CO₂ capture from industrial sources by high temperature sorbents

Matteo C. Romano, Giampaolo Manzolini, Stefano Consonni
Politecnico di Milano, Department of Energy
Group of Energy Conversion Systems (GECoS)

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SUMMARY

• High temperature sorbent systems for post-combustion capture
  - Integration in power plants
  - Integration in cement plants

• High temperature sorbent systems for pre-combustion capture
  - Sorption enhanced reforming for power generation and hydrogen production
  - Sorption enhanced WGS in power plants and integrated steel mills
  - Sorption enhanced gasification for biofuels production

• Conclusions
CALCIUM LOOPING PROCESS

\[ \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \quad \Delta H_{298 \text{K}} = -178 \text{ kJ/mol} \text{ (or 4.04 MJ/kg}_{\text{CO}_2}) \]
**CALCIUM LOOPING PROCESS**

- Fast carbonation kinetics at around 650°C
  \[ \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \]

- Regeneration in concentrated \( \text{CO}_2 \) atmosphere at >900°C
  \[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]

![Graph showing carbonation and calcination temperatures](image-url)
SORPTION ENHANCED WATER GAS SHIFT

SEWGS sorbents are suitable to $\text{CO}_2$ separation at average temperatures, typical of WGS reaction (350-400°C).
Sorbent regeneration by pressure swing, facilitated by steam purging.

Water-Gas Shift:  \[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \]

$\Rightarrow$ Carbonate Formation $\Rightarrow$

$\leftarrow$ Decarbonisation $\leftarrow$

$\Rightarrow$ $\text{H}_2$

$\leftarrow$ $\text{H}_2\text{O}$

$\Rightarrow$ $\text{H}_2\text{O}$

$\leftarrow$ $\text{CO}_2$

$\leftarrow$ CO

$\leftarrow$ H$_2$O

$\Rightarrow$ H$_2$
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CAL FOR COAL POWER PLANTS

STATE OF THE ART – TRL 6-7

• The technology has been demonstrated at 0.1-2 MW-scale in different lab-scale and pilot facilities and is technically ready for scale-up.

<table>
<thead>
<tr>
<th></th>
<th>La Pereda (Spain)</th>
<th>Darmstad (Germany)</th>
<th>IFK (Germany)</th>
<th>La Robla (Spain)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Thermal input</strong></td>
<td>1.7 MW\textsubscript{th} referred to carbonator</td>
<td>1 MW\textsubscript{th} referred to calciner</td>
<td>50-230 kW\textsubscript{th} referred to carbonator</td>
<td>300 kW\textsubscript{th} referred to the biomass fed to carbonator</td>
</tr>
<tr>
<td><strong>Configuration</strong></td>
<td>Calciner: CFB Carbonator: CFB</td>
<td>Calciner: CFB Carbonator: CFB</td>
<td>Calciner: CFB Carbonator: FFB\textsuperscript{<em>} and TFB\textsuperscript{</em>}</td>
<td>Calciner: CFB Carbonator: CFB</td>
</tr>
<tr>
<td><strong>Height</strong></td>
<td>Calciner: 15 m Carbonator: 15 m</td>
<td>Calciner: 11.4 m Carbonator: 8.6 m</td>
<td>Calciner: 10 m Carbonator: 10 m (FFB\textsuperscript{<em>}), 6 m (TFB\textsuperscript{</em>})</td>
<td>Calciner: 12 m Carbonator: 12 m</td>
</tr>
<tr>
<td><strong>Diameter</strong></td>
<td>Calciner: 0.75 m Carbonator: 0.65 m</td>
<td>Calciner: 0.4 m Carbonator: 0.59 m</td>
<td>Calciner: 0.21 m Carbonator: 0.21 m (FFB\textsuperscript{+}), 0.33 m (TFB\textsuperscript{+})</td>
<td>Calciner: 0.4 m Carbonator: 0.4 m</td>
</tr>
<tr>
<td><strong>Flue gas source</strong></td>
<td>Integrated with power plant</td>
<td>Flue gas from coal burner</td>
<td>Synthetic flue gas</td>
<td>Flue gas generated in carbonator</td>
</tr>
<tr>
<td><strong>Calciner operation</strong></td>
<td>Oxy-fired with coal</td>
<td>Oxy-fired with coal/propane</td>
<td>Oxy-fired with coal and flue gas recycle</td>
<td>Air-fired with biomass</td>
</tr>
</tbody>
</table>

