Present challenges for modern Cement Plants

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XXVII Technical Congress FICEM-APCAC
Agenda

- Energy-Efficiency
- CO$_2$-Emissions
- Clinker
- Cement
- Summary / Discussion
Efficiency levels of various industrial processes

- Cement plant
- "New" power plant
- "Existing" power plant
- "AF" power plant
- Waste incineration plant

Efficiency (%)

Source: vdz
Specific fuel energy requirement

![Graph showing specific fuel energy input over the years from 1950 to 2010. The graph indicates a significant decrease in fuel energy input, reaching a level of approximately 3600 kJ/kg clinker in recent years. The theoretical fuel energy requirement and drying process are also depicted.](source: vdz)
Targets for Decrease in Energy Intensity, 2010-2050
(World Business Council for Sustainable Development)
Change of circumstances for Cement Production (I)

- **30 years before**
  - 100 % fuel or coal
  - 1 fuel
  - simple power supply
  - 1 major product (CEM I)
  - $\text{CO}_2$ ?

- **Today**
  - 5 and more combustibles
  - spot quantities possible
  - peak-/off-peak-E-supply
  - special E-net-rates for atypical power consumption
  - large variety of composite cements
  - emission trading
  - $\text{CO}_2$ monitoring
CO$_2$-emissions in the cement industry

1. Raw material related emissions:
   
   - clinker: 0,53 t CO$_2$/ t clinker
   - cement: 0,40 t CO$_2$/ t cement

   ⇒ Decarbonation of limestone

2. Fuel related emissions:
   
   - 0,34 t CO$_2$/ t cement

   ⇒ Combustion of fossil fuels

3. Energy related emissions from electricity consumption:
   
   - 0,29 t CO$_2$/ t cement

   ⇒ Grinding, cooling air etc.
Targets for CO$_2$ total emissions, Gtonne 2010-2050
(World Business Council for Sustainable Development)
Cost optimization in the cement industry

Alternative Fuels

+ lower costs
+/- process
- logistics
- investments
- surveillance

Lower clinker content

+ lower CO₂ costs
- higher grade clinker
- logistics/storage
- investments ?
- quality control
- lower production costs ?
Change of circumstances for Cement Production

• 30 years before
  • 1 major product (CEM I)

• Today
  • large variety of composite cements
  • HPC also with composite cements
  • 42,5 R and 52,5 R
  • extreme fine grinding
  • combo grinding
  • high performing Clinkers required
Early strength

Higher fineness:

- CEM II/A-S (15 – 20 % S) + 200 to 500 Blaine
- CEM II/A-V (15 - 20 % V) + 800 to 1000 Blaine
- CEM II/A-LL (15 - 20 % LL) +1000 to 1200 Blaine

Activating grinding aids:

Possible gain of early strength 2 – 4 N/mm² (after 1 or 2 d)
Composite Cements

Grindability of different main constituents acc. Zeisel for 4000 Blaine

<table>
<thead>
<tr>
<th>Constituent</th>
<th>kWh/t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clinker</td>
<td>40 – 60</td>
</tr>
<tr>
<td>Fly ash &gt; 45 µm</td>
<td>20 – 30</td>
</tr>
<tr>
<td>Limestone</td>
<td>5 – 15</td>
</tr>
<tr>
<td>Slag</td>
<td>50 – 80</td>
</tr>
</tbody>
</table>
Targets for cement to clinker ratio, 2010-2050
(World Business Council for Sustainable Development)
Targets for alternative fuels use, 2010-2050
(World Business Council for Sustainable Development)
Alternative fuel utilization in German cement plants

Target for 2050 (WBCSD) 37%

Source: VDZ
Petcoke an “Alternativ fuel”

Secondary fuel from oil refinery coker units
  “Petroleum coke” or “Petcoke”
High Carbon content
  High calorific value (~ 30GJ/t)
  Low volatiles (<11%)
Low ash content
  Very low ash content <1%

High Sulfur content
  2-6% (price strongly depending on the S-content)
Going from coal to petcoke: What changes?

