Guidance for reducing and controlling emissions of mercury compounds in the cement industry

Cement Sustainability Initiative (CSI)

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Acronyms and abbreviations

APCD	air pollution control device
AST	annual surveillance test
ASTM	American Society for Testing and Materials
BAT-BEP	best available techniques and best environmental practices
CEM	continuous emissions monitor
CKD	cement kiln dust
CSI	Cement Sustainability Initiative
CUSUM	cumulative sum control
ESP	electrostatic precipitator
FLPE	fluorinated polythene
ID	induced draft
NESHAP	National Emission Standards for Hazardous Air Pollutants
ppb	parts per billion
PTFE	polytetrafluoroethylene
QAL	quality assurance level
SCR	selective catalytic reduction
UNEP	United Nations Environmental Programme
US EPA	United States Environmental Protection Agency
WBCSD	World Business Council for Sustainable Development
WHO	World Health Organization

1. Introduction

1.1 Objective

The objective of this document is to provide guidance in measuring and controlling mercury emissions from cement manufacturing. Mercury is a toxic pollutant. It is reported (Munthe, 2010) that cement industry could contribute approximately 10% of all anthropogenic mercury emissions. However, emissions are highly variable depending on the fuels and raw materials used to make cement. The industry has considerable experience in preventing and minimizing inputs of mercury to and controlling releases from kilns. This Guidance is designed to help operators quantify emissions and track and control them efficiently and effectively.

The information was compiled from available literature, actual experiences and industry knowledge. This document complements other information, including the best available techniques and guidance on the best environmental practices (BAT-BEP) methods for adoption developed by the United Nations expert group under the Minamata Protocol. This guidance is specifically intended to assist cement plant operators in implementing techniques that can effectively reduce mercury emissions to the air. The cement plant operator should be cognizant that their plant could also be releasing mercury to the environment through mercury contained in disposed waste, including electrical and electronic equipment, batteries, laboratory waste, or residual waste from calibration materials or equipment, and should take appropriate action to properly dispose of and minimize these sources of solid waste.

1.2 Mercury in the environment

Mercury is a heavy metal that occurs naturally in the environment in various chemical forms. It averages around 50 parts per billion (ppb) in the Earth's crust. It can be found in its pure, or elemental, form or in combination with other elements (Kline 2013). At ambient temperatures, mercury occurs as a liquid. When in contact with air, mercury evaporates slowly into mercury vapors. In the natural environment, mercury occurs in both organic and inorganic forms (Lafarge 2007). The most common compound found in nature is mercury sulfide, commonly known as cinnabar. In the past, cinnabar was mined in order to produce pure mercury (Kline 2013). Small amounts of mercury are found in the raw materials and fuels used to produce cement.

It is estimated that roughly one-third of the mercury in the atmosphere and ecosystem comes from natural phenomena such as volcanic activity and the erosion of rocks (generally in the form of vapor). Human activity accounts for another third through various industrial and domestic processes. The final third of mercury in the atmosphere comes from reemission, such as from forest fires, biomass combustion, evaporation, etc. The principal anthropogenic releases are from: mining (especially gold-mining (Lafarge 2007)); fossil fuel combustion; and the thermal processing of materials where mercury is present as an impurity in the raw materials and fuels used.

1.3 Mercury's use

Mercury continues to be widely used throughout the world in a variety of products and processes, including small-scale mining of gold and silver; chlorine and caustic soda production; dental amalgam fillings; and the manufacture of manometers for pressure measurement and control, thermometers, electrical switches, fluorescent lamps, etc.

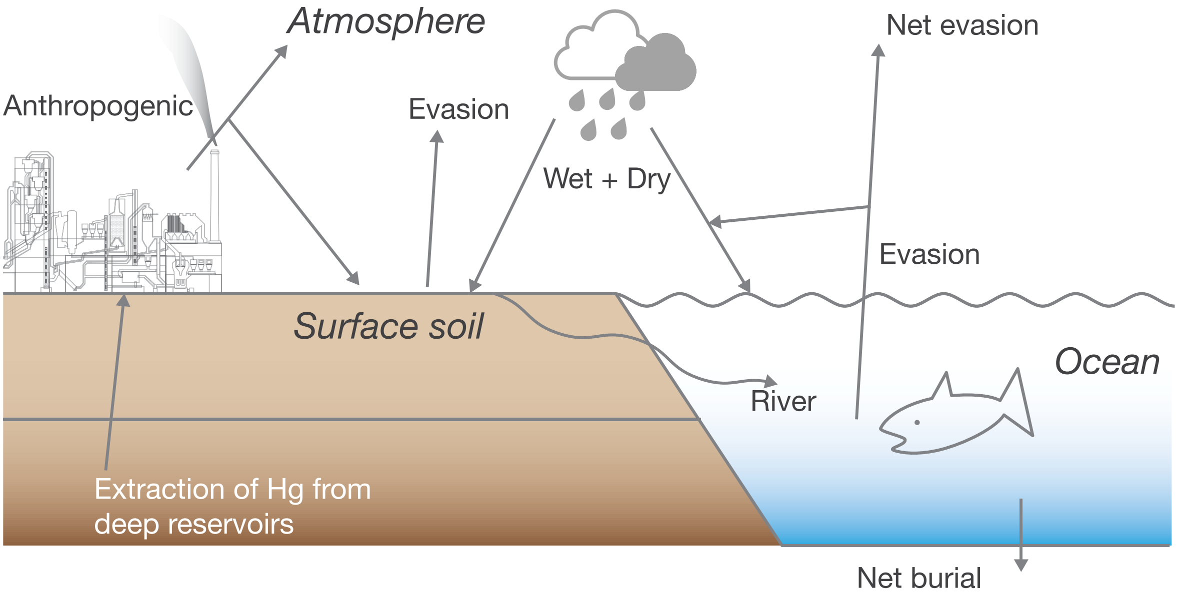
1.4 Health impacts

Mercury is a toxic substance that affects the nervous system. The main reasons why mercury is a chemical of global concern include: its ability to travel long distances in the atmosphere; its persistence in the environment; its ability to accumulate in ecosystems, including in fish; and its significant negative effect on human health and the environment (WHO 2013).

Methylmercury (CH_3Hg^+) is the most toxic form of mercury. Methylmercury is formed directly in chloralkali and other chemical processes. It is also formed in nature through the anaerobic digestion of inorganic or elemental mercury by organisms present in surface water and soils.

Methylmercury bioaccumulates in the food chain when predatory animals and fish ingest food and absorb the mercury in their prey. Higher predatory fish, such as swordfish and sharks, have the most significant amounts of methylmercury. For people working directly with mercury, the breathing of vapors can also be a significant pathway. **Figure 1** shows elements of the mercury cycle in nature, including anthropogenic release, deposition and reemission from soils and surface water, and bioaccumulation primarily in aquatic species.

Figure 1: The mercury life cycle (From Mason and Sheu 2002)



The consumption of fish and marine mammals is the largest source of human exposure to methylmercury. Methylmercury is easily absorbed in the digestive tract where it forms a complex with the amino acid cysteine, which enables entry into the body's cells. Methylmercury will accumulate in the brain and cause damage to the central nervous system, as well as cardiac and respiratory problems. In humans, this methylmercury-cysteine complex is eventually transported to the liver where it is secreted in the bile and after which enzymes break the complex down into its amino acid and methylmercury parts. Methylmercury is naturally removed from the body over long periods of time (Griesbauer 2007).

1.5 Minamata Convention

Minamata is a small town on the western edge of Japan's southern island of Kyushu. The Minamata Bay incident occurred between 1932 and 1968 when Chisso Corporation released methylmercury into the bay, poisoning the entire food chain, including the people who were living nearby. This resulted in 900 deaths and almost 3,000 people being directly affected by "Minamata disease" (mercury poisoning) (McCurry 2006). The effects are still being felt there today.

