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european cement research academy

Sources of mercury, behavior in cement process and abatement options

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Cement Industry Sector Partnership on Mercury
Partnership Launch Meeting

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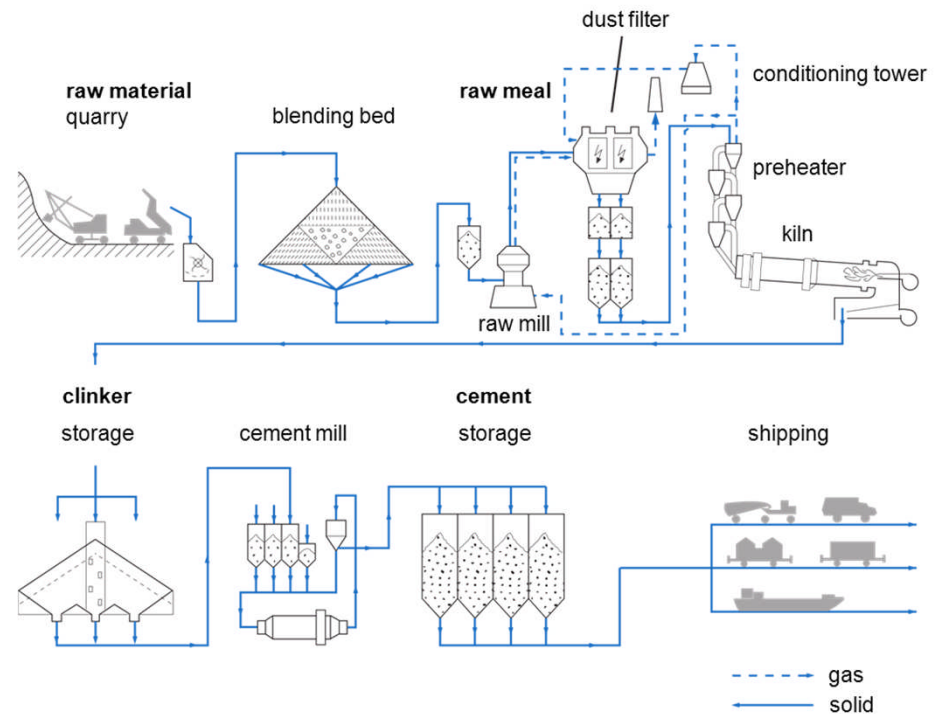
Agenda

- 1** Cement production process
- 2** Behaviour of mercury in Cement Production Process
- 3** Mercury abatement techniques
- 4** Monitoring of mercury emissions
- 5** Mercury emission inventories
- 6** Best Available Technique and Best Environmental Practice

1 Cement production process

General principle:

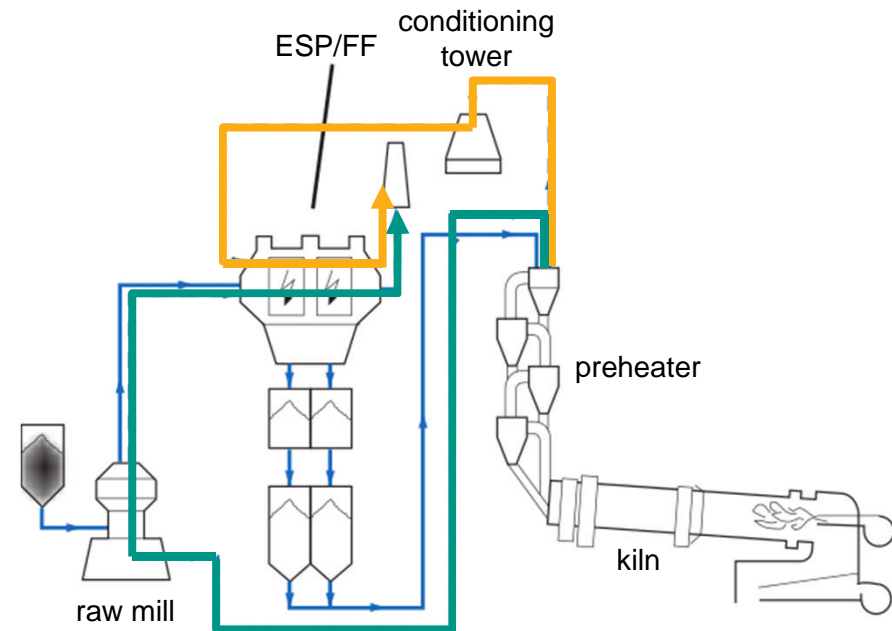
- Raw materials: limestone, clay, lime marl
- Thermal treatment to produce cement clinker (1450°C)
 - Commonly in rotary cement kilns
 - Regular fuels: black coal, lignite, petroleum coke, natural gas, heavy fuel
 - Alternative fuels: plastics, mixed industrial wastes (RDF), tyres, ...



