IECM Technical Documentation:

Calcium Looping Cycle for Post-Combustion CO2 Capture

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Acknowledgements

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Calcium Looping CO₂ Capture

Objective of this Report
This document provides details of performance and cost models of the calcium looping cycle (CaL) for post-combustion CO₂ capture.

Calcium looping Performance Models

Figure 1 shows the conceptual process flow diagram of the calcium looping process:

Figure 1. Conceptual flow diagram of a calcium looping CO2 capture process.
Table 1 lists the main variables used in the mass balance model:

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<th>Symbol</th>
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<td>$\eta_{CO2}$</td>
<td>CO2 capture efficiency</td>
</tr>
<tr>
<td>$X_{carb}$</td>
<td>Fraction of CaO converted to CaCO3 in the carbonator (Similar to “rich-loading”)</td>
</tr>
<tr>
<td>$X_{ave}$</td>
<td>Maximum possible conversion of CaO to CaCO3 in the carbonator</td>
</tr>
<tr>
<td>$X_{calc}$</td>
<td>Fraction of CaCO3 in the calciner outlet stream (not calcined, similar to “lean-loading”)</td>
</tr>
<tr>
<td>$f_{carb}$</td>
<td>Degree of carbonation (0-1) – Delta-loading in carbonator/maximum delta-loading ($X_{carb} - X_{calc}$)/($X_{ave} - X_{calc}$)</td>
</tr>
<tr>
<td>$f_{calc}$</td>
<td>Degree of calcination (0-1) – Delta-loading in calciner/maximum delta-loading ($X_{carb} - X_{calc}$)/$X_{carb}$</td>
</tr>
<tr>
<td>$f_m$</td>
<td>Ratio of make-up CaCO3 flow/Recirculating sorbent flow</td>
</tr>
<tr>
<td>$a_{sorbent}$</td>
<td>Purity of limestone (fraction)</td>
</tr>
</tbody>
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**Mass Balance Model**

The goal of mass balance model is to calculate the amount of sorbent circulating between the reactors.

Fix $\eta_{CO2}$, $f_{carb}$, $f_{calc}$ and $f_m$ and $a_{sorbent}$.

Calculate $X_{ave}$.

$X_{ave} = f_{calc} \left( \frac{f_m + 1}{f_m + f_{calc}} \right) \left[ \frac{0.100813 f_m}{f_m + 0.0178 f_{carb} f_{calc}} + \frac{0.48654 f_m}{f_m + 0.2095 f_{carb} f_{calc}} + 0.07709 \right]$ (1)

Calculate $X_{carb}$ and $X_{calc}$.

$X_{carb} = \frac{f_{carb}}{1 - (1 - f_{carb})(1 - f_{calc})} X_{ave}$ (2)

$X_{calc} = (1 - f_{calc}) X_{carb}$ (3)

**Carbonator mass balance**

Inlet – subscript “1”. Outlet – subscript “2”.

All calculations are for molar flows.

Carbonator inlet flows (solids):

Inlet stream contains CaO, uncalcined CaCO3, impurities in limestone (considered inert here), CaSO4 and ash. Molecular weight of sorbent impurities is assumed to be the same as that of CaCO3.
SO₂ in the flue gas reacts with CaO more readily than CO₂. So, the CaO available for carbonation is lesser. Also, CaSO₄ is stable and will not disintegrate into CaO and SO₂. So CaSO₄ is treated as inert.

\[
\text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CaSO}_4
\]

One mole of SO₂ reacts with one mole of CaO

\[
F_{\text{CaO, avail}} = F_{\text{CaO,1}} - F_{\text{SO2, fluegas}} \quad (4)
\]

The rest of CaO is available for carbonation. Maximum conversion is limited (Xₐᵥₑ), depending on activity of recycled sorbent and the amount of fresh sorbent input. Actual conversion (Xₐₙₑ < Xₐᵥₑ) depends on degree of carbonation and calcination.

\[
\text{CaO} + \text{CO}_2 \rightleftharpoons \text{CaCO}_3
\]

One mole of CaO reacts with one mole of CO₂ to form one mole of CaCO₃. Therefore the amount of CaCO₃ formed in the carbonator is equal to the amount of CO₂ captured.

\[
F_{\text{CaCO}_3, \text{formed}} = \eta_{\text{CO2}} F_{\text{CO2, fluegas}} = X_{\text{carb}} F_{\text{CaO, avail}} = X_{\text{carb}} (F_{\text{CaO,1}} - F_{\text{SO2, fluegas}}) \quad (5)
\]

From this equation, inlet CaO can be expressed in terms of input variables:

\[
F_{\text{CaO,1}} = \frac{\eta_{\text{CO2}} F_{\text{CO2, fluegas}}}{X_{\text{carb}}} + F_{\text{SO2, fluegas}} \quad (6)
\]

Since Xcalc is the fraction of CaCO₃ in the inlet sorbent flow (CaO and CaCO₃), inlet CaCO₃ flow also can be expressed as:

\[
F_{\text{CaCO}_3,1} = \frac{X_{\text{calc}}}{1 - X_{\text{calc}}} F_{\text{CaO,1}} \quad (7)
\]

Equations for CaSO₄ and ash in the carbonator inlet will be found later.

Make-up sorbent flow can now be calculated as:

\[
F_{\text{CaCO}_3, \text{makeup}} = f_m (F_{\text{CaO,1}} + F_{\text{CaCO}_3,1}) = \frac{f_m}{1 - X_{\text{calc}}} F_{\text{CaO,1}} \quad (8)
\]

\[
F_{\text{inert, makeup}} = \frac{1 - a_{\text{sorbent}}}{a_{\text{sorbent}}} F_{\text{CaCO}_3, \text{makeup}} \quad (9)
\]

\[
F_{\text{sorbent, makeup}} = \frac{1}{a_{\text{sorbent}}} F_{\text{CaCO}_3, \text{makeup}} \quad (10)
\]

Carbonator outlet flows (solids) or Calciner inlet flows

\[
F_{\text{CaCO}_3,2} = F_{\text{CaCO}_3,1} + F_{\text{CaCO}_3, \text{formed}}
\]
\[ F_{\text{CaCO}_3,2} = F_{\text{CaCO}_3,1} + \eta_{\text{CO}_2} F_{\text{CO}_2,\text{fluegas}} \] (11)

Or

\[ F_{\text{CaCO}_3,2} = F_{\text{CaCO}_3,1} + X_{\text{carb}} (F_{\text{CaO},1} - F_{\text{SO}_2,\text{fluegas}}) \]

(12)

One mole of \( \text{SO}_2 \) in fluegas forms one mole of \( \text{CaSO}_4 \).

\[ F_{\text{CaSO}_4,2} = F_{\text{CaSO}_4,1} + F_{\text{SO}_2,\text{fluegas}} \]

(13)

The other inert is ash from the calciner and the impurities in the sorbent.

\[ F_{\text{ash},2} = F_{\text{ash},1} \]

(14)

\[ F_{\text{inert},2} = F_{\text{inert},1} \]

(15)

One mole of \( \text{CaO} \) in the inlet forms one mole of \( \text{CaCO}_3 \). One mole of \( \text{SO}_2 \) in the fluegas consumes one mole of \( \text{CaO} \).

\[ F_{\text{CaO},2} = (1 - X_{\text{calc}})(F_{\text{CaO},1} - F_{\text{SO}_2,\text{fluegas}}) \]

(16)

Or

\[ F_{\text{CaO},2} = \frac{1 - X_{\text{carb}}}{X_{\text{carb}}} \eta_{\text{CO}_2} F_{\text{CO}_2,\text{fluegas}} \]

(17)

Calciner outlet flows (solids)
Inlet – subscript “2”. Outlet – subscript “3”.

