Fully Integrated Simulation of a Cement Plant
with a Carbon Capture Ca-looping Process

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2012/20/08
**Carbon Capture for Cement Industry**

**CO₂ Emission from Cement Industry**
- Cement is a key construction material (3.78 billion tons in 2012).
- Large industrial source of CO₂ emission (5% of worldwide emission).
- Around 50% of the total emission accounts for calcination of limestone in raw material.
- Energy efficiency improvements are limited, essential to deploy a carbon capture technology to reduce CO₂ emission up to 90%.

**Technical Options for Carbon Capture**
- **Oxy-combustion**
  - Technical uncertainty in operating cement kiln under the condition of oxy-combustion
- **Post-combustion amine process**
  - Stripper steam should be generated with an external boiler. → new boiler, FGD, SCR
- **Post-combustion Ca-looping process**
  - The absorbent is one of the cement raw materials → purge CaO can be used for cement manufacture
  - The operating condition of a carbonator can be found in cement plant.
### Chemical Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H$ (kJ)</th>
<th>For 1kg of</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO$_3$ (Calcite) $\rightarrow$ CaO + CO$_2$(g)</td>
<td>+1782</td>
<td>CaCO$_3$</td>
</tr>
<tr>
<td>AS4H (pyrophyllite) $\rightarrow$ $\alpha$-Al$_2$O$_3$ + 4SiO$_2$(quartz) + H$_2$O(g)</td>
<td>+224</td>
<td>AS4H</td>
</tr>
<tr>
<td>AS2H2 (kaolinite) $\rightarrow$ $\alpha$-Al$_2$O$_3$ + 2SiO$_2$(quartz) + 2H$_2$O(g)</td>
<td>+538</td>
<td>AS2H2</td>
</tr>
<tr>
<td>2FeO·OH (goethite) $\rightarrow$ $\alpha$-Fe$_2$O$_3$ + H$_2$O(g)</td>
<td>+254</td>
<td>FeO·OH</td>
</tr>
<tr>
<td>2CaO + SiO$_2$ (quartz) $\rightarrow$ $\beta$-C2S</td>
<td>-734</td>
<td>C2S</td>
</tr>
<tr>
<td>3CaO + SiO$_2$ (quartz) $\rightarrow$ C3S</td>
<td>-495</td>
<td>C3S</td>
</tr>
<tr>
<td>3CaO + $\alpha$-Al$_2$O$_3$ $\rightarrow$ C3A</td>
<td>-27</td>
<td>C3A</td>
</tr>
<tr>
<td>6CaO + 2 $\alpha$-Al$_2$O$_3$ + $\alpha$-Fe$_2$O$_3$ $\rightarrow$ C6A2F</td>
<td>-157</td>
<td>C6A2F</td>
</tr>
<tr>
<td>4CaO + $\alpha$-Al$_2$O$_3$ + $\alpha$-Fe$_2$O$_3$ $\rightarrow$ C4AF</td>
<td>-105</td>
<td>C4AF</td>
</tr>
</tbody>
</table>

- The enthalpy of formation of 1kg of a Portland cement clinker is around $+1757$ kJ/kg.

Phase Change in Cement Plant

Pre-heaters
- 30% sulphur reacts with oxygen
- Partial CaCO₃ calcination
- Partial clay minerals decomposition

Pre-calciner
- CaCO₃ calcination (>90%) and clay mineral decomposition completed.
- Partial conversion of CaO to C₂S.

Kiln
- C₂S to C₃S conversion. C₃A and C₄AF formed.
- Aluminate and Ferrite melting.

Fig. 3.1 Schematic diagram showing the variations in typical contents of phases during the formation of Portland cement clinker, loosely based on a figure by Wolter (W9).

Mass and Energy Balances

**Mass Balance**

- 1.67 kg/s of raw meal is required to produce 1 kg/s of clinker.

<table>
<thead>
<tr>
<th>Mass in</th>
<th>kg/s</th>
<th>Mass out</th>
<th>kg/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw meal</td>
<td>52.41</td>
<td>Clinker</td>
<td>31.45</td>
</tr>
<tr>
<td>Air</td>
<td>99.71</td>
<td>Flue gas</td>
<td></td>
</tr>
<tr>
<td>Fuel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet coal to</td>
<td>2.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pre-calciner</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet pet-coke</td>
<td>1.18</td>
<td>Excess Air</td>
<td>44.00</td>
</tr>
<tr>
<td>to kiln</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total in</td>
<td>155.55</td>
<td>Total out</td>
<td>155.55</td>
</tr>
</tbody>
</table>

**Energy Balance**

- The required thermal energy for unit clinker production is 3.18 MJ/kg clinker.

<table>
<thead>
<tr>
<th>Enthalpy in [GJ/h]</th>
<th>Sensible Heat</th>
<th>Heat by combustion</th>
<th>Sensible Heat</th>
<th>Heat of Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Meal</td>
<td>1.82</td>
<td></td>
<td>Clinker</td>
<td>5.09</td>
</tr>
<tr>
<td>Air</td>
<td>3.23</td>
<td></td>
<td>Flue gas</td>
<td></td>
</tr>
<tr>
<td>Fuel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet coal to pre-calciner</td>
<td>0.12</td>
<td>218.78</td>
<td>From fuel drying</td>
<td>4.63</td>
</tr>
<tr>
<td>Wet pet-coke to kiln</td>
<td>0.05</td>
<td>141.06</td>
<td>From raw Mill</td>
<td>74.13</td>
</tr>
<tr>
<td>Overall heat of reaction</td>
<td></td>
<td></td>
<td>Excess Air</td>
<td>46.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Heat lost by radiation and convection</td>
<td>53.29</td>
</tr>
<tr>
<td>Total in</td>
<td>365.06</td>
<td>Total out</td>
<td>365.06</td>
<td></td>
</tr>
</tbody>
</table>

