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Technical Report

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Guidance Document on BAT-BEP for Mercury in the Cement Industry

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1 Regulatory Framework

1.1 Minamata Convention

The Minamata Convention on Mercury as a global and legally binding treaty targets at the worldwide reduction of mercury emissions regulating their anthropogenic causes. It was initiated by the UNEP Governing Council in 2009.

The import, export and production of mercury containing products such as batteries, switches, some medical devices and cosmetics will be banned by 2020. Plans to reduce and eliminate mercury emissions from artisanal and small-scale gold mining shall be established by countries, promoting mercury-free alternatives. Plans to minimize mercury emissions from existing industrial mercury emitters such as coal-fired power plants, cement factories or waste incinerating plants are to be drawn up while new facilities are to install the Best Available Techniques.

The Convention was agreed upon in January 2013 in Geneva, Switzerland at the Intergovernmental Negotiating Committee's 5th session (INC5) and will be open to signature in October 2013 in Minamata, Japan to come into force after being ratified by 50 countries.

1.2 European Union

In the European Union, mercury emissions from cement plants co-incinerating waste fuels (alternative fuels) are regulated by the new Industrial Emissions Directive 2010/75/EU (IED) that brings together Directive 2008/1/EC (the 'IPPC Directive') and six other directives in a single directive on industrial emissions. It was to be transposed into the Member States' legislations by 7 January 2013. No mercury limits have been fixed for cement plants using only regular fuels.

The Directive is based on several principles¹, namely

- a) An **integrated approach** meaning that permits must take into account the whole environmental performance of the plant, covering all aspects of the plants environmental impact to ensure a high level of protection of the environment taken as a whole.
- b) **Best Available Techniques** on which permit conditions and emission limits must be based on. The reference for setting permissions shall be documents containing information on the emission levels associated with the best available techniques (BAT conclusions). These are relevant for plants not using waste fuels as well.
- c) **Flexibility** allowing the licensing authorities to set less strict emission limit values in specific cases where the achievement of emission levels associated with BAT as described in the BAT conclusions would lead to disproportionately higher costs compared to the environmental benefits.
- d) **Environmental inspections** by authorities on a regular basis
- e) The public's **right to participate** in the decision-making process, and to be informed of its consequences

¹ see <http://ec.europa.eu/environment/air/pollutants/stationary/ied/legislation.htm>

Installations for the production of cement clinker in rotary kilns with a production capacity exceeding 500 tonnes per day or in other furnaces with a production capacity exceeding 50 tonnes per day, which are co-incinerating waste fuels, are subject to a mercury emission limit of 0.05 mg/Nm³ at 10% O₂ over a sampling period of 30 minutes to 8 hours.

National legislative bodies may tighten this limit further, as it was by way of example implemented in Germany:

Two mercury emission limit values are in place for cement plants co-incinerating waste.²

- A daily mean average limit of 0.03 mg/Nm³ at 10% O₂ must be met.
- A half-hour mean average of 0.05 mg/Nm³ at 10% O₂ specifically limits short-time peaks.

A higher daily limit of 0.05 mg/Nm³ at 10% O₂ can be granted by the authorities if the operator can show that the above mentioned limit value cannot be met due to mercury input from raw materials. Cement plants using only regular fuels are subject to a mercury emission limit (daily rate) of 0.05 mg/Nm³ at 10% O₂.³

1.3 USA

Since 2005, for cement kilns using hazardous waste as a fuel, a 12-hour rolling average limit for the mercury feed has to be established based on test run averages limiting the mercury content of the hazardous waste feed to 3.0 ppmw⁴ for existing kilns and 1.9 ppmw for new kilns. Additionally mercury emissions are limited either to 120 µg/dscm⁵ corrected to 7% oxygen, 12-hour rolling average when continuously monitored or to a hazardous waste feed maximum theoretical emission concentration (MTEC) of 120 µg/dscm.

The standard for cement plants not burning hazardous wastes was revised to come into force in September 2010 for new sources and in September 2013 for existing sources introducing new limits based on the amount of produced clinker, see **Table 1**. However in February 2013 the compliance date for existing sources was postponed to September 2015 /FED 13/.

Table 1 US-ELV for mercury emissions to be met by September 2015 /FED 11/

existing sources	new sources (after 6 May 2009)
55 lb/MM t (US) of clinker 27.5 mg/t, 30-day rolling average, equivalent to about 11 µg/Nm ³	21 lb/MM t (US) of clinker 10.5 mg/t, 30-day rolling average, equivalent to about 4 µg/Nm ³

Until the new standards come into force, cement plants with a commenced construction or reconstruction on or after 2 December 2005 must meet mercury emissions of 41 µg/dscm or alternatively use a packed bed or wet scrubber⁶ /FED 13/.

² subject to 17. BImSchV

³ subject to TA Luft, currently under revision and expected to take over regulations established in 17. BImSchV

⁴ parts per million by weight

⁵ dry standard cubic meter

⁶ at 7% O₂, based on a performance test or as "maximum theoretical emission concentration" based on the measured performance of the wet scrubber

1.4 Other countries

As shown in Table 2 not only ELVs themselves vary significantly from country to country and are to be distinguished by the use of waste derived fuels, but they also differ in influencing circumstances such as measurement technique or reference conditions.