\( \text{CaO} \) is formed in the calciner by calcination of \( \text{CaCO}_3 \) (from carbonator as well as make-up \( \text{CaCO}_3 \)). \( \text{SO}_2 \) from oxy-combustion of coal also consumes \( \text{CaO} \).

\[ F_{\text{CaO},3} = F_{\text{CaO},2} + F_{\text{CaCO}_3,\text{calcined}} - F_{\text{SO}_2,\text{oxy}} \]

\[ F_{\text{CaO},3} = F_{\text{CaO},2} + (F_{\text{CaCO}_3,2} + F_{\text{CaCO}_3,m} - F_{\text{CaCO}_3,3}) - F_{\text{SO}_2,\text{oxy}} \]

Adjusting the above equation:

\[ F_{\text{CaO},3} + F_{\text{CaCO}_3,3} = F_{\text{CaO},2} + F_{\text{CaCO}_3,2} + F_{\text{CaCO}_3,m} - F_{\text{SO}_2,\text{oxy}} \]

By definition, \( X_{\text{calc}} = F_{\text{CaCO}_3,3}/(F_{\text{CaO},3} + F_{\text{CaCO}_3,3}) = F_{\text{CaCO}_3,1}/(F_{\text{CaO},1} + F_{\text{CaCO}_3,1}) \)

\[ F_{\text{CaO},3} \] can be derived as:

\[ F_{\text{CaO},3} = F_{\text{CaO},1} + (1 - X_{\text{calc}})(F_{\text{CaCO}_3,m} - F_{\text{SO}_2,\text{fluegas}} - F_{\text{SO}_2,\text{oxy}}) \]

(18)

From this and definition of \( X_{\text{calc}} \),

\[ F_{\text{CaCO}_3,3} = \frac{X_{\text{calc}}}{1 - X_{\text{calc}}} F_{\text{CaO},3} \]

(19)

Or
\[ F_{\text{CaCO}_3,3} = \frac{x_{\text{calc}}}{1-x_{\text{calc}}} F_{\text{CaO,1}} + x_{\text{calc}} (F_{\text{CaCO}_3,m} - F_{\text{SO}_2,\text{fluegas}} - F_{\text{SO}_2,oxy}) \]  \hspace{1cm} (20)

The first term on the right hand side is equal to \( F_{\text{CaCO}_3,1} \).

(If complete calcination happens, \( x_{\text{calc}} = 0 \), hence no \( \text{CaCO}_3 \) in the calciner outlet).

Other components flows (\( \text{CaSO}_4 \) and ash) can be calculated as:

\[ F_{\text{CaSO}_4,3} = F_{\text{CaSO}_4,2} + F_{\text{SO}_2,oxy} \]

\[ F_{\text{CaSO}_4,3} = F_{\text{CaSO}_4,1} + F_{\text{SO}_2,\text{fluegas}} + F_{\text{SO}_2,oxy} \] \hspace{1cm} (21)

\[ F_{\text{ash,3}} = F_{\text{ash,2}} + F_{\text{ash,oxy}} \]

\[ F_{\text{inert,3}} = F_{\text{inert,2}} + F_{\text{inert,makeup}} \]

Hence,

\[ F_{\text{ash,3}} = F_{\text{ash,1}} + F_{\text{ash,oxy}} \] \hspace{1cm} (22)

\[ F_{\text{inert,3}} = F_{\text{inert,1}} + F_{\text{inert,makeup}} \] \hspace{1cm} (23)

All components are accounted for.

Purge flows
Since purge stream is taken from calciner outlet stream, flow rate of purge will be the difference between flow rates of calciner outlet (3) and carbonator inlet (1) flows.

\[ F_p = F_3 - F_1 \]

Hence,

\[ F_{\text{CaO,p}} = F_{\text{CaO,3}} - F_{\text{CaO,1}} \]

\[ F_{\text{CaO,p}} = (1 - x_{\text{calc}})(F_{\text{CaCO}_3,m} - F_{\text{SO}_2,\text{fluegas}} - F_{\text{SO}_2,oxy}) \] \hspace{1cm} (24)

\[ F_{\text{CaCO}_3,p} = F_{\text{CaCO}_3,3} - F_{\text{CaCO}_3,1} \]

\[ F_{\text{CaCO}_3,p} = x_{\text{calc}} (F_{\text{CaCO}_3,m} - F_{\text{SO}_2,\text{fluegas}} - F_{\text{SO}_2,oxy}) \] \hspace{1cm} (25)

\[ F_{\text{CaSO}_4,p} = F_{\text{CaSO}_4,3} - F_{\text{CaSO}_4,1} \]

\[ F_{\text{CaSO}_4,p} = F_{\text{SO}_2,\text{fluegas}} + F_{\text{SO}_2,oxy} \] \hspace{1cm} (26)

\[ F_{\text{ash,p}} = F_{\text{ash,3}} - F_{\text{ash,1}} \]

\[ F_{\text{ash,p}} = F_{\text{ash,oxy}} \] \hspace{1cm} (27)

\[ F_{\text{inert,p}} = F_{\text{inert,makeup}} \] \hspace{1cm} (28)

(The purge equations for \( \text{CaSO}_4 \) and ash prove the mass balance of the entire system – sulfur coming in through fluegas and oxycombustion goes out through purge, ash coming through oxycombustion goes out through purge).

Since purge is taken from calciner outlet stream (3), the fractions of different solids in the total flow will be the same for streams 1, 3 and p.

\[ F_{\text{CaSO}_4,1}/F_{\text{CaCO}_3,1} = F_{\text{CaSO}_4,p}/F_{\text{CaCO}_3,p} \]

So,

\[ F_{\text{CaSO}_4,1} = F_{\text{CaSO}_4,p}(F_{\text{CaCO}_3,1}/F_{\text{CaCO}_3,p}) \]
This can be derived as:

\[ F_{CaSO4,1} = \frac{F_{CaO,1}}{1 - X_{calc}} \left( F_{SO2,fluegas} + F_{SO2,oxy} \right) \]  
(29)

Similarly,

\[ F_{ash,1} = \frac{F_{CaO,1}}{1 - X_{calc}} \left( F_{ash,oxy} \right) \]  
(30)

\[ F_{inert,1} = \frac{F_{CaO,1}}{1 - X_{calc}} \left( F_{inert,makeup} \right) \]  
(31)

Total flow of solids at carbonator inlet is calculated as follows:

\[ F_{total,1} = F_{CaO,1} + F_{CaCO3,1} + F_{CaSO4,1} + F_{ash,1} + F_{inert,1} \]

\[ F_{total,1} = \frac{F_{CaO,1}}{1 - X_{calc}} \left( 1 + \frac{F_{SO2,fluegas} + F_{SO2,oxy} + F_{ash,oxy} + F_{inert,makeup}}{F_{CaCO3,makeup} - F_{SO2,fluegas} - F_{SO2,oxy}} \right) \]  
(32)

In order to solve this system of equations, two variables have to be known – \( F_{SO2, oxy} \) and \( F_{ash, oxy} \). They depend on the amount of coal burnt in oxy-combustion calciner. The amount of coal depends on the heat requirement of calciner. So a heat balance of the calciner is needed to solve for those. Those calculations will follow.

