Observed Rate Kinetics of Calcium Carbonate Decomposition in High CO$_2$ Partial Pressures

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Introduction

Limestone calcination rate at high partial pressures of CO\textsubscript{2}

Steam or nitrogen as additional gases

Atmospheric pressure fluidised bed reactor, \(u/u_{mf}=11.7 @ 950^\circ\text{C}\)

Small samples rapid addition at high temperature

Investigate effect of:
- Bed temperature
- Particle size
- Steam/nitrogen partial pressure
- Sample mass
- Limestone type
Reactor set up - Steam

- Heating control boxes
- Steam Probe
- HPLC pump
- Transformer
- Fluidised bed reactor
- Steam generator
- Heated gas lines
Steam System Design

- Sample Cylinder
- Gas Preheating line
- Heated water bath
Reactor set up - Nitrogen
# Limestone Characterisation

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Longcliffe</th>
<th>Havelok</th>
<th>Cadomin</th>
<th>Imeco</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CaCO$_3$ mol% by XRF</strong></td>
<td>98.89</td>
<td>96.30</td>
<td>95.46</td>
<td>98.74</td>
</tr>
<tr>
<td><strong>BET surface area (m$^2$/g)</strong></td>
<td>0.057 ± 0.0085</td>
<td>0.46 ± 0.0028</td>
<td>1.05 ± 0.0051</td>
<td>0.21 ± 0.0037</td>
</tr>
<tr>
<td><strong>Porosity (%)</strong></td>
<td>3.06 ± 0.0057</td>
<td>2.38 ± 0.0017</td>
<td>2.07 ± 0.0063</td>
<td>2.42 ± 0.0066</td>
</tr>
<tr>
<td><strong>Skeletal density (g/cm$^3$)</strong></td>
<td>2.82 ± 0.0038</td>
<td>2.92 ± 0.0017</td>
<td>2.90 ± 0.0063</td>
<td>2.94 ± 0.0066</td>
</tr>
<tr>
<td><strong>Envelope density (g/cm$^3$)</strong></td>
<td>2.73 ± 0.0069</td>
<td>2.85 ± 0.0080</td>
<td>2.84 ± 0.0053</td>
<td>2.86 ± 0.0083</td>
</tr>
</tbody>
</table>
Experimental Results
Effect of Temperature

Increasing Temperature

20% Steam, 500-710µm, 0.25g

20% N₂, 500-710µm, 0.25g
**Effect of Temperature – Activation Energy**

\[ E_a = 166.48 \text{ kJ mol}^{-1} \]

20% **Steam**, 500-710µm, 0.25g

\[ E_a = 299.01 \text{ kJ mol}^{-1} \]

20% **N\textsubscript{2}**, 500-710µm, 0.25g
Effect of Gas Concentration

Steam, 950°C, 500-710µm, 0.25g  

\[ \text{N}_2, 950°C, 500-710\mu m, 0.25g \]

Increasing CO\(_2\) concentration
Effect of Particle Size

**20% Steam**, 950°C, 0.25g

**20% N₂**, 950°C, 0.25g
Effect of Sample Mass

Increasing mass

20% Steam, 950°C, 500-710µm

20% N₂, 950°C, 500-710µm
Effect of Limestone Type

20% Steam, 950°C, 500-710µm, 0.25g

20% N₂, 950°C, 500-710µm, 0.25g
1. Limestone calcination in steam is consistently faster due to the adsorption of H$_2$O on the active sites\textsuperscript{1}, thereby weakening the bonding between CO$_2$ and CaO, resulting in an increased decomposition rate.

\begin{equation}
CaCO_3 + H_2O \Leftrightarrow CaCO_3^* \cdot H_2O \Leftrightarrow CaO + CO_2 + H_2O
\end{equation}

\begin{equation}
CaCO_3 + N_2 \Leftrightarrow CaCO_3^* + N_2 \Leftrightarrow CaO + CO_2 + N_2
\end{equation}

* = Active site

2. Catalytic effect of steam combined with a smaller physical effect on the thermal properties.

\textsuperscript{1} Junjun Yin, Xin Kang, Changlei Qin, Bo Feng, , Ananthanarayanan Veeraragavan, Dmitry Saulov (2014) - Modeling of CaCO3 decomposition under CO2/H2O atmosphere in calcium looping processes. DOI: 10.1016/j.fuproc.2014.03.036.
Modelling
Shrinking Core Model

