Carbonation-Calcination Reaction (CCR) Process for High Temperature \( \text{CO}_2 \) and Sulfur Removal

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CO₂ Capture from Fossil Fuel Based Plants

Post Combustion
- Coal or Natural Gas
- Boiler → Steam Generator → CO₂ Capture

Oxy Combustion
- Coal or Natural Gas
- Air
- ASU
- Boiler → Steam Generator
- Gasifier
- Gas Cleanup → WGSR → CO₂ capture → Reforming → PSA → FT Reactor
- Electricity
- Electricity CO₂ free Flue Gas → CO₂ Compression, Transportation and Sequestration

Pre Combustion
- Coal or Natural Gas
- Electricity
- N₂ and Steam
- Gas Turbine → Steam Turbine → Hydrogen
  - Ammonia Synthesis
  - Hydrogenation
  - Other chemicals synthesis
- Liquid Fuels
General Overview

- Coal-fired power plants generate 50% of electricity in United States and accounts for 33% of United States CO$_2$ emissions

- Generate 41% of world’s electricity and accounts for 42% of world’s CO$_2$ emissions

- Necessary to develop economic, post-combustion CO$_2$ removal technology for existing power plants to sustain energy demand while protecting environment
  - Solvent based scrubbing
  - oxyfuel
  - adsorbents
  - Membranes
  - reactive sorbents
Use of metal oxide (CaO) in a reaction-based cyclical capture cycle

- **Carbonation:** \( \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \)
- **Sulfation:** \( \text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4 \)
- **Calcination:** \( \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \)

**Advantages of Carbonation/Calcination Reaction (CCR)**

- Operation under flue gas conditions
- High equilibrium capacities of sorbent
- Calcination produces pure \( \text{CO}_2 \) stream
- Low sorbent cost
- Simultaneous \( \text{CO}_2/\text{SO}_2 \) removal
- High-temperature operation allows for heat utilization
# Demonstration Project Team

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Basic Reactions

Based on high-temperature, reversible reaction of metal oxide (CaO)

**CARBONATOR**
- Dehydration: \( \text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O} \)
- Carbonation: \( \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \)
- Sulfation: \( \text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4 \)
  
  450°C – 650°C

**CALCINER**
- Calcination: \( \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \)
  
  900°C – 1200°C

**HYDRATOR**
- \( \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \)
  
  500°C, P ~ 1 atm

Energy flows through the system, with CO2 to sequestration and waste CaO/CaCO3/CaSO4 being recycled.

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Single cycle (once-through) testing

- Multiple sorbents
- Solids loading (Ca:C ratio)
- Residence time
- Reaction Temperature
Sub-pilot Plant Set-up

- Sorbent Injection
- Gas sampling system
- Coal Stoker
- Baghouse
- Clean Flue Gas To Atmosphere
CO₂ Removal by Ca Based Sorbents

% CO₂ Removal

Ca:C Mol Ratio

- Calcium Hydroxide
- Pulverized Ground Lime
- Ground Lime

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SO$_2$ Removal by Ca-based Sorbents

![Graph showing SO$_2$ removal efficiency for different Ca:C mol ratios with data points for Calcium Hydroxide, Pulverized Ground Lime, and Ground Lime.]
Effect of Residence Time

CO₂ Removal vs. Reaction Residence Time

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Multicyclic Testing
Calcination under Realistic Conditions

- Sorbent reactivity reduced to half during calcination
- Effect of sintering reduced by steam calcination
- Increase in steam concentration improves reactivity

- Calcination at 900°C with 50% steam and 50% CO₂
- Reduced sintering over multiple cycles
- Reactivity reduced to half in 4 cycles
CCR with hydration

- Sorbent reactivity reduced to a third after calcination at 1000°C
- Calcined sorbent regenerated completely by hydration
Cyclic Studies Set-up

- Coal Stoker
- Rotary Calciner
- Sorbent Injection
- Baghouse

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Multicyclic CO$_2$ and SO$_2$ Removal
Aspen Simulation Assumptions

- 500 MWe power plant
- Coal Composition: Pittsburgh #8
- 20% Excess Air
- 41% Turbine Efficiency
- 10% in-house electricity consumption
- 119 kWh/tonne CO₂ for compression to 14 MPa (~140 atm)

Parasitic Energy Consumption = 
\[
\frac{\text{(Net Electricity Generation w/o CO₂ Control)} - \text{(Net Electricity Generation w/CO₂ Control)}}{\text{Net Electricity Generation w/o CO₂ Control}} \times 100
\]

1. Wong, S. "CO₂ Compression and Transportation to Storage Reservoir”. Asia-Pacific Economic Cooperation. Building Capacity for CO₂ Capture and Storage in the APEC Region. Module 4
Aspen Simulation of CCR Process

Pittsburgh #8 Coal, 1506.84 MWh input
1.33:1 Ca/C mol ratio
90% CO2/100% SO2 removal
3% purge stream
698.7 MWh from Boiler
647.6 MWh from CCR
90% Heat Extraction
582.8 MWh
41% Turbine efficiency
525.4 MW Gross
10% in-house consumption
472.8 MWs
51.3 MWs compression (119 kWh/tonne CO2)
421.5 MWs NET
Parasitic Energy Consumption = 15.8%

Temperature (°C)
Pressure (atm)
Mass Flow Rate (tons/hr)
Duty (MW)
Q Duty (MW)

CO2/SO2 Lean Flue Gas to Stack

ASH PCD

CO2/SO2 REMOVAL

PURGE/RECYCLE

CALCINER

15% - 20% Parasitic Energy Consumption (with compression)
Overall Electricity Production Efficiency

Net Efficiency, HHV (%)

- Air Fired SC/Air* Base
- Air Fired USC/Air*
- Econoamine SC/Air*
- Oxy Fuel SC/ASU*
- CCR SC/Air

*Ciferno et al. 2008

Sakadjian et al, 2009

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Conclusions

- Greater than 90% CO₂ and ~100% SO₂ Removal at a C:C of 1.3
- Ca(OH)$_2$ has highest reactivity leading to low Ca:C and residence time
- 13 hours of continuous operation conducted and repeatable results obtained
- Sorbent reactivity maintained constant over multiple cycles
- Reduction in sorbent circulation and make up rate
- Low parasitic energy requirement of 15% -20% for CCR depending on heat integration
- Competitive with existing CO₂ control technologies