**Heat Balance Calculations**

All variables are known except \( F_{SO2, oxy} \). The calculations which depend on \( F_{SO, oxy} \) are:

- \( F_{CaSO4,1} \)
- \( F_{CaSO4,2} \)
- \( F_{ash,1} \)
- \( F_{ash,2} \)
- \( F_{CaO,3} \)
- \( F_{CaCO3,3} \)
- Purge flows

Calcination reaction happens at higher temperature (900-950°C) than carbonation (600-650°C). Heat input to the calciner should be sufficient to heat the incoming streams to the calcination temperature and supply the calcination reaction heat (168,500 kJ/kmol). The incoming streams include – solid stream from carbonator, solid stream of make-up \( \text{CaCO}_3 \) and recycled flue gases.

Assuming the heat of reaction is supplied by oxy-combustion of coal, the following expressions can be written:

\[ H_{calc} = \frac{m_{coal} \cdot HHV_{coal}}{\eta_{comb}} \text{ (kJ/s)} \]

Where, \( H_{calc} \) is the heat required in calciner, \( m_{coal} \) is the mass flow rate of coal (kg/s as-burnt, wet basis) and \( HHV_{coal} \) is the higher heating value of coal and \( \eta_{comb} \) is the efficiency of oxy-combustion.
m\text{coal} \text{ can be expressed in terms of molar contents of its constituents:}
\[m_{\text{coal}} = F_i \left( \frac{\text{MW}_i}{w_i} \right) .\]

Where, \(F_i\) is the inlet molar flow of a component (C, S, H\text{2}, ash etc), \(\text{MW}_i\) is the molecular weight and \(w_i\) is the weight fraction of the component in coal, obtained from the ultimate analysis data of coal (wet basis).

Hence, inlet molar flow rates of components can be expressed in terms of \(H_{\text{calc}}\) and HHV. For example:
\[
F_{C,\text{in}} = \left( \frac{H_{\text{calc}}}{\text{HHV}_{\text{coal}}} \right) \left( \frac{w_C}{12} \right) \quad (33)
\]
\[
F_{S,\text{in}} = \left( \frac{H_{\text{calc}}}{\text{HHV}_{\text{coal}}} \right) \left( \frac{w_S}{32} \right) \quad (34)
\]
\[
F_{\text{H\text{2},in}} = \left( \frac{H_{\text{calc}}}{\text{HHV}_{\text{coal}}} \right) \left( \frac{w_{\text{H\text{2}}}}{2} \right) \quad (35)
\]
\[
m_{\text{ash, in}} = \left( \frac{H_{\text{calc}}}{\text{HHV}_{\text{coal}}} \right) \left( \frac{w_{\text{ash}}}{\text{MW}_{\text{ash}}} \right) \quad (36)
\]

The following reactions take place in the oxy-combustion calciner:
\[
\begin{align*}
\text{CaCO}_3 & \leftrightarrow \text{CaO} + \text{CO}_2 \\
\text{C} + \text{O}_2 & \rightarrow \text{CO}_2 \\
\text{S} + \text{O}_2 & \rightarrow \text{SO}_2 \\
\text{H}_2 + \frac{1}{2} \text{O}_2 & \rightarrow \text{H}_2\text{O} \\
\text{CaO} + \text{SO}_2 + \frac{3}{2} \text{O}_2 & \rightarrow \text{CaSO}_4
\end{align*}
\]

Combining the above reaction with SO\text{2} formation reaction, we get:
\[
\text{CaO} + \text{S} + 3/2 \text{ O}_2 \rightarrow \text{CaSO}_4
\]

The amount of O2 input to the calciner can be written as:
\[
F_{\text{O\text{2},in}} = (1+x_a) (F_{C,\text{in}} + F_{S,\text{in}} + \frac{1}{2} F_{\text{H2, in}})
\]
Where \(x_a\) is the excess air ratio for oxy-combustion.

\[F_{\text{N\text{2,in}}} = (0.05/0.95)F_{\text{O\text{2,in}}} \]

The gaseous products’ flow rates from the calciner are:
\[
\begin{align*}
F_{\text{CO2,p}} &= F_{\text{CaCO3, calcined}} + F_{C,\text{in}} \\
F_{\text{H2O,p}} &= F_{\text{H2, in}} \\
F_{\text{SO2,p}} &= 0 \\
F_{\text{O2,p}} &= F_{\text{O2, in}} - (F_{C,\text{in}} + 3/2 F_{S,\text{in}} + \frac{1}{2} F_{H2,\text{ in}}) \\
F_{\text{O2,p}} &= x_a(F_{C,\text{in}} + \frac{1}{2} F_{H2,\text{ in}}) + (x_a - \frac{1}{2}) F_{S,\text{in}}
\end{align*}
\]

Assuming no NO\text{x} is formed,
\[F_{\text{N2,p}} = F_{\text{N2,in}} \]

These are the gaseous products of calciner reactions. A fraction of these gases will be recycled to the calciner to maintain the temperature from oxy-combustion. A part of heat input to the calciner goes into heating of the recycle stream ‘\(r\)’. If \(x_r\) is the fraction of recycled gases, the flow rates of gases in the recycled stream can be derived as:
\[ F_{\text{CO}_2,r} = \frac{x_r}{1-x_r} \left( F_{\text{CaCO}_3,\text{calcined}} + \frac{w_C}{12} \frac{H_{\text{calc}}}{\text{HHV}_\text{coal}} \right) \]  

\[ F_{\text{H}_2\text{O},r} = \frac{x_r}{1-x_r} \left( \frac{w_{\text{H}_2}}{2} \frac{H_{\text{calc}}}{\text{HHV}_\text{coal}} \right) \]  

\[ F_{\text{O}_2,r} = \frac{x_r}{1-x_r} \left( \frac{H_{\text{calc}}}{\text{HHV}_\text{coal}} \right) \left( X_\alpha \left( \frac{w_C}{12} + \frac{w_{\text{H}_2}}{4} \right) + \left( X_\alpha - \frac{1}{2} \right) \frac{w_S}{32} \right) \]  

\[ F_{\text{N}_2,r} = \frac{x_r}{1-x_r} \left( \frac{H_{\text{calc}}}{\text{HHV}_\text{coal}} \right) \left( 1 + X_\alpha \left( \frac{w_C}{12} + \frac{w_{\text{H}_2}}{4} + \frac{w_S}{32} \right) \right) \]  

If values for \( x_r \) and \( x_\alpha \) are assumed, then all the recycled gas flows are expressed in terms of \( H_{\text{calc}} \) and known parameters.

