Sulfation Behavior of Calcium-based Sorbents Under Oxy-Combustion Conditions at High Pressures

Xiaojing Yang and Sarma Pisupati*
John and Willie Leone Family Department of Energy and Mineral Engineering, and the EMS Energy Institute, The Pennsylvania State University, PA, USA

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Presentation Outline

• Background
  – High pressure oxy-combustion
  – Direct sulfation and understanding on high pressure behavior
  – Factors affecting sulfation

• Key research questions

• Experimental methodology

• Results

• Conclusions
• Oxy-Combustion: combustion in oxygen without nitrogen
  – reduces fuel consumption and emissions
  – high pressure:
    • reduces the size of the system at scale
    • Ready-to-sequester stream of CO₂ to attempt zero emission

• Ability to use limestones and dolomites in the FBC system to capture SO₂.
Direct Vs Indirect Sulfation Mechanisms

In an atmospheric FBC reactor, limestone sulfation undergoes the following reactions pCO₂ > equilibrium pressure, T < 920 °C, calcination is inhibited

- **Calcination**
  - CaCO₃ → CaO + CO₂

- **Sulfation**
  - CaO + SO₂ + ½ O₂ → CaSO₄

**Direct sulfation:**

- CaCO₃ + SO₂ + ½ O₂ → CaSO₄ + CO₂

**Dolomite sulfation:**

- CaMg(CO₃)₂ → CaCO₃·MgO + CO₂

- CaCO₃·MgO + SO₂ + ½ O₂ → CaSO₄·MgO + CO₂

Pore plugging is dominating for indirect sulfation. Direct sulfation leads to a higher conversion than indirect.

(Snow et al., 1988; Tullinet al., 1993; Fuertes et al., 1994a, 1994b, 1995; Rahmani and Sohrabi, 2006).
Sulfation process. (a) Direct sulfation; (b) indirect sulfation (Hu et al., 2007)

SEM photograph of CaSO$_4$ product layer. (a) Direct sulfation of limestone; (b) indirect sulfation of limestone. (Chen et al 2009)

Pressure, Gas Concentration, Temperature and Sorbent Particle Size Affect Sulfation

Factors studied in this work

- Sulfation Conversion
  - Effect of CO\textsubscript{2}/O\textsubscript{2} ratio at high pressures
  - Sulfation Pattern (SEM and petrographic analysis) and Sulfur penetration depth (SEM-EDS cross-section)

Previous Studies

- Sulfation Pattern

Factors studied in this work

- Total pressure (unclear)
- Gas concentrations (CO\textsubscript{2} (negative) and SO\textsubscript{2} (positive))
- Direct sulfation temperature (850-920 °C)
- Particle sizes

Key Research Questions

• Will direct sulfation achieve a higher conversion at high pressures than at atmospheric pressure?
• Will CO$_2$ have a negative effect on conversions at high pressures similar to that at atmospheric pressure?
• How will dolomite behave at high pressures?

Controls: SO$_2$ concentration, temperature, particle size.
Three Raw Sorbents were Selected and Characterized

Graymont limestone, Ohio Dolomite and Michigan Limestone

• Compositional Analysis of Sorbents
  – Elemental: Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)
  – Crystalline phase: XRD
• Hardgrove Grindability Index (HGI)
  – Dimensionless measure the amount of energy required to grind the sample from a certain size to another
• Particle Size Measurement
• Petrographic Analysis
Test Apparatus for Sulfation Experiments

- High-Pressure Fixed-Bed Reactor
- Sample size = 1g > typical TGA 5-20mg
- Controls: 3000 ppm SO₂, 870 °C

• Pure CO₂: until 870°C is reached
• Pre-mixed gas: 9 bar or atmospheric pressure
## Composition analysis by XRD

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<tr>
<th>CO₂ Partial Pressure</th>
<th>Total Pressure (bar)</th>
<th>Sorbent</th>
<th>Before (g)</th>
<th>CaCO₃ (wt%)</th>
<th>CaMg(CO₃)₂ (wt%)</th>
<th>After (g)</th>
<th>SO₂ absorbed</th>
<th>CaSO₄ (wt%)</th>
<th>CaMg₂(SO₄)₃ (wt%)</th>
<th>MgO (wt%)</th>
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Effect of Pressure and Gas Concentration on Sulfation Depends on the Type of Sorbent

Graymont
- Increasing pO2 or decreasing pCO2 by 10%: increased sulfation by 15-16%
- Increasing total pressure to 9 bar increased sulfation by only 2%