Table 2 National ELVs for mercury emissions for cement manufacturing in mg/Nm³, status: 2010 /based on REN 10/

Country	without using waste	using waste	information
Argentina		no limit	
Australia	1.0		permit limit
Bangladesh	0.20		
Brazil		0.05	sum of Cd, Hg, and Tl: 0.2 or 0.28; at 7% O ₂
Chile		0.109	at 10% O ₂
Colombia		0.05	at 11% O ₂
Costa Rica		0.24	sum of Hg and Cd; at 10% O ₂
Ecuador			under review; reference value: 0.05; at 10% O ₂
El Salvador		0.05	at 10% O ₂
India	0.2		
Indonesia	5.0	0.2	at 7% O ₂
Korea	0.1		at 13% O ₂
Malaysia	10.0		at 12% CO ₂
Mexico		0.07	at 7% O ₂
Morocco	0.1	0.10	at 11% O ₂
Philippines	5.0		
Thailand		0.10	at 7% O ₂
Venezuela		0.05	at 10% O ₂
Vietnam		0.5	for waste incinerators

2 Behaviour of mercury in cement process

2.1 Description of cement production process

Clinker production

Limestone and clay or their natural mix, lime marl, which are the raw materials for cement clinker, are extracted from quarries typically close to the cement plant. They are comminuted, dried, and heated to 1450°C. This procedure triggers the chemical reactions that result in the formation of cement clinker. It later confers on the cement its hydraulic properties (setting whether it is exposed to air or submerged in water).

Most commonly, clinker is produced in rotary kiln plants which can be divided into wet kiln plants, semi-wet / semi-dry and dry process kiln plants. In the dry process, the raw material is fed to the preheater as finely ground meal. In preheater/precalcination kilns it is preheated to about 750°C to 850°C by the counter-current flow of the kiln exhaust gas.

Calcination, i.e. the separation of CO₂, mainly takes place in the calcining zone of the rotary kiln or in a separate calciner. In calciner kilns the hot meal is discharged from the second cyclone stage from the bottom and swept away by the hot gas flowing upward from the rotary kiln and conveyed to the calciner. In this process, the kiln exhaust gas is suddenly cooled from between about 1000 and 1100°C to the calcination temperature of approximately 850°C. For the endothermic calcination reaction to be maintained, fuels that may – depending on the kiln plant – account for a thermal input of up to 60% of the total fuel energy requirement, are supplied in the calciner.

In plants utilizing grate preheaters (semi-dry process), the raw material mix, which is dry at the beginning, is formed into pellets by adding water. In the grate preheater, these pellets, which are disposed on a travelling grate, are passed through a tunnel subdivided into a drying chamber and a hot chamber, from which they enter the rotary kiln.

Raw materials with a high moisture content may also be fed as a slurry directly into a long rotary kiln where drying occurs within the kiln or in a separate dryer/preheater. Since the wet slurry has to be dried, this wet process has a higher energy demand compared to the previously described processes.

As fuels commonly black coal, lignite, petroleum coke and to a lower extent natural gas and heavy fuel are used. However numerous alternative fuels such as plastics, mixed industrial wastes (RDF), tires, meat and bone meal or other waste derived fuels are used to preserve natural resources and to lower production costs.

Cement grinding

Clinker is ground together with other major (e.g. granulated blast furnace slag, fly ash, puzzolana, lime stone) and minor (e.g. filter or bypass dust) constituents in ball mills, vertical roller mills, high pressure grinding rolls or combined systems. The compositions of the cement as well as the allowed constituents are defined in the respective cement standards. Cement standards differ globally with respect to cement composition, properties and constituents. So e.g. some standards allow the intergrinding of kiln or filter dust in cement while others do not.

Exhaust gas utilization

For cement plants with an in-line raw mill there are two modes of operation. In mill on operation (raw mill on), the kiln exhaust gas' enthalpy is harnessed in the raw mill to dry raw materials cooling the exhaust gas temperature to 90 – 120°C. In mill off operation (raw mill off) the exhaust gas leaving the preheater with a temperature of about 300 – 400°C is cooled down in a conditioning tower to below 150 – 200°C. Dedusting takes place in a subsequent electrostatic precipitator (ESP) or fabric filter. If raw mill and evaporating cooler are in parallel circuit, the gas stream may be parted to suit the energy demand of the drying process within the raw mill.

The time of raw mill on and raw mill off operation depends on the raw meal quantity needed for kiln operation and therefore on the relation between installed mill and kiln capacity. The respective gas stream proportion led through the raw mill is determined by the raw materials' moisture content. The residual kiln exhaust stream bypasses the raw mill and is conditioned in a evaporating cooler.

As an example in Northern Europe, where raw materials are predominantly humid, raw mills are designed accordingly and due to the necessary drying, mill on operation makes up for 80 to 95% of the total time of operation.

In other regions where raw materials are dryer less exhaust gas is needed for drying and thus a bigger part of the exhaust gas bypasses the raw mill. The time of mill operation can be prolonged to a minimum mill shutdown time for higher system stability by reducing the throughput of the raw mill.

Some dry kiln systems are equipped with a so-called bypass system in order to limit a level of internal cycles of alkali, chloride or sulphates in the system. Therefore a small part of the kiln gases is removed from the kiln inlet and cooled to ca. 250 – 350°C in order to condense the salts. This salt containing dust is separated in an ESP or fabric filter. The clean bypass gas is led to the main stack or separate stack.

Dust utilization

The precipitated filter dust from the main filter is usually recirculated to the raw mill or the raw meal silo. In some cases and according to the respective cement standard a part of the dust is used in the cement mill serving as an additive to adjust the cement quality. Also bypass dust can be used as cement additive and ground together with clinker in the cement mill.

2.2 Behaviour of mercury in cement production

Mercury is ubiquitous and from a toxicological point of view very important substance and can originate from raw materials as well as fuels used in cement production. Its concentration can vary significantly from one raw material or fuel to another, from deposit to deposit or even within one quarry.

2.2.1 Where does mercury come from?

Mercury is introduced into the clinker burning process via both, raw materials and fuels. When using alternative fuels or materials, they substitute an equivalent proportion of natural constituents and also contain mercury. The following **Table 3** shows ranges of mercury contents found in certain regular and alternative fuels currently utilized in cement works.

Table 3 Typical composition of regular and alternative fuels used in the cement industry /REN 10 and references cited therein/

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

The comparison with regular fuels leads to the conclusion that alternative fuels can have both, higher or lower contents of mercury than regular fuels. The same applies for conventional and alternative raw materials. The following **Table 4** shows typical average values found in conventional and alternative raw materials currently used in cement works. Some of the alternative raw materials show significantly higher mercury concentrations than the standard raw materials limestone, marl and clay.