The calciner heat requirement (neglecting the flow of ash) can be written as:

\[ H_{\text{calc}} = F_{\text{CaCO}_3,\text{calcined}} \Delta H_{\text{carb}} + (F_{\text{CaO}_2} C_{p,\text{CaO}} + (F_{\text{CaCO}_3} + F_{\text{inert},2}) C_{p,\text{CaCO}_3} + F_{\text{CaSO}_4,2} C_{p,\text{CaSO}_4}) \Delta T_{\text{calc}} + \frac{F_{\text{CaCO}_3,m}}{a_{\text{sorbent}}} C_{p,\text{CaCO}_3} \Delta T_{\text{makeup}} + \sum F_{i,r} C_{p,i} \Delta T_r \]

Where, \( \Delta T_{\text{calc}} = T_{\text{calc}} - T_{\text{carb}}; \Delta T_{\text{makeup}} = T_{\text{calc}} - T_{\text{CaCO}_3,\text{makeup}}; \Delta T_r = T_{\text{calc}} - T_r. \)

\[ F_{\text{CaCO}_3,\text{calcined}} = F_{\text{CaCO}_3} + F_{\text{CaCO}_3,m} - F_{\text{CaCO}_3,3} \]

Only \( F_{\text{CaCO}_3,3} \) depends on \( F_{\text{SO}_2,\text{oxy}} \) (Eqn17). Hence, in the \( H_{\text{calc}} \) equation, \( F_{\text{CaCO}_3,\text{calcined}}, F_{\text{CaSO}_4,2} \) and \( F_{\text{CO}_2,r} \) depend on \( F_{\text{SO}_2,\text{oxy}} \).

The minimum calcination heat requirement is when there are no recycled gases or combustion products in the calciner. This heat is required to heat the recirculating solids from carbonator to calciner temperature, make-up sorbent to calciner temperature and supply the heat for calcination reaction.

The minimum heat requirement in the calciner can be obtained by making \( F_{\text{SO}_2,\text{oxy}} \) and \( x_r \) zero in the \( H_{\text{calc}} \) equation.

The expressions for \( F_{\text{CaCO}_3,\text{calcined}}, F_{\text{CaSO}_4,2} \) and \( F_{\text{CO}_2,r} \) (the terms containing \( F_{\text{SO}_2,\text{oxy}} \)) can be rewritten as:

\[ F_{\text{CaCO}_3,\text{calcined}} = (\eta_{\text{CO}_2} F_{\text{CO}_2,\text{fluegas}} + (1-X_{\text{calc}}) F_{\text{CaCO}_3,m} + X_{\text{calc}} F_{\text{SO}_2,\text{fluegas}}) + X_{\text{calc}} F_{\text{SO}_2,\text{oxy}} \]  

\[ F_{\text{CaCO}_3,\text{calcined,min}} = (\eta_{\text{CO}_2} F_{\text{CO}_2,\text{fluegas}} + (1-X_{\text{calc}}) F_{\text{CaCO}_3,m} + X_{\text{calc}} F_{\text{SO}_2,\text{fluegas}}) \]  

\[ F_{\text{CaSO}_4,2} = F_{\text{SO}_2,\text{fluegas}} + \frac{F_{\text{CaO},1}}{1-X_{\text{calc}}} \left( F_{\text{SO}_2,\text{fluegas}} \right) \left( \frac{F_{\text{CaCO}_3,m} - F_{\text{SO}_2,\text{fluegas}}}{F_{\text{CaCO}_3,m} - F_{\text{SO}_2,\text{oxy}}} \right) \]  

For simplifying the calculations, we can assume that

\[ (F_{\text{CaCO}_3,m} - F_{\text{SO}_2,\text{fluegas}})(F_{\text{CaCO}_3,m} - F_{\text{SO}_2,\text{fluegas}} - F_{\text{SO}_2,\text{oxy}}) = (F_{\text{CaCO}_3,m} - F_{\text{SO}_2,\text{fluegas}})^2 \]

Also, \( F_{\text{CaCO}_3,m} = f_m F_{\text{CaO},1}/(1-X_{\text{calc}}) \) (Eqn 8).
Hence $F_{\text{CaSO}_4,2}$ can be written as:

$$F_{\text{CaSO}_4,2} = F_{\text{SO}_2,\text{fluegas}} + \frac{F_{\text{CaO},1}}{1 - X_{\text{calc}}} \left( \frac{F_{\text{SO}_2,\text{fluegas}}}{F_{\text{CaCO}_3,m} - F_{\text{SO}_2,\text{fluegas}}} \right) + \frac{F_{\text{CaCO}_3,m}^2}{f_m(F_{\text{CaCO}_3,m} - F_{\text{SO}_2,\text{fluegas}})} F_{\text{SO}_2,\text{oxy}} \quad (43)$$

Similarly, $F_{\text{inert},2,\text{min}}$ is when there is no $F_{\text{SO}_2,\text{oxy}}$.

$$F_{\text{inert},2,\text{min}} = F_{\text{inert},1,\text{min}} = \frac{F_{\text{CaO},1}}{1 - X_{\text{calc}}} F_{\text{CaCO}_3,\text{makeup}} - F_{\text{SO}_2,\text{fluegas}} \quad (43a)$$

Substituting $F_{\text{SO}_2,\text{oxy}} = 0$ and $x_r = 0$ in these expressions, $H_{\text{calc},\text{min}}$ can be calculated as:

$$H_{\text{calc},\text{min}} = \left( \eta_{\text{CO}_2} F_{\text{CO}_2,\text{fluegas}} \right) + (1 - X_{\text{calc}}) F_{\text{CaCO}_3,m} + X_{\text{calc}} F_{\text{SO}_2,\text{fluegas}} ) \Delta H_{\text{carb}} + \left( F_{\text{CaO},2} C_{p,\text{CaO}} + (F_{\text{CaCO}_3,2} + F_{\text{inert},2,\text{min}}) C_{p,\text{CaCO}_3} + \left( \frac{F_{\text{CaO},1}}{1 - X_{\text{calc}}} F_{\text{CaCO}_3,m} - F_{\text{SO}_2,\text{fluegas}} \right) C_{p,\text{CaSO}_4} \right) \Delta T_{\text{calc}} + \frac{F_{\text{CaCO}_3,m}}{\alpha_{\text{sorbernt}} C_{p,\text{CaCO}_3}} \Delta T_{m} \quad (44)$$

From this, $H_{\text{calc}}$ can be expressed as:

$$H_{\text{calc}} = H_{\text{calc},\text{min}} + \frac{x_r}{1 - x_r} F_{\text{CaCO}_3,\text{calcined},\text{min}} C_{p,\text{CO}_2} \Delta T_{r} + F_{\text{SO}_2,\text{oxy}} \left( X_{\text{calc}} \Delta H_{\text{carb}} + X_{\text{calc}} \frac{x_r}{1 - x_r} C_{p,\text{CO}_2} \Delta T_{r} \right) + \frac{F_{\text{CaCO}_3,m}^2}{f_m(F_{\text{CaCO}_3,m} - F_{\text{SO}_2,\text{fluegas}})} C_{p,\text{CaSO}_4} \Delta T_{\text{calc}} + \frac{x_r}{1 - x_r} \left( \frac{H_{\text{calc}}}{\text{HHV}_{\text{coal}}} \right) \sum F_{i,r} C_{p,i} \Delta T_{r}$$

$F_{\text{SO}_2,\text{oxy}}$ is the same as $F_{\text{S,in}}$ and can be written in terms of $H_{\text{calc}}$ and HHV. Defining $A_{\text{oxy}}$ as the coefficient of $F_{\text{SO}_2,\text{oxy}}$ term and $A_{r}$ as the summation term in the previous equation,

$$A_{\text{oxy}} = X_{\text{calc}} \Delta H_{\text{carb}} + X_{\text{calc}} \frac{x_r}{1 - x_r} C_{p,\text{CO}_2} \Delta T_{r} + \frac{F_{\text{CaCO}_3,m}^2}{f_m(F_{\text{CaCO}_3,m} - F_{\text{SO}_2,\text{fluegas}})} C_{p,\text{CaSO}_4} \Delta T_{\text{calc}} \quad (45)$$

$$A_r = \frac{w_C}{12} C_{p,\text{CO}_2} + \frac{w_{H_2}}{2} C_{p,\text{H}_2} + \left( x_a \left( \frac{w_C}{12} + \frac{w_{H_2}}{4} \right) + \left( x_a - \frac{1}{2} \right) \frac{w_S}{32} \right) C_{p,02} + \frac{0.05}{0.95} (1 + x_a) \left( \frac{w_C}{12} + \frac{w_{H_2}}{4} + \frac{w_S}{32} \right) C_{p,N_2} \quad (46)$$

$$H_{\text{calc}} = \frac{H_{\text{calc},\text{min}} + \frac{x_r}{1 - x_r} F_{\text{CaCO}_3,\text{calcined},\text{min}} C_{p,\text{CO}_2} \Delta T_{r}}{1 - \frac{w_C}{12} A_{\text{oxy}} + \frac{x_r}{1 - x_r} A_r \Delta T_{r}} \quad (47)$$

All the parameters in the above equation are known and hence $H_{\text{calc}}$ can be calculated.