Japan's largest environmental disaster of the time eventually led to the Minamata Convention, an international treaty completed in January 2013 by the United Nations Intergovernmental Negotiating Committee. Its aim is to control mercury emissions by industries in order to protect human health and the environment.[1]

1.6 Mercury in the cement industry

The cement manufacturing process typically involves burning fuels to heat a mixture of limestone ($CaCO_3$) and additive materials to produce clinker, which in turn is mixed with gypsum to produce cement. The worldwide average emission factor for mercury from cement kilns has been reported as 35 mg/t cement (Renzoni et al. 2010). However, the quantity of mercury emitted by different cement plants can vary significantly. Specific emissions are dependent on the amount of mercury in the raw materials and fuels, as well as the manufacturing process (Schorcht et al. 2013). The range of mercury emissions from the European cement industry is reported to vary between levels that are below detection to 69 mg/t clinker (Munthe et al. 2010). However, emissions from a very small number of kilns worldwide have been reported to be many times higher than this figure. The rapid growth of cement production, especially in some areas of the world, increases the significance of cement manufacturing as a major contributor to mercury emissions.

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1. http://www.mercuryconvention.org/

2. Control of mercury emissions from the cement industry

2.1 Setting mercury emissions objectives

The primary objective of Article 8 of the Minamata Convention is to measure and reduce the quantity of mercury released to the environment from anthropogenic sources, including the cement industry. Such an objective is often achieved in manufacturing processes by limiting the maximum concentration of mercury that can be emitted in exhaust gases. As mercury emissions from cement manufacturing may vary over time, the industry should take a longer term approach to measuring and reducing these emissions.

Plant-specific objectives for mercury emissions levels and reductions should be set based on the lowest level indicated by the following:

- Local regulatory requirements
- BAT/BEP guidance for the specific plant technology
- Overall company targets
- Plant-specific criteria.

2.2 Mercury's behavior in cement manufacturing

The majority of the cement industry employs one of five different processes in the manufacture of Portland cement clinker, the primary ingredient in cement. In general, the various technologies used are, in decreasing order of prevalence:

- Preheater / precalciner process – used in plants built after 1970 and the primary configuration of plants built after 1980.
- Straight preheater process – used in plants built after 1960 and still used in some smaller sized plants today.
- Long-dry kiln process – typically used in plants built between 1940 and 1975, with a small percentage still in use.
- Semi-wet and semi-dry kiln processes – used in plants built after the 1950s and in wet process kilns retrofitted since the 1960s.
- Wet process – older plants or those using especially wet raw materials built before 1970, with a small percentage still in use.

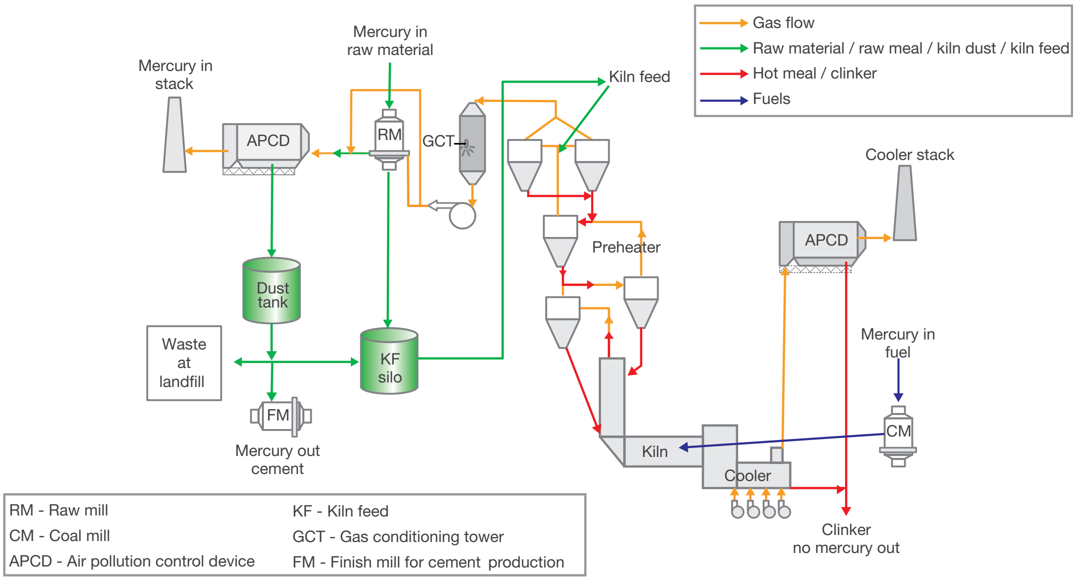
There are potential variations in each of the above processes, such as the number of preheater stages, the types of internals in long kilns (dry and wet), etc.

A technical description of each of the processes, along with the specific behavior of mercury within each process, can be found in the guidance document on BAT-BEP, by the UNEP expert group for implementation of the Minamata Convention (2015).

In summary, all the processes exhibit some common behaviors:

- Mercury enters the process from the raw materials and fuels. Although the concentration of the mercury in the input materials is generally very low (measured in parts per billion), the high volumes of materials processed result in significant amounts of mercury entering the kiln system.
- Virtually all of the mercury from the raw materials and fuels is volatilized in the clinkering process and exits the kiln system as a vapor.
- Practically all of the mercury that enters the kiln system will be emitted through the stack(s), unless there is a specific system for purging mercury.
- Mercury vapors are in an elemental form at high temperatures.
- Elemental mercury can form various mercury compounds when combined with other elements (most significantly halides) as the mercury vapors cool.
- Mercury vapors can adsorb onto solids as the kiln exit gases cool.
- Increased mercury adsorption occurs when the kiln exit gases are used for raw material and fuel drying.
- Mercury can also be adsorbed onto the dust collected in the kiln exhaust filter.
- The amount of mercury adsorption is a function of the form of mercury and the temperature of the gas stream.
- Adsorbed mercury is usually returned to the kiln system and can build up a significant cycle over time.

Figure 2: Diagram of a typical process flow of a preheater cement kiln



2.3 Mercury mass balance

A material or mass balance is an accounting of material over time. Balances are used in industry to calculate mass flow rates of different streams entering or leaving chemical or physical processes. Over longer periods of time, "all mercury in" is equal to "all mercury out". That is, the sum of mercury inputs from fuels and raw materials will equal the sum of mercury outputs in clinker, cement kiln dust (CKD) and stack emissions.

Over the long-term, mathematically;

All Mercury In = All Mercury Out (Eq. 1)

All Mercury In= Raw Materials Hg + Fuels Hg (Eq. 2)

All Mercury Out = Clinker Hg + Stack Hg + CKD Hg (Eq. 3)

Since Clinker Hg is often negligible, then,

CKD Hg = Raw Materials Hg + Fuels Hg – Stack Hg (Eq. 4)

Stack Hg = Raw Materials Hg + Fuels Hg – CKD Hg (Eq. 5)

Mass balances need to account for all the material streams, including any dust removed from the system, such as bypass dust or spray tower dust.

