CO$_2$ removal from industrial off-gas streams by fluidized bed carbonation

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Project Objectives

- To investigate practical solutions for direct \( \text{CO}_2 \) removal from single large sources
- Typical sources outside the power industry: Iron & steel, cement, chemicals, petroleum refining, pulp and paper
- Build on knowledge gained from existing Accelerated Carbonation Technology research to develop a continuous process using conventional Fluidised Bed Reactors
- Build a suitable two-phase reacting CFD model of the FBR to establish feasibility of design(s)
CO2 and Climate Change

- Around 50% of greenhouse gases are due to CO₂, mainly from power plants with fossil fuel combustion.
- Steelmaking (BOF, DRI-EAF, blast furnace) responsible for 1-12 tCO₂e per ton steel.
- Aluminium production responsible for 0.8% of all manmade CO2 emissions!
- Carbon capture and storage technologies are now of great research interest in view of forthcoming carbon credits legislation.
CO2 emissions in the U.S. in 2006

By far the largest source is fossil fuel combustion

Source: U.S. Greenhouse Gas Emissions Inventory
Accelerated Carbonation Technology (ACT)

- Award-winning University of Greenwich research for treatment of man-made oxide by products to inert state, using flue gas CO2
- Batch ambient temperature process used for land remediation
- Pulverised feeds include: power station fly ash, steel slags, cement-based material

Advantages:
- Zero energy requirement (excluding transport)
- Useful output material
- Basic technology

Disadvantages
- Batch process only at present
- Slow!

How can we speed up this process?
FBR Continuous Process Concept

Carbonator

Calciner

$F_{CO_2} E_{carb}$

$CO_2$

$F_{CaO} X_{carb}$

$F_{CaO}$

$F_0$

C. Abanades et al., 2008

CaO

CaCO$_3$
CO₂ capture using carbonation reactions can be retrofitted to existing power plants. Advantages:

- The original plant does not need to be altered to add this technology
- Plant operation is not affected
- SOx emissions are also removed; no need for separate unit and associated costs
- Carbonation releases large amounts of energy as heat that can be used downstream, e.g. in a Calciner

In terms of CO₂ capture, claimed CO₂ emissions reduction from,

- 0.781 Kg CO₂/净kW h to 0.122 Kg CO₂/净kW h
- Capture cost ~ 16 Euros/tonne CO₂,
- Increasing electricity cost from €37.9/MWh to €48.3/MWh
- The technology requires development, but similar equipment already exists for other processes.
- Potential for faster development compared to other CO₂ capture technologies.

Mathematical Model

- This is a 2-phase reacting problem
- An Eulerian/Lagrangian approach is used with interchange of mass, momentum and energy between the solid sorbent and the CO\textsubscript{2}-rich gas
- The solid and gaseous phases communicate through sources using the scheme (PSICEL) originally devised by C.T. Crowe
- A large number of particle tracks with a given size distribution is released to get statistically meaningful results
- Assuming a lightly loaded FBR, particle/particle interactions may be neglected
Continuous Phase Transport equations

- General transport equation for variable $\Phi$:

$$\frac{\partial (\rho \Phi)}{\partial t} + \nabla \cdot (\rho u \Phi) - \nabla \cdot (\Gamma \nabla \Phi) = S_\Phi + S_{\Phi p}$$

- Governing mass conservation, velocity components, temperature, CO2 concentration and turbulence ($k, \varepsilon$) quantities.

- Particle feedback on gas is represented via the source term, $S_{\Phi p}$.

- The FV code PHYSICA developed at Greenwich is used for all simulations.
Treating each particle in a Lagrangian fashion, velocity $u_p$ is computed from Newton’s law:

$$m_p \frac{du_p}{dt} = C_d \rho_g (u_g - u_p) |u_g - u_p| \frac{S_p}{2} + m_p g$$

where $m_p$ and $S_p$ are the particle mass and cross section, $\rho_g$ and $u_g$ are the gas density and velocity, $g$ is the gravity vector, and the drag coefficient $C_d$ for spheres is given by Clift et al.:

$$C_d = \frac{24}{Re} \cdot (1 + 0.15 Re^{0.687}) + \frac{0.42}{42500} \cdot \frac{1}{1 + \frac{Re^{1.16}}{42500}}$$

Dispersed Phase - Momentum

- Treating each particle in a Lagrangian fashion, velocity $u_p$ is computed from Newton’s law:

\[
m_p \frac{du_p}{dt} = C_d \rho_g (u_g - u_p) |u_g - u_p| \frac{S_p}{2} + m_p g
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\[
C_d = \frac{24}{Re} \cdot \left(1 + 0.15 Re^{0.687}\right) + \frac{0.42}{42500} \frac{1}{1 + \frac{Re^{1.16}}{Re}}
\]