1 Cement production process

Exhaust gas utilization

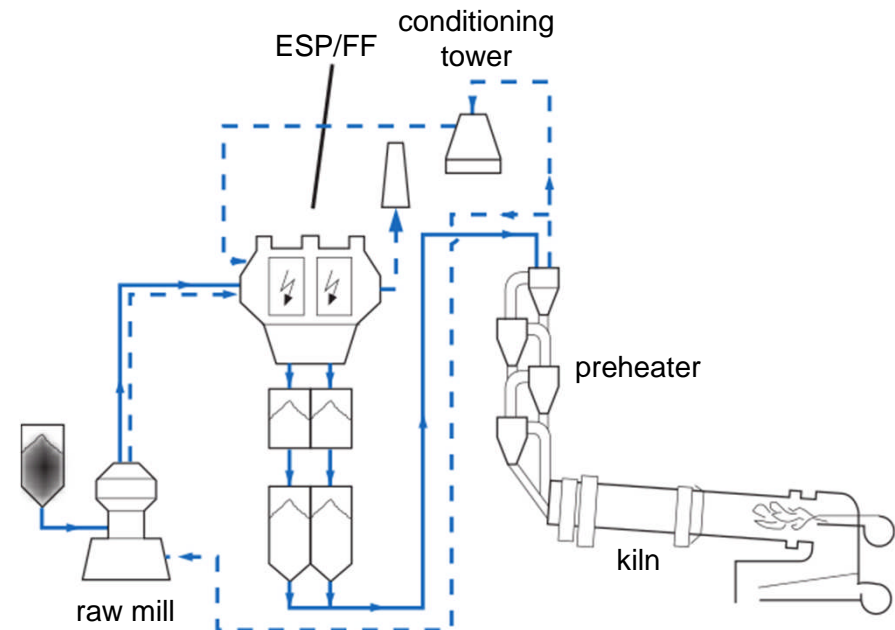
- Kiln exhaust gases are mainly used for drying of raw materials
- Two modes of operation:
raw mill on / **raw mill off**
- Raw mill gas stream determined by required heat ->raw material moisture
- Residual kiln exhaust stream bypasses raw mill and is conditioned in evaporating cooler
- Example: dry raw materials
 - Less exhaust gas needed for drying
 - More exhaust gas bypasses raw mill
- Ratio raw mill on/off operation mainly determined by ratio raw mill/kiln capacity