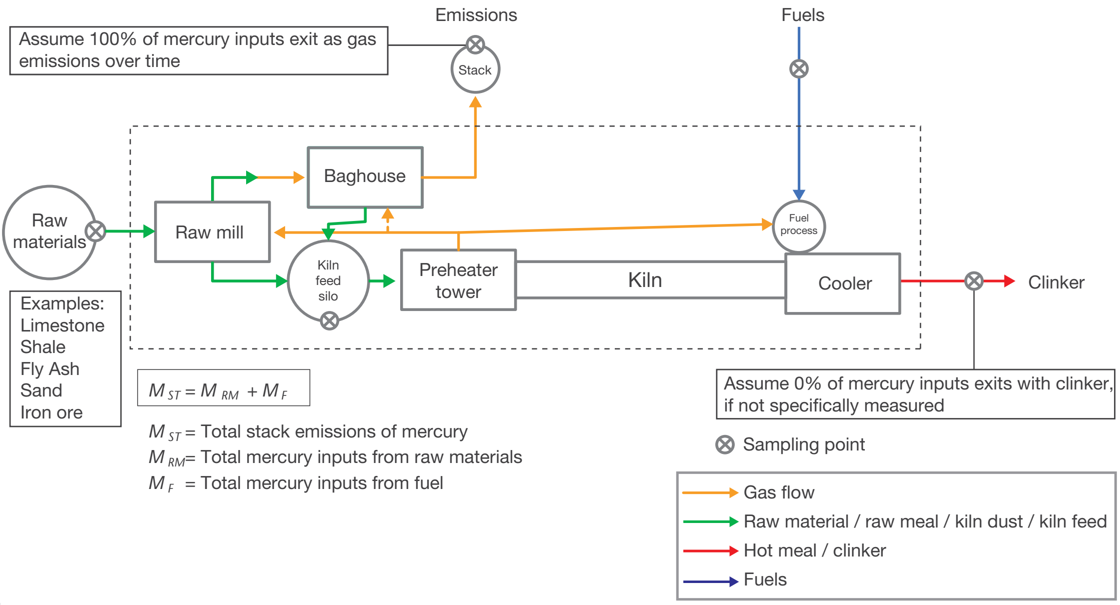
Mercury mass balances can be easily established in spreadsheet format, such as the one displayed in Appendix 1: Sample mercury feed tracking form. Once established, the mass balance can be used to demonstrate potential changes in emissions when raw materials and/or fuels are changed.

It is highly recommended to use a "Material Qualification Form" for each raw material and fuel. A sample of such a qualification form can be found in Appendix 2: Material qualification form. The frequency at which the mercury analysis needs to be updated is dependent on the variability of both the composition and the sources for the material. Materials subject to either source or composition change should be checked more frequently. All material qualification forms should be updated at least annually and when there are changes of supplier.

Creating an accurate material balance requires that representative samples of each raw material, fuel and dust stream be taken. The quantity of samples necessary as well as the frequency of sampling over the balance period will be dependent on the variation of mercury in the material and the size distribution of the stream being sampled. If wastes are co-processed, the variability could be greater and additional care must be observed when taking a representative sample. A site-specific sampling plan should be developed that takes into account all the factors mentioned above. In many cases, analyzing a composite made of 30 daily samples for each fuel and raw material stream will give adequate results.

The American Society for Testing and Materials (ASTM) has standards for coal sampling and for initial preparation of the coal sample for analysis (ASTM D2234[2] and ASTM D2013[3] standards) that can serve as a guide.

Figure 3: Mass balance methodology without dust removal



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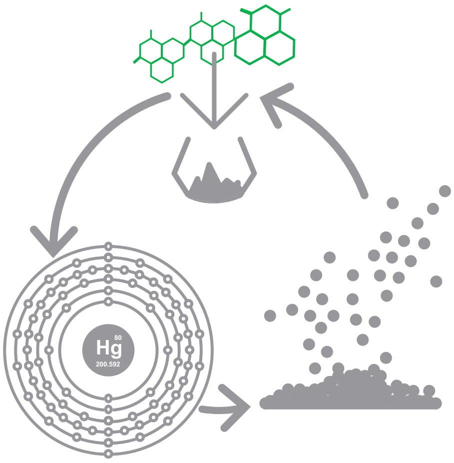
[2] http://www.astm.org/Standards/D2234.htm
[3] http://www.astm.org/Standards/D2013.htm



2.4 Mercury cycles

Mercury can cycle within the cement manufacturing process. Virtually all of the mercury from the raw materials and fuels is vaporized as elemental mercury (Hg^0) in the combustion zones of the kiln and precalciner. This vaporized mercury exits the kiln system with the exhaust gases. The elemental mercury often combines with other elements in the gas stream to form various mercury compounds, collectively called oxidized mercury (Hg^{2+}). Mercury speciation refers to the relationship between oxidized and elemental mercury in the gas stream. The mercury that adsorbs onto the surface of dust particles is known as particle-bound mercury.

The temperature and composition of the gas stream are of significant importance in determining mercury speciation. Minor elements in the gas stream, such as chlorine, can combine with the elemental mercury as it cools to form new oxidized mercury compounds. Oxidized mercury adsorbs more readily onto dust than elemental mercury. The vapor pressure of mercury drops significantly with temperature, which increases the rate of adsorption on dust, as shown in Figure 4.

2.4.1 Filter dust cycle

Kiln exhaust gases are dedusted in an air pollution control device (APCD), also known as the kiln filter. The most common types of kiln filters are baghouses and electrostatic precipitators. Mercury adsorbed on the collected dust does not make its way to the stack at this point. When collected dust is returned to the kiln system, it carries the adsorbed mercury with it. The adsorbed mercury is then combined with the raw material and fuel mercury, increasing the total mercury accumulated in the kiln system. In this manner the mercury inside the system continues to increase until either it is purged or an equilibrium is met. If the cycle is uninterrupted, it will build up over several weeks or months to reach an equilibrium where the amount of mercury emitted through the stack is equal to the inputs from fuels and raw materials.

Baghouses have been found to adsorb more mercury than electrostatic precipitators (US EPA 2005). This is believed to be due to the mercury laden gases passing through the dust cake on the filter bag. This intimate mixing of gas and material allows for increased adsorption of mercury onto dust.

Therefore, the filter dust can be concentrated in mercury. Often this dust is returned to the kiln feed system, creating a cycle in which mercury from the kiln exhaust gases is trapped and returned. Removing this dust from the system will remove some of the mercury from the cycle.