**Mass balance of gases**

**Carbonator outlet**

$F_{\text{CO}_2,2} = (1 - \eta_{\text{CO}_2}) F_{\text{CO}_2,\text{fluegas}}$
\[ \text{FO}_{2.2} = \text{FO}_{2,\text{fluegas}} - \text{FSO}_{2,\text{fluegas}} \]

All other gases’ flow rates do not change.

Calciner outlet

\[ F_{\text{CO}_2,\text{calc,\text{out}}} = \frac{1}{1-x_r} (F_{\text{CaCO}_3,\text{calcined}} + F_{\text{C,\text{in}}} ) \]
\[ F_{\text{H}_2\text{O,calc,\text{out}}} = \frac{1}{1-x_r} F_{\text{H}_2,\text{in}} \]
\[ F_{\text{SO}_2,\text{calc,\text{out}}} = 0. \]

\[ F_{\text{O}_2,\text{calc,\text{out}}} = \frac{1}{1-x_r} \left( x_a \left( F_{\text{C,\text{in}}} + \frac{1}{2} F_{\text{H}_2,\text{in}} \right) + \left( x_a - \frac{1}{2} \right) F_{\text{S,\text{in}}} \right) \]

Assuming no NOx is formed,

\[ F_{\text{N}_2,\text{calc,\text{out}}} = \frac{1}{1-x_r} F_{\text{N}_2,\text{in}} = \frac{1}{1-x_r} 0.05 F_{\text{O}_2,\text{in}} \]

\[ \text{CO}_2 \text{ product stream} \]

\[ F_{\text{CO}_2,\text{product}} = (1-x_r) (F_{\text{CO}_2,\text{calc,\text{out}}} + F_{\text{H}_2,\text{calc,\text{out}}} + F_{\text{O}_2,\text{calc,\text{out}}} + F_{\text{N}_2,\text{calc,\text{out}}}) \]

**Calculation procedure:**

1. User inputs are \( \eta_{\text{CO}_2}, f_{\text{carb}} \) (Range 0-1, but most likely 0.5-1), \( f_{\text{calc}} \) (Range 0-1 but most likely 0.8-1) and \( f_{\text{in}} \) (>0, but should not be most likely <0.5), \( a_{\text{sorbent}} \) (0.924, same as in the wet FGD system).
2. Calculate \( X_{\text{ave}}, X_{\text{carb}} \) and \( X_{\text{calc}} \) from equations 1 – 3.
3. Calculate \( F_{\text{CaO,1}} \) from Eqn 6.
4. Calculate \( F_{\text{CaCO}_3,1} \) from Eqn 7.
5. Calculate \( F_{\text{CaCO}_3,\text{makeup}} \) from Eqn 8 and \( F_{\text{inert,makeup}} \) and \( F_{\text{sorbent,makeup}} \) from Eqns 9 and 10. (Minimum \( F_{\text{CaCO}_3,\text{makeup}} = F_{\text{SO}_2,\text{fluegas}} + F_{\text{SO}_2,\text{oxy}} \). Since \( F_{\text{SO}_2,\text{oxy}} \) is not known initially, assume minimum \( F_{\text{CaCO}_3,\text{makeup}} = 2F_{\text{SO}_2,\text{fluegas}} \).
6. User inputs \( T_{\text{carb}} \) (600-650°C), \( T_{\text{calc}} \) (900-950°C), \( T_{\text{makeup}} \) (>ambient temp), \( T_r \) (around 120°C). Also, \( x_r \) (0-1 but most likely value is 0.6), \( x_a \) (0.05).
7. Calculate \( H_{\text{calc,\text{min}}} \) from Eqn 44, \( A_{\text{oxy}} \) from Eqn 45 and \( A_r \) from Eqn 46.
8. Calculate \( H_{\text{calc}} \) from Eqn 47.
9. Calculate \( F_{\text{SO}_2,\text{oxy}} \) from Eqn 34 and \( m_{\text{ash}} \) from Eqn 36. Assume a molecular weight of 70kg/kmol for ash and calculate \( F_{\text{ash,oxy}} \).
10. Calculate \( F_{\text{CaSO}_4,1}, F_{\text{ash,1}} \) and \( F_{\text{total,1}} \) from Eqns 29-32.
11. Calculate \( F_{\text{CaO,2}} \) from Eqn 16, \( F_{\text{CaCO}_3,2} \) from Eqn 11, \( F_{\text{CaSO}_4,2} \) from Eqn 13, \( F_{\text{ash,2}} \) from Eqn 14 and \( F_{\text{inert,2}} \) from Eqn 15.
12. Calculate calcliner outlet flows from Eqns 18, 20, 21, 22 and 23.
**Reactor Design**

This section provides the details used for reactor design, which is used to calculate the costs.

**Carbonator design**

An important factor in reactor design is the residence time of solids in the reactor. A few studies, both experimental and analytical, deal with this subject. Romano (2012) described a detailed fluid dynamics and kinetics model in order to calculate the residence time of solids in the carbonator. However, that model seems to be too complicated and involves making many assumptions. Rodriguez et al (2011) present the results of several experimental investigations for the carbonation process. Figure 4 of that work shows the efficiency of carbonation (normalized over equilibrium efficiency) as a function of “active space time”. Active space time can be roughly defined as residence time of active solids (CaO) in the carbonator, given by the following equation:

\[
\tau_a = \frac{N_{Ca} X_{active}}{F_{CO2, in, flues}}
\]

(48)

Where, \(N_{Ca}\) is the total number of moles of Ca-based solids (CaO and CaCO3) in the carbonator and \(X_{active} = X_{ave} - X_{carb}\), which is the fraction of CaO which is still available for CO\(_2\)-capture.

Data points were noted from the following figure (Fig 4 of Rodriguez et al, 2011, the CFB cases):

![Figure 2. Conversion data used for estimating residence time (Rodriguez et al, 2011).](image)

The above figure shows the amount of space time needed to approach equilibrium in the carbonator. The trend lines show a typical exponential function, of the form:
\[ \frac{\eta_{CO_2}}{\eta_{CO_2, eq}} = 1 - e^{-\frac{\tau_a}{\tau_{max}}} \]  \quad (49)

Where, \( \tau_{max} \) is the time at which the efficiency reaches an asymptotic value.