Raw coal
- Uniform blending petcoke/raw coal (if petcoke < 100%)

Coal mill
- Requires higher fineness (due to less volatiles)
- Affects mill capacity (different grindability and higher fineness, evaluate by trial)

Kiln
- Low ash and high CV
- Low reactive fuel, ignition delayed
- High sulfur causing more plugging (kiln inlet/preheater)
- Stable and controlled kiln process to minimize sulfur cycles

Clinker quality
- More $\text{SO}_3$ in clinker (better strength development, red. gypsum addition)
Rules: Basic potential & supply

Alkali/sulfur

For a first conservative approach, go for following total inputs:

<table>
<thead>
<tr>
<th>SO₃ inputs</th>
<th>&lt; 1.5 % (clinker basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar A/S</td>
<td>&gt; 0.8</td>
</tr>
</tbody>
</table>

On precalciner kilns even better result are achievable, under ideal conditions:

<table>
<thead>
<tr>
<th>SO₃ inputs</th>
<th>&lt; 2.5 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar A/S</td>
<td>down to 0.4</td>
</tr>
</tbody>
</table>

Petcoke supply

Top grade (2%S, HGI>55)
High grade (4%S, HGI>55)
Low grade (6/7% S, HGI 40)
Raw coal/pet coke preparation

**Controlled** mixing from two feed hoppers

Coal mill

**Recommended fineness for 100% pet coke**

<table>
<thead>
<tr>
<th>R 90 µ</th>
<th>&lt; 5 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>R 200 µ</td>
<td>&lt; 1%</td>
</tr>
</tbody>
</table>

Determine mill output by trial (HGI can be misleading) depending on the “shot”-amount
Curcuits inside rotary kilns
Hot meal – Indication of process stability

Risk of coating due to SO\textsubscript{3} and Cl concentration in hot meal

- Hot meal analysis
  - Adequate frequency, usually once per shift
  - Monitor LOI (decarbonation), SO\textsubscript{3}, K\textsubscript{2}O
  - SO\textsubscript{3} < 5 % (if chlorine < 0.5%)
Preheater care

Preheater cleaning

Add poking possibilities and air cannons (can be up to 100) where coatings occur.
Removing of heavy blockages can also be done with CARDOX blasting on demand.

Anti coating SiC-refractories in the riser duct
Observation of the Temperature-profile inside the inlet/rising duct
Clinker chemistry

Alkalisulfate on Alit
• $K_2SO_4$ has a melting point at 1069°C
• evaporation/condensation-circuits will develop

• low alkali/sulfate ratio may have an impact on setting
• high alkali/sulfate ratio $\Rightarrow K_2SO_4$

  - High solubility in water
  - much quicker than Hemihydrates or Anhydrite
  - may help the workability
### Reaction of Volatile Elements with Refractory Materials

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Sulfates</th>
<th>Chlorides</th>
<th>Alkalis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(sulfides)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basic bricks</td>
<td>reaction</td>
<td>infiltration</td>
<td>infiltration, reaction</td>
</tr>
<tr>
<td></td>
<td>($C_2S, C_3MS_2, CMS, KFeS_2$)</td>
<td></td>
<td>($KFeS_2$)</td>
</tr>
<tr>
<td>Alumina bricks</td>
<td>reaction</td>
<td>infiltration</td>
<td>reaction</td>
</tr>
<tr>
<td></td>
<td>($C_4A_3SO_3$)</td>
<td></td>
<td>($KAS_4, KAS_6$)</td>
</tr>
<tr>
<td>Castables</td>
<td>reaction</td>
<td>infiltration</td>
<td>reaction</td>
</tr>
<tr>
<td></td>
<td>($C_4A_3SO_3$)</td>
<td></td>
<td>($KAS_4, KAS_6$)</td>
</tr>
<tr>
<td>Kiln shell, Metallic anchors</td>
<td>reaction</td>
<td>catalytic reaction</td>
<td>reaction</td>
</tr>
<tr>
<td></td>
<td>($NiS, Cr_2S_3$)</td>
<td></td>
<td>(chromate formation)</td>
</tr>
</tbody>
</table>
Essential Chemical Reactions of Kiln Atmosphere Compounds with Basic Brick Compounds