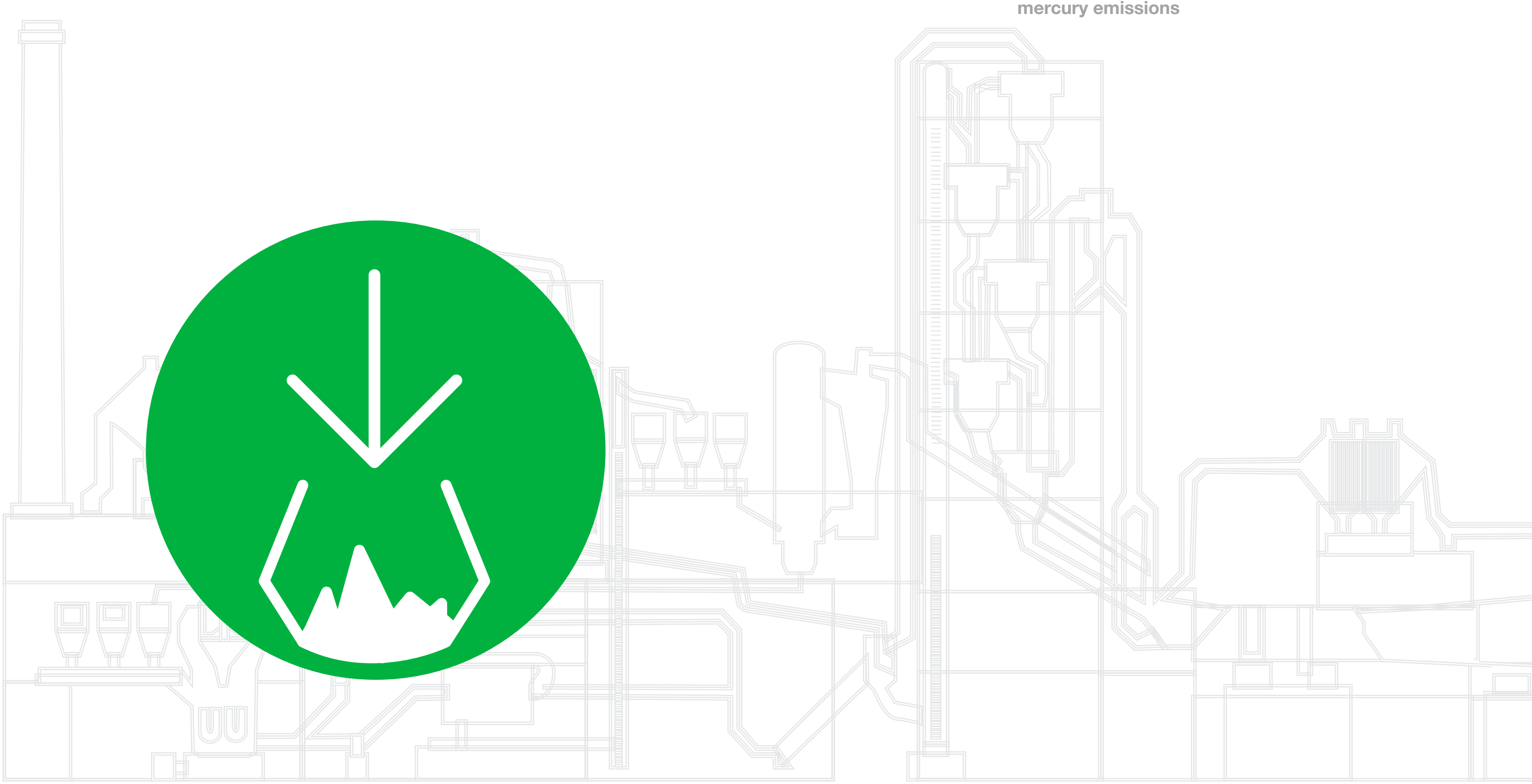
2.4.2 Raw mill cycle

Most modern cement plants utilize the kiln exhaust gases for raw material drying. This is usually accomplished in a vertical roller mill; however, other types of mill systems are also used. The extensive contact between the kiln exit gases and the ground raw materials, combined with the lower temperature of the mill, creates a high degree of mercury adsorption. Thus the mercury content of the gases leaving the raw mill circuit is reduced. The adsorbed mercury is returned to the kiln feed silo with the raw mill product. This cycle builds up over time, increasing the amount of mercury in the kiln feed. Equilibrium is eventually reached, but it can take from several weeks to months to occur.

When the raw mill is taken out of operation, the “raw mill off / direct operation” condition, the preheater exhaust goes directly to the main filter. The raw mill is no longer in the circuit and therefore the high material surface area at the lower gas temperature is not available to adsorb the mercury from the gas stream. The kiln filter then sees a sharp increase in mercury input, which often results in both high stack emissions and higher concentrations of mercury being adsorbed on the filter dust. Stack emissions can increase as much as tenfold, while filter dust concentrations can increase significantly as well (Schreiber and Kellett 2009). This variation creates unique challenges for the cement industry in measuring and therefore managing mercury emissions as an appropriate number of samples have to be taken in all relevant operation modes if spot stack testing is applied to assess mercury emissions over time.

2.4.3 Fuel mill cycle

In many cement plants a portion of the preheater exit gases are used to dry coal or coke in the fuel mill. In this case, the mercury in the gas stream from the preheater is almost entirely adsorbed onto the fuel particles according to the same mechanisms as in the vertical raw mill: low temperature and high surface area contact between the mercury laden gases and the fuel particles. The mercury content of the ground fuel will therefore increase over time as the mercury cycle builds in the kiln system.



3. Using abatement technologies to control mercury emissions

3.1 Control of mercury emissions through raw material and fuel inputs

Mercury is present in all material streams entering the kiln system – in natural and alternative raw materials as well as in conventional and alternative fuels. This means that, like all trace elements, mercury is introduced into the clinkering process via the feed, the main burner, and the secondary firing system. The amount of mercury coming from each raw material and fuel will be a function of the mass flow of that specific material and its mercury content.

The mass balance demonstrates that mercury emissions are directly related to the sum of the mercury inputs. The easiest 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.

3.1.1 Raw material substitution

Raw materials typically have lower mercury concentrations than fuels. However, as the raw material to fuel ratio is approximately 10 to 1, the raw material can often account for the majority of the mercury input. Mercury concentrations in raw materials (limestone, marl or clay) can vary significantly from quarry to quarry and even within a single quarry deposit. Mercury emissions can be reduced by substituting certain raw materials with others that contain less mercury. It is important to know the mercury content of each raw material as well as its variability.

The substitution of limestone, as the principal raw material, is usually not feasible as there is little flexibility in the source of the limestone. In cases where the mercury level in a quarry varies widely, it may be feasible to use selective mining techniques to maintain a target mercury concentration. If this is not possible, then the material with the higher mercury content may be considered as an additive to the cement mill or otherwise disposed of. (As a rough guide, from a mass balance with no abatement, 25 ppb of mercury in the limestone can contribute up to 0.014 mg/Nm^3 of mercury emissions at the stack).

Other raw materials such as shale, bauxite, iron ore or sand are often required to adjust the chemical composition of the raw mix. These raw materials are usually a small fraction of the total raw material requirements and are often transported to the plant from various offsite sources. Cement plants are not as dependent on these materials and in many cases may have access to substitute materials that can bring the same relevant chemistry with a lower concentration of mercury. The availability of suitable substitute materials must be determined on a on a site-by-site basis.

3.1.2 Alternative raw materials

Alternative raw materials are often by-products or wastes from other processes that can be used as substitute for natural raw materials used in cement manufacture. Alternative raw materials should be tested for mercury content as with all other fuels or raw materials. Alternative materials that exhibit higher levels of mercury should be avoided. The variability of mercury in alternative raw materials may be higher than natural materials and therefore they may need to be checked more frequently.

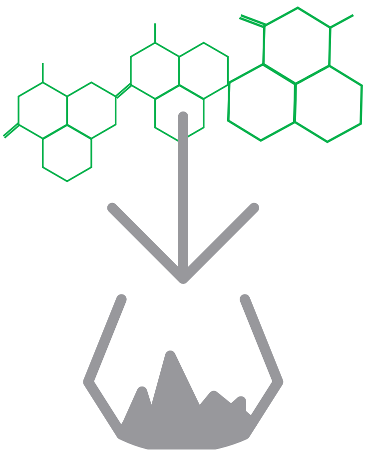
3.1.3 Conventional and alternative fuels

Cement production requires the use of fuels to provide the thermal energy needed for clinker production. This thermal energy can be provided by conventional fuels (such as coal, natural gas, petroleum coke, oil, etc.) or alternative fuels (such as tires, waste-derived fuels, etc.). As mentioned above, fuels are not usually the dominant source of mercury input to the cement kiln system. However, in some cases the fuel streams may be the highest contributor of mercury.

The concentration of mercury can vary significantly for a given type of fuel. For instance, the mercury concentration in coal is generally in the range of 10 to 50 ppb but in some cases may be as high as 2,000 ppb. Similarly, most alternative fuels have low concentrations of mercury, but there are cases of specific alternative fuels that contain unacceptably high concentrations of mercury and should be avoided (CSI 2014).

Selecting fuels, including alternative fuels, with low mercury content is required in order to minimize mercury emissions from the stack. For example, coal high in mercury can be substituted with another type of coal lower in mercury. Changing the fuel type used can also have a similar effect. For example, substituting coal with coke, which normally has extremely low mercury content, can often reduce mercury emissions. Finally, improving the thermal efficiency of the kiln process can reduce the total amount of fuel required, thus also reducing the total mercury input from fuel.