Figure 3 shows the region of interest in magnified form:

![Figure 3. Data points used for carbonator residence time.](image)

The exponential trend can be expressed in linear terms as follows:

\[ \tau_a = -\tau_{max} \ln(1 - \frac{\eta_{CO_2}}{\eta_{CO_2, eq}}) \]  \quad (50)

From figure 3, the data points were plotted and a linear regression model was developed, as shown in the figure 4.

![Figure 4. Regression equation for residence time of carbonator.](image)

Thus the regression equation for active space time is given as:
\[
\eta_{CO_2} = 1 - e^{-\frac{\tau_a}{0.0039}}
\]

Where \( \tau_a \) is in hours. This can also be written in the units of seconds:

\[
\eta_{CO_2} = 1 - e^{-\frac{\tau_a}{14.04}}
\]

Though the R\(^2\) value for the regression is very low, this equation is kept because it validates with experimental results from literature.

The actual data points and the points obtained from the new regression equation (for the trend) are plotted in figure 5, which seems very close to Figure 4 of Rodriguez et al (2011).

![Figure 5. Regression fit of the experimental data.](image)

Calculating carbonator solids inventory:
All calculations assume a perfectly mixed reactor, which means that the composition everywhere in the reactor is the same as the exit composition for both solids and gases.

Capture efficiency can be expressed in terms of inlet and outlet mole fractions of CO\(_2\) as follows:

\[
\eta_{CO_2} = \frac{y_{CO_2, in} - y_{CO_2, out}}{y_{CO_2, in}(1 - y_{CO_2, out})}
\]

Equilibrium mole fraction of CO\(_2\) depends on temperature and is given by the following equation:

\[
y_{CO_2, eq} = \frac{10^{7.079 - \frac{8308}{T}}}{P}
\]

Where T is temperature in K and P is pressure in atm. For this application, P = 1 atm.

Once the pressure and temperature of the carbonator are known, equilibrium CO\(_2\) mole fraction can be calculated and from there \( \eta_{CO_2, eq} \) can be calculated, to be substituted in the calculation of active space time. The actual capture efficiency is a design parameter.

Thus, active space time needed to achieve a desired CO\(_2\) capture at a particular temperature and pressure is given by the following equation:
\[ \tau_a(s) = \frac{14.04}{\ln \left(1 - \frac{\eta_{CO_2}}{\eta_{CO_2,eq}}\right)} \]  

(54)

From this, the number of moles of CaO and CaCO3 inside the carbonator can be calculated as:

\[ N_{Ca} = \frac{\tau_a F_{CO_2,fluegas}}{x_{ave} - x_{\text{carb}}} \]  

(55)

Out of this, \((1-X_{\text{carb}})\) is the fraction of CaO and \(X_{\text{carb}}\) is the fraction of CaCO3.

The other solids present in the reactor are CaSO4 and ash. The mole fractions of these inside the reactor are the mole fractions at the exit. Hence,

\[ x_{\text{CaSO}_4} = \frac{F_{\text{CaSO}_4,2}}{F_{\text{total},2}} \]  

And

\[ x_{\text{ash}} = \frac{F_{\text{ash},2}}{F_{\text{total},2}} \]  

The moles of total solids in the carbonator (solids inventory) can now be calculated as:

\[ N_{\text{solids,carb}} = \frac{\tau_a F_{CO_2,fluegas}}{(x_{\text{ave}} - x_{\text{carb}})(1-x_{\text{CaSO}_4}-x_{\text{ash}})} \]  

(56)

The solids residence time can now be calculated as

\[ t_{\text{res,carb}} = \frac{N_{\text{solids,carb}}}{F_{\text{total},1}} \]  

(57)

Total mass of solids in the carbonator can be calculated as:

\[ m_{\text{solids,carb}} = \frac{\tau_a F_{CO_2,fluegas} x_{\text{ave}} - x_{\text{carb}}}{x_{\text{CaSO}_4} - x_{\text{ash}}} \left( (1 - X_{\text{carb}})M_{W_{\text{CaO}}} + X_{\text{carb}}M_{W_{\text{CaCO}_3}} + \frac{x_{\text{CaSO}_4}M_{W_{\text{CaSO}_4}}}{1-x_{\text{CaSO}_4}-x_{\text{ash}}} + \frac{x_{\text{ash}}M_{W_{\text{ash}}}}{1-x_{\text{CaSO}_4}-x_{\text{ash}}} \right) \]  

(58)

Density of solids can be calculated from the outlet composition as:

\[ \rho_{\text{solids,carb}} = x_{\text{CaO}}\rho_{\text{CaO}} + x_{\text{CaCO}_3}\rho_{\text{CaCO}_3} + x_{\text{CaSO}_4}\rho_{\text{CaSO}_4} + x_{\text{ash}}\rho_{\text{ash}} \]  

(59)

The values of densities and molecular weights of these solids are given in the following table:

<table>
<thead>
<tr>
<th>Solid</th>
<th>Molecular weight (kg/kmol)</th>
<th>Density (kg/m3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>56.1</td>
<td>3320</td>
</tr>
<tr>
<td>CaCO3</td>
<td>100.1</td>
<td>2710</td>
</tr>
<tr>
<td>CaSO4</td>
<td>136.1</td>
<td>2964</td>
</tr>
<tr>
<td>Ash (assumption)</td>
<td>70</td>
<td>2860</td>
</tr>
</tbody>
</table>

**Calciner design**

Calciner solids inventory

Not many studies exist which deal with the reactor design of a calciner. Martinez et al (2013) present a simplified model to calculate the solids inventory in the calciner, which is explained
below.
They define calcination efficiency ($E_{\text{calc}}$) which is same as the degree of calcination ($f_{\text{calc}}$) defined earlier in this model.

\[ f_{\text{calc}} = \frac{f_a}{\ln(1 - f_a)} \]  

(60)

Where

\[ f_a = 1 - e^{-\frac{t^*}{\tau}} \]

\[ t^* = \frac{3X_{\text{carb}}}{k_c(C_{\text{CO}_2,eq} - C_{\text{CO}_2})} \]

\[ k_c = k_{c0}e^{- \frac{E_a}{RT}} \]

($k_{c0}$ is the kinetic rate constant, 2050 m$^3$/mol/s; $E_a$ is activation energy for the reaction, 112,000 kJ/kmol).

Solids residence time is given by the following equation, where $N_{\text{Ca,calc}}$ is the number of moles of CaO and CaCO$_3$ inside the calciner.

\[ \tau = \frac{N_{\text{Ca,calc}}}{F_{\text{CaO,2}} + F_{\text{CaCO3,2}} + F_{\text{makeup}}} \]

Assuming ideal gases,

\[ C_{\text{CO}_2,eq} - C_{\text{CO}_2} = (y_{\text{CO}_2,eq} - y_{\text{CO}_2}) \frac{p}{RT} \]

Where $p$ is the calciner pressure in Pa (1.0132x10$^5$ in this case) and $T$ is in K. $y_{\text{CO}_2}$ is the mole fraction of CO$_2$ in the calciner outlet gases.

\[ y_{\text{CO}_2} = \frac{F_{\text{CO}_2,\text{calc,out}}}{F_{\text{CO}_2,\text{calc,out}} + F_{\text{H}_2\text{O,calc,out}} + F_{\text{O}_2,\text{calc,out}} + F_{\text{N}_2,\text{calc,out}}} \]

Calciner efficiency can be expressed as:

\[ f_{\text{calc}} = 1 - e^{-\frac{t^*}{\tau}} \]  

(61)

For different values of $\frac{t^*}{\tau}$, $f_{\text{calc}}$ was plotted as follows, to which an exponential function fits very well, as shown in figure 6.