1 Cement production process

Dust utilization

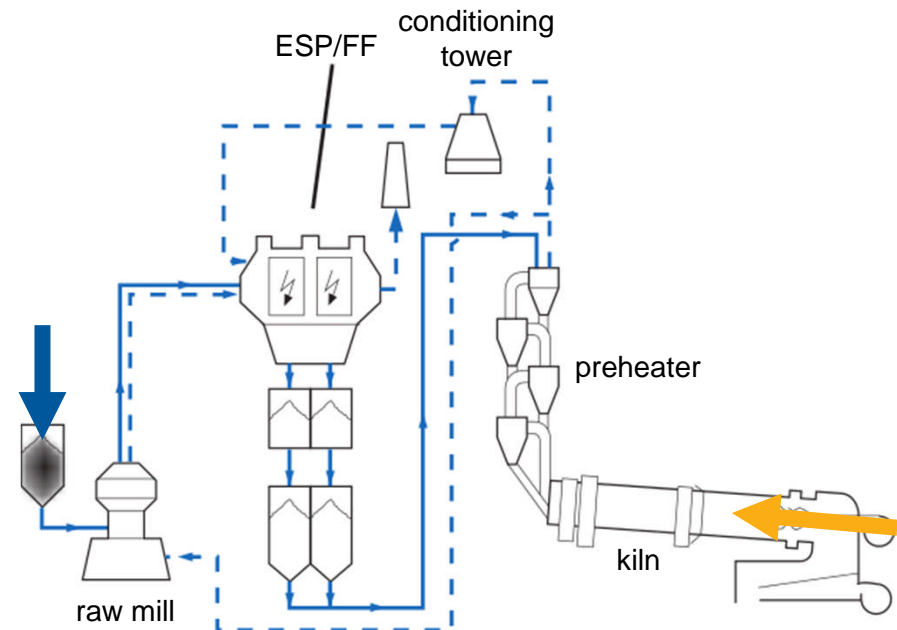
- Precipitated dust consists mainly of raw material
- **Raw mill on:** „dust“ is ground raw material
- **Raw mill off:** recirculation of filter dust to kiln feed or raw meal silo
- Dust can be used in cement mill to adjust cement quality
 - Depending on national cement standards and market conditions



2 Behaviour of mercury in cement production process

Origin of mercury:

- Mercury is introduced to the process via **raw materials** and **fuels**
- Concentrations may vary significantly between
 - fuels
 - raw materials
 - within deposits or quarries
- Alternative fuels and raw materials can have higher or lower mercury contents than regular/conventional ones



2 Behaviour of mercury in cement production process

Mercury content in fuels

Fuel	Mercury content in mg/kg
Coal	0.1 – 13
Lignite	0.03 – 0.11
Petcoke	0.01 – 0.71
Heavy oil	0.006
Liquid-waste derived fuel	< 0.06 – 0.22
Solid-waste derived fuel	< 0.07 – 2.77
Sewage sludge	0.31 – 1.45
Secondary fuel	0.04 – 10
Tire-derived fuel	0.01 – 0.4

- Due to fuel-raw material ratio, Hg intake through raw materials can be up to 10-fold higher
- Substitution of fuels commonly does not lead to rising mercury emissions

Mercury content in raw materials

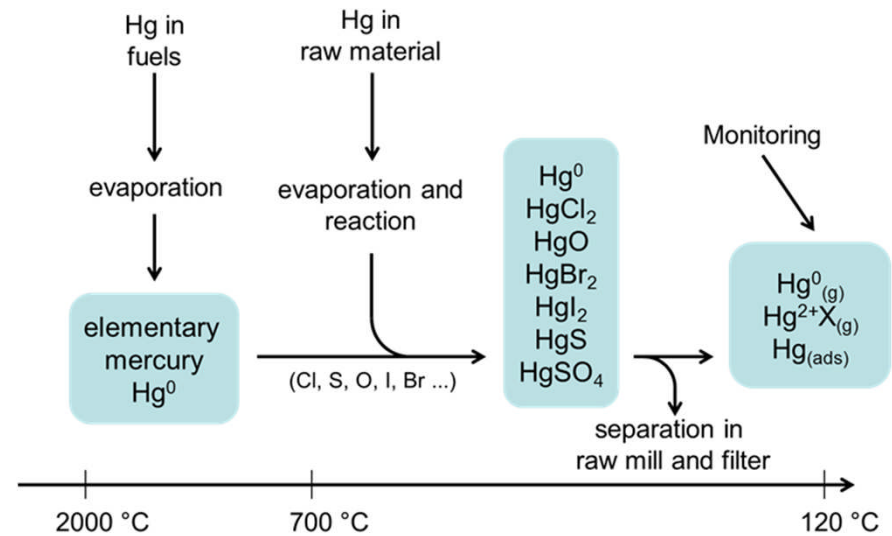
Raw material	Mercury content in mg/kg
Limestone, lime marl, chalk	< 0.005 – 0.40
Clay	0.002 – 0.45
Sand	< 0.005 – 0.55
Fly ash	< 0.002 – 0.8
Iron ore	0.001 – 0.68
Blast furnace slag	< 0.005 – 0.2
Pouzzolana	< 0.01 – 0.1
Burned oil shale	0.05 – 0.3
Shale	0.002 – 3.25
CaSO ₄	< 0.005 – 0,02
Gypsum (natural)	< 0.005 – 0.08
Gypsum (artificial)	0.03 – 1.3
Aggregates	< 0.01 – 0.1
Raw meal	0.01 – 1
Earth crust (avg.)	0.05, 0.08

