Equilibrium calculations in aqueous carbonation of oil shale waste – sulfur compounds

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Background I

The main energy source in the Republic of Estonia is the local fossil fuel - oil shale (OS) - which is used for the power as well as shale oil (SO) production.

As a consequence:
• large quantities of OS mineral waste
  ~8.0 MT of OS waste per 2013
• gaseous emissions of CO$_2$, SO$_x$ and NO$_x$ are produced.

Oil shale ash (OSA) is classified as a hazardous waste” in Estonian registry of waste due to the highly alkaline leachates (pH 12 - 13) formed at hydrotransportation and open-air deposition of OSA.
OS waste can be used as sorbents in the CO₂ mineralization process.

**Chemical stabilization of ashes** can be achieved.

Alkaline ash transportation water could be considered as a resource for the production of PCC (CaCO₃).
In order to minimize the environmental risks accompanied by utilizing OS wastes as a CO$_2$ trap and/or cheap Ca-source for PCC production the routes of sulfur compounds transformations have to be explored in different conditions.

To better understand OS waste leaching/carbonation process, that we could reliably design technological schemes.
Calculations methodology

Circulating fluidized bed ash (CFBCA)

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO&lt;sub&gt;free&lt;/sub&gt;</td>
<td>10.44</td>
</tr>
<tr>
<td>CaSO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>5.47</td>
</tr>
<tr>
<td>CaS</td>
<td>0.64</td>
</tr>
<tr>
<td>MgO&lt;sub&gt;free&lt;/sub&gt;</td>
<td>3.94</td>
</tr>
<tr>
<td>CaCO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>27.7</td>
</tr>
</tbody>
</table>

Solid heat carrier ash (SHCA)

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO&lt;sub&gt;free&lt;/sub&gt;</td>
<td>3.0</td>
</tr>
<tr>
<td>CaSO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.7</td>
</tr>
<tr>
<td>CaS</td>
<td>4.62</td>
</tr>
<tr>
<td>MgO&lt;sub&gt;free&lt;/sub&gt;</td>
<td>8.7</td>
</tr>
<tr>
<td>CaCO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>29.4</td>
</tr>
</tbody>
</table>

Direct aqueous (S/L=1/5 to 1/250) carbonation of OS wastes at 25 °C and 1 atm
RESULTS
Results

CO$_2$(g) binding potential at aqueous carbonation of OS wastes

![Graph showing pH averages and bound CO$_2$ amounts for different model flue gases.]

- **pH$_{\text{average}}$ = 8.42** for CFBCA - model flue gas 1
- **pH$_{\text{average}}$ = 8.40** for CFBCA - model flue gas 2
- **pH$_{\text{average}}$ = 8.59** for SHCA - model flue gas 1
- **pH$_{\text{average}}$ = 9.04** for SHCA - model flue gas 2

Bound CO$_2$(g) amount, mmol
OSA suspensions pH changes

Results

CFBCA – H₂O - model flue gas 1

Experimental results pH 12 → 6.8

SHCA – H₂O - model flue gas 1

Experimental results pH 12.28 → 7.5

CFBCA – H₂O - model flue gas 2

SHCA – H₂O - model flue gas 2

1/5 OSA/water  -  1/10 OSA/water  -  1/20 OSA/water  -  1/250 OSA/water
The behavior of Ca\(^{2+}\) ion and solid phase in OSA - H\(_2\)O – flue gas systems

Results

\[
\begin{align*}
\text{pH 12.28} & \rightarrow 8.45 \\
\end{align*}
\]

\[
\begin{align*}
\text{CaO + H}_2\text{O} & \leftrightarrow \text{Ca(OH)}_2 \leftrightarrow \text{Ca}^{2+} + \text{OH}^- \\
\text{Ca}^{2+} + \text{CO}_3^{2-} & \leftrightarrow \text{CaCO}_3
\end{align*}
\]
The behavior of sulfur in CFBCA - $\text{H}_2\text{O}$ systems

Results

The behavior of sulfur in CFBCA - $\text{H}_2\text{O}$ systems

The behavior of sulfur in CFBCA - $\text{H}_2\text{O}$ systems

The behavior of sulfur in CFBCA - $\text{H}_2\text{O}$ systems

The behavior of sulfur in CFBCA - $\text{H}_2\text{O}$ systems
Experimental results
OSA – H₂O – model flue gas systems; S/L = 1/10

Batch reactor

SO₄²⁻ = 45 mmol/L calculated

System pH, sulfate mmol/L and CO₂ in solid residue %

Input CO₂(g), mmol

System pH, sulfate mmol/L and CO₂ in solid residue %

H₂S(g)

System pH exp

System pH calculated

Binding potential ~400 calculated

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The behavior of sulfur in SHCA–H₂O systems

Results


0 100 200 300 400 500 600 700 800

H₂S(g), mmol; CaS, H₂S(a), HS-, S²-, mmol/L

Input CO₂, mmol

model flue gas 2

HS(-a)  H₂S(g)  S(-2a)  H₂S(a)  CaS

Conclusions

- Considering the amounts of deposited waste from OS sector, the mineral carbonation of acidic gases is a promising solution in reducing greenhouse gas emissions and utilizing OS waste, while monitoring the pH and oxidation potential of aqueous carbonation to minimise sulfur pollution.

- The study shows that oil shale waste are able to bind 264 – 308 kg of CO₂ per ton of mineral waste under certain conditions.

- SO₄²⁻—ions dominated (comparing with other sulfur species) in all OS waste – H₂O – acidic gases systems.

- The behaviour of sulfates were dependent on the system pH, while thiosulfates depended on the equilibriums of sulfide forms.

- If system pH < 9 sulfides were depleted.

- The HSC calculation results of model systems were in reasonable accordance with the experimental results.

- SHCA is not suitable for carbonation due to the high content of sulfide and because of the formation of bicarbonates.
Thank you for your kind attention.

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