Original paper

The effect of porosity on the reactivity of calcium sorbents

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Abstract. The current work presents the results of seven sorbent samples investigated with respect to SO_2 capture. The sorbents' reactivity and capacity indexes were determined, and the tests were carried out in accordance with the 'classical' procedure for limestone sorbents. The reactivity indexes (RIs) of the tested samples were in the range of 2.57 and 3.55 (mol Ca)/(mol S), while the absolute sorption coefficients as determined by the capacity index (CI) varied between 87.9 and 120.6 (g S)/(kg of sorbent). Porosimetric analysis was also carried out and the specific surface area of the samples was found to be between 0.2 and 1.7 m^2/g. The number of micro-, meso- and macro-pores in individual samples was determined from the corresponding pore size distribution histograms, and the values of sorbent RIs and CIs were correlated with the samples' total porosity and specific surface.

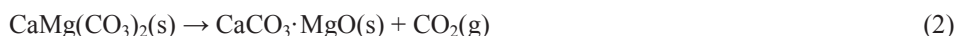*Key-words:* limestone, desulfurization, sorbent, reactivity, fluidization

1. Introduction

The Polish energy sector is still mostly based on coal-fired power plants, and in the second decade of the 21st century coal power plants produced approximately 130.3 TWh each year, corresponding to about 78% of the total national electricity production (Grudziński 2019). As for the electricity consumption, it continuously increased from around 159 TWh in 2012 to almost 169 TWh in 2016, while the consumption of hard coal and lignite in those years decreased and large-scale thermal power plants consumed approximately 94 million tons of coal in 2012 and some 90 million tons in 2016 for the production of electricity (Grudziński 2019).
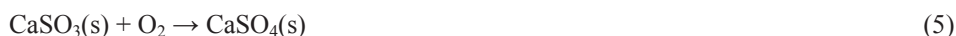
The burning of solid fuels in Poland is mainly responsible for the country's emission of sulfur dioxide, where the contribution of the energy sector is approximately 43.1%, while no-industry combustion is about 29.3%, and the industry sector 23.8%. The total emission into the atmosphere has been decreasing, however, and as presented by KOBiZE (2019), the decrease was approximately 18% – over 714,489 Mg of SO_2 was emitted in 2015, compared to 528,655 Mg in 2017.

For flue gas desulfurization, mainly limestone ($CaCO_3$) is used. In Poland, limestone is mainly mined in the Świętokrzyskie Voivodships (comprising over 60% of all known Polish limestone resources), as well as in the Łódź, Opole and Silesia regions. The total resources of industrial limestone are estimated at over 5.5 billion Mg and the exploited deposits at over 16,000 tons per year (Galos et al. 2016). In the case of dry desulfurization in the furnaces of fluidized-bed boilers, sorbents with grain sizes above 120 μm are usually used, while those of particle size less than 120 μm are consumed for wet flue gas desulfurization plants. The $CaCO_3$ content in the limestones for flue gas desulfurization is high, and in most cases exceeds 96%. The total demand for limestone sorbents for desulfurization was over 1.8 million Mg/year in 2014 (Galos et al. 2016), but that number significantly increased due to the construction and commissioning of new approximately 1,000 MW units in Poland, as well as further tightening of the SO_2 emission standards.

The dry method of flue gas desulfurization involves the introduction of 'dry' sorbent containing calcium carbonate into the combustion chamber. The additive injected is most often limestone or dolomite, since both decompose in boiler furnaces to form calcium or magnesium oxides (reactions (1)-(3)); the CaO and/or MgO then react with sulfur dioxide (sulfation) according to reactions (4)-(7).
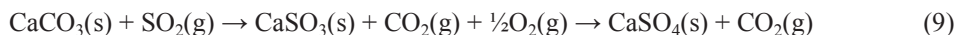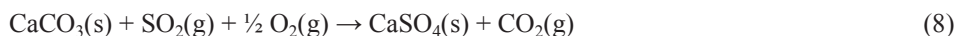
$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \tag{1}$$