Main source: Université de Liège, 2010

2 Behaviour of mercury in cement production process

Behaviour of mercury

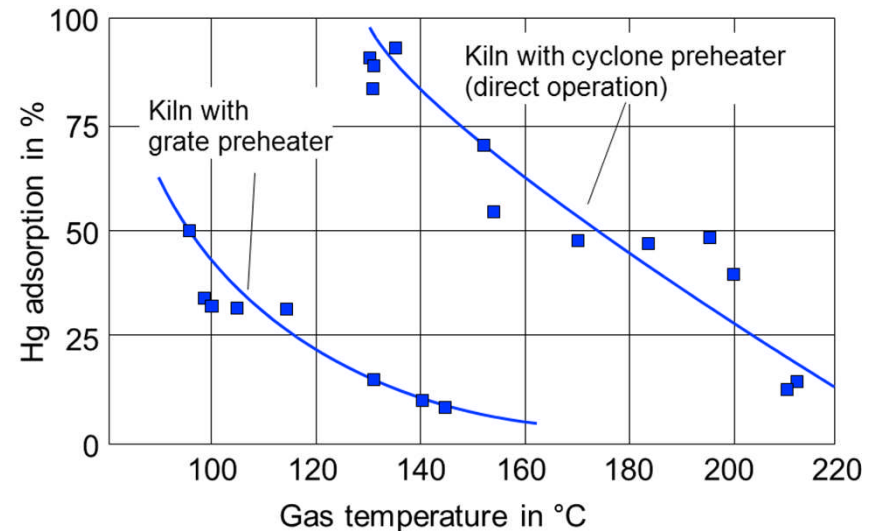
- Determined by thermal conditions between preheater, raw mill and dust precipitator:
 - Vaporization of Hg and its compounds in kiln or preheater
 - Depending on temperature and available reaction partners, HgCl_2 , HgO and HgSO_2 are formed



2 Behaviour of mercury in cement production process

Influence of temperature

- Decrease in temperature in raw mill
 - Condensation of Hg compounds on raw meal
 - Adsorption of elemental mercury on raw meal surface depending on availability and temperature
 - Example: adsorption in cyclone preheaters is most efficient below 140°C
- In mill off operation
 - Adsorption depends on temperature profile (conditioning tower/quenching)
 - Retention capacity significantly smaller (higher temperature, less available surface)



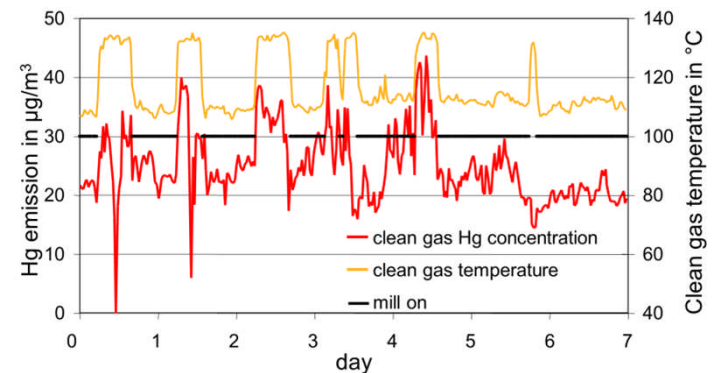
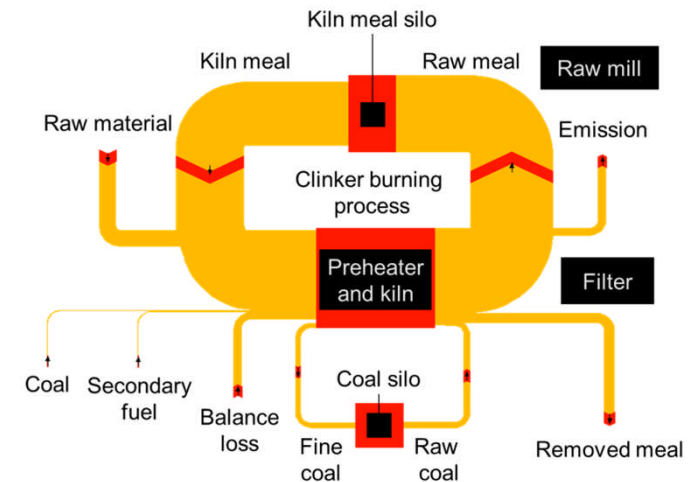
2 Behaviour of mercury in cement production process

