation exchange capacity (CEC) values range from approximately 4.5 mval/100 g to 6.7 mval/100 g. The clay content only in the aggregates obtained from the Triassic limestone of the Góraždže Formation exceeds 2%. In the remaining limestones, it is below 1%, which is a favourable feature. Higher amounts of clay decrease the mechanical properties of an aggregate. The Carboniferous limestone aggregates show slightly worse performance than the previous results (Hydzik-Wiśniewska et al., 2018) regarding water absorption, frost resistance, and CBR.

Tab. 6. Physical-mechanical properties of the aggregates studied

Physical-mechanical property	Sample							Unit
	1	2	3	4	5	6	7	
Fines content	0	0.95	8.15	11.02	9.34	2.07	3.27	%
Resistance to fragmentation (LA coefficient)	34	30	52	49	48	25	26	-
Bulk density	2.67	2.68	2.68	2.68	2.65	2.70	2.71	Mg/m^3
Water absorption	6.37	5.97	7.89	8.33	9.34	4.56	4.84	%
Frost resistance	3.9	3.8	18	26	23	1.1	1.1	%
CBR (after 96 h water absorption)	47	46	20	23	19	54	52	-
Specific surface area	51	54	154	136	142	86	71	m^2/g
Cation exchange capacity (CEC)	4.56	4.71	6.35	6.67	6.48	5.51	5.79	mval/100g
Clay content	< 1	< 1	2. 37	2.14	2.29	< 1	< 1	%

Results of sorption properties tests

The reactivity coefficient (RI) is 2.14 (sample 1) and 2.61 (sample 5), while the absolute sorption coefficient (CI) is 148.7 and 119.3, respectively (Tab. 7). To assess the significance of the results, they were compared with the Ahlstrom reference values (Hycnar, 2018) (Tab. 2). The comparison demonstrates excellent sorption properties of sample 1, representing Carboniferous limestone. Such outstanding features of this rock were previously communicated (Lewicka et al., 2020; Galos et al., 2016). Sample 5, which was collected from the Góraždže Formation of the Middle Triassic, has very good sorption properties. The RI and CI values obtained are better than indicated in many previous tests performed on limestone both from Poland and other countries (Anthony et al., 1997; Hycnar, 2018; Wichliński &Włodarczyk, 2021).

Tab. 7. Values of the reactivity index (RI) and the absolute sorption index (CI) for the studied samples

Sorption properties	Sample	
	1	5
RI (Ca/S moles)	2.14	2.61
CI (g S/1000g of a sorbent)	148.7	119.3

Discussion

Based on the results of the analyses performed, possible directions for the industrial use of the limestones studied were identified. Key applications were taken into account, namely as a raw material for the production of fertilizer, cement, glass, lime, aggregate (for construction and concrete production), animal feed additive, mine safety dust, sorbent for flue gas desulphurization, and as a component for the iron and steel industry.

The requirements for limestone use, which are given in standards and regulations of various types and sometimes result directly from long-term economic practice, include the $CaCO_3$ content in some applications and the CaO content in others. Therefore, to apply the XRF examination as a primary method, the required $CaCO_3$ content was converted to CaO when needed. For this purpose, a well-known and widely used stoichiometric conversion factor of 0.56 was applied (Sigma Aldrich, 2024, among others). The chemical properties of limestone, including the minimum CaO content (in the increasing sequence) converted from the minimum $CaCO_3$ content required in Poland for the various uses of this rock, are given in Tab. 8.

