Carbon Dioxide Control Technologies for the Cement Industry

Volker Hoenig, Düsseldorf, Germany

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Carbon Dioxide Control Technologies for the Cement Industry

1. Introduction
2. The cement clinker burning process
3. Assessment of carbon dioxide control technologies
   3.1 Pre-combustion technologies
   3.2 Oxyfuel technology
   3.3 Post-combustion technologies
4. Preliminary research results (Oxyfuel technology)
   4.1 Impact on raw meal decarbonation
   4.2 Modeling of the clinker burning process with Oxyfuel operation
The German Cement Works Association (VDZ)

Activities:
- Mortar and concrete
- Chemistry and mineralogy
- Environmental expertise
- Plant technology investigations
- Environmental measurements
- Certification
- Knowledge transfer

↑ The Research Institute of the Cement Industry, Düsseldorf / Germany

For further information: www.vdz-online.de
The European Cement Research Academy (ECRA)

• has been founded by VDZ in 2004
• Members (> 40) are cement companies and associations from Europe, Asia, Australia, US

• **objectives**
  → know how transfer
  → joint research

• **activities**
  → seminars and workshops
  → research programmes
    - carbon capture technologies for the cement industry
    - continuous measurement of biomass CO₂ in stack gases

For further information: www.ecra-online.org
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Production of cement

- Raw material: quarry, blending basin
- Raw meal: ESP
- Clinker: storage bin, cement mill
- Cement: storage bin, dispatch

Gas and solid production flowchart.
Clinker burning process

- Preheater exit gas
- Kiln feed
- Fuel
- Tertiary air
- Secondary air
- Cooler exhaust gas
- Primary air
- Fuel
- Cooling air
- Clinker
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3.1 Pre-combustion technologies

- **Natural gas**
  - Reforming process
  - $\rightarrow$ $H_2$
  - $\rightarrow$ $CO_2$
  - $\rightarrow$ Combustion process
  - $\rightarrow$ Storage

- **Coal**
  - Gasification process
  - $\rightarrow$ $H_2$
  - $\rightarrow$ $CO_2$
  - $\rightarrow$ Combustion process
  - $\rightarrow$ Storage
Scheme of gasification process

• Partial oxidation for heat supply
  \[ \text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + \text{H}_2 \]

• Gasification of solid carbonaceous matter
  \[ 2 \text{C} + \text{O}_2 \rightarrow 2 \text{CO} \]
  \[ \text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \]

• CO shift for hydrogen synthesis
  \[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]
Pre-combustion technologies: level of implementation

- Steam reforming is the predominant technology for H₂ production worldwide.
- IGCC (Integrated Gasification Combined Cycle) demonstration plants since the 1970s.
- IGCC can be realized with or without CO₂ capture.
- Today no IGCC plant with capture technology in operation.
- Two IGCC projects planned with CO₂ capture:
  - Australia (100 MW)
  - Germany (450 MW)
- CO₂ capture costs for new IGCC plant: 13-37 $/t CO₂ (CO₂ capture by physical absorption).
Applicability of pre-combustion technologies to clinker burning process (1)

Hydrogen from syngas of gasification processes as fuel for cement kiln burners?

- Hydrogen has different properties as actual fuels:
  - handling/feeding must be solved
  - pure $\text{H}_2$ cannot be used in kiln firing
- $\text{H}_2$ flames have low heat transfer by radiation
  - temperature profile in the kiln
  - injection of raw meal or clinker dust
Applicability of pre-combustion technologies to clinker burning process (2)

Hydrogen from syngas of gasification processes as fuel for cement kiln burners?

• New combustion technologies required:
  – non-carbonaceous flame ingredients
  – new burner technologies
    for increasing heat transfer

• Only abatement of fuel CO$_2$
  $\rightarrow$ only 1/3 of CO$_2$ emission is captured

$\Rightarrow$ hardly promising for clinker burning process
3.2 Oxy-fuel Technology

- Air-separation plant: $O_2$-production
- Combustion: $O_2/CO_2$-atmosphere
- Flue gas: $CO_2$, water steam

Diagram:
- Air separation
- Flue gas recirculation
- Clinker burning process
- N$_2$ for other use or to atmosphere
- Flue gas (CO$_2$-rich)
- Clinker
- To separation or liquefying

Raw materials:
- Air
- Fuel
- Raw material
Applicability of oxy-fuel technology to clinker burning process

- Oxygen production by air separation is state of the art (by freezing or membranes)
- Oxy-fuel technology is state of the art in other industries, e.g. for glass production
- New combustion technologies required, e.g.:
  - Oxy-fuel burner
  - Waste gas recirculation
- Modifications of plant design, e.g.
  - Dimensions of kiln, cooler, preheater
  - Gas recirculation including dedusting, cooling
- Impact on reactions (e.g. decarbonation) and clinker quality
3.3 Post-combustion technologies