The nature of the mercury input from natural and alternative raw materials and fuels has a critical impact on mercury emissions. It is therefore crucial that plant managers understand the nature of mercury in all their materials and fuels, especially when any changes are made. New sources of raw materials or fuels, changing quarry characteristics, or, most importantly, changing material characteristics due to changes at a source (for instance changes in coal at a power plant supplying fly ash to a cement plant) can greatly affect cement plant emissions and must be appropriately monitored.



3.2 Dust shuttling

3.2.1 Description

A proven technology to limit the build-up of a mercury cycle is the selective purging or “bleeding” of kiln dust, called dust shuttling. The removal of the filter dust from the kiln system carries the adsorbed mercury with it. In the pure sense, dust shuttling implies that the mercury-rich dust is then shuttled or added to the cement product. Some applications consider dust wasting, where the dust is disposed of, to be a form of dust shuttling. In this document “dust shuttling” refers to the addition of the filter and other mercury-laden dust sources to the cement product.

Mercury concentrations are highest in kiln / preheater exit gases. In long wet and long dry kilns, these gases often pass directly to the main filter. Therefore the dust from these filters may have elevated mercury content and allow for dust shuttling. However, the low level of gas to material contact limits the amount of mercury adsorption and therefore the effectiveness of dust shuttling for these kilns.

Dust shuttling is most effective when used in conjunction with preheater type kilns that include a raw mill in the circuit. The high level of gas to material contact combined with the lower operating temperatures of inline raw mills enables a high level of mercury adsorption. Most of the adsorbed mercury is returned with the raw mill product to the kiln feed silo when the raw mill is in operation. Some of the adsorbed mercury is in the filter dust as well.

When the inline raw mill is stopped, the kiln exhaust gases with higher concentrated mercury content pass directly to the main filter. This increase in filter inlet mercury often results in increased adsorption on the filter dust as well as increased mercury emissions. The stack emissions increase as not all of the incoming mercury can be adsorbed on the filter dust.

Dust shuttling is possible during “raw mill on” and “raw mill off” operations:

- Dust shuttling is most effective during a “raw mill off” operation when the collected dust comes from the preheater, which can have significantly higher mercury concentrations.
- It can be effective in “raw mill on” operation in cement plants in which a portion of the kiln gases bypass the raw mill and the dust is collected in a separate filter.
- It is less effective in “raw mill on” operation in cases where the collected dust is a combination of raw mill output and kiln dust.

Dust shuttling technology is most effective when the kiln filter gas temperature is kept below 140°C. In the “raw mill on” operation the gas temperature in the filter is usually between 90° and 120°C. In a “raw mill off” operation the temperature is usually between 140° and 170°C and can be as high as 200°C. Higher temperatures greatly reduce the amount of particle-bound mercury and thus the effectiveness of dust shuttling.

Plants using dust shuttling to reduce mercury emissions should consider the optimum temperature for the “raw mill off” condition. Reducing the gas temperature below 140°C by water conditioning can result in sulfuric and nitric acid condensation, causing corrosion. This potential corrosion can be prevented when the walls of the dust collector and ducting are well insulated, when the hoppers of the dust collector are heated, and/or when the internal metal parts are treated with corrosion resistant coatings.

The captured dust must be removed from the kiln system in order to reduce mercury emissions. The amount of dust to be removed will depend on the concentration of mercury in the dust and the emission reduction target. These can be determined by the mass balance. It may be possible to remove only a portion of the filter dust. In some electrostatic precipitators (ESPs), good results can be obtained by removing only the dust from the last section.

The dust to be removed should be collected in a separate bin in order to be flexible regarding its further usage. In many cement plants the dust is used as a mineral addition to the cement, which is in line with most cement standards, (e.g. European standards). If this is not possible, the dust may be used for other products, such as certain mortar binders. If the dust cannot be used in a product, then it must be wasted. Any wasted dust should be disposed of according to local regulations and in accordance with best practices for dust disposal.

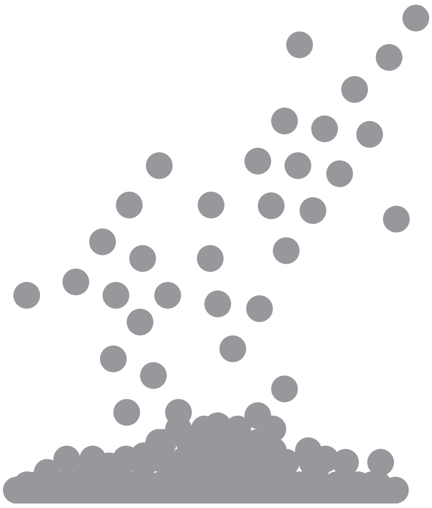
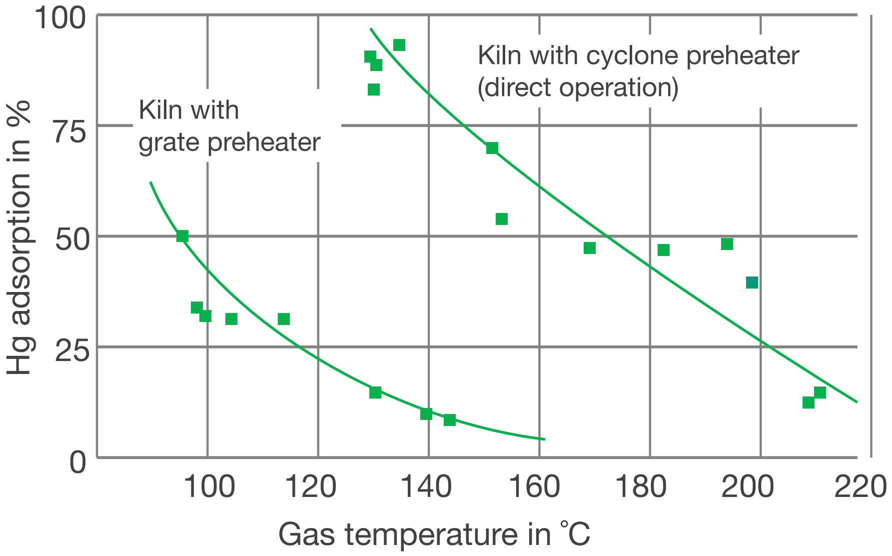


Figure 4: Comparison of mercury adsorption in grate and cyclone preheaters depending on clean gas temperature (Kirchartz 1994)



3.2.2 Applicability

Dust shuttling can be applied to all kiln types and can achieve mercury emissions reductions of 10 to 40%. The effectiveness of dust shuttling is directly related to the concentration of mercury in the dust and the quantity of dust removed. The highest mercury concentrations in filter dust are typically found in preheater / precalciner kilns with inline raw mills when operating in the “mill off” condition. The concentration of mercury in the filter dust depends on a number of parameters, such as:

- The relationship between oxidized and elemental mercury in the exhaust gas;
- The amount of time for “raw mill on or raw mill off” operations;
- The filter type; and
- The achievable exhaust gas temperature in “raw mill on or raw mill off” operations.

The removal efficiency needs to be determined over a longer time period as the dust removal impacts the mercury equilibrium of the system. An environmental side effect is that emissions of some other compounds, such as other volatile metals and ammonia, are reduced.

This method is applied in many cement plants in Germany and the US to specifically remove mercury from the process. Dust shuttling is almost exclusively used during a “mill off” operation, but in some cases where the raw mill dust is collected separately, the dust from the kiln filter may be removed continuously. Dust shuttling is less effective on long kilns where the exhaust gas is not utilized in the raw mill for drying.