181.62 (1.60 MJ/kg)
## Clinker Composition

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Bogue calculation [wt %]</th>
<th>Simulation [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alite (C(_3)S)</td>
<td>60.6</td>
<td>60.4</td>
</tr>
<tr>
<td>Belite (C(_2)S)</td>
<td>17.5</td>
<td>17.2</td>
</tr>
<tr>
<td>Tricalcium Aluminate (C(_3)A)</td>
<td>11.0</td>
<td>10.9</td>
</tr>
<tr>
<td>Tetracalcium Aluminate (C(_4)AF)</td>
<td>8.6</td>
<td>8.2</td>
</tr>
<tr>
<td>Free CaO</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>CaO·SO(_3)</td>
<td>2.3</td>
<td>2.5</td>
</tr>
<tr>
<td>Ash</td>
<td>0.0</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.0</strong></td>
<td><strong>100.0</strong></td>
</tr>
</tbody>
</table>

The simulated clinker compositions are in a good agreement with those estimated by Bogue equation.
• The flue gas temperature and CO₂ mole fraction varies over the process.
• The optimal flue gas stream for the capture process should be selected taking the operating condition of a selected capture unit, ease of heat integration, and CO₂ partial pressure into account.
The CO₂ concentration at the end-of-pipe stream is ~22 vol%.

The flue gas at the 3rd preheater exit has a higher CO₂ concentration (~35 vol%).

Flue gas needs to be heated up to 650°C. Relatively low CO₂ concentration.

Flue gas temperature is around 650°C → no preheating is required.
Process Integration in Retrofit Case

1) The flue gas from 3\textsuperscript{rd} Preheater is diverted to Ca-looping process for carbon capture.
2) CO\textsubscript{2} depleted flue gas from carbonator is routed to the 2\textsuperscript{nd} Preheater for the raw material preheating.
3) Part of excess air from the cooler is used for additional raw material heating.
4) Purge from the carbon capture calciner is sent to the kiln.
Ca-Looping Process

- Calciner needs to operate at 930°C for 100% calcination while carbonator operates at 650°C.
- CaO loses its capacity over the cycles → theoretical capture rate is determined by two flowrate ratios: $F_R/F_{CO2}$ and $F_0/F_{CO2}$.
- The operation conditions inside carbonator and calciner are also favourable to the $SO_2$ capture (effects of sulfidation on the maximum carbonation degree).
Carbonator Model

Two mathematical models for carbonator have been compared in the study;
- The simple model (all active fraction of CaO reacts with CO₂)
- The rigorous model¹:
  - CFB model operates in the fast fluidization regime
  - Particle distribution part has been applied from K-L model; lower dense region and upper lean region
  - The CO₂ concentration at the exit has been estimated from the gaseous material balance by considering the first order kinetic law of carbonation degree.

The effect of sulfidation was considering by adjusting the k and Xᵣ constants corresponding to sulfidation level of Piaseck limestone ² (valid up to 1% sulfidation)

\[ X_{\text{max},N} = \frac{1}{1/(1-X_r)+kN} + X_r \]

• To keep sulfidation rate maximum at 1%, the S content of fuel has been adjusted. (5.3% → 3.6%)
Carbonator Model

- All the mathematical models for the carbonator have been solved in Matlab, and the carbonator unit was incorporated into the Unisim process simulation (Unisim → Matlab → Unisim)

Unisim User Unit Operation for Carbonator Simulation

The interface of the model in Unisim
Simulation Basis

- Target: 90% CO₂ recovery in the carbonator and 95+% CO₂ purity.
- The total clinker production rate is kept constant.
- ASU: 95% O₂ purity.
- CO₂ product is compressed up to 150 bar.
Results

- The thermal requirement for the pre-calciner and kiln decrease → reduction in calcite fed to raw mill, and calcite is completely calcined in the calciner.
- The heat requirement for the calciner shows a minimum.
- The energy requirement for ASU and blower has decreasing trend → less gas flow into the carbonator.
• The gross power generation efficiency is estimated as 46 %.
• It is predicted that the power generated in steam cycle can exceed the power demand in the cement plant integrated with a Ca-looping process up to 2.9 $F_0/F_{CO_2}$. 
• The percentage of CO₂ avoided is between 92 – 99 %.
• Oxy-calciner only → no carbonator and all calcites are calcined in the calciner.
• The incremental energy consumption for 5.8 case is 5.3 GJ/ton CO₂ while that value can be estimated as 4.6 GJ/ton CO₂ for integrated MEA process.
• With heat recovery, the resulting energy consumption decreases to 2.3 GJ/ton CO₂ for 5.8 case.
Conclusions

- A way of capturing CO₂ from cement plants by integrating it with a Ca-looping process has been investigated.
- The clinker composition is in a good agreement with the Bogue equation.
- The gas stream leaving the 3rd preheater was selected to be a feed suitable for Ca-looping capture unit since
  - it does not have to be preheated
  - it has a higher CO₂ partial pressure and lower total volumetric flow rate
  - a simpler design of steam cycle for heat recovery is possible
- Low sulphur fuel is required to minimize CaO circulation.
Conclusions

- Given the 90% carbon capture in the carbonator, the CO₂ avoided in overall process ranges from 92% to 99% depending on the $F_0/F_{CO2}$ ratio.
- The fuel consumption of 2.3 to 3.0 GJ/ton CO₂ avoided which depends on the $F_0/F_{CO2}$ ratio with a heat recovery system is estimated.
- The estimation of heat recovery can be made more accurate by a follow-up study on a detailed steam cycle.