PRELIMINARY RESULTS OF USAGE POSSIBILITIES OF CARBONATE AND ZEOLITIC SORBENTS IN CO₂ CAPTURE

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ABSTRACT

This paper presents evaluations of carbonate and zeolitic materials usefulness from point of view application of them as carbon dioxide sorbents. For all selected materials mineralogical examinations (XRD, SEM analysis and observation in transmitted light) were conducted. Also textural characteristics (the BET surface area, mean pore diameter, pore size distribution and volume of pores) were carried out. An essential research has constituted CO₂ adsorption. CO₂ adsorption tests revealed that carbonate rocks have poor adsorption properties, their sorption capacity does not exceed 0.1 mmol/g. Therefore, they should be examined from the viewpoint of their application in mineral carbonation. However zeolites shown much better CO₂ adsorption parameters, thus, they can be subjected to further examinations (modification/activation) in order to determine selective and dynamic adsorption of CO₂.

KEYWORDS: CO₂ adsorption; Carbonate rocks; Synthetic zeolites; Sorbents; CO₂ capture

1 INTRODUCTION

The environmental impact of anthropogenic CO₂ emissions is regarded as the major risk to mankind, because its emissions into the atmosphere have been reported to account for half of the greenhouse effect which causes the global warming [1]. Over the past century its concentration in the atmosphere has increase significantly. The atmospheric level of CO₂ is rising at about 1.6 ppm per year while worldwide CO₂ emissions from fossil fuels combustion would amount to an increase of almost 3 ppm annually [2]. Therefore, reduction of CO₂ emission will be the greatest industrial challenge of the 21st century [3].

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There are exist three options to reduce total emission of CO₂ into the atmosphere e. i.: 1) reduction of energy intensity, 2) reduction of carbon intensity, 3) enhancing of CO₂ sequestration. The first option requires efficient usage of energy. The second, requires switching to using non-fossil fuels such as hydrogen and renewable energy. The third, involves the development of technologies to CO₂ capture and storage. It is believed that carbon capture and storage (CCS) technology is one of the obvious priority candidates for long term technology policies and enhanced R&D efforts to protect human against the risks associated with high environmental impacts of climate changes even widespread deployment of CCS requires decades to come.

Since the CO₂ separation/capture method is the first and most energy intensive step of CCS processes, many researches have targeted at improving the current technologies or developing new approaches of CO₂ separation and capture [4]. Many materials as sorbents of CO₂ are tested. These include natural and synthetic zeolites [5-8] (so far used in heavy metals [9] and ammonia ions removal from water solutions [10] or generally as acid gases sorbents [11]), limestones [3], opokas, glauconites [2, 7, 12], amines [4], activated carbons [13] (so far used in many applications i. e. for purification of water, air, and many chemicals etc. [14]). But, each materials need a different methods of modification or activation of them in order to received better CO₂ sorption properties.

2 MATERIALS AND METHODS

The main aim of this study was examination of carbonate materials occurring on Lublin vicinity and Roztoce in Poland (Fig. 1.) and synthetic zeolites (mixture of Na-P1 with Na-X and Linde-A, and mixture of Na-P1 with Linde-A) as potential carbon dioxide sorbents.

The carbonate research materials have constituted the following rocks: silica-carbonate rocks (opokas) from Kazimierz Dolny area, carbonate-silica rocks (detritic sandy limestone) from Józefów area, chalks from Chełm area and peelite marlstones from Rejowiec area.

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The zeolite material was a product of hydrothermal reaction of fly ash with NaOH water solution [15, 16]. It was obtained a mixture of three types of zeolites, in which dominates the zeolite Na-P1 accompanied by Linde-A zeolite and Na-X (Z-4 sample), and Na-P1 accompanied only by Linde-A (Z-5 sample). For Z-4 zeolitic mixture the
The following conditions were applied: 21 kg of fly ash, 12 kg of NaOH, 90 dm³ of water, temperature 75°C and time of reaction 36 h, whereas for Z-5 zeolitic mixture only time of reaction was different - 24h, rest of established parameters were the same.

For all tested materials mineralogical examinations such as XRD, SEM analysis and observation in transmitted light were conducted. Also textural characteristics were carried out. The BET surface area, mean pore diameter BJH, pore size distribution (PSD) and volume, average particle size, mean width of pores for each sample were determined.