Table 4 Typical composition of conventional and alternative raw material used in the cement industry /REN 10 and references cited therein/ compared to earth crust /UNEP 02/,/EHR 08 and reference cited therein/

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 ⁷ (avg.)	0.05, 0.08

In special cases higher or lower values may be found. It has to be kept in mind that these materials constitute only a small percentage of the whole raw meal mix. The comparison with the average Hg content in earth crust shows that these are in a similar magnitude as those of most alternative materials.

A study conducted by the Université de Liège, Belgium states that fuels do usually not represent the main input of mercury into the system /REN 10/. This is supported by studies conducted by Schäfer and Hoenig /SCH 01/ and VDZ /VDZ 96/ concluding that the mercury input to the cement production process through raw materials is often about 10-fold higher than through fuels.

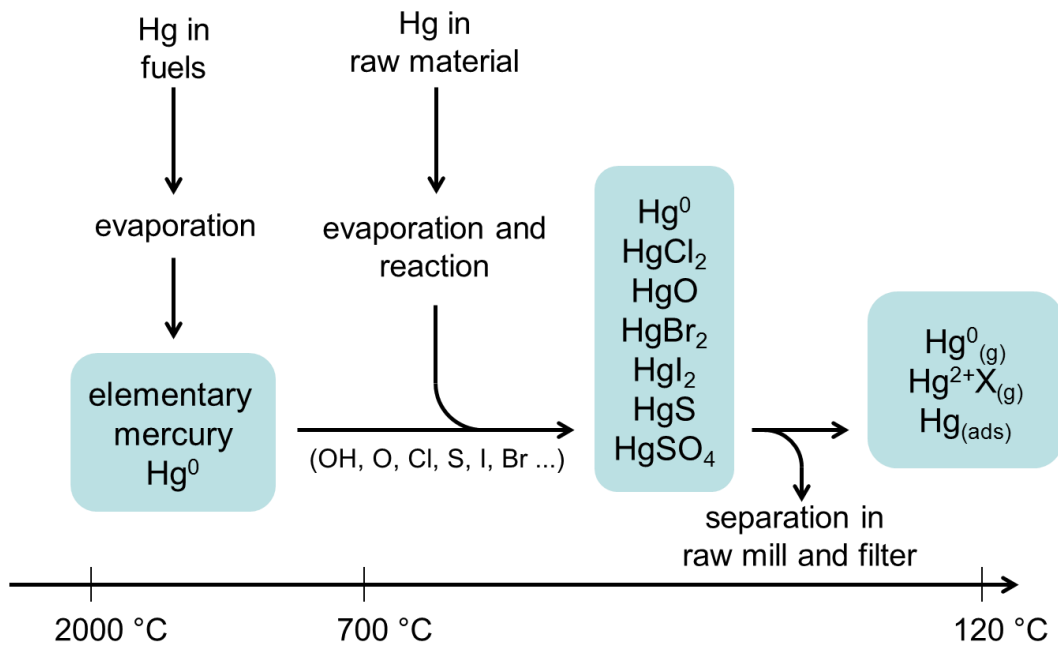
An investigation by the US Environment Protection Agency (EPA) states that non-limestone mercury from fuels and other raw materials accounted for more than 50% of the mercury emissions of about 55% of the investigated kilns. Though the principal volumetric input, limestone in many instances was not the dominant source of mercury. However for more than 70% of the investigated kilns, fuels contribute to less than 30% of the kilns' mercury emissions /FED 09/.

Concerning the impact of the use of waste materials as alternative fuels on mercury emissions, Schneider and Oerter /SCH 00/ analysing 58 test series and the Université de Liège's study analysing 649 values conclude that the substitution of fossil fuels with alternative fuels does not lead to rising mercury emissions.

2.2.2 Behaviour of mercury in the clinker burning process

The behaviour of mercury in the cement production process is mainly determined by thermal conditions between preheater, raw mill and dust precipitator.

Mercury and its compounds entering the process through raw materials and fuels are almost entirely vaporized in the kiln or in the preheater and therefore exit the hot section of the process with the gas stream. Depending on the temperature profile and the presence of oxygen, hydrochloric acid or sulphur compounds, some of the mercury reacts to mainly HgCl_2 , HgO and HgSO_2 , see Figure 1. Other mercury compounds listed may occur but play a minor role in the process.



Behaviour of mercury in the clinker burning process

Figure 1 Possible conversion reactions of mercury in the clinker burning process /VDZ 12/

With a decrease in temperature in the raw mill, mercury compounds condense on the raw meal in mill-on operation. To a smaller extent elemental mercury is adsorbed on its surface. The adsorption rate largely depends on temperature and available surface. A low temperature and a high dust load i.e. a high available surface favour the adsorption. **Figure 2** compares the mercury adsorption in a grate preheater and a cyclone preheater in mill off operation. Due to the by far higher available surface, adsorption in cyclone preheaters is most efficient at temperatures below 140°C.