Michigan and dolomite
- Increasing pressure is more effective than changing gas concentration (pO2 or pCO2)

This is due to
1. the type of sorbent (petrography) and
2. The participation of Mg in the sulfation process

In addition to confirm the existence of CaMg$_2$(SO$_4$)$_3$ (will discuss later)
Sulfation Performance depends on the Sorbent Petrographic Structure

Sulfation patterns
• determined by Scanning Electron Microscopy (SEM) across the cross-sections of the sorbents.
• indicate the sulfation penetrating depth and route

Sample Graymont SEM cross section (layered BSE, 20%O2, 9 bar)
Michigan Limestone Sulfation Patterns

EDS Layered Image 3

Sample Layered Image of Michigan (BSE, 20%O₂, 9 bar)

- unreacted core—a Ca rich particle
- network
- unreacted core—a Mg rich particle
- uniform

100μm

Ca, S, Mg, C, Electron
Dolomite Sulfation Patterns

Sulfur map of dolomite (90%CO₂, 9bar); S/Ca (mol) = 0.61

At high pressure, sulfur was able to penetrate deeper for unreacted-core particles.

How to quantify sulfur penetration depth?
Petrographic Analysis– Graymont

*sparite (sparry crystals, 5-20 µm) uniform or unreacted-core*

*Rock matrix: primarily of micrite (1-4 µm) Network*

Graymont limestone petrography sample pictures
Petrographic Analysis—Michigan

- micrite (1-4 µm) rich
- bioturbated micrite
- sparite (5-20 µm) rich

3 sulfation patterns were all present
Petrographic Analysis—Ohio dolomite

Mainly well bounded crystals (similar to sparite in limestones)

Uniform or unreacted-core!

Dolomite Matrix
SEM-EDS Analysis Confirmed the Observations (S/Ca ratios)

Energy Dispersive Spectroscopy (EDS): elemental wt% at the chosen site

S/Ca ratio:
- the average of S/Ca (mol) of 10 sites across the cross section (grid sampling)
- quantitatively analyzed the effectiveness of sulfation pattern

- How did the conversion improve?
  - increase in the sulfur penetration depth → improvement in conversion
### SO₂ absorbed

At High Pressures sulfation of Magnesium is evident in Dolomites as CaMg$_2$(SO$_4$)$_3$

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Up to 12%wt in Ohio dolomite sulfated products at 9 bar also present in the Michigan limestone.
XRD spectrum of Nittany dolomite samples.

A. the unsulfated Nittany dolomite;
B. the sulfated Nittany dolomite at atmospheric pressure;
C. the sulfated Nittany dolomite at 9 bar

Nittany Dolomite has ~96% dolomite (A, unreacted), no peak CaMg$_2$(SO$_4$)$_3$ was present (B, atmospheric pressure).

CaMg$_2$(SO$_4$)$_3$ in C makes up to 6.7%wt of the product (9bar)
Mg Sulfation Accounted for 14% of all the Absorbed $SO_2$

<table>
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<tr>
<th>CO$_2$ Partial Pressure</th>
<th>Sorbent</th>
<th>$SO_2$ absorbed by Mg/total SO$_2$ absorbed (mol)</th>
<th>Mg$<em>{sulfated}$/Mg$</em>{total}$ (mol)</th>
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<td>11.47%</td>
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<td>6.84%</td>
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<tr>
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<td>3.89%</td>
<td>7.70%</td>
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Conclusions

• High pressure could improve the conversion (2-15%) of sulfation by
  1. Improving sulfur penetration depth of the particles, especially for the particles with an unreacted core pattern.
  2. Improving Mg participation in the reaction

• With the decrease of CO₂ partial pressure, the direct sulfation was promoted by 5-15% in a pressurized system (within the testing range)

• Dolomite had a uniform-dominated sulfation pattern, and gave the highest conversion among all three under a given condition.

• Graymont (almost pure limestone), which had a network-dominated sulfation pattern and no unreacted-core pattern, had only 2% improvement at 9 bar.

• Mg participated in dolomite sulfation under pressurized system forming CaMg₂(SO₄)₃ phase. (this is also confirmed by the other experiments conducted in a fluidized bed at Penn State)
Acknowledgments

• The limestone samples and partial financial support for characterization were provided by Aerojet Rocketdyne, CA.

• The staff of EMS Energy Institute have helped in setting up the reactor.
Thank you! 谢谢

Questions?

Contact Information:
Sarma Pisupati  sxp17@psu.edu
Xiaojing Yang  xzy109@psu.edu

The Dolomites (http://www.lagazzettaitaliana.com/hill.aspx)