Tab. 8. Required or postulated properties of limestone for different ways of use in Poland

Way of use	Min. content $CaCO_3$/CaO [wt. %]	Max. content Cd [ppm]	Pb [ppm]	Cr [ppm]	Hg [ppm]	Ni [ppm]	As [ppm]	Cu [ppm]	Zn [ppm]	F [ppm]	Sb [ppm]	Fe_2O_3 [wt. %]	MgO [wt. %]	SiO_2 [wt. %]
Fertilizer	-/20.0	8/2*	200/120*	-/2*	-/1*	-/90*	-/40*	-/300*	-/800*	-	-	-	-	-
Cement	75.0/42.0	-	-	-	-	-	-	-	-	-	-	-	-	-
Glass	-/50.0	-	-	-	-	-	-	-	-	-	-	0.4	-	-
Lime	90.0/50.4	-	-	-	-	-	-	-	-	-	-	-	-	-
Aggregate	90.0/50.4	-	-	-	-	-	-	-	-	-	-	-	-	-
I&S industry	92.0/51.5	-	-	-	-	-	-	-	-	-	-	-	-	-
Feed add.	94.0/52.6	2/10*	10/20*	-	0.1/0.3*	-	2/15*	-	-	150/350*	-	-	-	-
Sorbent	94.0/52.6	-	-	-	-	-	-	-	-	-	-	0.4	1.0	-
MSD	95.0/53.2	-	50	-	-	-	10	-	-	-	5	-	-	3.0

*Explanation: * - the first value refers to the Polish requirements, whereas the second refers to the UE regulations; the CaO content converted from CaCO3 is underlined; I&S industry – iron and steel industry; Feed add. – Feed additive; MSD – mine safety dust*

Based on the XRF analyses, it is found that all limestones studied exceed the minimum CaO content required for fertilizers in the form of crushed rock (20%) and from limestone processing (40%) (MERP, 2010) (Tabs. 3 and 8). The content of trace elements is within the limits allowed in Poland (MARDRP, 2008**)**, and only in one case (sample 6) it is exceeded for chromium, according to EU regulations (EU 2019/1009, 2019) (Tabs. 4 and 8). Therefore, all limestones tested, except for limestone 6, can be used for fertilizer manufacturing. In Poland, depending on the variety, the fertilizers obtained from the limestone processing must also have the appropriate grain size (MARDRP, 2008). The chemical parameters of a fertilizer must be adapted to the properties of the soil, which is why this product comes in different varieties and is obtained from diverse raw materials. Therefore, the range and requirements for limestone used for this purpose differs between the countries (Abeysinghe, 1998; EU 2019/1009, 2019; ASTM C602-07, 2007; GI, 2013; MARDRP, 2024). Limestone-based fertilizers are applied to deacidify and enrich soil with calcium. They also help to remove aluminium ions from the soil, stimulate the activity of soil microorganisms and reduce the negative effects of phytotoxic elements **(**Crusciol et al., 2017).

The requirements for using limestone in the production of Portland cement have been standardized in Europe (PN-EN 197-1, 2012). All the rocks tested here meet the requirement for the CaO content (min. 42%) (Tabs. 3 and 8). The Carboniferous limestone and this from the Karchowice Formation are also characterized by a low clay content (<1%) (Tab. 6), making them potentially suitable for Portland cement production. Similar chemical characteristics of limestone applied for the production of Portland cement are also required in other countries, e.g., in the USA (ASTM C150M-18, 2018), Canada (CSA A3001-03, 2003), Australia (Abeysinghe, 1996), and India (GI, 2013). The Canadian standard allows limestone to be used in amounts up to 15% (CSA A3001-03, 2003, while the American standard only up to 5% (ASTM C150M-18, 2018), which is lower than the European standard allows for (max. 35%, depending on the variety) (PN-EN 197-1, 2012). A low limestone admixture (<10-15%) in Portland cement can increase compressive strength (Githachuri & Alexander, 2013; Lee et al., 2024). This is attributed to the improvement in particle packing efficiency due to their fine particle size, enhancing the hydration of the clinker by the filler effect. However, at higher admixtures, negative effects on mechanical properties are observed (Lothenbach et al., 2008; Githachuri & Alexander, 2013; Lee et al., 2024). It should be underlined that the use of Portland limestone cement can significantly contribute to reducing CO_2 emissions by reducing clinker production (Lee et al., 2024).