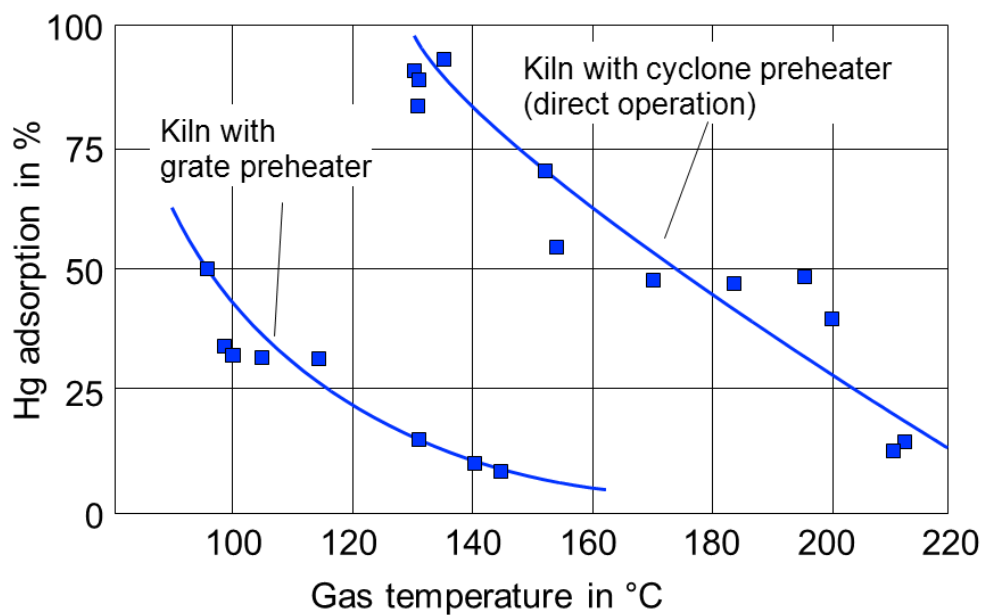


Figure 2 Comparison of mercury adsorption in grate and cyclone preheaters depending on clean gas temperature /KIR 94/

In mill-off operation or respectively in the part of the exhaust gas which is not led through the raw mill, mercury adsorption depends on the temperature profile which is determined by the water injection in the conditioning tower or by quenching with cold air. Also in this case the relationship between mercury adsorption and gas temperature shown in **Figure 2** is relevant. Due to the lower available surface in the absence of mercury adsorbing raw meal as well as higher temperatures, the retention capacity is significantly smaller in raw mill-off operation.

As the ground raw meal is fed to the kiln and precipitated dust is usually recycled to the kiln system, a mercury cycle is formed between preheater, raw mill and exhaust gas filter. Without measures the level of mercury concentration is higher the more gas is lead through the raw mill and the longer the mill-on operation lasts (**Figure 3**). After a change to mill off operation this cycle is relieved but the long term overall mercury mass flow is not influenced. Albeit clean gas mercury concentration may temporarily be lower in mill on operation, only the time of release is delayed through buffering in raw mill and kiln meal silo.

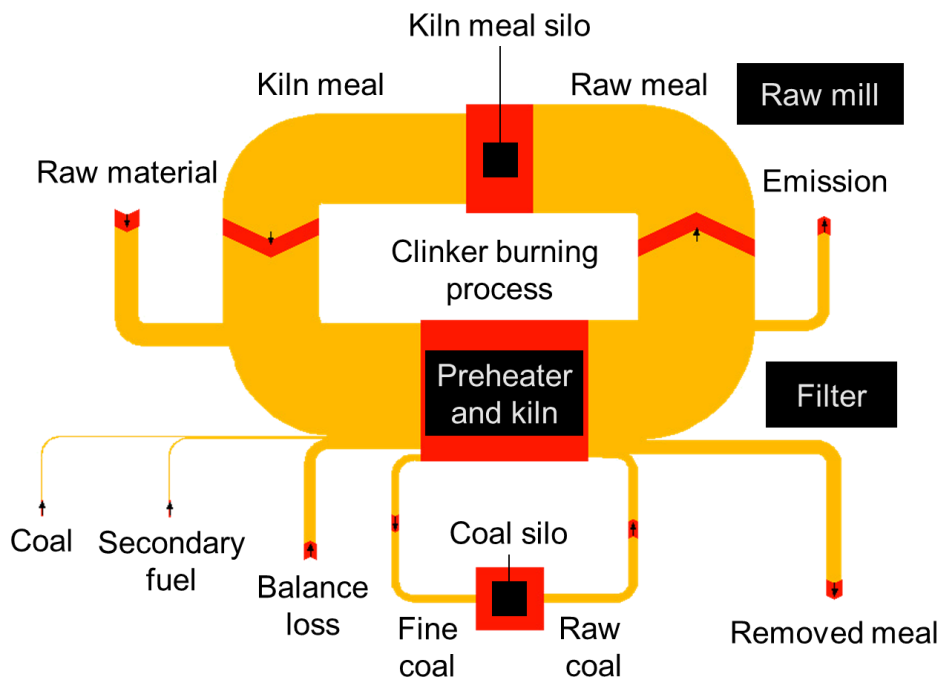


Figure 3 Mercury cycle in a preheater cement kiln in mill on operation /ECR 10/

Figure 4 shows this characteristic dynamic behaviour of mercury in a cement plant with comparatively high share of mill-on operation.