*Abanades et al., 2015. Emerging CO\textsubscript{2} capture systems. Int J Greenh Gas Con, 40, 126-166.*
KEY ISSUES ON Ca-LOOPING PROCESS IN COAL PLANTS

CHALLENGES:
• To reduce solids make-up and purge:
  → Keep high sorbent activity, e.g. through sorbent reactivation techniques (recarbonation)
  → Avoid coal ash buildup in the CaL loop

OPPORTUNITIES:
• To avoid oxyfuel calciner and therefore avoid ASU:
  → Indirectly heated calciner through high temperature heat exchanger
  → Directly heated calciner through high temperature circulating solids
• To increase power plant flexibility by exploiting CaO as high temperature thermochemical storage material.

Martínez, I. et al., 2016. Review and research needs of Ca-Looping systems modelling for post-combustion CO$_2$ capture applications. *Int J Greenh Gas Control* 50, 271-304.
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CA-LOOPING FOR CEMENT PLANTS

Key information on cement plants:

- 60% of CO₂ emissions derive from CaCO₃ calcination and cannot be reduced by fuel switch, fuel decarbonization or energy efficiency.
- Modern cement plants are thermally very efficient: waste heat is not enough to capture high amounts of CO₂ by conventional post-combustion amines.

![Graph showing global CO₂ emissions of the cement industry from 2010 to 2050.](source: IEA Cement Roadmap)

**Reduction by:**
- Increase of energy efficiency
- Alternative fuels use
- Reduction of clinker share

**CCS**
CA-LOOPING FOR CEMENT PLANTS

Ca-LOOPING PROCESS INTEGRATION OPTIONS:

1. **Cement plant-power plant coupling:** CaO-rich spent sorbent from a CaL power plant is used as feed for the cement plant in place of CaCO$_3$

2. **Post-combustion capture configuration:** CaL process is integrated in the cement plant with a conventional post-combustion capture configuration

3. **Integrated CaL configuration:** the CaL process is integrated within the cement production process by sharing the same oxyfuel calciner

No real need of reducing solids make-up and purge: CaCO$_3$ needed for cement production largely exceeds the CaL process needs.

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*Spinelli M. et al., 2016.* Integration of Ca-Looping systems for CO$_2$ capture in cement plants. *GHGT-13 Conference.*
TAIL-END CAL CONFIGURATION

- Carbonator removes CO₂ from cement plant flue gas → highly suitable for retrofit
- CaO-rich purge from CaL calciner used as feed for the cement kiln
- CFB CaL reactors: d₅₀=100-250 μm
  Particle size for clinker production d₅₀=10-20 μm → CaL purge milled in the raw mill at low temperature
INTEGRATED CaL CONFIGURATION

- CaL carbonator highly integrated within the preheating tower, on rotary kiln gas
- CaL calciner coincides with the cement kiln pre-calciner
- Calcined raw meal as CO$_2$ sorbent in the carbonator
- Sorbent has small particle size (d$_{50}$=10-20 μm) → entrained flow reactors
CA-LOOPING FOR CEMENT PLANTS

Ca-LOOPING PROCESS INTEGRATION OPTIONS:

1. Cement plant-power plant coupling:
   - Excellent expected performance ✓
   - Easily retrofittable with low cost ✓
   - Logistic problem: a very large power plant has to be built next to the cement plant ✗

2. Post-combustion capture configuration:
   - Low uncertainty in the feasibility of the process (very similar to application in power plants) ✓
   - Very high CO₂ capture expected ✓
   - Two calciners are present in the system, leading to high fuel consumptions ✗

3. Integrated CaL configuration:
   - High CO₂ capture efficiency without modifying rotary kiln operation (no need of kiln oxyfiring). ✓
   - Higher thermal efficiency and lower fuel consumptions expected (compared to option 2) ✓
   - New carbonator design and fluid-dynamic regime: fluid-dynamics, heat management and sorbent performance need verification ✗
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HT CaO-based sorbents for natural gas

Process integration strategies based on sorption-enhanced reforming are preferable with natural gas.

