The pressure granulation of dolomite decarbonates for the production of refractory materilas

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Introduction

Dolomite refractories attract an increasing interest due to its numerous valuable properties. They mainly consist of a high-temperature refractory phase such as MgO (melting temperature: 2840°C) and CaO (2570°C). These materials are characterized by the most alkaline nature among other commonly used refractories. Consequently, at high temperatures they are quite resistant to a corrosive effect of alkaline substances, for example some metallurgical slags. The production of dolomite refractories is particularly important in the countries rich in dolomite mineral deposits that at the same time do not have any magnesite resources useful for the production of high-temperature refractories. Poland is among such countries.

The minerals suitable for the production of high-quality dolomite refractories have to fulfil many requirements of which the most important are:

- an adequate chemical composition, i.e. possibly high content of MgO and CaO and low contribution of SiO_2, Al_2O_3 and Fe_2O_3
- an adequate microstructure characterised by relatively small sizes of crystals of carbonate phase, gradual transformations between less and more crystalline areas and small sizes of likely agglomerations of minor admixtures
- the optimum texture with a small capacity of open and close-type pores and clefts
- high homogeneity with reference to the chemical composition, microstructure and texture.

As it has been already mentioned, Poland is rich in dolomite deposits predominantly present in 3 areas (the region of Silesia and Cracow, the Świętokrzyski region and the Lower Silesia region). According to the analysis of the paper elaborated by Bąk et al. (2011), there are mainly average and inferior quality dolomite deposits regarding the needs of the refractory industry. Selecting an adequate technology for dolomite refractories production is among the methods for counteracting these limitations. They are currently produced as:

- materials with carbon bond, obtained by partial carbonisation of organic polymer adhesive
- materials with ceramic bond, obtained from high-temperature sintering of dolomite clinker.

For all kinds of dolomite materials, dense dolomite clinker obtained by thermal decomposition of dolomite, and then by high-temperature sintering of this half-product is a fundamental raw material. Two basic methods for the production of dolomite clinker are involved in the production of dolomite refractories with ceramic bond. The first method, known as a one-stage method, consists in sintering the raw dolomite in the form of lump in shaft or rotary furnaces at high temperatures reaching even 2000°C. The second method – described as a two-stage method – is based on preliminary decarbonisation of dolomite, and then, its milling and pressing in the form of briquettes and their sintering. The recent research studies (Goławski et al. 2011, Wyszomirski et al. 2011) have shown that in case of some dolomites from the region of Silesia and Cracow, which is traditionally considered to have the richest varieties useful in producing the refractories – the application of the two-stage method yields better results in comparison with the one-stage one. In the second case, the negative impact of the following properties of a raw material is minimised: high and changeable porosity and apparently increased and varied content of iron oxides. This purpose can be achieved by, inter alia, the proper pressure granulation of dolomite decarbonates. The test results from the pressure granulation are demonstrated later in this paper. The high compactness of clinker texture is necessary to require the highest possible hydration resistance and corrosive resistance of dolomite products. It is commonly known that the strong tendency towards the hydration affected by humidity – resulting mainly from extremely hygroscopic and free CaO (Kashaninia et al. 2011), is the principal disadvantage of dolomite products hindering, inter alia, their longer storage. The satisfactory sintering of clinker, thus obtaining the dense texture allows the significant increase in the hydration resistance, and hence the production of dolomite refractories of high quality.

Methodology

The chemical analysis of raw dolomite samples was carried out using principally X-Ray fluorescence spectrometry with the Instrumental Neutron Activation Analysis (INAA).

The dolomite decarbonate samples obtained at 1000°C were pressed in the die closed with two punches; the top punch was pressed and the bottom was a non-skid one. Before pressing, the decarbonised dolomite samples were subjected to grinding, and then screened through a 0.1 mm mesh sieve. The material with a mass of 3 g, prepared as described above, was filled into the die and pellets with a diameter of 20 mm were formed at applied axial pressures of 20 MPa, 50 MPa and 200 MPa.

The apparent density and porosity analyser GeoPyc type 1360 and the true density analyser AccuPyc type 1330 of the American company Micromeritics were used for tests on the structural and textural parameters of decarbonate samples after sintering at 1550°C, 1600°C and 1650°C.

The hydration resistance of sintered samples was analysed in the ESPEC LHL 113 environmental chamber. The tests were performed at 40°C and 70% relative humidity.