From the regression equation, an expression can be developed for $\frac{t^*}{\tau}$ as a function of $f_{\text{calc}}$, as follows:

\[ \frac{t^*}{\tau} = 2.179\ln\left(\frac{0.9933}{f_{\text{calc}}}\right) \]  

(62)

Since $f_{\text{calc}}$ is a design variable (user input), $\frac{t^*}{\tau}$ can be calculated from which $N_{\text{Ca,calc}}$ can be estimated.

\[ N_{\text{Ca,calc}} = \frac{3(F_{\text{CaO,2}} + F_{\text{CaCO3,2}} + F_{\text{makeup}})X_{\text{carb}}}{k_c(y_{\text{CO}_2,eq} - y_{\text{CO}_2}) \frac{p}{RT} (\frac{t^*}{\tau})} \]  

(63)
Hence, for a given calciner efficiency ($f_{calc}$), inlet solids flow rates, pressure and temperature, solids inventory in the calciner can be calculated.

Similar to the carbonator calculations, the total solids in the calciner can be calculated as:

$$N_{solids,calc} = \frac{N_{Ca}}{1 - x_{CaSO_4,3} - x_{ash,3}}$$

Molecular weight and density of solids inside the calciner can also be estimated similar to the carbonator:

$$MW_{solids,calc} = x_{CaO,3}MW_{CaO} + x_{CaCO_3,3}MW_{CaCO_3} + x_{CaSO_4,3}MW_{CaSO_4} + x_{ash,3}MW_{ash}$$

$$\rho_{solids,calc} = x_{CaO,3}\rho_{CaO} + x_{CaCO_3,3}\rho_{CaCO_3} + x_{CaSO_4,3}\rho_{CaSO_4} + x_{ash,3}\rho_{ash}$$

**Reactor design**

The purpose of reactor design is to calculate the volume of reactors for capital cost estimation and also to estimate the pressure drop in the reactors.

It is assumed that both carbonator and calciner operate as circulating fluidized bed (CFB) reactors operating in the fast fluidization mode. A typical CFB has a dense lower zone and lean upper zone. The solids fraction in the dense zone ($\varepsilon_{s,d}$) is fairly constant while the solids fraction in the lean zone ($\varepsilon_{s,l}$) undergoes an exponential decay towards an asymptotic value of $\varepsilon^*$.

$$\varepsilon_{s,l} = \varepsilon^*_s + (\varepsilon_{s,d} - \varepsilon^*_s)e^{-az}$$

Where, $a$ is a decay constant given and $z$ is the height along the lean zone.

Decay constant is calculated from $aU_g = \text{constant}$, typically between 2-4. We can assume 3 in this model.

$aU_g = 3$.

An average lean zone solids fraction can be calculated as:

$$\varepsilon_{s,l} = \varepsilon^*_s + \frac{(\varepsilon_{s,d} - \varepsilon^*_s)}{a(H_t - H_d)}$$

**Figure 6. Regression equation for calciner residence time.**
Typical values of $\varepsilon_{s,d}$ and $\varepsilon^*$ are 0.15 and 0.01, respectively (Romano, 2012). Ht and Hd are of the orders of a few meters, sometimes more than 10. The value of a is typically less than 1.

Hence, the lean zone solids fraction can be estimated to be 0.015, for typical applications. $\varepsilon_{s,l} = 0.015$.

The solids inventory of a reactor can be written as:

$$ m_{\text{solids}} = \rho_s A \left( \varepsilon_{s,d} H_d + \varepsilon_{s,l} (H_t - H_d) \right) \quad (65) $$

There are three unknowns in this equation – A, H_d and H_t. Romano (2012) assumes a constant value for H_t/D. However, considering the wide variation in H_t/D values for typical CFB boilers, this kind of design condition does not seem appropriate. On the other hand, for the solids flow rates in typical applications, H_t/H_d seems to be varying between 4 and 7, most likely between 5 and 6. In the CLC reactor design model, H_t/H_d was assumed to be 5 and we will keep that assumption here too. Area A can be calculated from gas flow rates and velocity. $H_t/H_d = 5$.

The following is the same as in CLC reactor design model.

$$ A_{\text{carb}} (m^2) = F_{\text{fluegas,in}} \times 22.4 \times (T_{\text{carb}} + 273.15) / (P_{\text{carb}} \times 273.15 \times U_g) \quad (66) $$

$$ A_{\text{calc}} (m^2) = (F_{\text{O2,in}} + F_{\text{recycle}}) \times 22.4 \times (T_{\text{calc}} + 273.15) / (P_{\text{calc}} \times 273.15 \times U_g) \quad (67) $$

where, $U_g$ is the superficial gas velocity. The most common value of $U_g$ for these kind of applications is 7m/s, though a range of 5 – 10m/s is possible [Fan, 2010].

Diameter of vessel D (m) = $\left(4 \times A / \pi \right)^{1/2}$.

Maximum diameter of a vessel is 8m [Fan, 2010]. If D > 8m, the air flow is divided in to multiple vessels.

From $U_g$, a can be calculated, $a = 3/U_g$ \hspace{1cm} (68)

Solids inventory can now be expressed as:

$$ m_{\text{solids}} = m_{\text{solids}} \left( \frac{H_t}{H_d} \right) \left( \varepsilon_{s,d} + \varepsilon_{s,l} \left( \frac{H_t}{H_d} - 1 \right) \right) \quad (69) $$

AHt is the volume of the reactor, V.

$$ V = \frac{m_{\text{solids}} \left( \frac{H_t}{H_d} \right)} {\rho_s \left( \varepsilon_{s,d} + \varepsilon_{s,l} \left( \frac{H_t}{H_d} - 1 \right) \right)} \quad (70) $$

Pressure drop in the reactors is:

$$ \Delta p (Pa) = m_{\text{solids}} \times 9.81 / A \quad (71) $$
Heat Recovery from CaL Process

Carbonation is an exothermic process, the heat from which can be used for steam generation. The design assumption is that water runs through a heat exchanger which is placed inside the carbonator to maintain a fixed carbonator temperature.

Flue gas leaving the carbonator and the CO2-rich stream leaving the calciner are at high temperatures, which also can be used to generate steam. The amounts of heats from these three sources are calculated as follows:

Heat of reaction of the carbonation reaction or the heat released in the carbonator:

\[
H_{\text{carb}} = (F_{\text{CO}_2,2} - F_{\text{CO}_2,\text{fluegas}})H_{f,\text{CO}_2} + (F_{\text{CaO},2} - F_{\text{CaO},1})H_{f,\text{CaO}} + (F_{\text{CaCO}_3,2} - F_{\text{CaCO}_3,1})H_{f,\text{CaCO}_3} + (F_{\text{N}_2,\text{fluegas}}C_{\text{pN}_2} + F_{\text{O}_2,\text{fluegas}}C_{\text{pO}_2} + F_{\text{H}_2\text{O},\text{fluegas}}C_{\text{pH}_2\text{O}} + F_{\text{CO}_2,\text{fluegas}}C_{\text{pCO}_2})(25 - T_{\text{fluegas}}) + (F_{\text{CaO},1}C_{\text{pCaO}} + F_{\text{CaCO}_3,1}C_{\text{pCaCO}_3} + F_{\text{CaSO}_4,1}C_{\text{pCaSO}_4} + F_{\text{ash},1}C_{\text{pash}})(25 - T_{\text{calc}}) + (F_{\text{N}_2,2}C_{\text{pN}_2} + F_{\text{O}_2,2}C_{\text{pO}_2} + F_{\text{H}_2\text{O}_2,2}C_{\text{pH}_2\text{O}_2} + F_{\text{CO}_2,2}C_{\text{pCO}_2} + F_{\text{CaO},2}C_{\text{pCaO}} + F_{\text{CaCO}_3,2}C_{\text{pCaCO}_3} + F_{\text{CaSO}_4,2}C_{\text{pCaSO}_4} + F_{\text{ash},2}C_{\text{pash}})(T_{\text{carb}} - 25)
\]

\[
H_{f,\text{CO}_2} = -393,509 \text{ kJ/kmol}
\]

\[
H_{f,\text{CaO}} = -635,090 \text{ kJ/kmol}
\]

\[
H_{f,\text{CaCO}_3} = -1,206,920 \text{ kJ/kmol}
\]