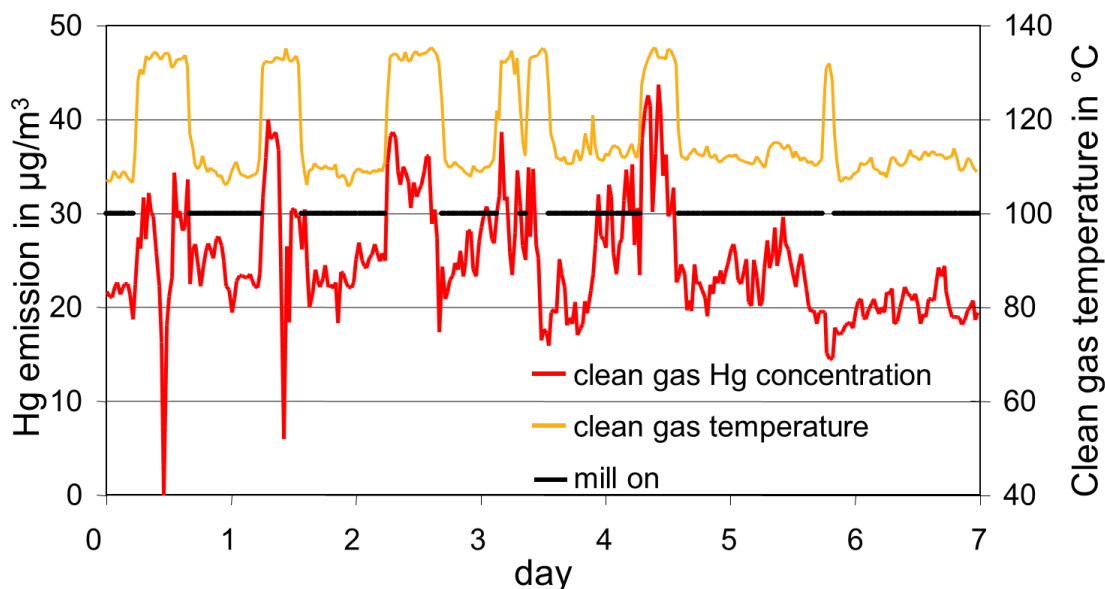


Figure 4 Mercury emissions from a European cement plant, in mill on and mill off operation, without meal removal /ECR 10/

2.2.3 Mercury releases from cement production

Mercury emissions from cement production as a whole, are determined by the overall mercury input through raw materials and fuels and can be expressed e.g. in yearly emissions as in section 2.2.4 below.

Short-time concentration levels are commonly used to describe emission limit values as in section 1. Mercury peak emissions from cement production vary with the type of kiln system in use. While long wet and dry kilns in general have lower and constant emissions, preheater/precalciner kilns tend to emit higher concentrations of mercury in mill off operation due to the previously described release of the built-up mercury cycle but lower concentrations in mill-on operation. According to /SCH 09/, an investigation of the mercury compounds showed that wet kiln emissions consist mostly of elemental mercury while emissions from dry kilns consist mostly of oxidized mercury.

2.2.4 Known inventories

According to the UNEP's Global Atmospheric Mercury Assessment 2013, the production of cement is responsible for about 9 % of the world's 1960 tonnes of mercury emissions /UNEP 13, reference year: 2010/. This can be distinguished further into regions as shown in **Table 5**. As the data for the cement industry have been calculated based on emission factors, a significant uncertainty can be assumed. With regard to information from Europe the values listed in the following table seem to overestimate the real situation as no real measurement results have been used. Furthermore the information from the study of the Université de Liège has not been taken into account.

Table 5 Worldwide anthropogenic mercury emissions from cement production /UNEP 13/

Region	Mercury emissions [t]	% of Cement related emissions	% Change from 2005
Australia, New Zealand & Oceania	0.7	0.40	0.0
Central America and the Caribbean	3.2	1.85	-4.1
CIS & other European countries	4.7	2.72	-1.1
East and Southeast Asia	102.4	59.16	40.5
EU25	13.1	7.57	-8.7
Middle Eastern States	13.4	7.74	43.7
North Africa	7.9	4.56	35.7
North America	2.3	1.33	-33.6
South America	5.1	2.95	35.3
South Asia	16.9	9.76	45.4
Sub-Saharan Africa	3.4	1.96	24.0
Cement Industry Total	173.1	–	30.4
World (all industries)	1960.0	–	–

2.3 Safe enclosure of mercury

The described behaviour of mercury in the clinker burning process leads to the fact that practically no mercury ends up in the clinker. If a part of the filter dust is removed from the hot process section and used in the cement mill, part of the mercury is included in the cement.

As the hardened cement paste shows an excellent binding capacity for heavy metals only a minor percentage of heavy metals is released from the final product concrete. In addition to that, the dense pore structure that concrete has makes it highly resistant to diffusion. This prevents the release of heavy metals dissolved in the pore water of the hardened cement paste. Research projects have shown for mercury amongst other metals that the values measured in leaching tests of new and crushed concrete are extremely low. The interpretation leads to the conclusion that mercury is solidly fixed in the hardened concrete matrix /VDZ 96/.

3 Mercury abatement techniques with regard to the European BAT Reference Document

Regarding metal emissions from the cement production process (including mercury) according to the European Commission's BAT Reference Document it is Best Available Technique to apply one of the following measures individually or in combination /BAT 10/:

- 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.

3.1 Methods for removing mercury

3.1.1 Cement kiln dust shuttling

A proven technology to limit the build-up of a mercury cycle is the selective shuttling or 'bleeding' of precipitated dust. It is most effective in preheater/precalciner kilns during mill off operation or in a "mill-off" – string, in case only a part of the exhaust gas is used in the raw mill. In other configurations, the technology can also be applied continuously if the precipitated dust from the kiln system is not intermixed with the kiln meal, e.g. at long dry kilns.

This method is systematically applied in many cement plants to specifically separate mercury from the process.

Extensive research by the Research Institute of the German Cement Industry of VDZ on cement plants with preheater systems was conducted to investigate the dynamic behaviour of mercury cycles between preheater, raw mill and filter system to entirely describe the context of mercury emissions /VDZ 08/ as well as the efficient application of the dust shuttling technology. As the relationship between mercury separation and gas temperature shown in **Figure 2** is also relevant for the dust shuttling technology, the efficiency of the mercury removal is higher the lower the temperature in the gas stream is and the higher the proportion of oxidized mercury is. This means, that in most cases the water or air quenching of the exhaust gas has to be optimized and temperature has to be reduced to 120 – 140°C. This leads to a significantly higher adsorption of mercury on the particles, so that with a given quantity of dust more mercury can be removed from the process.