- Turbulence coupling from Gosman & Ioannides model (1983)
Particle temperature governed by the enthalpy equation:

\[
m_p c_p \frac{dT_p}{dt} = \alpha (T_g - T_p) + \varepsilon \sigma (T_w^4 - T_p^4) A_p
\]

where \(T_g\) and \(T_w\) are the gas and wall temperatures, \(\varepsilon\) is the particle emissivity, \(\sigma\) is the Stefan-Boltzmann constant, \(A_p\) is the particle surface area;

The heat transfer coefficient between gas and particles \(\alpha\) is given by:

\[
\alpha = \pi k_g d_p \text{Nu}
\]

in which \(k_g\) is the gas thermal conductivity, \(d_p\) the particle diameter and \(\text{Nu}\) is provided by:

\[
\text{Nu} = 2(1 + 0.3\text{Re}^{0.5} \text{Pr}^{0.33})
\]
The rate of particle conversion for CaO particles is given by (Gemma et al. 2009):

$$\frac{dX}{dt} = \frac{k_s S_0 C(1-X)\sqrt{1 - \Psi ln (1 - X)}}{(1 - \varepsilon)\left[1 + \frac{\beta Z}{\Psi} \sqrt{1 - \Psi ln(1 - X)} - 1\right]}$$

where,

$$k_s = k_{s0} \exp\left(-\frac{E_{ak}}{RT}\right)$$

$$\beta = \frac{2k_s a \rho (1 - \varepsilon)}{M_{CaO} b D_p S_0}$$

$$D_p = \frac{b M_{CaO} D C}{a \rho}$$

$$D = D_0 \exp\left(-\frac{E_{AD}}{RT}\right)$$

We assume that as particles replace CaO with CaCO$_3$ in their pores, their density increases as a function of $X$, with the molecular weight changing from 56 to 100 on full conversion.
Interaction between the phases

- Momentum source:
  \[ S_{mom} = m_p (\Delta u + g_i \Delta t) \]

- Mass source:
  \[ S_{CO2} = \frac{\Delta X m_p^0 M_{W_{CO2}}}{\Delta t M_{W_{CAO}}} \]

- Heat source:
  \[ S_{heat} = \frac{\Delta X \Delta H_r}{\Delta t M_{CaO}} \]
Several (2D) designs of reactor were considered:

- straight tube reactor
- stepped section reactor
- straight + expanding section

<table>
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<tr>
<th>Description</th>
<th>Value</th>
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<tr>
<td>Particle density (kg/m³)</td>
<td>3340</td>
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<tr>
<td>Particle diameter (m)</td>
<td>100#150#200</td>
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<tr>
<td>Particles initial velocity (m/s)</td>
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<td>Gas inlet velocity (m/s)</td>
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<td>Gas initial temperature (°C)</td>
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<td>Bed width (m)</td>
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<tr>
<td>Bed height (m)</td>
<td>8.0</td>
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<tr>
<td>Particles sphericity</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Stepped FBR: Cumulative solid volume fraction

CaO Particle sizes
100μm
150μm
200μm
Particle residence time, momentum exchange and gas velocity along the reactor centreline.
a) Velocity and typical particle track
b) Normalised sorbent volume fraction
c) CO2 mass fraction
Conversion performance vs time

- Experimental data by G. Grasa et al. 2009
- Simulation result
- Carbonation model by G. Grasa et al. 2009
Gradually expanding reactor CaO volume fraction by size
Comparative performance for maximum capture

- 72% CO2 captured in the stepped reactor
- 68% CO2 captured in the gradually expanding reactor
- 64% of CO2 captured in the straight reactor
Conclusions

- A 2-phase Eulerian-Lagrangian model of a fluidised bed carbonator has been developed using the CFD code PHYSICA.
- The gas-solid contact has been studied with regard to the hydrodynamics of particle fluidization and mass transfer due to the carbonation reaction.
- The model predicts: hydrodynamic parameters of the reactor, gas concentration, reaction rate and CO2 capture.
- The results indicate that different solid zones exist inside the reactor corresponding to different particle sizes.
- The simulation can predict the correct reactor dimensions based on the ultimate conversion required.
Future Prospects

- Feasibility of CO2 capture in a flue gas stream by adsorption in a FBR has been shown theoretically to work, although many model developments still needed.
- Practical application is possible once consideration is given to separation/collection of reacted CaCO3 particles in a continuous process.
- Combination with a calciner for regeneration of CaO logistically and economically attractive.
- Other available materials may be used depending on industry (e.g. Steel slags, fly ash).
- Man-made materials would enhance process (viz. Recent hyperbranched aluminosilica research at Georgia Tec.)