Assuming fluegas can be cooled upto 50°C in a heat exchanger before going out of the stack, heat recovered from fluegas can be calculated as:

\[
H_{\text{fluegas}} = (F_{\text{N}_2,2}C_{\text{pN}_2} + F_{\text{O}_2,2}C_{\text{pO}_2} + F_{\text{H}_2\text{O}_2,2}C_{\text{pH}_2\text{O}_2} + F_{\text{CO}_2,2}C_{\text{pCO}_2})(T_{\text{carb}} - 50)
\]

Heat recovered from cooling of calciner output gases to T_r (assumed 120°C earlier),

\[
H_{\text{CO}_2,\text{cool}} = (F_{\text{N}_2,\text{calc.out}}C_{\text{pN}_2} + F_{\text{O}_2,\text{calc.out}}C_{\text{pO}_2} + F_{\text{H}_2\text{O}_2,\text{calc.out}}C_{\text{pH}_2\text{O}_2} + F_{\text{CO}_2,\text{calc.out}}C_{\text{pCO}_2})(T_{\text{calc}} - 120)
\]
Steam power generated from this waste heat recovery will depend on the steam cycle heat rate. Assuming all these heat streams (or steam generated) can be easily integrated in to the existing steam cycle, steam power generated is calculated as:

\[
ST_{\text{power}} = \frac{(-H_{\text{carb}} + H_{\text{tuegas}} + H_{\text{CO2,cool}})}{HR_{\text{steam}}}
\]

### Calcium looping Cost Model

The cost model is developed based on volumetric flow of gases as the scaling factor rather than the reactor volume. An atmospheric pressure CFB boiler as modeled in case S22A of the NETL baseline report on oxy-combustion plants (NETL, 2010), has been used as a basis for carbonator costs since carbonator also includes steam generating heat exchangers. An atmospheric pressure biomass CFB gasifier, has been used as the basis for calciner costs, since there are no heat exchangers inside the calciner.

Volumetric flow rate of gases can be expressed a function of molar flow rate, temperature and pressure. However, since a boiler and carbonator have similar operating conditions, temperature and pressure effects are not considered in cost estimation. Instead, just the molar flow rate is used.

\[
C_{\text{carb}} = C_{\text{ref}} \left( \frac{F_{g,\text{in}}}{F_{\text{ref}}} \right)^{0.6}
\]

\[C_{\text{carb}} = \$373,018,000 \text{ (2007)}\]
\[F_{\text{carb}} = 64,561 \text{ kmol/hr}\]

\[
C_{\text{calc}} = C_{\text{ref}} \left( \frac{F_{\text{calc, in}} P_{\text{ref}} T_{\text{calc}}}{F_{\text{ref}} P_{g,\text{in}} T_{\text{ref}}} \right)^{0.6}
\]

\[C_{\text{calc}} = \$29,838,000 \text{ (1990)}\]
\[F_{\text{calc}} = 3,687 \text{ kmol/hr}\]
\[P_{\text{ref}} = 1.4 \text{ bar} \text{ (} P_{g,\text{in}} = 1.1 \text{ bar)}\]
\[T_{\text{ref}} = 1143.15K\]
\[F_{\text{calc, in}} = F_{O2,\text{in}} + F_{\text{recycle}}\]

(Since volume of the reactor is affected by the volumetric flow rate of gases, the same exponent of 0.6 is used).

Limestone (CaCO3) unit cost \(C_{\text{limestone}} = \$25.8/\text{tonne}\) (same as used in FGD in IECM)
Initial limestone cost = \((m_{\text{carb}} + m_{\text{calc}}) \times C_{\text{limestone}}\) ($ from solids inventory calculations)
Make up OC = \(\text{MW}_{\text{CaCO3}} \times F_{\text{makeup}}\) (kg/hr)
Annual make-up OC cost = (capacity factor) \(\times \text{MW}_{\text{CaCO3}} \times F_{\text{makeup}} \times C_{\text{limestone}} \times 8760\)

### Additional costs to be considered:

Heat recovery steam generator (same as used in IGCC model)

\[
C_{HRSG} = 0.3146(ST_{\text{power,HRSG}}) \text{ ($M, 2011)}
\]
\[ S_{\text{power,HRSG}} = \left( H_{\text{fluegas}} + H_{\text{CO}_2,\text{cool}} \right) / H_{\text{steam}} \] (MW)

(In HRSG, heat is recovered only from cooling of flue gas and CO\(_2\). The cost for heat exchanger in carbonator cooling is already included in the carbonator capital cost).

**Figure 7. Cost model for HRSG.**

Steam turbine (same as used in PC plant model)

\[
C_{\text{ST}} = 0.9322 \left( S_{\text{power}} \right)^{0.7971} \] ($M, 2011)

\[
S_{\text{power}} = \left( -H_{\text{carb}} + H_{\text{fluegas}} + H_{\text{CO}_2,\text{cool}} \right) / H_{\text{steam}} \] (MW)

**Figure 8. Cost model for steam turbine.**

Coal handling equipment for ASU

\[
C_{\text{coal handling}} = 2.05 \left( m_{\text{coal,ASU}} \right)^{0.7201} \] ($M, 2011)

\[ m_{\text{coal,ASU}} \] (tonne/hr)

(The cost is different for different coals, but not by much. So an average cost is used here. Refer to figure below).
Solids handling equipment
Since limestone and lime are the solids that are transported in the CaL system, capital cost for solids handling could be estimated based on the dry solids flow rate in the dry FGD system. However, as can be seen in the figure below, solids handling equipment in dry FGD system is a strong function of both sorbent flow rate and sulfur content of coal. Since sulfur content of coal does not matter much in a CaL system, this method cannot be used. Instead, it is assumed that the capital cost of CaL solids handling equipment can be estimated similar to that of coal handling equipment and solids handling equipment. Only make-up sorbent and purged sorbent are transported using the solids handling equipment. The recirculating sorbent drops through stand pipes and loop seals.

\[ C_{\text{solids handling}} = 2.05 \left( m_{\text{make-up}} + m_{\text{purge}} \right)^{0.7201} \text{(SM, 2011)} \]

\[ m_{\text{make-up, purge (tonne/hr)}} \]

Other cost areas involved in the CaL process are CO₂ purification unit (CPU), CO₂ compressors and blowers.
Conclusion

This report presented the performance and cost models for a calcium looping process for post-combustion CO₂ capture. These models are incorporated into the Integrated Environmental Control Model (IECM).
References:


