CO$_2$ sequestration with the use of fly ash from hard coal and lignite combustion

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The Polish power industry is based on conventional fuels combustion: hard coal and lignite. This industry is the largest source of carbon dioxide emission in Poland. Power generation process creates considerable quantity of wastes, including fly ash which is used in various other industries. One method of using fly ash in Poland is placing it in a fly ash-water suspensions in underground coal mines. Fly ash in a mixture with water might be used for carbon dioxide fixation in mineral carbonation process.
The CaO and free CaO content decides largely about the usefulness of fly ashes in CO$_2$ bonding. On the basis of fly ashes analysis from Polish professional power industry, it has been stated that the fly ashes from lignite and fluidized bed boilers are characterized by the biggest CaO contents (10-29,2%). The lowest CaO content amounting to 0,86-6,2% is present in the fly ashes from conventional hard coal combustion.
Fly ashes used for CO$_2$ fixation need to have high calcium content, which directly reacts with water. As the result of fly ash hydration the Ca(OH)$_2$ and C-H-S phases form, which are reactive with carbon dioxide.

**Portlandite**

\[
Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O
\]

**Calcium silicates**

\[
CaO \cdot nSiO_2 \cdot mH_2O (C-S-H) + CO_2 \rightarrow CaCO_3 + SiO_2 + mH_2O
\]
A wide range of research has been carried out in order to determine the applicability of selected fly ash from Polish professional power industry to CO$_2$ sequestration via mineral carbonation including:

- determination of CO$_2$ absorption by ‘fresh’ ash-aqueous suspensions
- determination of CO$_2$ bonding rate
- determination of CO$_2$ influence on leachability of impurities from ash-aqueous suspensions
- determination of CO$_2$ influence on properties of ash-aqueous suspensions
### Chemical composition of fly ash selected for the purpose of research

<table>
<thead>
<tr>
<th>Component</th>
<th>Fly ashes from hard coal combustion in conventional boilers</th>
<th>Fly ashes from lignite combustion in conventional boilers</th>
<th>Fly ashes from hard coal combustion in fluidized bed boilers</th>
<th>Fly ashes from lignite combustion in fluidized bed boilers</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>58.4</td>
<td>41.5</td>
<td>31.4</td>
<td>38.0</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>4.0</td>
<td>4.5</td>
<td>3.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>14.0</td>
<td>4.8</td>
<td>14.7</td>
<td>28.0</td>
</tr>
<tr>
<td>CaO</td>
<td>5.3</td>
<td>30.0</td>
<td>20.0</td>
<td>16.0</td>
</tr>
<tr>
<td>MgO</td>
<td>3.0</td>
<td>4.5</td>
<td>2.2</td>
<td>2.0</td>
</tr>
<tr>
<td>CaO$_{free}$</td>
<td>1.3</td>
<td>7.1</td>
<td>6.7</td>
<td>5.0</td>
</tr>
</tbody>
</table>
Investigation system to determine the amount of absorbed CO₂
### Absorption of CO₂ by ‘fresh’ ash-aqueous suspension

<table>
<thead>
<tr>
<th>Suspension kind</th>
<th>Ash-water ratio</th>
<th>Seasoning time [h]</th>
<th>CO₂ absorption [g CO₂/100 g]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>after 24 hours</td>
</tr>
<tr>
<td>Suspension with fly ashes from hard coal combustion in conventional boilers</td>
<td>1.5</td>
<td>480</td>
<td>1.33</td>
</tr>
<tr>
<td>Suspension with fly ashes from lignite combustion in conventional boilers</td>
<td>2.0</td>
<td>408</td>
<td>4.81</td>
</tr>
<tr>
<td>Suspension with fly ashes from hard coal combustion in fluidized bed boilers boilers</td>
<td>0.6</td>
<td>614</td>
<td>7.85</td>
</tr>
<tr>
<td>Suspension with fly ashes from lignite combustion in fluidized bed boilers boilers</td>
<td>1.0</td>
<td>760</td>
<td>7.03</td>
</tr>
</tbody>
</table>

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Example chart of absorption

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In order to confirm CO$_2$ bonding by ash-aqueous suspensions, that is the ongoing processes of mineral carbonation, their phase composition has been examined by means of roentgenographic method, calcium carbonate content – thermogravimetry method and supplementary, the microstructure has been examined with the use of a scanning microscope. In the studies the presence of calcite and its content has been of a particular interest, which is the elementary product of mineral carbonation and phases – the products of ash hydration undergoing carbonation. Determination of phase composition helps to state whether carbonation will proceed.
CaCO$_3$ content

- Suspension with fly ashes from hard coal combustion in conventional boilers
- Suspension with fly ashes from lignite combustion in conventional boilers
- Suspension with fly ashes from hard coal combustion in fluidized bed boilers
- Suspension with fly ashes from lignite combustion in fluidized bed boilers

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Ash-aqueous suspension with the inserted CO$_2$

Noticeable ash grains covered with microcrystalline silicates hydration, distinguishable calcite

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Pb contents in leachates from ash aqueous suspensions ‘pure’ and with the inserted CO$_2$
Cr contents in leachates from ash aqueous suspensions ‘pure’ and with the inserted CO₂.
Impact of CO₂ on pH leachates from ash aqueous suspensions

- Suspension with fly ashes from hard coal combustion in conventional boilers
- Suspension with fly ashes from lignite combustion in conventional boilers
- Suspension with fly ashes from hard coal combustion in fluidized bed boilers
- Suspension with fly ashes from lignite combustion in fluidized bed boilers

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Impact of CO$_2$ on the compression strength of suspensions

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Impact of CO$_2$ on the time of bonding of suspensions

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Conclusions

Fly ash may be the material used for CO\textsubscript{2} sequestration. Regardless of a low extent of absorption, as for example in suspensions based on fly ash from hard coal combustion, waste is worth considering for CO\textsubscript{2} sequestration, because of its great amounts.

An important aspect of ash-aqueous suspensions use for CO\textsubscript{2} bonding is their subsequent economic usage, that will be limited by CO\textsubscript{2} influence on leachability of impurities and the impact on technological properties of ‘fresh’ and hardened suspensions.
Literature:


CO₂ Capture and Storage – Response to Climate Change