Behaviour of heavy Metals in Cement Kilns

Volutility
- Arsenic
- Nickel
- Chrome
- Copper
- Cobalt
- Cadmium
- Lead
- Thallium
- Mercury

Emissions
- solid, (bounded)
- bounded and gaseous

Enrichment on filter dust (%)
- non
- low
- light
- high

Volatility
Mercury – Emission Measurements at German Cement kilns

34 yearly averages from continuous control and 112 measurements from 44 plants. 5 Values below detection limit.

Exceptional Limit: 50 μg/Nm³ if caused by Raw Material

Limit: 30 μg/Nm³

Source: VDZ 2008
Mercury – Emission Measurements at US Cement kilns

Emissions Regulations
Impact on US Industry

• $ in costs
• Possible Closures

• Hg Existing Plants 55 lb/Mst cli (8-13 μg/Nm³)
• Hg New Plants 21 lb/Mst cli (3-5 μg/Nm³)

Source:
Mercury Emissions and Abatement
Daniel Crowley, Titan America, LLC

September 2015 Limits
Mercury Cycle in Cement Kilns – direct operation

- Hg-Sources: Fuels + Raw Meal
- Direct operation:
  - High mercury emissions
  - Adsorption on the dust (depends on the temperature)

Mercury evaporation from Raw Meal

Diagram showing the process:
- Fuels
- Raw Meal
- Clinker
- Mercury evaporation
- Filters
- Dust
- Silo

Graph showing mercury concentration (%) vs. temperature (°C)
Mercury Cycle in Cement Kilns – compound operation

- Hg-Sources: Fuels/Raw Materials/Meal
- Compound operation:
  - Enrichment in the outer cycle (depending on mill type, amount of kiln gas used for grinding)
  - Lower mercury emissions
Mercury - Typical Emission Behavior

Source: tkIS
Primary Mercury Abatement Technologies

➢ Reduce Mercury input into the System

**Fuels:**

could be possible

**Raw Materials:**

might be possible if a minor component is the source

but

hardly achievable if the Limestone Quarry is the Source
Primary Mercury Abatement Technologies

- Dust shuttling (typically in direct operation)

Exhaust gas cooling as a precondition

- Dust shuttling (typically in direct operation)
- Filter-dust to Clinker grinding or disposal
- Filter-dust back to process (Silo)
Primary Mercury Abatement Technologies

- Effect of Dust shuttling in direct operation

Source: ZKG 11 2001, 591-601
Secondary Mercury Abatement Technologies: ACI

- Dust Shuttling with ACI
  (typically in Direct Operation)

- Activated Carbon - Injection
  approx. 30-40mgAC/Am³
  @3000tpd Clinker ➔ 12-15kg AC/h

- Filter-dust to
  Clinker grinding or disposal
  approx. 10 t/h; 0,15% C
  @3000tpd Clinker and 8% Dust related to Clinker

- Filter-dust back to process
  (Silo)
Secondary Mercury Abatement Technologies: ACI

- Expected Hg-Removal with ACI from Industrial Trials
  (Landreth and Hardtke ZKG 11 2012, 46-51)

1 lb/MMacf equal to approx. 16mg/Nm³

Removal efficiency generally confirmed by plant operations
Secondary Mercury Abatement Technology: ACI

- ACI with two Baghouses

  Activated Carbon - Injection

  • improved efficiency
  • pure activated carbon
  • high investment

landfill recycling...

 Filter-dust back to process (Silo)
Secondary Mercury Abatement Technologies: ACI

- ACI - Hg-Removal Experience with two Baghouses

Fig. 7. Mercury emission Reduction performance in lbs/mmtons clinker

Source: Mercury Reduction - The Plant Experience
Terry Kerby, IEEE 2016
Secondary Mercury Abatement Technology – ACI with Hg-Desorption from Dust

Activated Carbon - Injection

Filter-dust back to process (Silo)

Hg-Desorption
Secondary Mercury Abatement Technology - Thermal dust treatment for Hg-Desorption by TKIS

- Waste minimization: High Hg Enrichment factor
- Extremely compact design, mobile full scale demonstration plant possible

**Diagram:**
- Feed
- Heat Exchanger
- Reactor
- Cyclone
- HT-Filter
- Product
- Clean Gas
- ACF

**Patent Information:**
- United States Patent
- Patent No.: US 8,728,207 B2
- Date of Patent: May 20, 2014
- Method and System for Separating Mercury from Waste Gases of a Cement Production Process
Secondary Mercury Abatement Technology - Thermal dust treatment for Hg-Desorption by TKIS

Indirectly heated Rotary kiln for thermal Treatment of EP-Dust

Industrial Installation in 1992
Mercury Online Measurement

Big discussions about accuracy in cement process in Germany.

- Very low concentration (µg/Nm³)
- Alternating concentrations
  - Different measurement ranges in compound and direct operation
- Interferences (newer analyser with underground compensation)
- Only detection of elemental mercury (photometer)
  - Ionic mercury hast to be converted to the elemental form
- Older analysers uses a converter material → Deactivation by the sample gas of the kiln exhaust
  - Newer analysers: Thermal conversation
Mercury in Cement Kilns

Conclusion

- Mercury is completely volatile in the preheater.
- During mill down times (direct operation), the outer cycle is partly unloaded.
- Dust Shuttling is the first step to reduce Mercury Emission.
- Low temperatures in the filter are advantageous.
- Activated Carbon Injection may further reduce Emissions.
- Plant specific emissions and the maximum allowable emission determine the suitable abatement technology.
Mercury in Cement Clinker Production –
Behaviour and Abatement Strategies

Thank you for your attention!

Any questions?

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