- Absorption technologies:
  - chemical absorption (Econamine®, Benfield®, etc.)
  - physical absorption (Selexol®, Rectisol®, etc.)
- Membrane processes
- Solid sorbent processes
  - physisorption processes
  - mineral carbonation
  - carbonate looping

→ the higher the CO₂ concentration the higher the capture efficiency
→ end-of-pipe technologies; retrofit to existing plants possible
Absorption technologies are most developed today

- Chemical absorption:
  - amines (e.g. MEA) or inorganic salt solutions (e.g. K₂CO₃) as absorbent
  - high energy demand for solvent regeneration
  - very low dust, SO₂ and NO₂ concentration required
  - CO₂ capture costs for new coal-fired power plants: 29-51 $/t CO₂

- Physical absorption:
  - solvents as absorbent (e.g. methanol)
  - high CO₂ content required

↑ CO₂ capture by chemical absorption (fertilizer plant in Malaysia)
Simplified flow sheet of chemical absorption process for CO$_2$ capture
Application of CO₂ capture with amine absorption in a Norwegian 3000 t/d cement plant (pilot study)

**Technical requirements**
- NOₓ abatement with SNCR
- SO₂ abatement with wet scrubber
- Waste heat recovery boiler
- CO₂ capture amine absorption
- Amine recovery with stripper
- Gas fired boiler

**Investment costs in mio €**

<table>
<thead>
<tr>
<th>Component</th>
<th>Cost in mio €</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste gas cleaning</td>
<td>8</td>
</tr>
<tr>
<td>Waste heat recovery boiler</td>
<td>7</td>
</tr>
<tr>
<td>CO₂ capture</td>
<td>32</td>
</tr>
<tr>
<td>CO₂ drying and compression</td>
<td>28</td>
</tr>
<tr>
<td>Boiler</td>
<td>28</td>
</tr>
<tr>
<td>Total</td>
<td>110</td>
</tr>
</tbody>
</table>

**Operating costs in mio €/year** | 32

**Total costs in €/t CO₂** | 45

2006 data
Carbonate looping

Raw material

Cement kiln

Fuel
Air
Energy

Clinker

Carbonator

CaO

CaCO₃

Exhaust gas (CO₂ poor)

Calciner

Exhaust gas (CO₂ rich)

Energy

Degraded CaO

Fresh CaCO₃
Synergy of cement and power plants

One 3,000 tpd kiln utilizes degraded sorbent (after 30 loops) of three 800 MW<sub>el</sub> power plants.
### Assessment of CO₂ capture technologies

<table>
<thead>
<tr>
<th>Capture technology</th>
<th>Availability on scale</th>
<th>Applicability in the cement industry</th>
<th>Reduction of CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>research</td>
<td>demo</td>
<td>industrial</td>
</tr>
<tr>
<td><strong>Pre-Combustion</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- reforming / gasification</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td><strong>Oxyfuel</strong></td>
<td>X</td>
<td>(X)</td>
<td></td>
</tr>
<tr>
<td><strong>Post-Combustion</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- absorption</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>- membranes</td>
<td>X</td>
<td>(X)</td>
<td></td>
</tr>
<tr>
<td>- solid sorption process</td>
<td>X</td>
<td>(X)</td>
<td></td>
</tr>
<tr>
<td><strong>Hybrid Systems</strong></td>
<td></td>
<td></td>
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<tr>
<td>- solar cement plant</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- carbonate looping (cement / power plant)</td>
<td>X</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Potential future application of CCS in the cement industry

• **Short-term:** no relevance due to
  - very high costs (> 50 $/t CO₂ avoided)
  - not existing availability of capture technologies
• **Medium-term:** depends on policy decisions and technical developments
  - climate policy (incl. USA, China, India)
  - cost reductions due to technical developments (target value: 20-30 $/t CO₂)
• **Long-term:** high relevance possible if
  - other options are exhausted
  - worldwide comparable costs for cement production would be introduced
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Modeling of the clinker burning process

- clinker burning process (dry)
- chemical / mineralogical reactions
- heat transfer
- process technology
- energy and material balances
  (approximately 1000 balance spaces)
Schematic diagram of the clinker burning process (reference)
Schematic diagram of the clinker burning process with oxyfuel operation (based upon assumptions for the simulation calculations)
Summary and outlook

• CO₂ capture technologies are not technically available for the cement industry
• Pre-combustion technologies are not promising because only fuel CO₂ would be captured
• Oxy-fuel technology is state-of-the-art in a few other industry sectors and seems to be promising for new kilns
• Post-combustion technologies are state-of-the-art in other industry sectors, but on relatively small scale
• From a today's point of view CCS is by far too expensive for the cement industry
• Huge research efforts would be/are necessary to develop CO₂ capture technologies for the cement production process

Ecra research project shall enable the cement industry to give scientifically based reliable answers to political requirements in the future