NOx in Cement Clinker Production - Formation and Measures to minimize NOx-Emission

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NOx – Emissions by Source in EEA member countries (2009)

Fig. 4: Sector share of nitrogen oxides emissions (EEA member countries)

- Road transport: 38.4%
- Commercial, institutional and households: 14.8%
- Travel and product use: 0.3%
- Waste: 0.0%
- Agriculture: 1.8%
- Energy production and distribution: 22.1%
- Energy use in industry: 13.4%
- Industrial processes: 2.1%
- Non-road transport: 7.1%
- Other: 0.0%

Emissions Cement Plants are contributing to
Development of NO\textsubscript{x} Limits for Cement Plants in Germany

Nm\textsuperscript{3} = dry at 10% O\textsubscript{2}. Conversion to 10% O\textsubscript{2} permitted in Germany only until 2012.
Capability of NOx-Abatement Technologies in Cement Plants

- **Emission without Abatement**
- **MSC**
- **MSC+SNCR**
- **SCR**
**NOx Sources in the Clinker Burning Process**

**Calciner firing**
- Low oxygen levels
- Substoichiometric at the ignition zone
- Flameless oxidation
- Uniform temperature
  - No thermal NO\(_x\)
  - Fuel NO\(_x\) only
  - Partly reduction of (kiln) NO\(_x\)

**Sintering zone**
- High temperatures
- High oxygen levels at the flame
  \[ N_2 + O_2 \rightarrow 2 \text{ NO} \]
  \[ (N_2 + 2 \text{ O}_2 \rightarrow 2 \text{ NO}_2) \]
  - Formation of thermal NO\(_x\) unavoidable
Measures to influence the NO\textsubscript{X} emission – Theory of Low NO\textsubscript{X} Burner

- High temperatures
- High oxygen levels at the flame

\[ \text{N}_2 + \text{O}_2 \rightarrow 2 \text{ NO} \]
\[ (\text{N}_2 + 2 \text{ O}_2 \rightarrow 2 \text{ NO}_2) \]

- Formation of thermal NO\textsubscript{x} unavoidable

Theory of Low NO\textsubscript{X} Burner:

**Reduce flame temperature**
- Switch to low reactivity fuel, increase particle size
- Increase flame length (reduce swirl)

**Reduce oxygen content**
- Reduce primary air
- Reduce momentum of primary air
Options for lowering the thermal NOx formation in the sintering zone are limited, as clinker quality is always affected.

→ NOx emission should be adjusted in the calciner by MSC

Theory of Low NOx Burner:
NO\textsubscript{x} Development in the Calciner

\begin{align*}
\text{Calciner Fuel N} & \rightarrow \text{HCN} \\
\text{HCN} & \rightarrow \text{NHi - radicals} \\
\text{NHi - radicals} & \rightarrow \text{NO}\textsubscript{x} \\
\text{NO}\textsubscript{x} & \rightarrow \text{Air Excess} \\
\text{N}_2 & \rightarrow \text{Lack of Air}
\end{align*}
MSC Multi-Stage-Combustion - A Primary Measure for NOx-Abatement

1. Air excess number below 1
2. High temperature in substoichiometric zone
3. Long retention time in substoichiometric zone

top air: ~ 0,85-0,95, lower values possible
meal staging for flexible temperature control
retention time of ~ 1 second

Area of reduced combustion condition with flexible temperature control and sufficient retention time
Latest References for MSC-Calciner Systems of TKIS

- Natural Gas: < 500 mg/Nm³
- RDF: ~ 500 mg/Nm³
- Coal (40%): 500 mg/Nm³
- Coal (28%): ~ 650 mg/Nm³
- Coal (21%)/Pet coke: ~ 800 mg/Nm³

> 30 units sold
SNCR - Selective Non Catalytic Reduction – Secondary Measure for NOx-Abatement

\[
2 \text{NO} + 2 \text{NH}_3 + 0.5 \text{O}_2 \rightarrow 2 \text{N}_2 + 3 \text{H}_2\text{O} \\
2 \text{NO} + \text{CH}_4\text{N}_2\text{O} \rightarrow 2 \text{N}_2 + 2 \text{H}_2\text{O} + \text{CO}
\]
SNCR - Selective Non Catalytic Reduction – Secondary Measure for NOx-Abatement
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Risk of secondary Emissions at higher Reduction levels

Increase of CO likely

Decreasing calciner cross-section

Urea is up to 50% less effective; high risk of secondary emission
SCR - Selective Catalytic Reduction – Secondary Measure for NOx-Abatement

\[ 4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \]
**SCR - Selective Catalytic Reduction – Secondary Measure for NOx-Abatement**

**High Dust (HD)**

+ Lowest investment costs
+ Suitable flue gas temperature
+ No interference with main process
+ Easiest option for retrofits
- Frequent cleaning of catalyst

**Semi Dust (SD)**

+ Suitable flue gas temperature
+ Easier cleaning of catalyst
- Higher cost of installation
- Complex duct routings in retrofits
- Additional power for ESP

**Tail End (TE)**

+ No dust cleaning required
+ Longer lifetime of catalyst
- Highest cost of installation
- Requires reheating of flue gas
- Complex system
- Higher operating costs
SCR References / Projects of Elex CemCat

- Monselice (2006)
- Mergelstetten (2010)
- Joppa (2013)
- Rezatto (2014)

Start up of SCR-Systems in 2017:
Solnhofen, Phönix, Göllheim
**SCR versus SNCR - Performance of NOx Abatement**

[Graph showing SCR and SNCR performance with NH₃/NO and NO-Abatement [%] axes.]
CemCat a Joint Venture of Elex and TKIS (Polysius)

- Catalysts
- Preheater / Calciner
- Combustion/Fuels
- SNCR
- New products
- Patents
Conclusion - NOx in Cement Clinker Production
Formation and Measures to minimize Emissions

- Primary NOx Emission can be reduced significantly with modern MSC Calciners down to 500 – 800 mg/Nm³

- SCNR is effective for NOx abatements of 50-60%, further reduction only with secondary emissions, mainly NH₃

- SCR abatement is nearly unlimited, secondary Ammonia emissions are not only avoided, but Ammonia is effectively used for the NO reduction

- High Dust is the favorite solution:
  - lowest investment
  - no extra energy
  - TOC oxidation
  - positive effect on downstream Hg capture
NOx in Cement Clinker Production
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Thank you for your attention!

Any questions?

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