An essential research has constituted CO₂ adsorption test at static condition with 750 mmHg pressure, that allowed to determine the usefulness of selected materials to application of them as CO₂ sorbents.

The chemical composition of carbonate rocks was determined using X-ray fluorescence spectrometer for wavelength-dispersive WD XRF. Induction source was a X-ray lamp with a dual Cr-Au anode about a maximum power of 3 kW.

Microscopic observations in transmitted light were carried out using an optical microscope Olympus BX60 equipped with camera, using zooms: 5x, 10x, 20x.

Observations of the mineral composition and examined samples surface (morphology) were made in FEI Qanta 250 FEG scanning microscope additionally equipped with a chemical composition analysis system (used for zeolitic materials) based on energy dispersion scattering – the EDS EDAX.

XRD analysis of the rocks and zeolitic materials were performed using a Philips X’pert APD diffractometer with the PW 3020 goniometer, Cu lamp, and graphite monochromator. The analysis was performed within the angle range of 5-40°.

Textural investigations of the specific surface areas and the associated pore size distribution were performed using Micromeritics ASAP 2020 analyser at temperature of 77°K. The samples before analysis were degassed at low pressure and temperature of 373.15°K during 6 hours period of time. After that, for each sample, cold and warm free spaces using helium were measured. Equilibration interval was 30 seconds. Weight of each samples ranged from 2.4 g to 2.9 g. Saturation pressure p₀ were calculated from temperature values enclosed in database of the analyser.

The main textural parameters (surface area, volume of pores, pore size distribution and average pore diameter) were evaluated by the following calculating methods: Langmuir model, BET equation, single point method surface area, BJH adsorption/desorption.

The values of the BET surface area and pore size distribution parameters were determined on the basis of the shape of adsorption/desorption isotherms of nitrogen vapour at 77°K. The BET surface area was calculated using Brunauer-Emmett-Teller’s multilayer adsorption theory [17] at p/p₀ between 0.06 and 0.3 (p - equilibrium pressure, p₀ - saturation pressure).

Volumes of pores were determined from the volume of adsorbed nitrogen at the pressure of p/p₀ = 0.98. Pore
diameters were calculated according to the following formula $D_p = 4V_p/S_{BET}$ (where: $V_p$ – pore volume, $S_{BET}$ – the BET surface area).

CO$_2$ sorption measurements were made using an analyser for precise measurements of physical sorption and chemisorption, equipped with additional device to vapor sorption, and mass spectrometer - AUTOSORB-I-C (Quantachrome Instruments, USA). Before the measurements samples were rinsed with helium and calcinated at 373.15$^\circ$K for 4 h. The scope of works included the appointment of CO$_2$ adsorption isotherms in temperature 273$^\circ$K.

For zeolitic samples, from adsorption isotherm of carbon dioxide, following parameters were determined: volume of pores with a diameter less than 0.7 nm, micropores volume, adsorption energy in micropores and the linear dimension of the micropores. The volume of pores with a diameter less than 0.7 nm was calculated from the points of adsorption isotherm for the relative pressure $p/p_0 > 0.029$. Parameters of microporous structure (pores with a diameter up to 2 nm) were determined according to the Dubinin-Radushkevich methodology [18]. These parameters were calculated according to the following standards: NIST 2006, ISO 9277:2010 (E), ISO 15901-3:2007 (E) [19-21].

3 RESULTS AND DISCUSSION

3.1. Chemical composition

The chemical composition of carbonate rocks is dominated by calcium oxide (associated with calcite), the largest amount of it was found in chalks (above 50 % wt.), while the opoka includes the smallest amount (less than 35 % wt.). In significant quantities there is also silica, with the biggest amount occured in opoka (almost 34 % wt.), slightly smaller amounts were found in limestone and marlstone (within 20 % wt.). The smallest number was observed in the chalk rocks. The content of aluminum oxide in the carbonate samples ranges from 2 - 2.5 % wt. with the exception of sandy-limestone from Józefów area (0.45 % wt.). Other ingredients such as MgO, Na$_2$O, K$_2$O, SO$_3$, TiO$_2$, P$_2$O$_5$, SrO are present in much smaller quantities (in marlstones and opokas) and quartz (in each rock sample). (in marlstones and opokas) and quartz (in each rock sample).