The desired chemical properties of limestone used in the glass industry depend on the type of glass, and rock that contains at least 50% CaO and a maximum of 0.4% Fe_2O_3 is required in Poland (Burkowicz et al., 2013) (Tab. 8). However, limestone with 54% CaO (97% $CaCO_3$) and a maximum of 0.04% Fe_2O_3 is generally in demand in Poland and other countries, especially when used for the production of colourless glass, as the iron oxides have a colouring effect on glass (Abeysinghe, 1998; Longcliff, 2024; McGrath, 2024). Considering the above, all of the limestones studied, except limestone 3 (Tables 3 and 8), can be used in glass production as inferior raw materials (Burkowicz et al., 2013). As the size of the grains influences glass homogeneity, finely ground limestone (so-called limestone flour) is used (West, 2012). The rock should be of high purity as it acts as a stabilizer and CaO supplier, making the glass more durable and resistant to weather conditions (Lewicka et al., 2020). The use of limestone also has an important economic sense, as it is less expensive compared to alternative alkaline materials, such as sodium carbonate/bicarbonate and caustic soda (McGrath, 2024).

It is suggested that the minimum carbonate content ($CaCO_3$+$MgCO_3$) in the limestone used for lime production should be 80% (Simoni et al., 2022). However, a much higher purity (≥92%) is usually required (Abeysinghe, 1998; Bureš, 2017), as impurities in the rock are transferred to lime. In Poland, limestone with a $CaCO_3$ content ≥90% (that is ≥50.4% CaO) is used in the lime industry (Brzeziński, 2023). Therefore, Triassic limestones 4-7 (Tabs. 3 and 8) represent a very good raw material for lime production. Rock with a fraction of

≥20 mm is used (Domaracká, 2018). The chemical purity of limestone directly affects the chemical purity of lime and its reactivity (Manocha & Ponchon, 2018; Sandström et al., 2024). The surface layer of limestone is disproportionately rich in impurities compared to the rest of the rock; therefore, it should be removed before inserting the batch into the kiln (Sandström et al., 2024). Limestone crystallinity, texture, and porosity also significantly influence the calcination process and the properties of the resulting lime (Manocha & Ponchon, 2018; Bhattacharyya et al., 2024).

In Poland, limestone used in the iron and steel industry should have a high $CaCO_3$ content. However, this parameter is not normalized. The product is prepared according to the individual needs of the recipient. According to information obtained from the manufacturers, 92% $CaCO_3$ (51.5% CaO) content is taken as the minimum value. Considering all of this, Triassic limestones 4-6 (Tabs. 3 and 8) are a high-quality raw material for the analyzed use. Also on the international scale, metallurgical industry needs limestone with a content of at least 92% $CaCO_3$ (≥51.5% CaO), but rocks containing ≥95% $CaCO_3$ (≥53.2% CaO) with low SiO_2 content are required most frequently (Manocha & Ponchon, 2018; Sivrikaya, 2018; Mao et al., 2018; Bhattacharyya et al., 2024). Limestone (similarly to lime) is used as a flux to promote fluidity and remove impurities in the form of slag. Therefore, it should be possibly pure (Sivrikaya, 2018). Limestone is used in both the basic oxygen furnaces (BOF) and the electric arc furnaces (EAF) (Mao et al., 2018; Gupta et al., 2024). To achieve complete rock decomposition, the rock fraction should not exceed 20 mm (Gupta et al., 2024).

When considering limestone used as an additive to animal feed, carbonate content is not a normative parameter in Poland; however, $CaCO_3$ content of at least 94% (52.6% CaO) is generally in demand (Tab. 8), as known from the product data sheets. This purity, as well as the Polish and European criteria for acceptable levels of undesirable constituents (MARDRP, 2024; EU 2002/32/EC, 2002) (Tab. 8), are met by the Triassic limestones 4 and 6 (Tab. 3 and 4). Limestone 5 is sufficiently rich in CaO but exceeds the permissible Pb content (Tabs. 4 and 8). In other countries, limestone, which is an animal feed component, should also be rich in calcium carbonate and contain minimal amounts of heavy metals, iron, aluminium and silica (Abeysinghe, 1998; ASTM 706-02, 2008).

