Best Practices to Reduce Mercury Emissions in the Cement Industry

Information-sharing session - Virtual event
Opening remarks and scene-setting
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- Teeraporn Wiriwutikorn, Ministry of Natural Resources and Environment, Thailand, Co-chair of the Partnership Advisory Group
- Zaigham Abbas, Ministry of Climate Change, Pakistan, Co-lead of the Partnership Area on Mercury Releases from the Cement Industry

- Best Available Techniques and Best Environmental Practices for reducing mercury emissions under the Minamata Convention, by Eisaku Toda, Minamata Convention Secretariat

- Question and Answer Session

- Global Cement and Concrete Association Sustainability Guidance for reducing and controlling emissions of mercury compounds in the cement industry, by Volker Hoeing, Association of German cement manufacturers (VDZ)

- Question and Answer Session

- National perspective from Pakistan, by Zaigham Abbas, Ministry of Climate Change, Pakistan, Co-lead of the Partnership Area on Mercury Releases from the Cement Industry

- Question and Answer Session

Closure
Best Practices to Reduce Mercury Emissions from the Cement Industry

Teeraporn Wiriwutikorn
Ministry of Natural Resources and Environment, Thailand, Co-chair of the Global Mercury Partnership Advisory Group
Zaigham Abbas
Ministry of Climate Change, Pakistan
Co-lead of the Partnership Area on Mercury Releases from the Cement Industry
Best Available Techniques (BAT) and Best Environmental Practices (BEP) in the Minamata Convention on Mercury

Best Practices to Reduce Mercury Emissions From the Cement Industry
Online, 23 June 2022
MINAMATA CONVENTION ON MERCURY

The Parties to this Convention,

*Recognizing* that mercury is a chemical of global concern owing to its long-range atmospheric transport, its persistence in the environment once anthropogenically introduced, its ability to bioaccumulate in ecosystems and its significant negative effects on human health and the environment,

*Recalling* decision 35/5 of 20 February 2009 of the Governing Council of the United Nations Framework Convention on Climate Change action to manage mercury,

*Recalling* parties to the United Nations Conference on Environment and Development which called for an international legally binding instrument to deal with mercury,
Global mercury supply and demand, 2015

Article 3: Supply source

Article 3: Trade

Article 7: ASGM

Article 8: Emissions

Article 9: Releases

Article 11: Waste

Note: Units (rounded) for the mercury pathways are in tonnes. They are means (averages) within varying ranges of uncertainty (not shown), depending on the pathway.
Article 8 – Emissions

- Controls the emissions of total mercury from point sources listed in Annex D:
  - Coal-fired power plants;
  - Coal-fired industrial boilers;
  - Smelting and roasting processes used in the production of non-ferrous metals (lead, zinc, copper and industrial gold);
  - Waste incineration facilities;
  - Cement clinker production facilities

- New sources – require the use of best available techniques and best environmental practices (BAT/BEP) no later than 5 years after the entry into force (EIF)

- Existing sources – implement control measures no later than 10 years after EIF
  - Quantified control/reduction goals
  - Emission limit values
  - Use of BAT/BEP
  - Multi-pollutant control strategy
  - Alternative measures

- Each Party shall establish an inventory of emissions from relevant sources no later than 5 years after EIF

- COP shall adopt guidance on
  - BAT/BEP
  - Methodology for preparing inventories of emissions
Article 2
Definitions

(b) “Best available techniques” means those techniques that are the most effective to prevent and, where that is not practicable, to reduce emissions and releases of mercury to air, water and land and the impact of such emissions and releases on the environment as a whole, taking into account economic and technical considerations for a given Party or a given facility within the territory of that Party. In this context:

(i) “Best” means most effective in achieving a high general level of protection of the environment as a whole;

(ii) “Available” techniques means, in respect of a given Party and a given facility within the territory of that Party, those techniques developed on a scale that allows implementation in a relevant industrial sector under economically and technically viable conditions, taking into consideration the costs and benefits, whether or not those techniques are used or developed within the territory of that Party, provided that they are accessible to the operator of the facility as determined by that Party; and

(iii) “Techniques” means technologies used, operational practices and the ways in which installations are designed, built, maintained, operated and decommissioned;

(c) “Best environmental practices” means the application of the most appropriate combination of environmental control measures and strategies;
Guidance under Article 8