HIGH TEMPERATURE HEAT FROM CARBONATION EFFICIENTLY CONVERTED INTO CHEMICAL ENERGY BY STEAM METHANE REFORMING
**Benchmark Pre-combustion Capture Configuration**

Pre-combustion CO$_2$ capture plants based on conventional reforming technologies:

- **SMR / ATR**
  
  \[
  \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad (\text{SMR}) \quad \Delta H^\circ_r = +205.9 \text{ kJ/mole}
  \]

- **HT-WGS**

- **LT-WGS**

- **CO$_2$ absorption**

• 3 reactors for H$_2$-rich syngas production
• Additional process for CO$_2$ separation
SORPTION ENHANCED REFORMING OF NATURAL GAS

\[
\begin{align*}
\text{CaCO}_3(s) & \rightarrow \text{CaO}(s) + \text{CO}_2 \quad \Delta H^{\circ}_r = +179.2 \text{ kJ/mole} \\
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2 \text{ (SMR)} \quad \Delta H^{\circ}_r = +205.9 \text{ kJ/mole} \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \text{ (WGS)} \quad \Delta H^{\circ}_r = -41.2 \text{ kJ/mole} \\
\text{CaO}(s) + \text{CO}_2 & \rightarrow \text{CaCO}_3(s) \text{ (carb)} \quad \Delta H^{\circ}_r = -179.2 \text{ kJ/mole} \\
\text{CH}_4 + 2\text{H}_2\text{O} + \text{CaO}(s) & \rightarrow \text{CaCO}_3(s) + 4\text{H}_2 \quad \Delta H^{\circ}_r = -14.5 \text{ kJ/mole}
\end{align*}
\]

Process intensification:
• Contemporary H\textsubscript{2} production and CO\textsubscript{2} separation in a single adiabatic reactor
• High hydrogen yield in a single step thanks to CO\textsubscript{2} removal
SORPTION ENHANCED REFORMING OF NATURAL GAS

Sorption enhanced reforming works nicely in the hydrogen production step. Challenges are in the sorbent regeneration step.

- **Hydrogen should be produced at high pressure** because hydrogen compression is very energy expensive, **BUT** sorbent regeneration at high pressure requires **too high temperatures** for the stability of sorbent and catalyst.
- **Packed beds** allow easier pressure swing, **BUT** heat management with high reaction heat is challenging.
- **Fluidized beds** allow easier heat management (uniform temperatures in reactors), **BUT** pressure swing is very challenging (especially at high temperatures).
- **Hydrogen may be produced in interconnected fluidized beds at low pressure** to avoid pressure swing, **BUT** hydrogen compression is needed for most industrial uses.
Sorption Enhanced Reforming of Natural Gas

- Regeneration requires temperatures of 850-900°C at atmospheric pressure.
  - High temperature heat has to be provided to the calciner.

- Oxyfuel combustion is an option, but oxygen production is expensive and may lead to hot spots, causing materials degradation.

- Indirect heating of the calciner is another option, but very high temperature heat transfer surfaces are needed.

- Heating by an additional high temperature CLC loop is also an option, but an additional CLC material is needed and increased process complexity.

In addition to process development, materials development is key challenge of Sorption Enhanced Reforming processes.
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SEWGS FOR INTEGRATED STEEL MILLS

Key information on integrated steel mills:
• Iron and steel industry is also among the largest industrial CO\textsubscript{2} emitters

SEWGS FOR INTEGRATED STEEL MILLS

How does an integrated steel mill work:

Coke produced in coke oven

Iron reduced by coke in a blast furnace producing pig iron

Carbon and impurities removed in BOF by oxygen injection

Excess process gases are burned in a power plant (steam or combined cycle)
SEWGS FOR INTEGRATED STEEL MILLS

CO₂ emissions:

- Coke oven: 15-20%
- Hot stoves: 15-30%
- Sinter plant and lime kiln: 10-25%
- Power plant: 40-70%
A first straightforward application of SEWGS process is to decarbonize the steel mill gas (mainly BFG) used in the power plant.

BFG has a very high carbon content: 20-30%CO, ~25%CO₂, 40-55%N₂. Specific emissions from a BFG combined cycle: ~1400 kg/MWh (~2x the specific emissions from an advanced coal steam plant)

Operating on the power plant gases does not affect the steel production process.

Hydrogen separation technologies are not suitable for BFG decarbonization, due to the high BFG N₂ content. SEWGS is a CO₂ separation technology.