Mercury cycle

- Recycling of precipitated dust to kiln system
 - Forming of dynamic cycle: preheater/kiln – raw mill – exhaust gas filter
- In mill off operation:
 - Higher temperature
 - Less available surface
 - Cycle is partly relieved

Safe enclosure of mercury

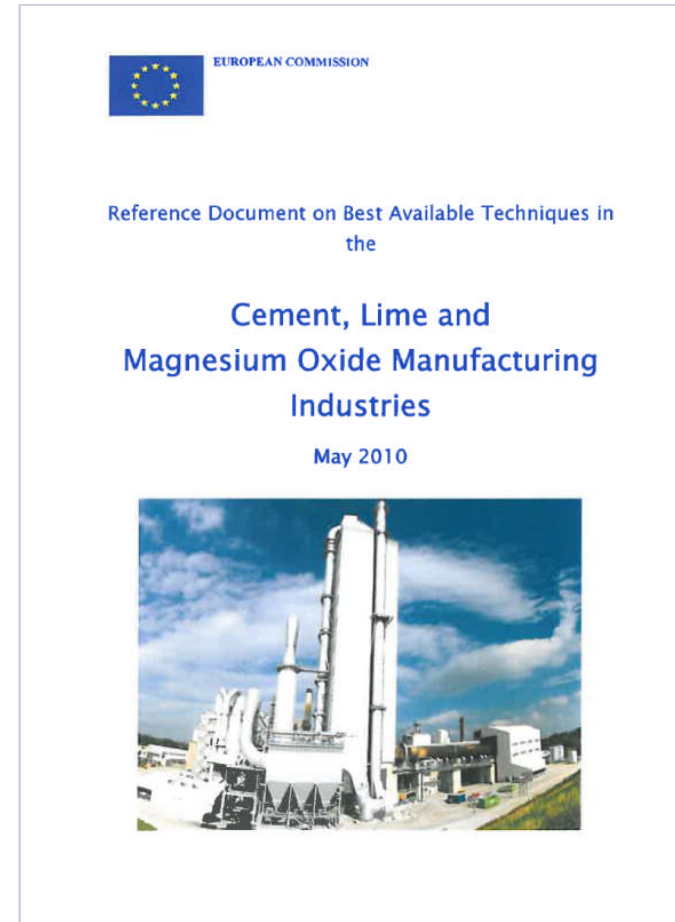
- Mercury is partially bound to filter dust
 - Can be used in cement mill
 - Is safely enclosed in cement matrix and leaching is negligible
- Almost no mercury is found in clinker