- BAT/BEP - Introduction
- BAT/BEP - Common Techniques
- BAT/BEP - Monitoring
- BAT/BEP - Coal-fired power plants and coal-fired industrial boilers
- BAT/BEP - Smelting and roasting processes used in the production of non-ferrous metals (lead, zinc, copper and industrial gold)
- BAT/BEP - Waste incineration facilities
- BAT/BEP - Cement clinker production facilities
- BAT/BEP - New and emerging techniques
- Support for parties in implementing the measures for existing sources of mercury emissions
- Guidance on criteria that Parties may develop on a relevant source
- Guidance on the methodology for preparing inventories of emissions
• Presents guidance on BAT and BEP to assist parties in fulfilling their obligations under Article 8.
• Does not establish mandatory requirements, nor attempts to add to, nor subtract from a Party's obligations under article 8.
• In determining BAT, each Party will take account of its national circumstances. It is recognized that some of the control measures described in this guidance may not be available to all parties for technical or economic reasons.
• Financial support, capacity building, technology transfer, or technical assistance are made available as elaborated in Articles 13 and 14 of the Convention.
The process for selecting and implementing BAT could be expected to include the following general steps.

- **Step 1**: establish information about the source, or source category.
- **Step 2**: identify the full range of options of emission control techniques.
- **Step 3**: identify technically viable control options.
- **Step 4**: select the control technique options which are the most effective for the control and reduction of emissions.
- **Step 5**: determine which of these options can be implemented under economically and technically viable conditions.
BAT/BEP measures

► Primary measures to control input of mercury - Limit values and QA/QC for raw materials and fuels, avoiding the use of high Hg waste, etc

► Secondary measures to reduce Hg emissions during production – **Dust shuttling, solvent injection**

► Mercury removal by co-benefit of multi-pollutant control measures – **wet scrubber, selective catalytic reduction, activated carbon injection.**

“The indicative performance level associated with best available techniques and best environmental practices (BAT/BEP) in new and existing cement clinker production facilities for control of mercury emissions to the air is **below 0.03 mg Hg/Nm³** as a daily average, or average over the sampling period, at reference conditions 273 K, 101.3 kPa, 10 per cent oxygen and dry gas.”
Guidance on the methodology for preparing inventories of emissions pursuant to Article 8

Methodology to establish an emissions inventory typically involves many or all of the following steps:

- Plan the approach for development of inventory, within available resources, and consider how to collect, handle and review data, including any quality control and quality assurance processes.
- Collect existing emissions data as a useful starting point.
- Identify relevant sources within each source category.
- Establish facility-based emissions reporting requirements.
- Collect the emissions reports from facilities on a periodic basis (e.g. annually).
- Develop a database to store the reported emissions data.
- Facilitate analysis of the results.
- Make the data publicly accessible and searchable.

The guidance mentions pollutant release and transfer register (PRTR) as information source for mercury emission inventories.

**UNEP inventory toolkit** could be a good starting point for parties developing their own emissions inventories.
Article 9: Releases

► Article 9 concerns controlling and reducing releases of mercury and mercury compounds to land and water from the relevant point sources not addressed in other provisions of the Convention.

► Parties have an obligation to:
  • Identify relevant point sources no later than 3 years after EIF
  • Take measures to control releases which may include: release limit values; the use of BAT/BEP; multi-pollutant control strategy; or alternative measures
  • Establish inventory of releases no later than 5 years after EIF.

► Article 9 provides that COP shall adopt guidance on BAT/BEP and methodologies for inventories

► COP-2 established a group of technical experts that will prepare a report including a list of any significant anthropogenic point source of release categories.

► COP-3 agreed on the roadmap, the group will further develop draft guidance on standardized and known methodologies for preparing inventories.

► COP-4 adopted the inventory guidelines, which include a list of potentially relevant point source categories, and requested the expert group to develop draft guidance on BAT/BEP.
COP-4 decision MC-4/5 on Releases

COP

• Invited parties to consider the list of potentially relevant point source categories of releases when identifying relevant point source categories pursuant to paragraph 3 of article 9.