The specifications and test methods for aggregates are standardized in the UE countries (PN-EN 13043, 2004; PN-EN-12620+A1, 2010; PN-EN-13242+A1, 2010) and the USA (ASTM D1073, 2016; ASTM C33/C33M-18, 2018; ASTM C144-18, 2018; ASTM D692/D692M–20, 2020; ASTM D2940/D2940M-20, 2020), among others. They depend on the intended use of an aggregate. These specifications do not include $CaCO_3$/CaO content. However, the purity of limestone is important information on the possible use of this rock as an aggregate. Varieties rich in aluminium or iron oxides have worse physical-mechanical parameters, which exclude them. In Poland, the $CaCO_3$ content ≥90% (≥50.4% CaO) is treated as a threshold value (Guzik & Figarska-Warchoł, 2023) (Tab. 8). As the limestones studied contain approximately 50% CaO and more, they were all subjected to the tests of the physical-mechanical parameters. Given the European regulations PN-EN 13043, 2004; PN-EN-12620+A1, 2010; PN-EN-13242+A1, 2010), the aggregates obtained from the Carboniferous limestone (samples 1 and 2) are characterized by high values of physical-mechanical parameters, which classifies them as construction aggregates. The high load-bearing capacity (CBR) and very good resistance to fragmentation (Tab. 6) allow them to be used to build road embankments. These aggregates are also characterized by moderate water absorption and average resistance to climate conditions (resistance to freezing). The small specific surface also provides grounds for defining them as resistant to environmental conditions (physical weathering, aggressive environmental influences, etc.). Aggregates produced from the limestone representing the Triassic Górażdże Formation are featured by poor physical and mechanical parameters compared to others, which prevents them from being used as construction aggregates. Aggregates obtained from the limestone that occurs in the Triassic Karchowice Formation are high-quality construction aggregates. The high CBR value and resistance to fragmentation (Tab. 6) mean that they can be used in building embankments, mainly due to their high resistance to mechanical effects (weathering and crushing). These aggregates are also characterized by moderate water absorption and very high resistance to freezing.

Under Polish conditions, mine safety dust obtained from limestone must have an acceptable content of trace elements (Pb, As, Sb) (Tab. 8) (PN-G 11020:2019-10, 2019), which can be known from the XRF analysis. It should also contain ≥95% $CaCO_3$ and ≤3% of free SiO_2. Both parameters can be determined by the XRD analysis. Such requirements are met by the Carboniferous limestone 1 (Tabs. 4 and 5). Limestone 5 from the Górażdże Formation contains an excess amount of Pb (Tabs. 4). Limestone dust is obtained by grinding limestone rock to a fraction of less than 1.0 mm, so that 70% of the material should pass through a sieve with a mesh of 0.075 mm (PN-G 11020:2019-10, 2019). The specifications used in the UK and the USA do not include the percentage of calcium carbonate, but they indicate the maximum level of silica, which is 3% and 4%, respectively (Abeysinghe, 1998; ASTM C737-22, 2022). Moreover, particle size is also taken into account, as the effective dispersion of the dust particles is critical to mitigate a dust explosion. Limestone powder with a particle size below 0.1 mm is particularly desirable due to its excellent dispersion characteristics (Huang & Honaker, 2016). Limestone dust is a better inertant than dolomite dust for suppressing coal dust explosions (Sahu & Mishra, 2024).

Due to the fact that the sorbent performance is dependent on limestone purity (Lim et al., 2020), and there is also a need to identify the Fe_2O_3 and MgO content in the rock, the suitability of limestones for use as a sorbent was assessed based on the results of XRD and XRF analyses. The tests of the sorption properties were then performed. In Poland, limestone to be used as a sorbent for flue gas desulfurization (FGD) should contain not less than 94% $CaCO_3$ (52.6% CaO) and possibly low amounts of Fe_2O_3 (max. 0.4%) and MgO (max. 1%) (Szlugaj & Galos, 2021) (Tab. 8). As the XRF examination showed, the CaO content in the Carboniferous limestone 1 is below the required level but the other two oxides are within the permissible amounts (Tabs. 3 and 8). The XRD analysis indicated high purity of the rock (Tabs. 5 and 8), and the sorption tests – excellent quality (Tabs. 2 and 7). Therefore, the rock was qualified as suitable to be used as a sorbent. Triassic limestone 5 meets all the requirements regarding $CaO/CaCO_3$ as well as Fe_2O_3 and MgO content (Tabs. 3, 5 and 8), and shows very good sorption properties (Tabs. 2 and 7), also being usable as a sorbent. Similar rock purity, as in Poland, is also required elsewhere (Lim et al., 2020). Currently, fine-grained limestone sorbents, with grain size less than 100/120 µm, are used in the wet desulfurization systems, which are most widely used around the world, while coarse-grained sorbents, with grain size greater than 100/120 µm, find their use mainly for fluidized bed boilers (Szlugaj & Galos, 2021). It is found that limestones from the same deposit often have a different SO_2 capture, although their $CaCO_3$ content is similar (Hycnar, 2018). Thus, the estimation of their usability for FGD should not only focus on the proportion of calcium carbonate (and other chemical components, if needed) but also include the examination of sorption properties.

As discussed above, the limestones studied from three selected deposits located in southern Poland have broad economic usability, which is summarized in Fig. 8. The results also show that the chemical properties of limestone can vary significantly within a deposit, indicating the occurrence of rock varieties that can be used in different ways. This raises the importance of the selective exploitation of deposits to make fuller use of their resources and to meet the quality requirements of diverse customer groups.

Fig. 8. The economic uses of the limestones studied from different deposits of southern Poland

The use of the methodical algorithm presented in this study can reduce the time and cost of the tests performed. The description of macroscopic features gives general information on the properties of the rock. It can be followed by microscopic characteristics if the details regarding structural-textural features are needed. The XRF examination, which can be the principal method for identifying industrial uses of limestone, is quick and relatively simple. The results of the XRF analysis may serve to select rock varieties, which should be subjected to further physical-mechanical tests aimed at identifying (or excluding) their suitability as aggregates, as well as the varieties for the XRD examination, when necessary. The qualitative and quantitative XRD phase composition tests should be carried out, especially when high rock purity is required, and the content of mineral phases other than calcite should be known, or when the XRF measurements give results that are close to the normative values and they need to be confirmed by an additional method. Based on the XRD results, the rock varieties for the sorption properties tests can be chosen. The proposed algorithm cannot include the threshold values of any parameter, as they result from the regulations that exist in a given country. It also does not cover the processing operations necessary to obtain a product of the required grain size, as these may also vary between the countries.

Conclusions

On the basis of the work carried out, the following conclusions can be drawn:

1. The investigated Carboniferous and Middle Triassic limestones coming from the deposits located in southern Poland are generally characterized by high purity (CaO content ≥49.95 wt.%; $CaCO_3$ content ≥93.8%), and low proportion of admixtures (mainly SiO_2 as well as Al_2O_3, Fe_2O_3, MgO and Na_2O).
2. The rocks studied have a broad scope of applications. Depending on their origin and properties, they can be used for the production of cement and lime, as a road aggregate, fertilizer, animal feed additive,

mine safety dust or a sorbent for flue gas desulphurization in the iron and steel industry, as well as a component for glass production. This demonstrates the very high economic potential of their deposits in terms of the rock quality.

3. The X-ray fluorescence (XRF) analysis can be applied as an effective principal tool for assessing the suitability of limestone for various economic purposes. On this basis, the rock varieties can be selected for further investigation, including the X-ray diffraction (XRD) analysis and tests of the physical-mechanical and sorption properties.

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