$$CaMg(CO_3)_2(s) \rightarrow CaCO_3 \cdot MgO(s) + CO_2(g) \tag{2}$$

$$CaCO_3 \cdot MgO(s) \rightarrow CaO \cdot MgO(s) + CO_2(g) \tag{3}$$

As for the sulfurization, it may be realized in two ways: CaO reacts with SO_2 forming $CaSO_3$, and then the $CaSO_3$ reacts with oxygen forming $CaSO_4$, according to reactions (4)-(5):

$$CaO(s) + SO_2(g) \rightarrow CaSO_3(s) \tag{4}$$

$$CaSO_3(s) + O_2 \rightarrow CaSO_4(s) \tag{5}$$

or sulfur dioxide is oxidized to SO_3 and then the SO_3 reacts with CaO (reactions (6)-(7)):

$$SO_2(g) + \tfrac{1}{2} O_2(g) \rightarrow SO_3(g) \tag{6}$$

$$SO_3(g) + CaO(s) \rightarrow CaSO_4(s) \tag{7}$$

In case the temperature in the boiler furnace is lower than required for the decomposition of the calcium carbonate, or the concentration of CO_2 is too high, direct reaction between $CaCO_3$ and SO_2 may occur according to reactions. (8)-(10):

$$CaCO_3(s) + SO_2(g) + \tfrac{1}{2} O_2(g) \rightarrow CaSO_4(s) + CO_2(g) \tag{8}$$

$$CaCO_3(s) + SO_2(g) \rightarrow CaSO_3(s) + CO_2(g) + \tfrac{1}{2}O_2(g) \rightarrow CaSO_4(s) + CO_2(g) \tag{9}$$

$$CaSO_3(s) + \tfrac{1}{2} O_2(g) \rightarrow CaSO_4(s) \tag{10}$$

The direction in which reactions (8)-(10) occur depends on reactions (1), (4) and (5), that is, on the formation of CaO and the production of CO_2, which is then evolved to the

particle surroundings. Much of the data in the literature suggest that there is a relationship between the processes of calcination and sulfation (e.g. Tullin 1989; Oin 1995; Olas 2006; Montagnaro et al. 2010).

As a result of the sulfation of CaO, a layer of $CaSO_4$ is formed on the sorbent particle surface and in the pores. Due to its higher molar mass, the layer may thus lead to the 'blockage' of sorbent's active surface and a deceleration of the process of sulfation. In case of short sorbent particle residence time in the boiler furnace, some of the CaO may remain unreacted, since it may be surrounded by a continuous $CaSO_4$ product layer (cf. Fig. 1). Such a phenomenon is in most cases unwelcome, since it increases the desulfurization costs and limits possible application of the fluidized-bed ashes.
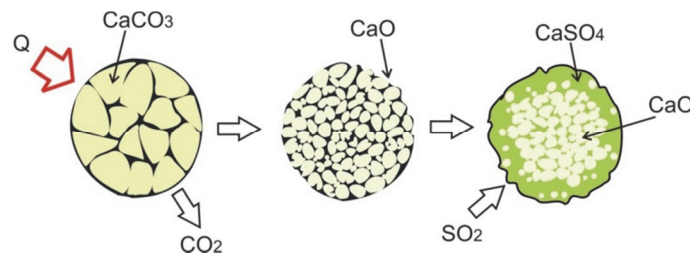

Fig. 1. The schematics of the sulfation of a CaO particle.

Investigation of the possibility of using limestone-containing sorbents for the reduction of the emission of SO_2 was carried out by numerous research groups. In all of those studies, the investigation of the sorbent's specific surface, as well as its porosity, were claimed to be of great importance (Adanez et al. 1997; Davini 2002; Lee et al. 2012; Han et al. 2015).