• Adopted the guidance on the methodology for preparing inventories of releases pursuant to paragraph 7 of article 9 of the Convention, and invites parties to take into account of the guidance when preparing their inventory of releases from relevant sources pursuant to paragraph 6 of article 9;

• Requested the expert group to develop draft guidance on best available techniques and best environmental practices to control releases from relevant sources, with a view to its adoption pursuant to paragraph 7 of article 9 of the Convention;
Article 11: Mercury waste

Each Party shall take appropriate measures so that mercury waste is managed in an environmentally sound manner, taking into account the Basel Convention guidelines, and in accordance with requirements that COP shall adopt in an additional annex.

Mercury wastes means substances or objects:
(a) Consisting of mercury or mercury compounds;
(b) Containing mercury or mercury compounds; or
(c) Contaminated with mercury or mercury compounds, in a quantity above the relevant thresholds defined by COP that are, are intended to be, or are required to be disposed of.

This definition excludes overburden, waste rock and tailings from mining, except from primary mercury mining, unless they contain mercury or mercury compounds above thresholds defined by COP.

Basel Convention COP in June 2022 adopted an updated Technical Guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with mercury or mercury compounds.
Thank you for your attention

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#MakeMercuryHistory
GGCA Sustainability Guidance for reducing and controlling emissions of mercury compounds in the cement industry

Volker Hoenig
UNEP Global mercury partnership webinar
“Best practices to reduce mercury emissions from the cement industry”
23 June 2022
1. Mercury behaviour and mass balance
2. Control of mercury emissions
   2.1 Reducing mercury input
   2.2 Dust shuttling
   2.3 Sorbents
   2.4 Process integrated thermal desorption (PITD)
3. Material sampling and analysis
4. Stack analysis methods
   4.1 Isokinetic sampling
   4.2 Continuous emissions monitoring
   4.3 Sorbent traps
1 The cement clinker burning process
1 Mercury input

- Mercury enters the process with all materials
- All Hg entering the process is volatized
- Mercury vapors are in elemental form at high temperatures
- Elemental mercury can form various mercury compounds when combined with halides and
- ... adsorb onto solids as the gas flow cools
1 Mercury input: variation in concentration can be huge!

Examples: limestone and pretreated industrial wastes (RDF)

<table>
<thead>
<tr>
<th></th>
<th>weighted average</th>
<th>10th percentile</th>
<th>90th percentile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>0.024</td>
<td>0.003</td>
<td>0.050</td>
</tr>
<tr>
<td>Pretreated industrial wastes</td>
<td>0.142</td>
<td>0.069</td>
<td>0.309</td>
</tr>
</tbody>
</table>

Source: VDZ
1 Mercury mass balance

Over the long-term, mathematically:

\[
\text{All Mercury In} = \text{All Mercury Out (Eq. 1)}
\]

\[
\text{All Mercury In} = \text{Raw Materials Hg} + \text{Fuels Hg} \quad (\text{Eq. 2})
\]

\[
\text{All Mercury Out} = \text{Clinker Hg} + \text{Stacks Hg} + \text{CKD Hg} \quad (\text{Eq. 3})
\]

Since Clinker Hg is often negligible, then,

\[
\text{CKD Hg} = \text{Raw Materials Hg} + \text{Fuels Hg} - \text{Stack Hg} \quad (\text{Eq. 4})
\]

\[
\text{Stack Hg} = \text{Raw Materials Hg} + \text{Fuels Hg} - \text{CKD Hg} \quad (\text{Eq. 5})
\]

- Over longer periods of time, “all mercury in” is equal to “all mercury out”
- In practical balances, e.g. over 2 or 3 days, you will always find a significant balance deficit
  - Appendices 1 and 2 to be used for material tracking and qualification
  - Appendices 3 and 4 to be used for preparing a mass balance exercise
  - Appendices 5 and 6 give guidance regarding sampling details
1 Mercury behaviour

- Mercury sorption depends on
  - Gas temperature
  - Binding form (elemental or oxidized)
  - Dust concentration in the gas flow (available reactive surface area)
- Elemental mercury is adsorbed on the surface at low temperature (e.g. in the raw mill)
- Bound (oxidized) mercury is condensed on the particle surface
Mercury cycles are dynamic, i.e. varying over time.

