An investigation on CO$_2$ capture by lime mud from paper mill in calcium looping process

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The utilizing situation of the lime mud from paper mill

- Lime mud (LM) is the insoluble material that results from the causticization reaction in alkali recycling process of paper mill:
  \[ \text{Na}_2\text{CO}_3 + \text{CaO} + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{CaCO}_3 \text{ (lime mud)} \]

- The main disposal is landfills:
  - Lead to water, soil and air contamination.
  - Landfill is not a suitable method to deal with the LM.
  - How to reuse the LM in environmentally sound methods?

As sorbent for \( \mathrm{CO}_2 \) capture in calcium looping process?
CO₂ capture by LM in calcium looping process

Reaction conditions:
Carbonation: 700℃, 15% CO₂+85% N₂
- CO₂
Calcination: 850℃, N₂

Particle size: <0.125 mm

\(X_N\) denotes conversion of CaO in the sorbent to CaCO₃ after \(N\) calcination/carbonation cycles and is calculated according to mass change of the sample after calcination and carbonation.
The carbonation conversion of the LM is relatively low during the previous cycles.

Carbonation: 700 °C, 40 min;
Calcination: 850 °C, 15 min;
Particle size: <0.125 mm

<table>
<thead>
<tr>
<th>Sample</th>
<th>CaO</th>
<th>MgO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>SO₃</th>
<th>Ti₂O</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>Cl</th>
<th>others</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>LM</td>
<td>52.39</td>
<td>0.7</td>
<td>2.52</td>
<td>1.49</td>
<td>0.29</td>
<td>0.31</td>
<td>0.056</td>
<td>0.013</td>
<td>0.14</td>
<td>0.88</td>
<td>0.049</td>
<td>41.16</td>
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<td>limestone</td>
<td>52.08</td>
<td>1.32</td>
<td>3.32</td>
<td>0.53</td>
<td>0.03</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.02</td>
<td>--</td>
<td>--</td>
<td>42.23</td>
</tr>
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</table>
Pre-wash treatment to decrease Na and Cl

LM

100g

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<td>0.88</td>
<td>0.049</td>
<td>41.16</td>
</tr>
<tr>
<td>PLM</td>
<td>52.52</td>
<td>0.73</td>
<td>2.64</td>
<td>1.71</td>
<td>0.27</td>
<td>0.3</td>
<td>0.066</td>
<td>0.013</td>
<td>0.044</td>
<td>0.30</td>
<td>0.051</td>
<td>41.36</td>
</tr>
</tbody>
</table>

Distilled water

400ml

2 h at ambient temperature

Distilled water

200ml

2 h at ambient temperature

Pre-washed lime mud (PLM)
CO$_2$ capture behavior of LM and PLM

In DFR;
- Carbonation: 700 °C, 40 min;
- Calcination: 850 °C, 15 min;
- Particle size: <0.125 mm

$X_N$

$N$

0.36

0.20
The effect of prolonged carbonation on the CO$_2$ capture capacity of LM and PLM

- The CO$_2$ capture capacity of LM is enhanced by pre-wash treatment.

- Moreover, it is necessary to further improve the cyclic carbonation rates and conversions of LM and PLM by some simple methods.

- It has been found that calcium-based sorbent can be reactivated by a prolonged carbonation process

- We attempt to increase the CO$_2$ capture capacity of the LM and PLM by a prolonged carbonation process at the 1st cycle.
The prolonged carbonation process

- The carbonation reaction was prolonged for **3-12 h in the 1st cycle.**
  - Carbonation: 100% CO₂; 700 ℃
  - Calcination: 15 min; 100% N₂; 850 ℃

- **For the other cycles, the carbonation time is 20 min.**
  - Carbonation: 15%CO₂+85%N₂; 700 ℃
  - Calcination: 15 min; 100% N₂; 850 ℃

- After prolonged carbonation, the carbonation reactions of LM and PLM at 2nd and 15th cycles were investigated in TGA.
The effect of the carbonation time in the 1st cycle on CO$_2$ capture capacity

In DFR;
Carbonation: 700 °C, 20 min except the 1st cycle;
Calcination: 850 °C, 15 min;
Particle size: <0.125 mm

In the Figure, LM-n Car denotes the LM undergone n hour carbonation at the 1st cycle.
The effects of prolonged carbonation on the carbonation rates and conversions

In TGA; Carbonation: 700 °C; Calcination: 850 °C, 15 min;
Particle size: <0.125 mm

The prolonged carbonation process mainly increase the carbonation rates of the LM and PLM during the chemical reaction controlled stage.
We also do another experiment. **Not only the 1st but also the 20th** carbonation were prolonged.
The effect of prolonged carbonation on microstructure of the calcined LM and PLM

<table>
<thead>
<tr>
<th></th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LM</td>
<td>7.65</td>
<td>0.018</td>
</tr>
<tr>
<td>PLM</td>
<td>12.20</td>
<td>0.036</td>
</tr>
</tbody>
</table>

Surface area and pore volume of the calcined sorbents

- LM
- PLM
- LM-9h Car
- PLM-9h Car
Future work

- Cyclic CO$_2$ capture of LM and PLM in a dual fluidized bed reactor
- Particle attrition of LM and PLM
- The long-term CO$_2$ capture capacity of LM and PLM
Acknowledgments

• This research is supported by National Natural Science Foundation of China (51006064)
Thank you for your attention!

Any questions?