3 Mercury abatement techniques

European Commission's BAT Reference Document

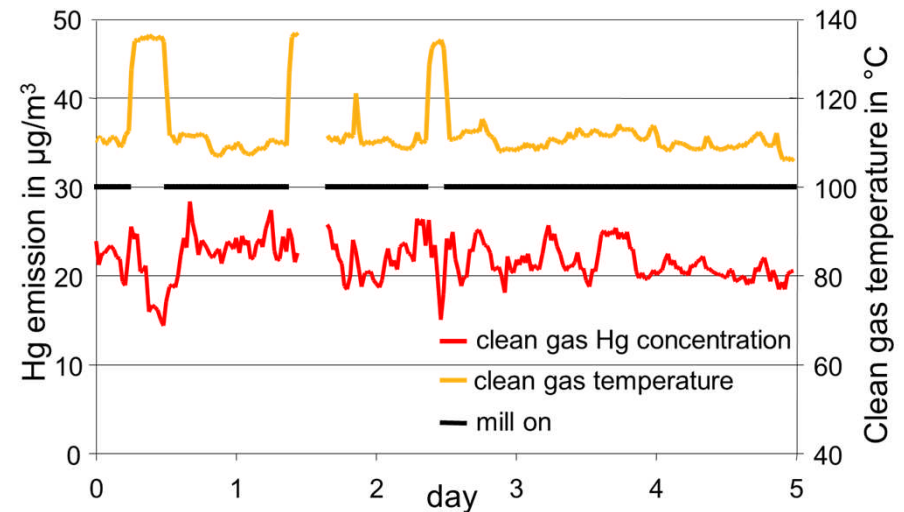
- Selecting materials with a low content of relevant metals and limiting the content of relevant metals in materials, especially mercury
- Using a quality assurance system to guarantee the characteristics of the waste materials used (in case of using alternative materials)
- Using effective dust removal measures/techniques



3 Mercury abatement techniques

Selective dust shuttling

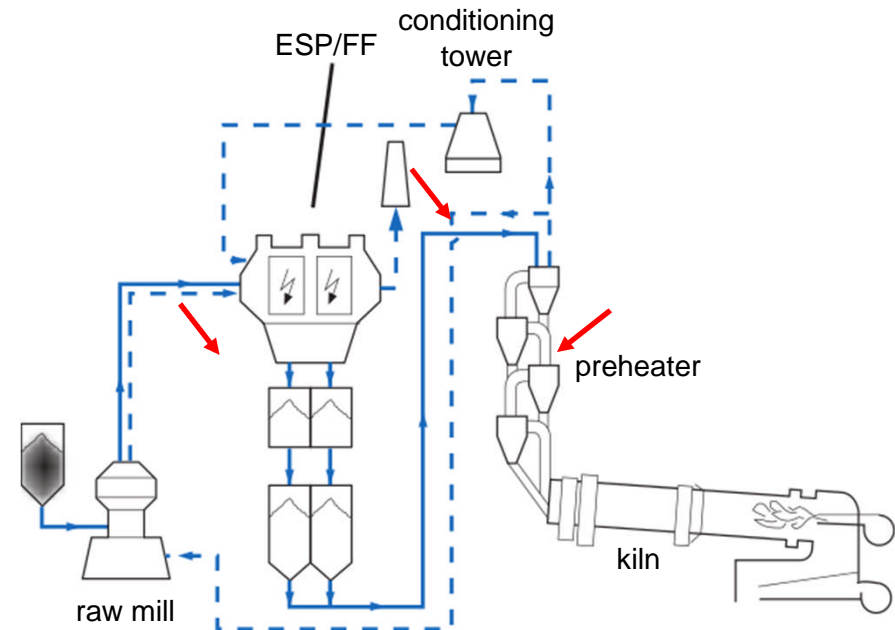
- Mercury is partially bound to dust circulating between kiln/preheater raw mill and dust precipitator
- Selective shuttling or “bleeding“ may limit build-up of cycles
- Method is proven and systematically applied in many cement plants to specifically separate mercury from the process
- Most effective at a low temperature of 120–140°C with a high proportion of oxidized mercury
- Shuttling efficiency is higher if mercury enrichment in the system/respective gas stream is high => usually more effective in raw mill off-operation



3 Mercury abatement techniques

Activated carbon/sorbent injection

- Injection into gas stream before dust filter
- Mercury and other pollutants are captured on the sorbent's high surface
- Frequently used in power plants or waste incinerating plants
- Little experience in cement industry
- General applicability not demonstrated
- **Not easily extrapolated to cement industry due to recirculation/utilization of removed dust**
 - Activated carbon may influence cement properties and must be removed from the kiln system
 - Calcium-based sorbents are expected to have only little influence on cement when blended