Two relevant cycles: raw mill/dust filter cycle and fuel mill cycle.
2.1 Control of mercury emissions - reducing mercury input

- The most effective means to reduce mercury emissions may be to reduce the total inputs into the kiln system. This can be achieved by:
  - Selecting raw materials and/or fuels with a lower mercury concentration
  - Reducing the consumption of fuels as a result of improved efficiencies in thermal energy production and
  - To a lesser degree, reducing the consumption of raw materials due to improved efficiencies in their use.
- Raw material substitution: limited potential with regard to main raw materials
- Conventional fuel and AF/ARM substitution: usually easier, but nevertheless often limited due to limited availability of substitutes or economic reasons
2.2 Control of mercury emissions – dust shuttling

- Dust shuttling can be applied to all kiln types and can achieve mercury emissions reductions of 10 to 40%.

- The concentration of mercury in the filter dust depends on:
  - Relationship between oxidized and elemental mercury in the exhaust gas
  - Amount of time for “raw mill on” or “raw mill off” operation
  - Filter type
  - Achievable exhaust gas temperature in “raw mill off” operation

- Adsorption capacity can be increased by additives (e.g. bromine, sulfur) which promote the formation of mercury compounds (oxidized mercury)
2.3 Control of mercury emissions - sorbents

Support of dust shuttling by sorbent injection

- Injection into gas stream before dust filter
- Most effective in direct operation at low temperatures (< 140°C) to capture mercury peaks
- Mercury (and other pollutants) are captured on the sorbent's high surface
- Emissions reductions of 70 to 90% have been demonstrated
- Sorbents can influence cement properties if enclosed (coloring, air entraining agents)
- Types: activated carbon, activated coke, calcium hydroxide, trass, etc. or intermixtures thereof

<table>
<thead>
<tr>
<th>Sorbents</th>
<th>Zeolite</th>
<th>Lime products</th>
<th>Activated lignite</th>
<th>Activated carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size</td>
<td>0 - 50 μm</td>
<td>0 - 2 mm</td>
<td>0 - 0,4 mm</td>
<td>0 - 0,2 mm</td>
</tr>
<tr>
<td>Specific surface</td>
<td>400 - 600 m²/g</td>
<td>1 - 50 m²/g</td>
<td>300 m²/g</td>
<td>500 - 1600 m²/g</td>
</tr>
</tbody>
</table>

Source: VDZ
2.4 Control of mercury emissions - PITD

PITD = “Process integrated thermal desorption” for kiln dust treatment

- Filter dust is sent to a “split pre-heater”
- Dust is reheated by a small amount of hot gases extracted from the lower part of the main pre-heater
- Hg is evaporated
- Mercury-free dust is separated in a high-efficiency cyclone and a hot-gas filter
- Dust is returned to the main preheater
- Dust-free exhaust gas containing the Hg is rapidly cooled down and sorbent is added to capture the mercury
- Bag filter separates the sorbent from the clean-gas
- Highly concentrated sorbent has to be disposed

Source: Scheuch website
3 Material sampling and analysis

- Sampling program: fundamental goal is to collect samples that are representative for the materials

  - Time frame for mass balance:
    - Establish the initial mass balance over a 30-day period
    - Each individual raw material and fuel, as well as clinker and any solid stream being removed from the system
    - Stack emissions can be verified using a sorbent trap system or through stack sampling.

- Sampling locations
  - Appendix 3: Example of sampling inputs and outputs for mass balance.

- Limit of quantification: usually in the range of 5-10 ppb but recommended LOQ for mercury is 1 ppb for Hg mass balance
4.1 Isokinetic sampling

- Particle bound mercury is captured with the dust
- Gaseous mercury is condensed and captured in liquid agents
- Limited representativity with regard to sampling period and location (e.g. raw mill on or off operation)

4.2 Continuous mercury emissions monitors

- Allow instantaneous mercury emission readings
- Allow continuous control of sorbent injection
- CEMs are installed in Germany and Austria due to legal requirements

4.3 Sorbent traps

- Collect Hg samples over a specified time period
- Cannot be used for control of sorbent injection
- Are required for compliance in the US
Thank you for your attention

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Best Practices to Reduce Mercury Emissions from the Cement Industry

National perspective from Pakistan

Zaigham Abbas, Ministry of Climate Change, Pakistan
Co-lead of the Partnership Area on Mercury Releases from the Cement Industry
Closing Remarks

Co-leads of the Partnership Area on Mercury Releases from the Cement Industry

Secretariat of the Global Mercury Partnership