<table>
<thead>
<tr>
<th>Content in wt. %</th>
<th>marblestone</th>
<th>chalk</th>
<th>opoka</th>
<th>limestone</th>
<th>Z-4</th>
<th>Z-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>18.91</td>
<td>8.11</td>
<td>33.85</td>
<td>20.81</td>
<td>49.31</td>
<td>44.05</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>2.49</td>
<td>2.33</td>
<td>2.10</td>
<td>0.47</td>
<td>32.00</td>
<td>38.64</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.54</td>
<td>0.40</td>
<td>0.46</td>
<td>0.15</td>
<td>6.36</td>
<td>4.46</td>
</tr>
<tr>
<td>CaO</td>
<td>42.79</td>
<td>53.84</td>
<td>34.66</td>
<td>45.40</td>
<td>2.78</td>
<td>2.24</td>
</tr>
<tr>
<td>MgO</td>
<td>0.42</td>
<td>0.22</td>
<td>0.46</td>
<td>0.48</td>
<td>3.92</td>
<td>3.56</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.02</td>
<td>0.02</td>
<td>0.04</td>
<td>0.01</td>
<td>4.28</td>
<td>6.00</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.39</td>
<td>0.28</td>
<td>0.36</td>
<td>0.08</td>
<td>0.77</td>
<td>0.55</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.01</td>
<td>0.03</td>
<td>0.17</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.05</td>
<td>0.03</td>
<td>0.05</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.17</td>
<td>0.19</td>
<td>0.11</td>
<td>0.13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SrO</td>
<td>0.15</td>
<td>0.13</td>
<td>0.16</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LOI</td>
<td>33.67</td>
<td>33.92</td>
<td>27.27</td>
<td>31.80</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Microstructure of examined carbonate rocks (Fig. 2.) observed using scanning microscopy showed a very fine-grained nature of the tested materials and especially for the chalk and marlstone. Examined rocks are characterised by a high level of porosity. The microscopic images reveal their organic origin (chalk) and explicit participation of organisms in the process of these rocks formation (opoka, limestone).

Zeolitic materials are finer grained than carbonate rocks. Aggregation of these minerals rarely exceed the size of 2 µm and individual crystals, most often lamellar, sometimes needle-like, far less rarely isometric, reach the size of 0. X µm.

The mineral composition of carbonated rocks is shown in the Fig. 3. The main mineral component is calcite, that amount riches 92 % wt. in chalk rocks. Significant quantitative part have silica minerals such as CT opal especially occurring in opoka and marlstone. Besides it were observed clay minerals from smectite and illite group (in marlstones and opokas) and quartz (in each rock samples).

The mineral composition of the zeolite samples is shown in Fig. 4. In the composition of both zeolite samples the dominant zeolite phase is Na-P1 which in the sample Z-4 is accompanied by zeolite of the faujasite group (Na-X) and Linde-A type zeolite. And in Z-5 sample besides Na-P1 phase there occurs only Linde-A phase. The mineral composition is supplemented in both cases by the residue after the synthesis reaction which is a mixture of mullite, quartz, the remnants of aluminosilicate glass, and recrystalized calcite.
FIGURE 2 - Microstructures of tested materials
3.3. Textural parameter

Determined textural parameters are presented in Table 2. The differentiation of average particle size is clearly visible and these values for carbonate rocks are much higher in comparison with synthetic zeolite materials (from 113.401 nm for the opoka to 3415.177 nm for detritic limestone from the Józefów area). For zeolites, these values amounted 16.327 nm for Z-4, and 35.329 nm for Z-5, respectively. For an average pore diameter these values are varied regardless of the type of research materials, ranging from 6.444 nm for Z-4 to 13.513 nm for Z-5. For the most of carbonate materials, these values range within 9-10 nm. Determining the average pore width for carbonate rocks, due to the fact that the difference between the average pore size value and the examined parameter is small, it can be concluded that spherical shape of the pores is characteristic for these rocks. Differences between these parameters for zeolites are much higher, suggesting the elongated/oval shape of the pores. The values of the volume of mesopores (pore size 2-50 nm) for the carbonate rocks are very small which indicates a macroporous nature of the rocks. The exception is the opoka (0.129 cm³/g), where this value is similar to values obtained for zeolitic sample Z-4 (0.114 cm³/g). The volume of mesopores for the Z-5 is twice as high in comparison to Z-4.

