SORPTION CAPACITY OF NATURAL CZECH LIMESTONES FOR USE IN CARBONATE LOOP

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In these days the carbon dioxide emissions are growing, important and discussed problem. In industrial scale the high carbonate looping technology can be one of possible solution. This process should be used in industrial for carbon dioxide and other acidic substances removal from the flue gases. Therefore, the main goal of this technology is the decrease of carbon dioxide emission and simultaneously capturing of pure CO₂ (95%) which can then be used as a raw material in chemical industry.

In this technology the materials with suitable composition are used, they are allowed to create a chemical bond with carbon dioxide and appropriate carbonates are formed. This technology is sorption process, concretely chemisorption process. The most usual sorbent is calcium oxide and for this sorbent the carbonation proceeds at 850 - 700 °C and the calcination is carried out at 900 - 1 000 °C [1 - 4].

Tested Limestones

We tested ten different natural limestone materials based on calcium carbonate from these areas in Czech Republic (Fig.1):

- quarry Brandýzovy
- quarry Četnovy schody
- quarry Holy vrch
- quarry Hvězdátka
- quarry Libotín
- quarry Mofina
- quarry Na Špíče
- quarry Tetín
- quarry Upolňavy
- quarry Vítolov

Fig. 1: Chosen Limestone quarries in Czech Republic

The samples were crushed using jaw crusher and classified by sieving into several fractions. For chemisorption tests two fractions were chosen: 0.5 - 1.0 mm and 1.0 - 2.0 mm.

Sorption of CO₂

The chemisorption tests were performed on special sorption system Quantachrome ASIQ.

Before chemisorption tests all samples must be prepared. Samples were calcined in muffle furnace at 950°C for 12 hours. The calcination proceeds according the reaction:

\[ CaCO_3 \rightarrow CaO + CO_2 \]

During preparation on CO₂ sorption the carrier gas (helium) flowed through the calcined sample (ca. 1 g) in the sample cell. Then the sample was evacuated and heated up to 650 °C. After that the carrier gas (helium) was switched to adsorptive gas (carbon dioxide) and began the carbonation. The carbonation proceeds according the reaction:

\[ CaO + CO_2 \rightarrow CaCO_3 \]

The exactly given volumes of carbon dioxide were dosed into the sample cell and a sorption isotherm was measured – one point of isotherm for one volume of CO₂, when the balance was achieved [5].

Results

Samples of all quarries (0.5 - 1.0 mm fraction) were calcined (12 hours, 950 °C) and then analyzed by X-ray fluorescence analysis. Results of this analysis are shown in table 1.

For each sample it was compared the theoretical consumption and real consumption of carbon dioxide. The real consumption was derived from measurement and the theoretical one was calculated from measured content of calcium oxide and magnesium oxide in each limestone sample (X-ray analysis).

<table>
<thead>
<tr>
<th>Sample</th>
<th>CaO %</th>
<th>MgO %</th>
<th>Al₂O₃ %</th>
<th>SiO₂ %</th>
<th>Fe₂O₃ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brandýzový</td>
<td>98.41</td>
<td>0.70</td>
<td>0.13</td>
<td>0.25</td>
<td>0.21</td>
</tr>
<tr>
<td>Četnovy schody</td>
<td>99.01</td>
<td>0.61</td>
<td>0.21</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Holy vrch</td>
<td>77.17</td>
<td>4.03</td>
<td>0.78</td>
<td>16.91</td>
<td>0.39</td>
</tr>
<tr>
<td>Hvězdátka</td>
<td>69.82</td>
<td>2.50</td>
<td>2.58</td>
<td>20.79</td>
<td>1.80</td>
</tr>
<tr>
<td>Libotín</td>
<td>97.94</td>
<td>0.88</td>
<td>0.10</td>
<td>0.61</td>
<td>0.06</td>
</tr>
<tr>
<td>Mofina</td>
<td>91.23</td>
<td>4.35</td>
<td>1.07</td>
<td>2.22</td>
<td>0.50</td>
</tr>
<tr>
<td>Na Špíče</td>
<td>83.99</td>
<td>1.89</td>
<td>3.18</td>
<td>7.38</td>
<td>2.25</td>
</tr>
<tr>
<td>Tetín</td>
<td>97.06</td>
<td>1.52</td>
<td>0.22</td>
<td>0.47</td>
<td>0.20</td>
</tr>
<tr>
<td>Upolňavy</td>
<td>68.27</td>
<td>1.17</td>
<td>7.60</td>
<td>18.80</td>
<td>1.92</td>
</tr>
<tr>
<td>Vítolov</td>
<td>97.93</td>
<td>0.59</td>
<td>0.37</td>
<td>0.72</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Conclusion

Measurements and calculations showed that all limestone samples had higher theoretical sorption capacity than real consumption of carbon dioxide. The theoretical consumption correlates with the real one and the difference is ca. 0.1 - 0.3 g CO₂/g sample.

The best tested samples for using in high temperature carbonate looping technology, based on the sorption capacities of carbon dioxide, were Libotín, Četnovy schody and Tetín. Samples with the lowest real sorption capacity were Upolňavy, Holy vrch and Hvězdátka.

It has been also proved that the particle size does not have an important effect on sorption capacity of carbon dioxide under conditions of our testing. It should be mentioned that in larger scale it will probably not achieve the exact balance like during measurement on tested sorption system and the type of fraction could have an effect on sorption capacity of carbon dioxide.

All of tested samples will be tested in a larger scale to examine the effect of particle size and mainly the effect of repeatedly applied.

Acknowledgement

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References


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