Maximum CO₂ capture efficiency is limited by steam availability for high steam consuming technologies (e.g. MEA). SEWGS requires low amounts of steam.
SEWGS IN INTEGRATED STEEL MILLS POWER PLANT

Steel Plant

SEWGS: WGS+CO₂ separation

Gas humidification and HT-WGS

H₂/N₂/H₂O to gas turbine

Capture

Steel mill off-gas

CO₂ cooling and compression

Rinse & purge steam

Power Island

Steel mill gas compression
## SEWGS IN INTEGRATED STEEL MILLS POWER PLANT

<table>
<thead>
<tr>
<th>Power balance, MWₑ</th>
<th>Ref, no capt.</th>
<th>Post-comb. MEA capt.</th>
<th>Pre-comb. MDEA capt.</th>
<th>SEWGS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Net efficiency, %₁₀₀_LHV</td>
<td>52.3</td>
<td>38.6</td>
<td>34.6</td>
<td>37.7</td>
</tr>
<tr>
<td>CO₂ emission, kg/MWhₑ</td>
<td>1339</td>
<td>871</td>
<td>147</td>
<td>149</td>
</tr>
<tr>
<td>CO₂ avoided, %</td>
<td>-</td>
<td>35.0</td>
<td>89.3</td>
<td>88.9</td>
</tr>
<tr>
<td>SPECCA, MJ₁₀₀_LHV/kgCO₂</td>
<td>-</td>
<td>5.20</td>
<td>2.94</td>
<td>2.24</td>
</tr>
</tbody>
</table>

- With conventional MEA process, maximum CO₂ avoidance is limited by steam shortage, while MDEA and SEWGS can achieve ~90% of CO₂ capture efficiency.
- SEWGS allows achieving much higher efficiency and better SPECCA (specific primary energy consumption for CO₂ avoided).

*Gazzani et al., 2015.* CO₂ capture in integrated steelworks by commercial-ready technologies and sewgs process. *Int. J. Greenh. Gas Control, 41, 249-267.*
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Solid material with Ca-based sorbent is circulated between the gasifier-carbonator and the combustor-calciner to:
- produce a N\textsubscript{2}-free syngas with no need of pure oxygen production and external heating of the reactor;
- absorb CO\textsubscript{2} in the gasifier and adjust C/H content in the syngas.

**SORPTION ENHANCED GASIFICATION (SEG)**
Possibility of CO₂ capture and storage by oxyfuel combustion in the SEG combustor.

Gasifier-carbonator
600-700°C

- Biomass
- Steam

Syngas
(N₂-free syngas)

CaCO₃ + char
Solid circulation

Combustor-calciner
800-900°C

- Oxygen
- CO₂/H₂O
- CaO
- Bed material
- Limestone
- Biomass (if needed)
Sorption Enhanced Gasification (SEG)

By controlling the SEG process parameters (solid circulation, Ca/C ratio in the gasifier, gasifier temperature, S/C ratio), syngas composition can be adjusted to match with the downstream synthesis process.

Martínez et al., 2016. Energy, 113, 615-630.
SEG + SEDMES PROCESSES FOR BIO-DME

Biomass to DME with conventional process

Biomass → Gasification process → Tar/PM removal → WGS unit → CO₂ separation → H₂S separation

Air (if ind. gas) → O₂ → H₂/CO/CO₂ recycle

MeOH synthesis → MeOH separation → MeOH recycle

DME synthesis → DME separation → DME

Biomass recycle H₂/CO/CO₂ recycle

Optional CO recycle (smaller for given yield)

Biomass to DME by FLEDGED process

Biomass → SEG process → Tar/PM removal → H₂S separation → SE-DME synthesis → DME separation → DME

ASU

Air
If integrated with an electrolysis unit providing renewable hydrogen, SEG process parameters can be adjusted to produce syngas suitable for SEDMES process.

Contribution to electric grid stability by power-to-liquid
CONCLUSIONS

• High temperature CO$_2$ sorbent systems are applicable through a wide variety of process integration options.

• Promising application of post-combustion Ca-looping processes are power plants with improved flexibility and cement plants. For cement plants, technical demonstration is needed for the highly integrated Ca-looping process (TRL2-3).

• Sorption enhanced reforming with high temperature sorbent systems appears as the preferable option for natural gas plants. A wide variety of possible (still immature: TRL3-4) process integration options exists, to be assessed in conjunction with material development.

• SEWGS process (now at TRL4-5) is ready for demonstration in integrated steel mills (TRL6). This appears as the most promising application for SEWGS that may open further opportunities for application in power plants and hydrogen plants.

• SEG process is not new, but flexible operation to provide electric grid service has to be demonstrated. This represents an opportunity in electric mix with high share of intermittent renewables.
Thank you

Contact: matteo.romano@polimi.it

www.polimi.it

www.gecos.polimi.it
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