Oxidizing Atmosphere

2 $C_2S + MgO + SO_3 \rightarrow CaSO_4 + C_3MS_2$

$C_3MS_2 + MgO + SO_3 \rightarrow CaSO_4 + 2 CMS$

$CMS + MgO + SO_3 \rightarrow CaSO_4 + M_2S$

2 $CaSO_4 + K_2SO_4 \rightarrow 2 CaSO_4K_2SO_4$

3 $MgO.Al_2O_3 + 4 CaO + SO_3 \rightarrow 4CaO.3Al_2O_3SO_3 + 3 MgO$
Essential Chemical Reactions of Kiln Atmosphere Compounds with Basic Brick Compounds

Reducing Atmosphere

\[
\begin{align*}
4 \text{MgO} + 2 \text{K}_2\text{O} + 4 \text{FeO.Al}_2\text{O}_3 &+ 8 \text{SO}_2 &\rightarrow & 4 \text{KFeS}_2 + 4 \text{MgO.Al}_2\text{O}_3 + 11 \text{O}_2 \\
\text{MgFe}_2\text{O}_4 + \text{K}_2\text{O} + 4 \text{SO}_2 &\rightarrow & 2 \text{KFeS}_2 + \text{MgO} + 6 \text{O}_2 &\text{red. (1)} \\
2 \text{KFeS}_2 + 8 \text{O}_2 &\rightarrow & \text{K}_2\text{SO}_4 + \text{Fe}_2\text{(SO}_4)_3 &\text{ox. (2)} \\
\text{PbO} + \text{SO}_3 &\rightarrow & \text{PbS} + 2 \text{O}_2 \\
2 \text{CO} &\rightarrow & \text{CO}_2 + \text{C} &\text{(Boudouard’s equilibrium)}
\end{align*}
\]
Essential Chemical Reactions of Kiln Atmosphere Compounds with Alumina Brick Compounds

\[
\begin{align*}
A_3S_2 + 16 SiO_2 + 3 K_2O & \rightarrow 3 KAS_6 \quad \text{(feldspar formation)} \\
A_3S_2 + 10 SiO_2 + 3 K_2O & \rightarrow 3 KAS_4 \quad \text{(leucite formation)} \\
2 A_3S_2 + 8 SiO_2 + 6 K_2O & \rightarrow 6 KAS_2 \quad \text{(kalsilite formation)} \\
11 Al_2O_3 + K_2O + Na_2O & \rightarrow (K,N)A_{11} \quad \text{(ß-corundum formation)} \\
K_2SO_4.2CaSO_4 + H_2O & \rightarrow CaSO_4.K_2SO_4.H_2O \quad \text{(syngenite formation)} \\
2 CaSO_4 + K_2SO_4 & \rightarrow 2CaSO_4.K_2SO_4 \\
\end{align*}
\]
Spalling of a basic brick caused by elasticity differences due to infiltrations

Corrosion by sulfates

Crack formation due to elasticity differences

Infiltration and condensation of chlorides
Conflicting goals?
POSIBLE MEASURES TO REACH GOAL

- Reduction in the clinker to cement ratio
- Lower clinker burnability
- Higher quality clinker
- CO2 reduction
- Reduction in energy intensity
- Use of fluxing agents?
- Higher energy consumption for clinker production
- Lower clinker burnability
- Higher C₃S content
- Changes in clinker chemistry
- Higher quality clinker
- Reduction in the clinker to cement ratio
Conflicting goals?

POSIBLE MEASURES TO REACH GOAL

- CO2 reduction
  - Reduction in energy intensity

Use of fluxing agents?

CONFLICT

- Higher energy consumption for clinker production
- Lower clinker burnability
- Higher C₃S content
- Changes in clinker chemistry
- Higher quality clinker

Reduction in the clinker to cement ratio
Conflicting goals?

POSIBLE MEASURES TO REACH GOAL

- Finer Grinding
  - Increased wear of grinding media
  - Increased energy consumption in cement grinding

- Reduction in the clinker to cement ratio

- CO2 reduction
- Reduction in energy intensity
Wherever in the world you are, the road ahead is full of new challenges.

But you are not alone

Refratechnik is there, to help you meet these challenges!
Thank you very much for your kind attention