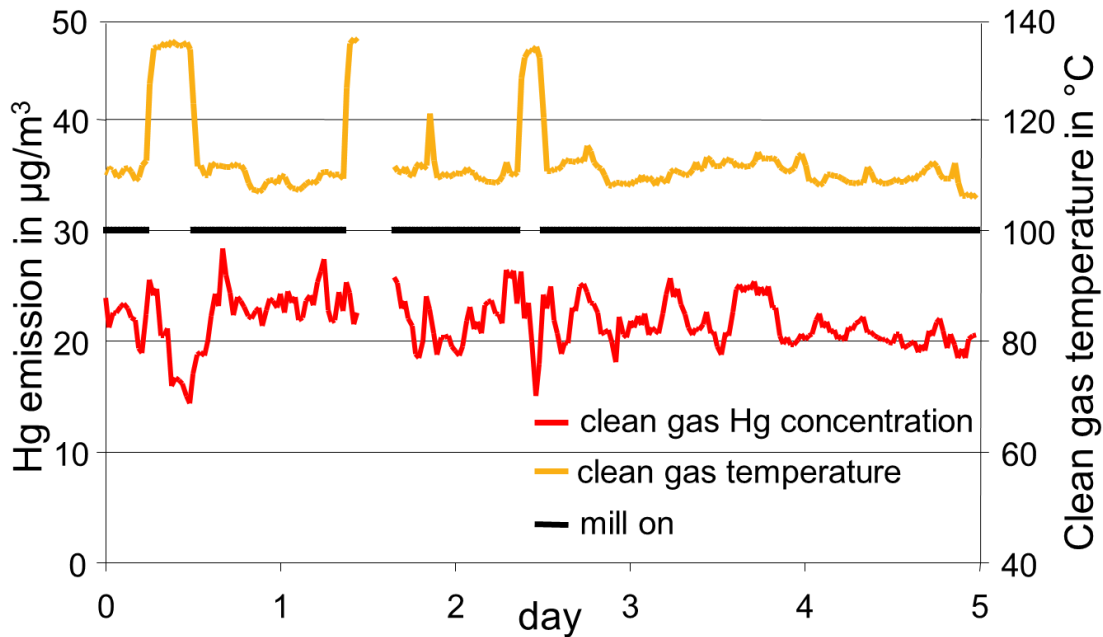


Figure 5 Mercury emissions with meal removal /ECR 10/

As shown in Figure 5 peak emissions during mill-off operation can be successfully reduced if dust shuttling is applied in a well-directed way. On the other hand dust shuttling is more efficient the higher the level of mercury enrichment in the system. A lower enrichment means that more dust or meal has to be removed from the system. Finally it is influenced by the duration of mill off operation, temperature and rate of dust shuttled.

3.1.2 Enhanced trapping and removal using sorbents

The described process of dust shuttling may be enhanced by adding sorbents with a high surface area or specific chemical properties to increase the rate of mercury bound to particles.

3.1.2.1 Injection of activated carbon (ACI) or other sorbents

The injection of activated carbon is applied increasingly in some industries such as coal-fired power plants or waste incinerating plants for the successful reduction of mercury emissions. The sorbent is injected into the gas stream before the particulate matter control system and mercury among other emissions is captured physically on the activated carbon's high surface area with high reduction rates.

However in cement industry, this measure is not easily applied since the majority of the removed dust is commonly recirculated within the production process. Usually, shuttled dust can be used in the cement mill but activated carbon content may cause undesirable colouring of the cement or interfere with air-entraining agents. Therefore activated carbon contaminated dust must be removed from the kiln system.

To ensure a proper adsorption and to avoid the danger of carbon fires, the temperature at the injection area would have to be kept considerably below 200°C /REN 10/.

A solution to both issues would be the installation of the ACI system tail-end just before the stack with a separate polishing filter. But as this solution is very cost intensive, it probably would not be suitable for most cement plants.

Alternative concepts suggest a separate thermal treatment of precipitated dust in a separate installation to remove mercury from the process. Mercury is re-volatilized and subsequently separated again. The scale of this installation would be by far smaller than a tail-end ACI injection system. To date this technology is in research or pilot phase; no information on a feasible operation of such an installation is available.

Only very few cement plants globally are using sorbents to minimize mercury emissions so far and there are no independent and conclusive findings to which extent this technology may be successfully applied in cement production.

Other sorbents such as lignite, metakaolin, calcium hydroxide, zeolites or combinations thereof are also options to be considered and may be feasible with different levels of efficiency. Of the mentioned, calcium based sorbents are expected to have only little if any influence the cement's properties when blended.

Currently, an alternative concept using a sorbent polymer composite in fixed modules has been developed which may be installed either in a separate installation tail-end or inside a wet scrubber. Mercury enriched modules would have to be disposed of as hazardous waste. According to the manufacturer field tests are planned. No industrial scale application is known.

3.1.2.2 Use of oxidizing agents

Since the adsorption rate of oxidized mercury on sorbents is higher, their adsorption capacity may be further increased by additives such as bromine, sulphur or more complex compounds with similar chemical properties. They may for example be used as an additive to or as an impregnation on the sorbent.

Elemental mercury is bound to the acidic component by chemisorption which increases the effectiveness of the adsorption. The resulting more efficient sorbent's capability to capture mercury leads to an increased removal through dust shuttling.

So far there is no certainty if the added oxidizing agent or the sorbent influences the cement's quality if enclosed.

3.1.3 Lignite coke filter (Polvitec)

Polysius' Polvitec technology uses a packed bed activated coke to separate SO₂, organic compounds, metals (including mercury) and NH₃ by adsorption. The cleaned gas is led through the activated coke in a cross current flow and the remaining dust content is further decreased. All the mentioned emission components were reduced to below the detection limit /ROS 95/.

Though technically highly efficient, the system is only installed at one cement plant in Europe (Siggenthal, Switzerland, since 1994). Its operation is economically only feasible because

about 30% of the investment was carried by the nearby city of Zürich for the burning of the city's sewage sludge. /BAT 10, REN 10/

3.1.4 Interactions with other gas cleaning technologies

In the following section two technologies originally developed for the abatement of other emissions are presented since they influence mercury emissions. Not suitable for the sole purpose of mercury emission reduction, their influence may be utilized in a multi-abatement strategy.