3 Mercury abatement techniques

Oxidizing agents

- Oxidized mercury is adsorbed more effectively than elemental mercury
- Bromine, sulphur or other compounds with similar properties may enhance adsorption rate by oxidizing elemental mercury
- Could be injected directly, as an additive to sorbents or as an impregnation on them
- No certainty if agents influence cement properties if enclosed
- Separate polishing filter (tail-end) for sorbents would be needed

Thermal treatment of shuttled dust

- Separate polishing filter (tail-end) for sorbents not suitable for most cement plants
- Treatment of shuttled dust
- Volatilization of Hg from shuttled dust
- Activated carbon injection + additional polishing filter
- Smaller scale than tail-end treatment facility for entire clean gas stream
- In research/pilot phase

These techniques are not proven in the cement industry!

3 Impact of other abatement techniques on mercury

Selective catalytic reduction (SCR)

- New technology in the cement industry for NO_x abatement
- Oxidization of mercury with acidic compound on catalyst surface
- May increase efficiency of dust shuttling because
- Adsorption of mercury compounds is higher than of elemental mercury
- Catalyst manufacturers are developing and introducing special mercury catalysts for other industries (waste incinerators, power plants)
- Further investigation required

Wet scrubbers

- Used primarily for SO₂ abatement
- Very common in other industries
- Side effect: soluble mercury compounds are washed out
- Elemental mercury remains in gas stream
 - Effect in cement plants may vary significantly case by case
- Not reasonable for mercury abatement **only** but effect may be utilized
- 2010: six scrubbers in European and 2 in US cement plants in operation

4 Monitoring of mercury emissions

Spot and continuous measurements must detect total mercury emission

Ratio of particle-bound mercury in stack emissions is very small (low dust content)

Manual mercury spot measurements

- European Standard EN 13211 for mercury and EN 14385 for a set of heavy metals
- US EPA methods 101 A for mercury and method 29 for a set of heavy metals
- Speciation of elemental and oxidized mercury:
US ASTM 6784-02 (Ontario Hydro); in Europe not standardized

Continuous emission monitoring systems (CEMS)

- Basic principle: detection of elemental Hg with UV photometers
 - prior reduction of mercury compounds necessary
- Continuous measurement not classified as BAT in European BAT Reference Document
- Ambitious tightening of US emission standards advances developments of mercury CEMS

Highly complex systems demand continuous, sophisticated maintenance and highly available support which may be difficult to provide outside Europe or North America

5 Mercury emission inventories

UNEP Global Mercury Assessment 2013

- Overall worldwide emissions: 1,960 tonnes in 2010
- Cement industry: 173 tonnes (9%)
- Based on country specific by-product emission factors derived from national data or global factors on raw material and fuel Hg content, fuel/raw material mix and applied technology

Université de Liège – Mercury in the Cement Industry, 2010

- Based on 1,681 spot measurements in 62 countries collected 2005–2007 by CEMBUREAU and CSI
- suggests 0,035 g/t cement → 115.5 tonnes
(worldwide production of cement in 2010 (est.): 3,300 MM tonnes)

Cembureau/PwC data base: Hg spot measurements

- Measurements from 204 European cement plants in 2010
- 0,015 g/t cement (0,020 g/t clinker; clinker-cement ratio: 0.74)

6 Best Available Technique and Best Environmental Practice

- **Limit mercury input** into the cement production process by careful monitoring and selection of fuels and raw materials
 - Difficult if regular fuels and natural materials are used
- **Dust Shuttling** for high concentrations
 - Reduction of exhaust gas temperature to below 140°C and removal of filter dust in mill off operation
 - Removed dust can be used to specifically influence cement properties
 - Procedure is covered by many cement standards but not possible in a few countries due to market reasons
 - Procedure is a proven and safe way to reduce mercury emissions
 - **Global acceptance in markets and standards is desirable**
- Cement plants struggling with very high emissions should consider the use of sorbents in conjunction with dust shuttling

Thank you for your attention! Questions welcome!