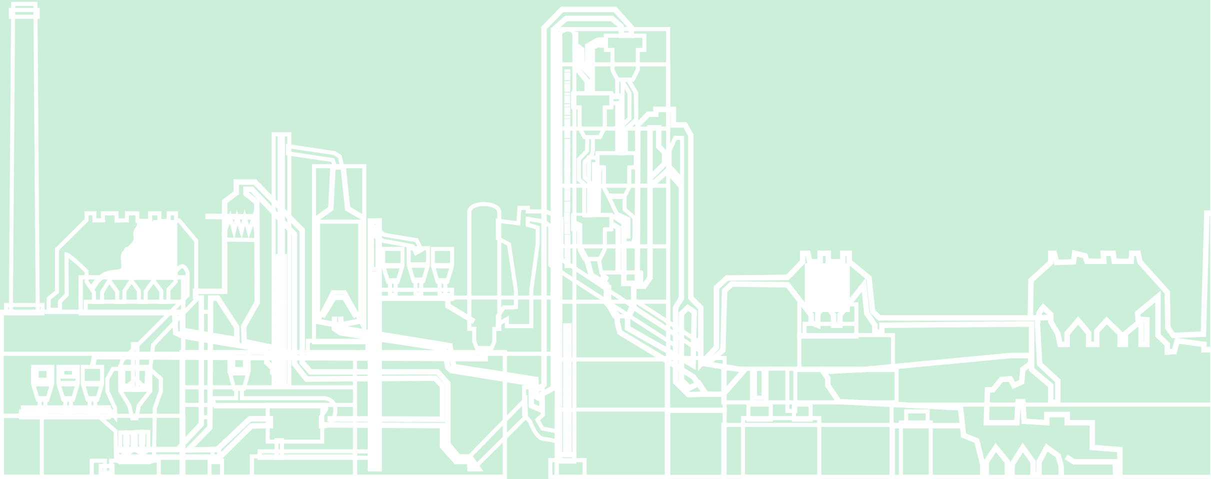
3.2.3 Enhanced mercury oxidation

The concentration of mercury in the filter dust is dependent on the form of mercury and the temperature of the gases. Oxidized mercury is more readily adsorbed than elemental mercury. The adsorption capacity may be further increased by additives such as bromine, sulfur or other chemicals that promote the formation of mercury compounds (oxidized mercury). These oxidizing agents are often added to the gas stream after the preheater induced draft (ID) fan, and can be added continuously or only when the dust is being shuttled. The most common oxidizing agent in use is aqueous calcium bromide ($CaBr_2$).

3.2.4 Other considerations when adding CKD as a mineral addition to cement

When the shuttled dust is used as an additive to cement, the mercury will be shifted to the final product. If the dust is distributed evenly in the final product, then the mercury concentration will be similar to that in the original raw materials and should be in the parts per billion range. Once the cement is hydrated, the mercury will be bound in the cement matrix. If the filter dust cannot be used in the final product, then it will have to be disposed of appropriately.

Cemex US experience on use of dust shuttling



Cemex's objective in dust shuttling is to beneficially use the dust that is removed from the kiln process by shuttling it to the cement grinding process and thus avoiding landfilling any dust that is removed from the kiln process. In 2010, one of Cemex's US plants started dust shuttling along with the use of a mercury mass balance to demonstrate compliance with a state limit on a 12-month rolling average. The kiln system is equipped with an inline raw mill. The procedure that the plant uses to show compliance is:

1. Analyze the mercury content in monthly composite samples of each raw material, each fuel and baghouse dust (also known as cement kiln dust, CKD);
2. Perform a mass balance to calculate the quantity of the mercury inputs and the quantity of mercury which is required to be removed with baghouse dust shuttling to maintain stack mercury emissions below the state limit;
3. Shuttle baghouse dust from the kiln filter to the cement mill;
4. Repeat the process.

Dust shuttling has proven to be an effective method to reduce mercury emissions and maintain compliance with mercury emission limits on this particular cement kiln. Only once did the kiln experience higher than normal mercury emissions. A subsequent technical evaluation determined that the baghouse operating temperature (APCD in Figure 2) was too high and the adsorption of mercury onto the dust was reduced. The lower mercury concentration at a constant dust removal rate reduced the amount of mercury removed from the system and thereby increased the quantity of mercury emitted from the stack. Once the temperature was lowered, mercury emissions were again under control.

Economics

Dust shuttling systems consist of the equipment required to remove the dust from the filter system(s) and to transport it to the cement mill area where it will be added to the milling process. Sufficient storage is required to allow for continuous addition to cement mills. Dust shuttling costs depend on the quantity of dust to be transported and stored, the transport distance, and the number of cement mills to be fed. Simple systems feeding one mill can cost in the 1 to 2 million euro range. Operating costs are negligible as the loss of raw material becomes a gain in cement production, unless the dust cannot be returned to the system where dust wasting can be quite costly.

In some cases, the model indicated that dust shuttling needed to be combined with raw material substitution to lower stack mercury emissions to the levels required for compliance. This is due to limitations on the amount of dust that can be added to the cement.

3.3 Mercury control by using sorbents

Sorbents can be used to enhance the adsorption of mercury from the gas stream. These specially developed materials are injected into the mercury-laden exhaust gases, typically ahead of the main filter. Mercury sorbents are specifically designed to enhance mercury capture with different formulations for different applications. The sorbents can capture a large percentage of the mercury in the gas stream under the proper conditions. The sorbents can be shuttled with the filter dust to the cement or disposed of through other means. Sorbents have been used effectively in the power industry, where they are injected into exhaust gas streams from coal fired utilities.

In the cement industry, sorbents are used in a limited number of plants today. Many plants can control mercury emissions through raw material and/or fuel selection. Dust shuttling is also an inexpensive means to control mercury emissions. Sorbents are typically used only when other means will not meet the objectives. Many of the sorbents commonly used today are based on activated carbons. However, several other non-carbon based sorbents are available and more are being developed.

3.3.1 Mercury emissions reductions with sorbents

Mercury emissions reduction efficiency varies widely from plant to plant as there are a large number of variables that affect the adsorption of mercury, including:

- Mercury speciation and concentration;
- The sorbent's physical and chemical properties;
- The quantity and dispersion of the sorbents used and
- The plant-specific process conditions.

Sorbents can be used with any kiln system and are normally injected in the exhaust gases ahead of the filter. As with dust shuttling, sorbents work best at lower temperatures and may be more effective with bag filters. Some cement plants with inline raw mills have been able to control mercury emissions using sorbent injection only in the “raw mill off” condition. There are some plants that bypass a portion of the kiln (preheater) exhaust around the raw mill and collect the dust in a separate filter. These plants may be able to inject sorbents in the mill bypass stream on a continuous or semi-continuous basis. The sorbent-impregnated dust needs to be removed from the system in order to remove the mercury.

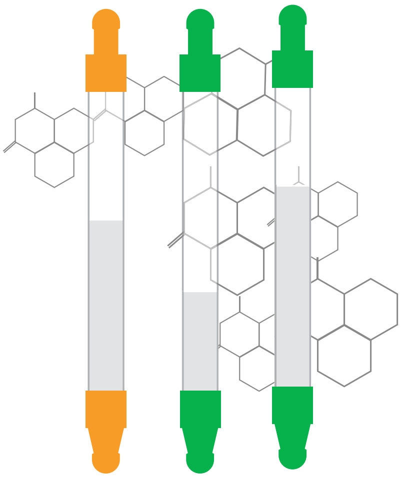
In extreme cases it may be necessary to inject sorbents on a full time basis. In these situations, a second filter can be installed after the main dedusting filter. The sorbent is injected after the main dedusting filter and ahead of the second filter (often called a polishing filter). In this arrangement, the normal dust can be returned to the kiln system while the sorbent is collected separately. The Ash Grove Company (US) invested in such a polishing filter system at the Durkee plant.