3.1.4.1 Wet scrubbers

Wet scrubbers are primarily used to reduce the SO₂ content of a flue gas by absorption in a spray tower using calcium carbonate slurry with gypsum as a product. Commonly used in coal fired power plants and other industries, very few are installed in cement production at plants using raw materials with high low volatile sulphur content. Depending on their initial level, SO₂ emissions are reduced up to 95%. Additionally wet scrubbers can reduce HCl and NH₃ emissions

A side effect known from experiences in power plants and waste incinerators is the additional reduction of metal (and mercury) emissions. Soluble mercury compounds such as HgCl₂ are washed out to remain in the slurry while highly-insoluble elemental mercury, mainly remains in the desulphurized gas stream. Therefore mercury reduction in wet scrubbers at cement kilns may vary widely from case to case.

Installations of wet scrubbers imply relatively high investment and increased operational costs, an increased water consumption and higher CO₂ emissions due to the chemical reaction forming gypsum. Therefore the reduction of mercury in wet scrubbers can be seen as a secondary benefit and an optimization can be explored if the technology is present for its main purpose.

As of 2010 six wet scrubbers were installed at European cement plants and two at US Cement plants /BAT 10, REN 10/. Gypsum resulting from the wet scrubbing process from desulphurization in power and cement plants is added to the cement to replace natural gypsum.

3.1.4.2 Selective catalytic reduction (SCR)

SCR is a new technology in the cement industry to reduce NO_x emissions by injecting NH₃ or urea into the gas stream to react on the surface of the catalyst. On the catalyst surface elemental mercury is oxidized in the presence of acidic compounds, mainly HCl.

Currently extensive research is carried out to proof the applicability of SCR technology in the cement industry. Investigations at European (Germany, Austria, Italy) cement plants indicate that most of the elemental mercury contained in the gas stream is already oxidized after the first catalyst layer as shown in **Figure 6**. If SCR is installed for NO_x abatement, this side-effect might be utilized in combination with dust shuttling since adsorption of mercury compounds is higher than of elemental mercury. Quantification of this effect requires further investigation.

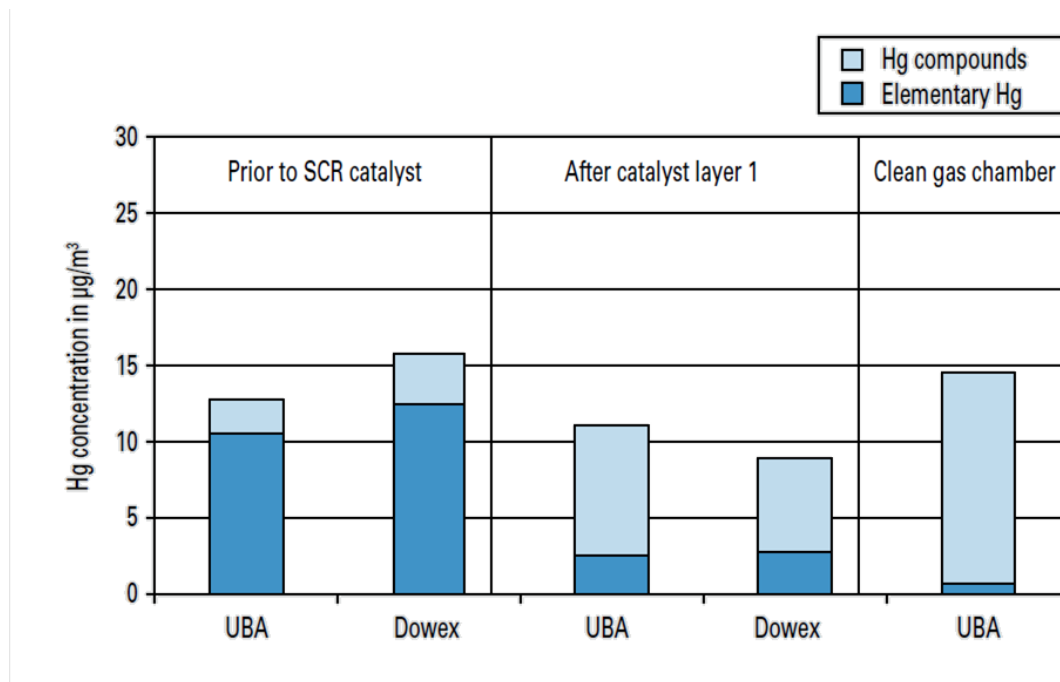


Figure 6 Example of the use of various speciation methods (UBA and Dowex) in a rotary kiln plant with SCR-Denox catalyst /VDZ 12/

Currently in Europe four SCR installations are in operation (2 of them in demonstration) and around the world several are in the planning phase.

3.2 Emission monitoring

3.2.1 Monitoring of mercury emissions

The measurement of mercury emissions in the exhaust gas of cement kilns is particularly challenging as mercury arises in different forms. Generally a distinction has to be made between particle-bound mercury, elemental mercury and oxidized mercury. While elemental (Hg^0) and oxidized mercury [$Hg(I)$ or $Hg(II)$] comprise the vapor-phase mercury, the particulate mercury represents the fraction which is condensed onto particulate matter.

Manual methods for mercury spot measurements as well as continuous emission monitoring systems (CEMS) must be able to detect the total mercury emissions independent from their form of appearance. Due to the low level of particulate emissions in the exhaust gas of cement kilns the ratio of particle-bound mercury of the total mercury emissions is very small and in most cases even below the detection limit. While the manual sampling methods strictly consider the possible amount of particle-bound mercury the sampling methodology of CEMS in most cases provides a dust filter at the inlet of the sampling probe in order to protect the subsequent measuring system. Though the particle-bound mercury is not considered the measurement error should be minimal.