Isotherms of nitrogen adsorption/desorption were also plotted for the examined carbonate materials (Fig. 5). Analysis of isotherms for carbonate rocks show that these rocks are characterized by Type IV isotherms according to IUPAC classification (International Union of Pure and Applied Chemistry), indicating the meso/microporous nature of the rocks, while the hysteresis loops can be categorized as Type H2/H3 that confirms the blind spherical and ink bottle shape of pores [23]. Pore size distribution for the carbonate rocks was determined in the range from 1.7 to 300 nm (Fig. 6). It is clearly visible that for opoka and marlstone observed variation in pore diameter varies from 2 - 40 nm, with a predominant pore diameter of 10 - 15 nm for opoka while for marlstone dominate the pores with a diameter of 2 - 12 nm. Pore distribution for opoka is homogeneous while it is bimodal for marlstone. For chalk and limestone very little variation in pore diameter from 2 -5 nm was observed. However, for chalk dominate pores with 4 nm in diameter and for limestone with 2 nm in diameter. In both cases, the pore distribution is homogeneous.

The isotherms analysis for the examined zeolitic materials (Fig. 7) revealed that, as in the case of carbonate rocks, zeolites are characterized by Type IV isotherms according to IUPAC classification indicating a meso/microporous nature of the rocks, while the hysteresis loops represent the Type H2/H3 which indicates a spherical shapes of pores (blind spherical and ink bottle shapes of pores) [23].

### Table 2 - Textural parameters of tested materials

<table>
<thead>
<tr>
<th>Rock samples</th>
<th>Average Particle Size [nm]</th>
<th>Mesopore volumes [cm³/g]</th>
<th>Average pore diameter BJH 4V/nm [nm]</th>
<th>S_{BET} surface area [m²/g]</th>
<th>Average width of pores 4V/nm by BET [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalk from Chelm</td>
<td>924.945</td>
<td>0.015</td>
<td>9.049</td>
<td>6.487</td>
<td>8.5166</td>
</tr>
<tr>
<td>Opoka from Kazimierz Dolny</td>
<td>113.401</td>
<td>0.129</td>
<td>8.958</td>
<td>52.910</td>
<td>9.7776</td>
</tr>
<tr>
<td>Detritic limestone from Józefów</td>
<td>3415.177</td>
<td>0.005</td>
<td>10.763</td>
<td>1.757</td>
<td>10.2529</td>
</tr>
<tr>
<td>Marlstone from Rejowiec</td>
<td>240.333</td>
<td>0.059</td>
<td>9.460</td>
<td>24.965</td>
<td>9.3732</td>
</tr>
<tr>
<td>Z-4</td>
<td>16.327</td>
<td>0.115</td>
<td>6.444</td>
<td>403.783</td>
<td>2.5721</td>
</tr>
<tr>
<td>Z-5</td>
<td>35.329</td>
<td>0.308</td>
<td>13.513</td>
<td>169.831</td>
<td>7.2546</td>
</tr>
</tbody>
</table>
FIGURE 5 - N₂ sorption/desorption isotherms of carbonate rocks

FIGURE 6 - Pore size distributions of carbonate rocks
FIGURE 7 - N₂ sorption/desorption isotherms of zeolites

FIGURE 8 - Pore size distributions of zeolites
The variability of the pores in the PSD (pore size distribution, Fig. 8) is observed in the range from 4 - 50 nm for Z-4 and from 2 - 20 nm for Z-4. For Z-4 dominant are pores with a diameter of 4.5 nm, while for Z-5 with a diameter of 2.5 nm. The distribution of pores in both cases is bimodal.

3.4. CO₂ adsorption

The CO₂ sorption experiments carried out on carbonate rocks showed that the carbonate rocks adsorb negligible amount of CO₂ therefore it was impossible to calculate pore structure parameters. Chalk and limestone show isotherms layout characteristic for Henry’s isotherms, while the sorption isotherms for the opoka, marlstone and zeolite samples are similar to Langmuir isotherm.