Applicability
- Non porous particles
- Fast reaction rate
- Minimal diffusion resistance through CaO product pores

Limitations
- Sharp / diffuse reaction boundary
- Assume Isothermal particle

Derivation and Parameters

1. Diffusion of steam/N\textsubscript{2} through the film surrounding the particle to the surface of the solid.

\[
\frac{t_{\text{film in}}}{\tau_{\text{film in}}} = X_{\text{film in}} \quad \tau_{\text{film}} = \frac{\rho_{\text{CaCO}_3} R}{3b k_g C_{Ag}}
\]

2. Reaction of the solid at the reaction surface.

\[
\frac{t_r}{\tau_r} = 1 - \left(1 - X_r,\text{CaCO}_3\right)^{\frac{1}{3}} \quad \tau_r = \frac{\rho_{\text{CaCO}_3} R}{b k'' C_{Ag}}
\]

3. Diffusion of CO\textsubscript{2} and steam/N\textsubscript{2} through the film surrounding the particle away from the surface.

\[
\frac{t_{\text{film out}}}{\tau_{\text{film out}}} = X_{\text{film out}} \quad \tau_{\text{film}} = \frac{\rho_{\text{CaCO}_3} R}{3b k_g C_{Ag}}
\]
Derivation and Parameters - Continued

Sherwood number: Ranz & Marshall equation

\[ Sh = \frac{2k_g R}{D_{CO_2}} = 2 + 0.6Re^{1/2}Sc^{1/3} \]

Schmidt number

\[ Sc = \frac{\mu_g}{\rho_g D_{CO_2}} \]

Multi-molecular viscosity

\[ \mu_{mix} = \sum_{\alpha=1}^{N} \frac{x_\alpha \mu_\alpha}{\sum_{\beta} x_\beta \phi_{\alpha\beta}} \]

Bulk multi-molecular diffusion\(^3\) of CO\(_2\) & H\(_2\)O or CO\(_2\) & N\(_2\)

\[ D_b = 0.001858 \times \sqrt{\frac{T^3 \left( \frac{1}{M_1} + \frac{1}{M_2} \right)^{1/2}}{P \sigma_{12}^2 \Omega^{(1,1)*}}} \]


Derivation and Parameters

\[
\tau_{\text{film in Steam}} \approx 0.39 \text{s} \quad \tau_{\text{film out CO}_2/\text{H}_2\text{O}} \approx 0.10 \text{s}
\]

\[
\tau_{\text{film in N}_2} \approx 0.52 \text{s} \quad \tau_{\text{film out CO}_2/\text{N}_2} \approx 0.13 \text{s}
\]

\[\tau_r \gg \tau_{\text{film in}} + \tau_{\text{film out}}\]

Reaction term of shrinking core model is dominant.

Least squares fitting

Used Excel solver to minimise sum of the squares by changing the value of \( k'' \)

\[
k'' = Ae \left( -\frac{E_a}{RT} \right)
\]
Model Predictions – Effect of Bed Temperature

20% Steam, 500-710µm, 0.25g

20% N₂, 500-710µm, 0.25g
Model Predictions – Effect of Gas Concentration

Steam, 950°C, 500-710µm, 0.25g

N₂, 950°C, 500-710µm, 0.25g
Model Predictions – Effect of Particle Size

20% Steam, 950°C, 0.25g

20% N₂, 950°C, 0.25g
Model Predictions – Effect of Sample Mass

20% Steam, 950°C, 500-710µm

20% N₂, 950°C, 500-710µm
Model Predictions – Effect of Limestone Type

20% Steam, 950°C, 500-710µm, 0.25g

20% N₂, 950°C, 500-710µm, 0.25g
Heat Transfer Limitations

Biot number

\[
Bi = \frac{hL_C}{k_b} \quad L_C = \frac{V_{\text{body}}}{A_{\text{surface}}} \quad \text{Bi} \approx 0.33
\]

• Particles are non isothermal – Unsteady state model needed
• Shrinking core model is only a starting point
• Reaction is very endothermic and must be accounted for
Preliminary Heat Conduction Model in Matlab

Graphical representation of heat conduction through the spherical particle
Conclusions

- Calcination kinetics in the presence of steam are significantly enhanced
- Steam mole fractions > ~10% display minimal improvement to overall rate
- Steam is a catalyst for limestone calcination
- Modelling with the shrinking core model has shown promising initial results
- Obviously a heat and mass transfer model needs to be developed because of the system being very endothermic
Thank you

Any questions?

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