3.2.2 Manual methods for mercury spot measurements

Depending on the measurement task different international guidelines and standards have to be considered. The European Standard EN 13211 is a standard reference method for the measurement of the total mercury emissions. It uses an acid aqueous solution of potassium permanganate or potassium dichromate for the sampling of vapor-phase mercury as well as

a filter paper for the collection of particle bound mercury. In Europe this standard has to be used for all legally required short-term mercury measurements. The sampling time should be 30 minutes up to 2 hours. In principle the European standard EN 13211 is comparable with the US EPA methods 101 A. Combining the European Standards EN 13211 and EN 14385 not only mercury but also a set of other relevant heavy metals can be measured. This procedure is comparable with the US EPA method 29.

If the speciation of elemental and oxidized mercury is required the only available standard is ASTM 6784-02 (Ontario Hydro) which uses a set of impinger bottles filled with different aqueous acid solutions in order to collect the different forms of mercury separately. As these speciation measurements are not legally binding in Europe no special standard exists. In literature a wet-chemical method, the so-called "UBA-method" is described which is basically comparable to the Ontario-Hydro method.

Besides these wet-chemical methods for the speciation of mercury emissions it is also possible to use sorbent traps filled with different materials. While oxidized mercury can be collected in a first trap filled with adsorber resins the elemental mercury will pass to a second trap filled with iodized carbon. In Europe this procedure is known as "Dowex-Jodkohle-Verfahren", which is similar to the procedure described in Appendix K to part 75 (formerly US EPA method 324). Besides the Appendix K method is appropriate for long-term mercury measurements up to a sampling time of 14 days in order to monitor low levels of mercury emissions.

Due to the growing importance of sorbent traps for the measurement of mercury emissions the European Committee for Standardization (CEN) has just established a working group for the elaboration of a European Standard "Stationary source emissions – Mercury monitoring using sorbent traps".

3.2.3 Continuous emission monitoring systems (CEMS) for long-term mercury measurements

CEMS for mercury measurements must be able to determine a complex mixture of different mercury components. Based on the measurement principle in all CEMS for mercury UV photometers are used which can only detect the elemental form of mercury (Hg^0) on a wavelength of 253.7 nm. The prior reduction of all the other gaseous mercury compounds into elemental mercury is therefore essential for the complete measurement of the overall mercury emissions. This preparatory step is decisive for the quality and long-term stability of the continuous mercury detection.

Continuous measurement of mercury emissions is not classified as Best Available Technique in the European BAT Reference Document for the Cement, Lime and Magnesium Oxide Industry. Nevertheless, in Germany cement kilns using alternative fuels must be equipped with mercury CEMS since the year 2000. These CEMS previously have undergone a suitability test pursuant to EN ISO 14956 (or the newer EN 15267) and have been acknowledged by the competent authorities. The first generation of mercury CEMS was developed in the 1990s and underwent their suitability tests between 1996 and 2001. The experiences in the following years have shown that, despite the successful completion of the suitability testing, difficulties arose in practice with regard to the stable long-term operation of the measurement devices. Instrument modifications based on experiences gained as part of multiple emission

measurements, calibrations and functional tests enabled an improved adaption to the features of the exhaust gas of cement kilns. Despite the efforts of suppliers, cement plants and measurement bodies not all issues have been able to be conclusively clarified.

In the light of this – but also due to the drastic tightening of the emission limit values for combustion plants discussed in the USA since the end of 2011 – various instrument manufacturers brought newly developed mercury CEMS onto the market.

Due to the complexity of the technology and the addressed issues still present after more than ten years of CEMS in place in a few countries, like e.g. Germany, the systems demand a continuous sophisticated maintenance and a highly available technical support which may be difficult to provide in regions outside Europe or North America.

A distinction must be made between the three fundamentally different designs of mercury CEMS.

3.2.4 Thermo-catalytic devices

Oxidized mercury is converted to the elemental form by using a thermal catalyst in the temperature range of 200 to 400 °C. These devices may be equipped with a sample gas dilution robin order to prevent a premature contamination of the catalyst and the associated loss of activity. This also reduces possible cross-sensitivities by other exhaust gas components, e.g. SO₂. Some of these devices are also equipped with a gold amalgamation in order to improve the sensitivity for lower mercury concentrations.

3.2.5 High temperature cell

For this newly developed measuring principle sampled gas is fed into a quartz measuring cell that is heated to 1 000 °C. Mercury compounds are immediately reduced to elemental mercury at these temperatures and can be measured directly in the photometer. Any cross-sensitivities are eliminated.

3.2.6 Wet-chemical devices

For the reduction of mercury compounds to elemental mercury a liquid agent (usually tin(II) chloride) is used. The liquid agent is a consumable which has to be replaced regularly. It has to be expected that no new installations of this sort of equipment will be realized.

The newly developed instruments can be equipped with automatic adjustment devices that perform a daily check of the CEMS function with mercury test gases. Furthermore this option allows the requirements of EN 14181 to be fulfilled with regard to the regular quality control (QAL 3) by the plant operator.

4 Best Available Technique and Best Environmental Practice

The first measure to limit mercury emissions is to limit the input of mercury into the cement production process by carefully monitoring raw materials and fuels. On the other hand, this is most often very difficult as far as natural raw materials and regular fuels are used.

If albeit the efforts mercury emissions continue to be on a high level, it is Best Environmental Practice to reduce the exhaust gas temperature to below 140°C and remove dust from the filter in mill off operation. The removed dust can be used to specifically influence the cement's properties and the low average mercury level in the input materials is reflected in the output materials. While this is not possible due to market reasons in a few countries, the procedure is covered by national cement standards in many countries in the world. Since the measure is a proven safe way to reduce mercury emissions, global acceptance in markets and in standards is desirable.

Cement plants struggling with very high mercury emissions should consider the use of sorbents in conjunction with dust shuttling to limit their mercury emissions. The sorbent has to be selected carefully dependent on the present input level and desired output level, ensuring that in case of an incorporation of the sorbent, it must not influence the cement's quality.

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