<table>
<thead>
<tr>
<th>Rock samples</th>
<th>Sorption capacity at pressure of 750 mmHg, [mmol/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalk from Chelm</td>
<td>0.0281</td>
</tr>
<tr>
<td>Opoka from Kazimierz Dolny</td>
<td>0.0717</td>
</tr>
<tr>
<td>Detritic limestone from Jozefow</td>
<td>0.0717</td>
</tr>
<tr>
<td>Marlstone from Rejowiec</td>
<td>0.3915</td>
</tr>
<tr>
<td>Z-4</td>
<td>0.9117</td>
</tr>
<tr>
<td>Z-5</td>
<td>0.0281</td>
</tr>
</tbody>
</table>

Sorption capacity (Table 3) for carbonate rocks ranges from 0.0216 mmol/g for samples of chalk to 0.0990 mmol/g for the opoka rocks. Zeolites however showed significantly bigger sorption capacity 0.3915 mmol/g for Z-5, and 0.9117 mmol/g for Z-4, respectively.

Better sorption capacity for zeolitic samples allowed to calculate following parameters from the isotherms of carbon dioxide adsorption: volume of pores with a diameter < 0.7 nm, micropore volume, adsorption energy in micropores and determination of micropores’ linear dimension, x. The results are compared in Table 4.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Z-4</th>
<th>Z-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of pores about diameter below 0.7 nm [m²/g]</td>
<td>0.043</td>
<td>0.018</td>
</tr>
<tr>
<td>Volume of micropores, V_m [cm³/g]</td>
<td>0.054</td>
<td>0.019</td>
</tr>
<tr>
<td>Adsorption energy in micropores, E [kJ/mol]</td>
<td>34.3</td>
<td>26.1</td>
</tr>
<tr>
<td>Linear dimension of micropores, x [nm]</td>
<td>0.76</td>
<td>0.99</td>
</tr>
</tbody>
</table>

TABLE 4 - Textural parameters of zeolitic materials calculated from CO₂ isotherms adsorption

4 CONCLUSIONS

Performed tests were aimed at determining the suitability of two types of materials (carbonates and zeolites) to use them in CO₂ capture technologies. These tests constituted only preliminary research in order to select appropriate further examination method for each tested materials. Due to the fact that the tested materials (carbonates and zeolites), significantly differ from each other, both in terms of chemical composition and mineral structure of the pore and textural properties, disparate results of adsorption of CO₂ were achieved.

Carbonate rocks contain mainly CaO in their chemical composition and thus calcite dominates in their mineral composition. While zeolites are mainly built by silicates, which are suitable zeolitic phases, and therefore SiO₂ and Al₂O₃ dominate in their chemical composition. For carbonate rocks i.e. chalk or limestone results showed a very low specific surface area of a few m²/g. Higher values were obtained for opoka and marlstone, respectively 24 m²/g and 53 m²/g which is probably associated with the presence of clay minerals in their mineral composition. Zeolites however have a much higher the BET specific surface area of Z-4 - 403.7 m²/g and Z-5 - 169.8 m²/g. Zeolites also have a much smaller particle size where average values are more than ten times as much lower than the values obtained for carbonate rocks.

CO₂ adsorption tests revealed that carbonate rocks have poor adsorption properties, their sorption capacity does not exceed 0.1 mmol/g. Therefore, they should be examined from the viewpoint of their application in mineral carbonation to neutralization of CO₂ but only after calcining them into CaO and then using them to carbon dioxide capture [8]. However zeolites shown much better CO₂ adsorption parameters (their sorption capacity is 0.9 mmol/g for Z-4 and 0.4 mmol/g for Z-5, respectively), thus, they can be subjected to further examinations (modification/activation) in order to determine selective and dynamic adsorption of CO₂ [8, 24, 25].

Therefore, testing materials so different from each other indicate that, depending on whether they will be used carbonate rocks or synthetic zeolites, a different method of neutralization of CO₂ should be applied. For carbonate rocks it should be utilization method, i.e. mineral carbonation, while zeolites could be used in adsorption methods in order to separate carbon dioxide.

In further consideration the thermal and IR (infrared) analysis will be conducted. Also for carbonate rocks the test of mineral carbonation is planned. However for zeolitic samples modification of their surface properties using amine solutions (MEA or IPA) will be carried out in order to improve their adsorption properties.

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The authors declare no conflict of interest

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