SEM analysis was made using Nova Nano SEM 200 scanning electron microscope with a field-emission (FEG – Schottky field emission gun) (manufacturer: FEJ EUROPE COMPANY). Its resolution limit is ca. 2 nm, vacuum at 60 Pa, and the possible magnification ranges from 70 to 500,000 x. The analysed sample was fixed to a brazen base and then, it was plated with a thin layer of coal to obtain the electric conductivity of a non-conductive material.

The sample material

Triassic dolomite samples from Brudzowice (sample 1115), Ząbkowice Będzińskie (1120) and Żelatowa (1104) deposits, Devonian dolomite from Brudzowice deposit (1114) and early Palaeozoic dolomite from Ołdrzychowice (1124) were tested. Their chemical composition is shown in Table 1.

Table 1

Chemical analysis of dolostones studied

Name of deposit	Brudzowice	Brudzowice	Ząbkowice	Żelatowa	Ołdrzychowice
Sample no.	1115	1114	1120	1104	1124
Calcination loss %	46.4	46	46.41	47.17	46.58
SiO_2 %	0.18	0.15	1.07	0.12	0.23
$Al._2O_3$ %	0.07	0.07	0.23	0.14	0.07
Fe_2O_3 %	1.06	0.28	0.45	0.31	0.09
TiO_2 %	<0.005	<0.005	0.009	<0.005	<0.005
CaO %	30.59	30.7	30.08	30.44	30.76
MgO %	20.02	20.95	20.76	22.00	21.88
MnO %	0.12	0.04	0.05	0.03	0.04
K_2O %	0.01	0.01	0.04	0.02	0.02
Na_2O %	0.04	0.04	0.04	0.05	<0.01
P_2O_5 %	0.01	<0.01	<0.01	<0.01	0.02

1-2 cm pieces of these raw materials were decarbonised in the Superkanthal furnace at 1000°C for one hour. The pellets with a 2-cm diameter were formed in the closed die from decarbonate with a mass of ca. 3g under three different pressing pressures applied (20 MPa, 50 MPa, 200 MPa), and later burned at 1550°C, 1600°C and 1650°C. More precise information on the conditions for sample formation was presented in the "Research Methodology" chapter.

Consolidation characteristics, specific work and side thrust coefficient

The response of granulated material to the standard pressure has a fundamental importance during the pressure granulation of particle media. The imposed pressure changes the medium density resulting in its decreased porosity. The bulk medium is transformed into the solid one which exhibits reduced porosity, becomes coherent, elastic and adopts quasi-solid properties. So, it is crucial to show how a specific particle medium responses to consolidation during the exposure to external forces. Such tests should enable the performance of the consolidation characteristic, the measurement of side thrust coefficient, and the determination of energy input necessary to achieve the assumed change in density. Figure 1 illustrates the structure of a genuine test stand for determining the side thrust coefficient. It consists of elements for applying the standard pressure (parts 1, 2, 3, 4), elements (5, 6) providing axiality of a punch (4), sliding mould elements (1, 2), supporting system (7, 8, 10, 11) and the measurement system (12, 13). A screw 7 and a screw cap 8 are used to exert the initial pressure on movable elements of a die (1, 2) and to adjust it.

The tested material was placed in a rectangular chamber having dimensions of 10 x 10 mm. The material sample with a mass providing its height of 10 mm at a standard pressure per specific unit value was filled to the hole. The test stand enables the pressure within a range from 5 to 400 N/mm^2 (5-400MPa) to be applied on the samples. The exerted standard pressure results in the occurrence of side thrusts. However, they do not induce the shift of die movable elements (1, 2). The punch shift is recorded with the accuracy up to 0.01 mm. The pressure of a punch is measured with the accuracy of 2% at 5 N/mm^2 (5 MPa) pressure and 0.2% in the upper measurement range. The measurement of the punch pressure and the height of a compacted sample allows the compaction characteristics in the following systems: standard pressure [kN/cm^2] – density [g/cm^3] and standard pressure [kN/cm^2] – volume mass [cm^3/g]. Figure 2 illustrates the consolidation characteristics for dolomite decarbonate samples in a standard pressure [kN/cm^2] – volume mass [cm^3/g] system that enables the calculation of the specific work.

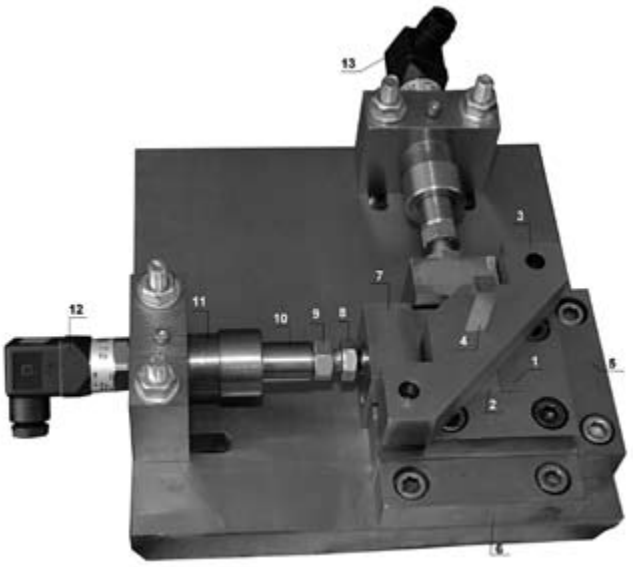

Fig.1. Test stand for testing of consolidation characteristics and side thrust
1 - part of a movable die, 2 – part of a movable die, 3 – stable element blocking die, 4 – punch, 5 – right-side guide, 6 – left-side guide, 7 – thrust bearing, 8 – adjusting screw, 9 – blocking screw cap, 10 – cylinder piston, 11- cylinder, 12 – electronic pressure converter, 13 - electronic pressure converter.

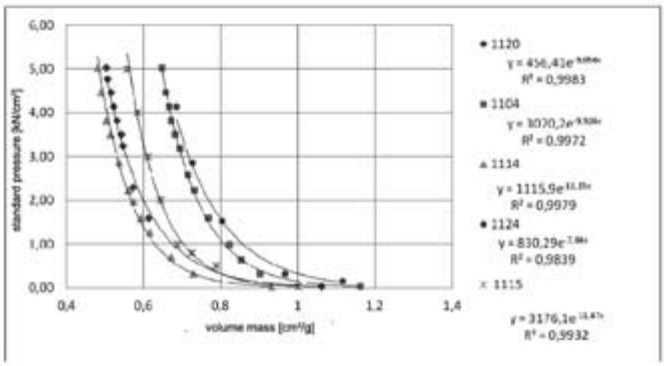

Fig.2. Consolidation characteristics of decarbonizated dolomite samples

Applied enumeration of samples: 1115 – decarbonate of Triassic dolomite from Brudzowice, 1114 – decarbonate of Devonian dolomite from Brudzowice, 1120 – decarbonate of Triassic dolomite from Ząbkowice Będzińskie, 1104 – decarbonate of Triassic dolomite from Żelatowa, 1124 – decarbonate of dolomite from Ołdrzychowice.

When the consolidation characteristics were completed, the function describing the relation of agglomerate volume mass to standard pressure inducing its changes was established. According to the performed tests, the exponential function expressed as an equation (1) describes very precisely the dependence of the standard pressure on inverse density of agglomeration obtained under its impact.

$$p_n = a \cdot e^{b \cdot v} \quad (1)$$

where:

a, b – coefficients determined from regression equations

v – volume mass

The unit densification work [J/g] reducing the volume mass and providing an adequate density is calculated as definite integral from the equation (1) within the integration boundaries corresponding to the initial v_i and final v_f volume according to the dependence (2).

$$A = \int_{vf}^{vi} a e^{bv} d(v) + C \quad (2)$$

where: v_i - initial volume mass; v_f - final volume mass, C – constant of integration

The constant value of integration was calucated from initial conditions assuming that the value of initial work was equal to zero at the beginning of the granulation process. For such a formulated assumption, constant C was calculated from the equation (3)

$$C = (-)\frac{a}{b} e^{bvp} \quad (3)$$

Figure 3 shows the calculation results of the specific work required to exert unit pressures of 20, 50 and 200 MPa on selected samples of dolomite decarbonate.

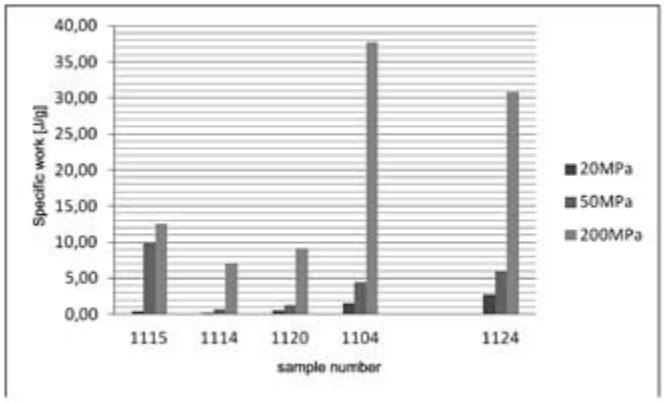

Fig. 3. Specific work of granulation process of decarbonizated dolomite samples

Applied enumeration of samples: 1115 – decarbonate of Triassic dolomite from Brudzowice, 1114 – decarbonate of Devonian dolomite from Brudzowice, 1120 – decarbonate of Triassic dolomite from Ząbkowice Będzińskie, 1104 – decarbonate of Triassic dolomite from Żelatowa, 1124 – decarbonate of dolomite from Ołdrzychowice.

All samples demonstrated minor values of unit work for pressures of 20 MPa. For the pressure value of 50 MPa, the value of specific work was considerably higher for the sample 1115 in comparison with others. The highest value of specific work was observed for the sample 1104 at 200 MPa pressure. A particular attention was paid to the sample 1115 which did not demonstrate any dramatic difference in the specific work for pressure values of 50 and 200 MPa. The tests on side thrust coefficient were carried out for this sample to find the response of its particle structure to consolidation under pressures within a range from 5 to 200 MPa.

Figure 4 illustrates the measurement results of the side thrust coefficient for decarbonate of Triassic dolomite from Brudzowice (sample 1115).

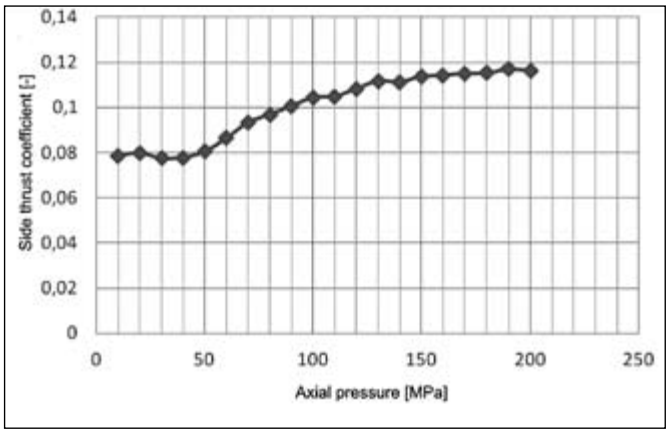

Fig. 4. The relation between side thrust coefficient and standard pressure in the consolidation process of decarbonate of Triassic dolomite from Brudzowice (sample 1115)

Three intervals of various responses of the consolidated material can be distinguished while analysing the data presented in Figure 4. For the axial pressure up to 50 MPa, the continuous side thrusts of low value occur, which may indicate the displacement of particles in empty inter-particle spaces. For axial pressures within a range of 150 – 200 MPa, the steady side thrusts are observed, which suggests an elastic form of solid matter. Finally, within a range of intermediate axial pressures (50 – 130 MPa), granulate behaves as elastic-plastic solid matter. Such properties of the consolidated medium decided on using three levels of unit pressures applied in the pressure granulation process, that is pressures of 20.0 – 50.0 and 200.0 MPa.

Effect of pressing pressure on hydration resistance of sintered dolomite decarbonates

Formed pellets were burned at 1550°C, 1600°C and 1650°C and kept at maximum temperature for one hour. Such prepared samples were tested on their hydration resistance in the environmental chamber. The results are presented in Figures 5÷8 in the following system: relative growth rate (%) – time (days).

The performed tests showed that decarbonate agglomerates of Triassic dolomite from Brudzowice demonstrate the greatest hydration resistance. It is related to increased content of Fe_2O_3 in initial dolomite - 1.06 % in this case (Tab.1). Iron content in other tested samples was smaller and their hydration resistance was lower. The presence of Fe_2O_3, despite resulting in improved sintering of the sample, is undesirable due to the negative impact of this oxide on the refractoriness of dolomite products.

The noticeable impact of the formation pressure on the hydration resistance is presented in graphs (Figs 3÷8). For samples formed under the lowest pressure (20 MPa), the growth rate is distinctly higher in comparison with other pellets, regardless of their sintering temperature. On the other hand, the samples obtained under 200 MPa pressure demonstrated the lowest hydration resistance, which was also observed for all three burning temperatures.

These findings are also verified by the observation with the scanning electron microscope SEM (Figs 9, 10). The sample formed under the pressure of 20 MPa is characterised by higher heterogeneity and increased porosity in comparison with the sample formed under the pressure of 200 MPa. Furthermore, these results are consistent with data from structural and textural tests presented in Table 2. The systematic decrease in agglomerate porosity was observed at gradual increase in the formation pressure. For the formation pressure of 20 MPa, the total porosity exceeds 20 % while the significant reduction in its porosity is caused by increasing this pressure to 50 MPa, and specifically to 200 MPa.