Experience on emissions reductions is available from Germany where sorbents were tested in several cement plants by Verein Deutscher Zementwerke (VDZ). In two plants, a reduction efficiency of 30 to 90% was achieved, whereas in another two plants very little reduction was achieved. Brominated-activated carbon was also tested in one other plant where mercury capture was more than 90%. In the Cement and Lime BREF document (Schorcht et al. 2013) it is stated that “by using powdered activated carbon injection, mercury is adsorbed by carbon. Removal efficiency for mercury (metallic and ionic) of about 85 and 95% is reported for this measure / technique.” This technique has limited industrial references, being used successfully in Switzerland and Germany and in a couple of plants in the USA.

The Cement Sustainability Initiative's (CSI) report on mercury (Renzoni et al 2010) in the cement industry describes a plant where 0.03 mg/Nm^3 was achieved by using a sorbent in the "raw mill-off" mode. In this case the mercury concentration in the raw materials was between 100 and 300 ppb. Activated carbon was injected (40 to 50 kg per hour) between the gas conditioning tower and the dust collector during the "raw mill off" mode at different temperatures. The tests reinforced that lowering the temperature increases removal efficiency. In the "raw mill off" mode, the temperature had been reduced to 125°C and all the dust was removed.

An important consideration in the use of sorbents to enhance mercury removal is the disposition of the sorbent-laden dust. The dust must be removed from the kiln system in order to remove the adsorbed mercury. Dust may be shuttled to the cement mill, but in such cases it is necessary to understand how the sorbent may affect cement properties. It has been noted that activated carbon will suppress the effectiveness of the air-entraining agents required in many concrete applications. The normal variability of the quantity of activated carbon in the cement can make control of the dosage of the air entraining agent difficult, which could result in inconsistent concrete quality. Most sorbent suppliers are aware of this potential issue and are developing new sorbents that are more concrete friendly.

An additional consideration is that the activated carbon has a tendency to float to the top of the concrete and can detrimentally affect the appearance of the final concrete. If these quality issues cannot be overcome, the collected dust containing activated carbon may need to be landfilled. Any dust that is landfilled should be checked for potential leachate issues and disposed of accordingly. Most tests to date indicate that mercury leaching from sorbents is not a problem. Needless to say, the disposal of dust will result in increased material consumption and cost.



3.3.2 Sorbent types

Several sorbent types are available today, such as activated carbon from coals (bituminous and lignite) and other biomass, zeolites and reactive mineral mixtures. The sorbents are often impregnated or doped with bromine or sulfur in order to improve the removal efficiency. The selection of a sorbent should be carefully studied based on all of the factors described herein. Sorbent suppliers can often assist with sorbent selection. It is recommended to test several sorbents in situ prior to making a final sorbent supply arrangement.

The capture capacity is related to the physical and chemical characteristics of the sorbents. Gossman (2007) states that:

> "Generally the physical properties of interest are surface area, pore size distribution, and particle size distribution. The capacity for mercury capture generally increases with increasing surface area and pore volume. The ability of mercury and other sorbates to penetrate into the interior of a particle is related to pore size distribution. The pores of the carbon sorbent must be large enough to provide free access to internal surface area by Hg^0 and Hg^{2+} while avoiding excessive blockage by previously adsorbed reactants. As particle sizes decrease, access to the internal surface area of the particle increases along with potential adsorption rates.
>
> "Carbon sorbent capacity is dependent on temperature, the concentration of mercury in the flue gas, the flue gas composition, and other factors. In general, the capacity for adsorbing Hg^{2+} will be different than that for Hg^0. The selection of a carbon for a given application would take into consideration the total concentration of mercury, the relative amounts of Hg^0 and Hg^{2+}, the flue gas composition, and the method of capture (electrostatic precipitator (ESP), or bag house). An important factor for some cement kilns will be the levels of hydrocarbons and the need

> to account for their sorption on to the carbon reducing the capacity of the carbon to adsorb mercury. In addition, bench-scale research shows that high SO_2 concentrations diminished the adsorption capacity of activated carbons. Both of these issues could prevent Activated Carbon Injection (ACI) from being an effective control on some cement kilns."
>
> "There has been only limited testing of ACI on low concentration mercury gas streams as are typical of cement kilns. Most of this work has been done on power plant boilers achieving control efficiencies of 25–95% depending on the type of coal being burned and a wide number of other factors. In many cases these plants already had some mercury control via the particulate control systems in place and enhanced control via ACI was as low as a 10% improvement.
>
> "ACI has the further disadvantage of requiring the disposal of the mercury contaminated spent carbon. Whether the carbon is cleaned and reactivated for reuse or disposed of, the ultimate fate of the mercury needs to be assessed to insure that the mercury will not be reintroduced into the global mercury cycle through some other means."

It should be noted that considerable experience has been gained since the comments above were made.

Sorbents are typically made up of activated carbon or other materials with a high surface area. The specific surface areas of some sorbent types are listed in **Table 1** below. Although the physical characteristics of sorbents, such as pore size and surface area, are important, experience shows that sorbents are rarely saturated and therefore capture capacity may be less important than good dispersion and contact between the mercury and sorbent.

Brominated activated carbons are widely used as the bromine enhances the adsorption of elemental mercury. However, bromine is a corrosive element that has been found to cause increased metal attack in downstream systems, such as filters.

As seen above, the selection of sorbents is driven by a combination of factors, including: the raw gas composition, gas temperature, mercury sorbent contact time, mercury concentration in the raw gas, the sorbent distribution into the gas stream, the mercury species, the requested removal efficiency, the filter construction and potential impacts (e.g. corrosion, life time of filter bags) and the utilization of the filter dust. Non-carbon based sorbents are expected to have less influence on cement and concrete, though it should be noted that only limited experience is available in the cement industry.

3.3.3 Summary of the use of sorbents for mercury control

Sorbent injection has been shown to be an effective means of reducing mercury emissions in coal fired power plants. Experience in cement plants has been more limited but also shows promising results. In both cement and power, mercury emissions reductions of 70 to 90% have been demonstrated, but some plants have achieved very little reduction. Proper sorbent selection is based on many plant-specific criteria and should be carefully studied. Long-term experience is missing in general; further investigations are needed on the impact of sorbents on the cement and filter units.

Economics

Sorbent injection systems typically consist of a sorbent storage and dosing unit, transport system and injection equipment. Many sorbent suppliers and third parties supply packaged sorbent injection systems that consist of a storage silo, complete with dosing and pneumatic transport equipment and all electrical and instrumentation equipment mounted in one unit. That leaves transport lines and injection equipment to be customized per plant. These systems cost between 0.5 and 2 million euros depending on the amount of storage required, the transport distance, and the number of injection points. Operating costs are based primarily on the sorbent usage and can cost between 0.1 and 1.0 euro per tonne of clinker.

Table 1: The specific surface areas of some sorbent types

Sorbents	Zeolite	Lime products	Activated lignite	Activated carbon
Grain size	0 - 50 µm	0 - 2 mm	0 - 0,4 mm	0 - 0,2 mm
Specific surface	400 - 600 m^2/g	1 - 50 m^2/g	300 m^2/g	500 – 1600 m^2/g

3.4 Co-benefits from other abatement technologies

3.4.1 Selective catalytic reduction

Selective catalytic reduction (SCR) technology is used primarily for NO_x control but also shows some benefits in reducing mercury emissions. SCR technology uses a catalyst to enhance the combination of NO_x and ammonia compounds to form N_2 and water vapor. The SCR catalyst usually consists of a ceramic body which is doped with catalytically reactive compounds such as vanadium oxide (V_2O_5). SCR catalysts can also oxidize elemental mercury in the gas stream. Oxidized mercury is more likely to be collected in the filter system; therefore the use of SCR technology can enhance dust shuttling systems. It can also enhance mercury capture by sorbents due to the same mechanism.