The size of sorbent particles used for dry flue gas desulfurization depends on the boiler type and furnace hydrodynamics, where the main goal is to assure efficient use of the calcium contained in the sorbent. The reactivity of fine limestone is relatively low, and in most cases 25-35%. Therefore, in order to capture over 90% of the SO_2, it is necessary to use more sorbent than required stoichiometrically, and in most cases the Ca/S ratio at industrial installations is maintained at the level of 3 to 4 (Bis 2010). If stricter sulfur emission standards are implemented and, for example, at least 95% desulfurization is required, the Ca/S ratio may even exceed 5 or 6. Unfortunately, the increase of the Ca/S ratio brings about higher operational costs for boilers and higher emission of other pollutants, such as NO_x, due to the catalytic activity of the excess CaO. Apart from that, higher consumption of sorbent is also associated with lower boiler efficiency and increased combustion byproduct management costs (Bis 2010).

Those costs may be reduced by the application of more reactive and more porous sorbents, with the investigation in this regard representing the main goal of the present paper.

2. Methodology

Seven limestone samples from some chosen Polish mines were used to investigate sorbent porosity. The tests were carried out for sorbent fraction with a particle size of 125-250 μm. The sorbent reactivity studies were carried out according to the commonly known

Alstrom sorbent reactivity test (Olas 2006). The sorbents were introduced into a previously heated (850°C) electric furnace, where they were subjected to calcination in a synthetic flue gas composed of 16% CO_2, 3% O_2, and approximately 81% N_2. After 30 minutes of calcination, the sample was sulfated due to the addition of some 1,870 ppm of SO_2 to the synthetic flue gases. The sample sulfation lasted 60 minutes. Later on, the sample was weighed, the content of sulfur in the samples was determined (Leco TruSpec analyzer) and the sorbent reactivity index (RI) [mol/mol] and the capacity index (CI) [(g S)/(kg of sorbent)] were calculated from the experimental data (Olas 2006; Kobyłecki et al. 2011; Włodarczyk et al. 2018). Sample reactivity investigations were carried out with the use of a mercury porosimeter (Quantachrome PoreMaster 33). The results of the investigation of sorbent reactivity were then compared with the Alstrom sorbent classification table (cf. Table 1).

The RI and CI were calculated according to the formulae:

$$RI = \frac{m_p \cdot \eta \cdot C_{Ca} \cdot M_S}{M_{Ca} \cdot m_k \cdot S^k \cdot 100} = \left[\frac{mol\,Ca}{mol\,S}\right] \tag{11}$$

$$CI = \frac{m_k \cdot S^k \cdot 10}{m_p} = \left[\frac{g\,S}{kg\,sorbentu}\right] \tag{12}$$

where m_p is the initial mass in g, η represents the $CaCO_3$ content in the limestone in g/g, C_{Ca} is the Ca content in $CaCO_3$ as a percentage value, M_S represents the molar mass of sulfur in g/mol, M_{Ca} is the molar mass of Ca in g/mol, m_k represents the mass of the sample after the test in g, and S^k is the sulfur content in the sample after the test as a percentage value.

3. Results and analysis

The results of the sorbent reactivity tests are shown in Table 2. The results indicate that the RI reactivity coefficients were in the range of 2.57 mol/mol (sample D) to 3.55 mol/mol (sample F). The highest values of the absolute sorption (the coefficient CI) were obtained for sample D and yielded 120 g/kg. The lowest sorption capacities were determined for samples F and G, at approximately 88 g/kg. According to the sorbent classification (cf. Table 1), the limestones could be classified as very good (samples B, C, D and E) and good (samples A, F and G; cf. Table 2). From the presented results, it may be pointed out that the RI and CI values determined from the laboratory-scale tests are similar to the values obtained from industrial installations.

TABLE 1

Classification of the sorbent reactivities according to the Alstrom test (Olas 2006).

	RI, (mol Ca)/(mol S)	CI, (g S)/(kg of 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
Poor	> 5.0	< 60

TABLE 2

The reactivity of the investigated sorbents.

Sample	RI [mol/mol]	CI [g/kg]
A	3.02	107.2
B	2.71	116.9
C	2.84	111.4
D	2.57	120.6
E	2.72	115.3
F	3.55	87.9
G	3.51	88.3

TABLE 3

Total porosity and sorbent surface area.

Sample	Total porosity [%]	Specific surface area [m^2/g]
A	5.451	0.2587
B	7.718	1.035
C	7.482	0.9831
D	9.015	1.7537
E	8.107	1.5438
F	6.314	0.5979
G	3.085	1.1836

The results of the investigation of sorbent porosity are shown in Table 3. The highest values of total porosity (9.015%) were determined for sample D, while the lowest total porosity values (3.085%) were obtained for sorbent G. As for the specific surface area, the highest values were determined for sample D (1.7537 m^2/g), while the lowest surface area (approximately 0.259 m^2/g) was measured for sorbent A (cf. Table 3).

From the mercury porosimetry investigations, it was also possible to obtain histograms of the pore size distribution of the investigated sorbent samples.

Analysis of the results for sorbent A (cf. Fig. 2) indicated a lack of mesopores and macropores of diameter below 0.2 μm. The sorbent contained a significant amount of macropores approximately 0.2-0.9 μm in size. Such a large number of macropores was the reason why the values of the total porosity and specific surface of the sorbent were relatively low, at slightly over 5.4% and 0.2587 m^2/g, respectively. The data obtained for sorbent B indicated that the sample contained a small amount of mesopores (pore size: 0.03-0.05 μm) and a large number of macropores characterized by two pore size ranges: 0.6-1 μm and 3-10 μm. The uniform distribution of macropores and the presence of mesopores in sorbent sample B resulted in the total porosity and specific surface area being higher than in the case of sorbent A and yielded 7.718% and 1.035 m^2/g, respectively. In the case of sorbent C, the number of mesopores was smaller than in the case of sorbent B. As a result, the total porosity of that sample was 7.482% and the specific surface area was

determined as 0.9831 m^2/g. Furthermore, sorbent C contained more macropores than sorbents A and C, particularly in the size range of 0.1-2 μm.
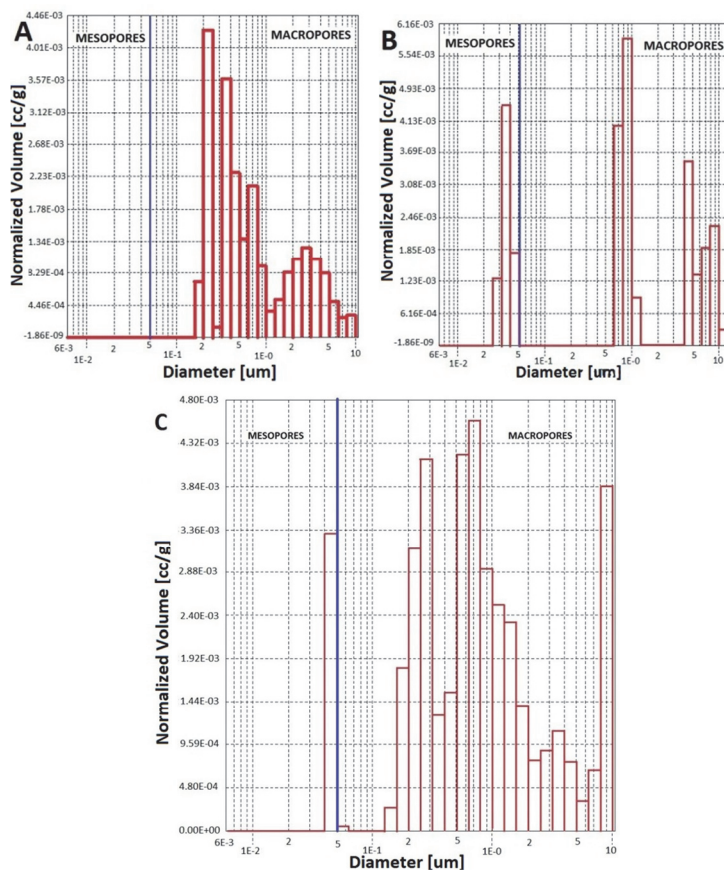

Fig. 2. Histograms of the pore size distributions of sorbents A, B and C.

The histograms of samples D and E (cf. Fig. 3) were quite similar, with both sorbents characterized by practically the same number of macropores; the main differences between those samples only became visible in case of the mesopores, since there were very few mesopores in the case of sorbent E, while in sorbent D the mesopores were determined in larger quantity. The data indicated that the varying number of mesopores was probably responsible for the differences in the values of specific surface area of both samples – in the case of sorbent D, the specific surface area was 1.7537 m^2/g, while in the case of sample E, the corresponding value was 1.5438 m^2/g.

In the case of the histograms for samples F and G, it was observed that both contained a similar amount of macropores. However, sorbent F lacked macropores smaller than 1 μm, while the macropores of that size were clearly visible in sample E. The data also indicated that there were virtually no mesopores either in sorbent E or F. As a result, the sorbents were characterized by quite small specific surface areas, approximately 0.6 m^2/g (sample F)

and 1.1836 m^2/g (sample G). However, the porosity of sample G was the lowest among all the tested sorbents, at slightly above 3% (3.085%). The sorbent sample was characterized by extensive mesopores, but contained just a few macropores, particularly those with diameters above 1 mm, and also – contrary to the other sorbent samples – lacked pores larger than 10 mm in size.
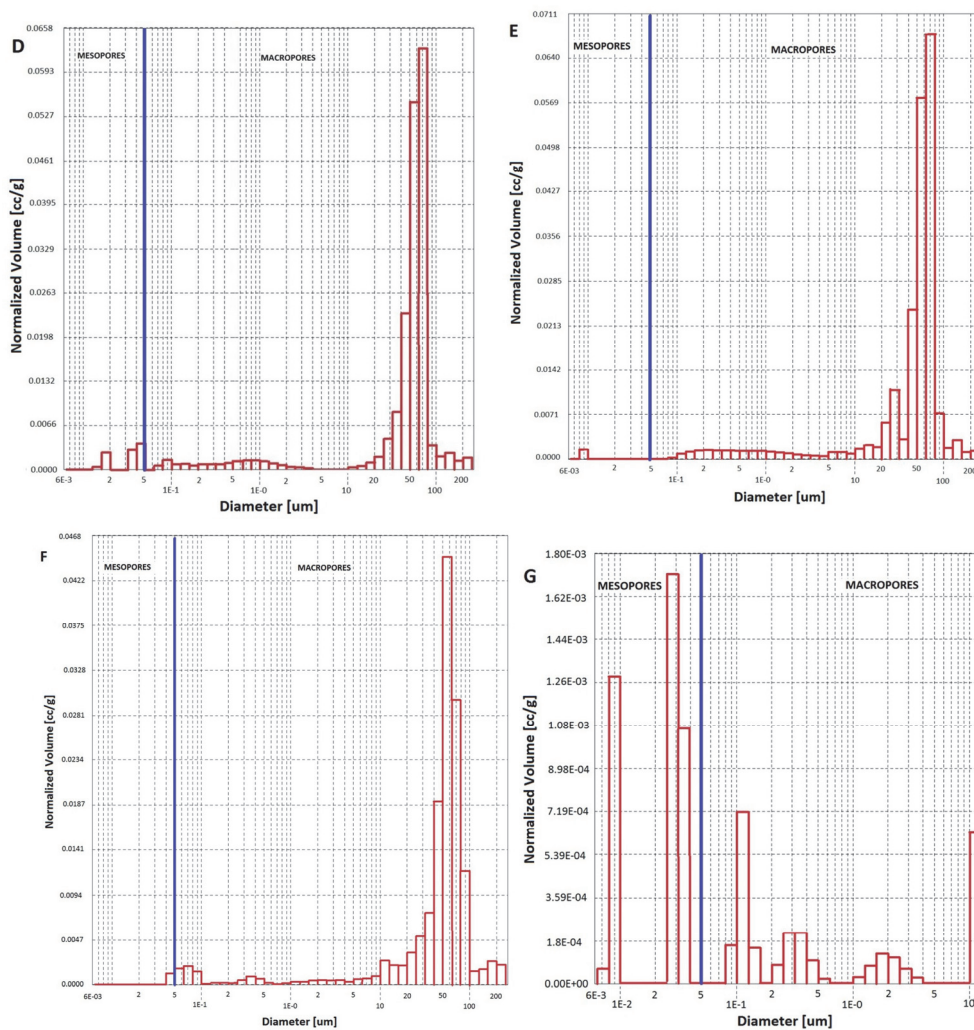

Fig. 3. Histograms of the pore size distributions of sorbents D, E, F and G.

The comparison of the results of the investigation of sorbent morphology (carried out by mercury porosimeter) and sorbent reactivity (characterized by the coefficients RI and CI) indicated (cf. Fig. 4) that sorbent D was the least reactive among all the investigated samples (RI = 2.57 mol/mol), but was characterized by the highest porosity (9.015%) and specific surface area (1.75 m^2/g). The sorbent samples B, C and E were characterized by

similar reactivity values (RI ranging from 2.5 to 3 mol/mol), as well as similar porosities and total surface areas. Sorbents A, F and G were characterized by lower total porosities compared to the other investigated samples, and thus were less reactive with respect to the capture of sulfur (cf. Table 2). Furthermore, compared to the other sorbents, sorbents A and F were also characterized by quite small specific surface areas. As for sorbent G, although it had a relatively well-developed specific surface area, it was also characterized by the lowest porosity among all the investigated samples and, as a result, the RI and CI values of that sample were quite poor.
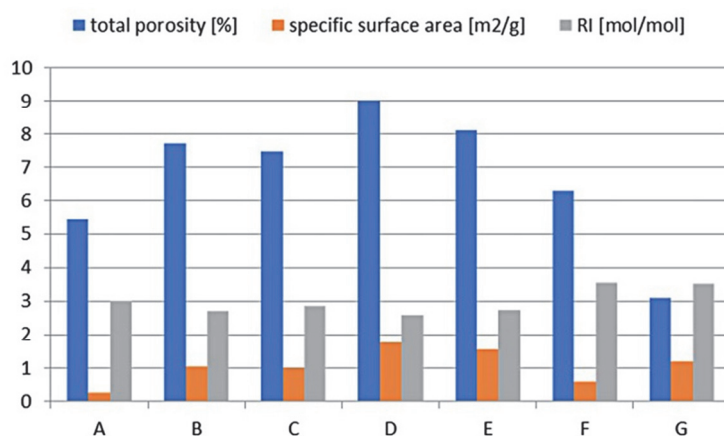

Fig. 4. Comparison of the reactivity, total porosity and surface area of the investigated sorbent samples.

4. Summary

The results presented and briefly discussed in the current paper indicate that the majority of sorbents having high total porosity and well-developed specific surface area were also characterized by very good reactivities, according to Alstrom's limestone sorbent sulfur capture and reactivity test (information on the test details was briefly discussed by Olas (2006), for example). It has to be emphasized that the application of porous and highly reactive additives in most cases brings about a reduction of the operational and maintenance costs for the plant. However, the relationship is not always straightforward, since among the investigated sorbent samples, there were also sorbents that were characterized by a well-developed specific surface area, or a high total porosity but their reactivity was lower than expected. One of the possible reasons for this may be a maldistribution of the pores in those samples (indicated by the corresponding sample histograms), or that the sorbents contained only macropores and just a few mesopores (as per the case of samples A and F). Another reason for the poor sorbent reactivity may be the lack of macropores in the sample, as per the case of sorbent G for example, which essentially contained only mesopores and almost no macropores. The discrepancies between the reactivity coefficients of the sorbents classified, according to the Alstrom test, as very good and characterized by similar specific

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surface and total porosity values were probably the result of the different chemical compositions of the individual sorbents. Due to the space limitations, the results of the investigations on the effect of the sorbent composition on its reactivity were not discussed in the current paper, with analysis in this regard the subject of another publication that is currently under preparation.

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