The determined true density of 3.45 g/cm^3 is an intermediate value between the density of pure MgO (3.56 g/cm^3) and CaO (3.30 g/cm^3) (Manecki 2004). It reflects the molar fraction of both phases in the tested agglomerates which is equal to 1:1.

Table 2

True and apparent density as well as total, open and closed porosity of decarbonate of Triassic dolostone of Brudzowice deposit and products of its sintering

Parameter	Decarbonate (1000°C)			1550°C			1600°C			1650°C		
	20 MPa	50 MPa	200 MPa	20 MPa	50 MPa	200 MPa	20 MPa	50 MPa	200 MPa	20 MPa	50 MPa	200 MPa
d_{true} [g/cm^3]	3.34	3.31	3.29	3.46	3.45	3.45	3.44	3.44	3.44	3.46	3.45	3.45
d_{ap} [g/cm^3]	1.31	1.45	1.77	2.55	3.16	3.24	2.67	3.21	3.27	2.76	3.21	3.27
P_{tot} [%]	60.6	56.1	46.2	26.4	8.5	5.9	22.2	6.8	4.9	20.2	7.1	5.0
P_{open} [%]	n.d.	n.d.	n.d.	25.6	3.3	3.1	22.1	2.1	0	19.5	2.0	2.6
P_{closed} [%]	n.d.	n.d.	n.d.	0.8	5.2	2.8	0.1	4.7	4.9	0.7	5.1	2.4

n.d. not determined due to hydration of these samples

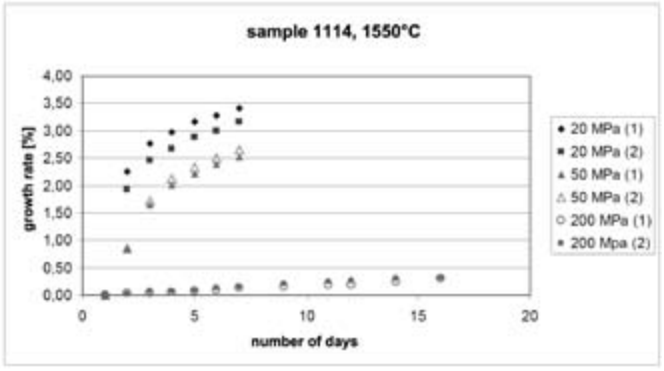

Fig. 5. Relationship between time and relative growth rate of sintered decarbonate of Devonian dolostone from Brudzowice obtained at 1550°C. For each pressure measurements were carried out for two samples

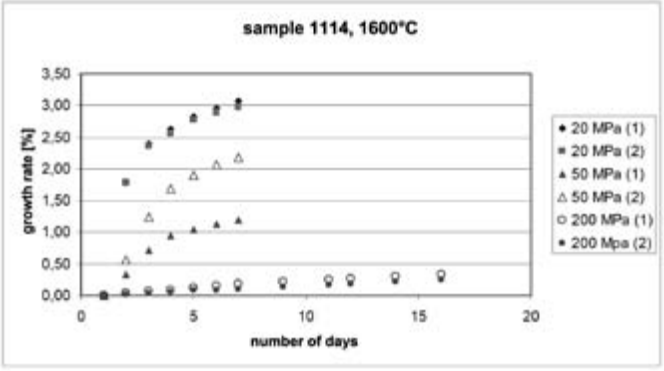

Fig. 6. Relationship between time and relative growth rate of sintered decarbonate of Devonian dolostone from Brudzowice obtained at 1600°C. For each pressure measurements were carried out for two samples

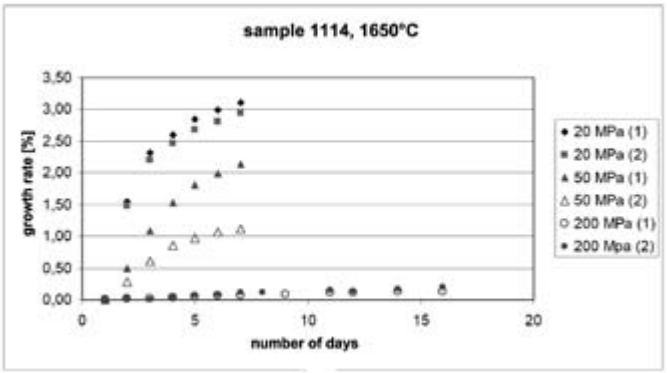

Fig. 7. Relationship between time and relative growth rate of sintered decarbonate of Devonian dolostone from Brudzowice obtained at 1650°C. For each pressure measurements were carried out for two samples

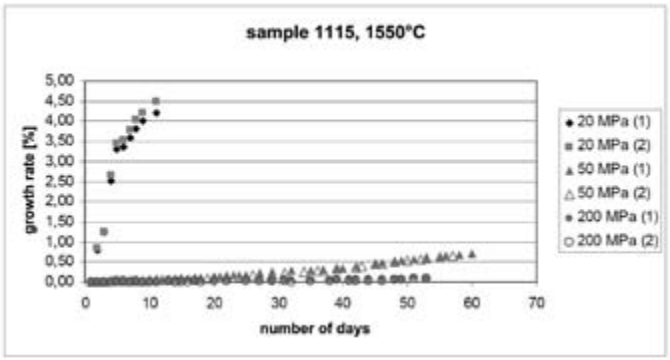

Fig. 8. Relationship between time and relative growth rate of sintered decarbonate of Triassic dolostone from Brudzowice obtained at 1550°C For each pressure measurements were carried out for two samples

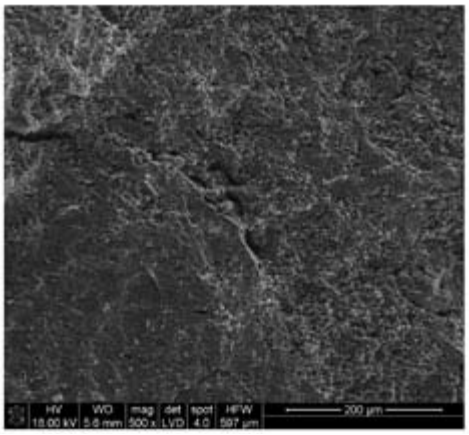

Fig. 9. Sample fracture of decarbonate of Triassic dolostone from Brudzowice (sample 1115) after its forming under pressure 20 MPa and sintering at 1650°C. SEM

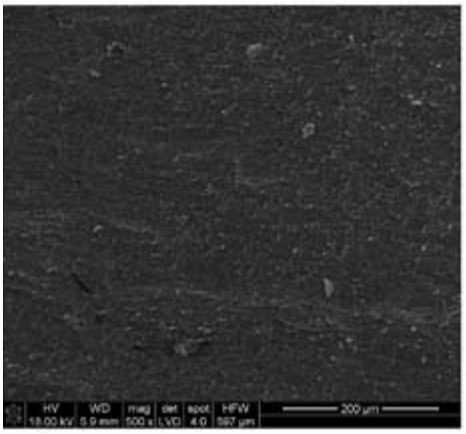

Fig. 10. Sample fracture of decarbonate of Triassic dolostone from Brudzowice (sample 1115) after its forming under pressure 200 MPa and sintering at 1650°C. SEM

Conclusions

The input of a specific work of 10 and 13 J/g respectively is required to form decarbonates of Triassic dolomite from Brudzowice under the pressure of 50 MPa and 200 MPa. The samples subjected to sintering at three temperatures demonstrated the satisfactory hydration resistance. This does not only refer to pellets formed under the highest pressure of 200 MPa, but also to considerably lower pressure (50 MPa) (Fig. 8).

For decarbonates of Devonian dolomite from Brudzowice, the formation process under the pressure of 20 and 50 MPa requires a minor input of the specific work (< 1 J/g), and the hydration rate of the samples is rapid (Figs 5÷7). The increase in formation pressure to

200 MPa contributed to the significant improvement of hydration resistance. In this case, the specific work necessary for the formation of decarbonates increased to 7 J/g.

The process of obtaining pellets from decarbonates of dolomite from Żelatowa and Ołdrzychowice under the pressure of 200 MPa requires a considerably greater input of the specific work: 37.5 and 31 J/g respectively. For samples from Żelatowa, the formation pressure increased to 200 MPa, which resulted in their reduced susceptibility to destruction at 40°C while exposed to 70% moisture. The hydration of sintered samples from Ołdrzychowice dolomite is a rapid process. It is even observed for samples obtained under the highest pressure applied in the formation pressure tests (200 MPa), and then sintered at 1650°C. The application of this outstandingly pure dolomite will require sintering temperatures considerably exceeding 1650°C.

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