SCR technology works by injecting ammonia (NH_3) or urea into the gas stream. These compounds react with NO_x on the surface of the catalyst at a temperature range of between 300 to 400°C. SCR technology is widely used for NO_x abatement in other industries (coal fired power stations, waste incinerators) and was introduced to the cement industry in the 1990s. In 2016, about 10 cement plants worldwide (Austria, Germany, Italy and the US) employ SCR technology. The primary issue with SCR technology in the cement industry is the plugging of the catalyst.

Two SCR systems are considered for use in the cement industry today: the clean side configuration, where the SCR unit is downstream of the filter, and the dirty side configuration, where the SCR unit is upstream of the filter. Clean side installations have fewer issues with plugging, but often require reheating the gases to the reaction temperature range. Clean side applications are not beneficial for mercury capture as the SCR unit comes after the filter.

Dirty side installations are often installed after the preheater, where the gases are in a good temperature range for the catalyst. These installations are more prone to material build-up and catalyst deactivation due to higher dust concentrations. However, dirty side applications can enhance mercury oxidation. Investigations at European cement plants have confirmed the oxidizing effect of the SCR technology in cement plants.

Economics

SCR technology has an installed cost of around 10 million euros per unit and an operating cost level of 1.25 to 2.00 euros per tonne of clinker, depending on the plant size and the NO_x removal efficiency required. The SCR units typically require an additional power demand of 5-6 kWh/t clinker. The economics of the SCR technique is dominated by the investment costs and the consumption of catalytic material, in other words the lifetime of the catalysts. Care must also be taken in the disposal of the SCR catalyst due to the metal content. Although SCR technology can enhance mercury capture, it should only be considered as a mercury control device when also necessary for NO_x control.

3.4.2 Wet scrubber

The European best available techniques reference document (Schorcht et al. 2013) notes that a wet scrubber is a proven technique for flue gas desulphurization in the power sector. In the cement industry, some 15 to 20 kilns worldwide are equipped with wet scrubbers due to high initial SO_2 concentrations in the exhaust gases. Wet scrubbing is based on the following chemical reaction:

$$SO_2 + \tfrac{1}{2}\, O_2 + 2\, H_2O + CaCO_3 \Rightarrow CaSO_4 \bullet 2\, H_2O + CO_2 \quad \text{(Eq. 6)}$$

The SO_2 is absorbed by a liquid / slurry which is sprayed in a spray tower. The absorbent is often calcium carbonate. Wet scrubbing systems provide very high removal efficiencies (>90%) for SO_2 and soluble acid gases. Wet scrubbers also significantly reduce other acidic gases like HCl as well as NH_3 emissions, to a lesser extent.

Gaseous compounds of oxidized mercury (Hg^{2+}) are water-soluble and can absorb in the aqueous slurry of a wet scrubber system. Therefore, a fraction of gas-phase mercury Hg^{2+} vapors may be captured. Gaseous elemental mercury (Hg^0) is insoluble in water and, therefore, does not absorb in such slurries. In wet desulfurization processes, gypsum is produced as a by-product that can be used as a natural gypsum replacement added to the clinker in the finish mill.

Wet scrubbers are known to capture soluble Hg compounds in the power industry. The capture efficiency strongly depends on the ratio of soluble to insoluble Hg compounds. As different cement kilns are known to have widely varying speciation of mercury (Hg^0 versus Hg^{2+}) and the speciation may even change in the same kiln under various operating conditions, the added benefit of using a wet scrubber for mercury abatement will be very much kiln dependent, with some kilns having substantial benefit and others relatively little.

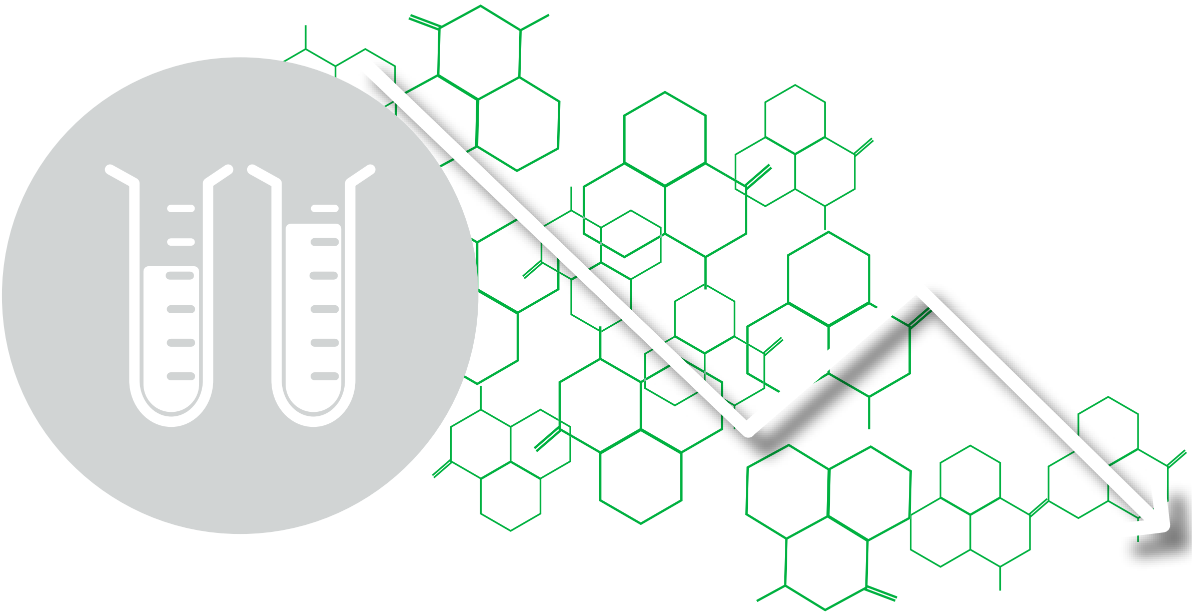
Therefore the wet scrubber is only used in cement plants with very high SO_2 emissions. Hg capture in a wet scrubber can be seen as a co-benefit for some installations. The high cost and inconsistent nature of Hg capture would preclude the use of a wet scrubber as a primary mercury abatement device. Additionally, the use of wet scrubber technology can have other negative consequences, including:

- Increased energy consumption;
- Increased waste production from flue-gas desulphurization (FGD);
- Increased CO_2 emissions;
- Increased water consumption;
- Potential emissions to water and increased risk of water contamination and
- Increased operational costs.

Dry scrubbers and dry sorbent injection systems are also used to reduce SO_2 emissions from cement plants. These systems often use hydrated lime as the sorbent and are not as efficient as wet scrubbers. These systems have a limited effect on mercury emissions as the hydrated lime is not a mercury sorbent and there is no slurry to absorb the oxidized mercury (Hg^{2+}).

Economics

Wet scrubber technology has an installed cost of 10 to 30 million euros per unit and an operating cost level of 1.00 to 2.00 euros per tonne of clinker, depending on the plant size and the SO_2 removal efficiency required. Wet scrubbers typically require an additional power demand of 7 to 10 kWh/t clinker. The economics of wet scrubber technology is dominated by the investment costs, the consumption of limestone, and the disposal of wastes. Care must be taken in the disposal of the solid and liquid wastes due to the metal content and other contaminants. Although wet scrubber technology can enhance mercury capture, it should only be considered as a mercury control device when also necessary for high levels of SO_2 control.



4. Material sampling and analysis

Sections 2.1 and 2.2 describe how mercury enters a kiln system with the raw materials and fuel. The raw materials and fuel contain low concentrations of mercury but as these materials are used in high volumes, a substantial quantity of mercury can enter the kiln system. It is therefore critical that these low concentration levels, which could be as low as a few parts per billion, can be measured accurately. Accurate data is necessary for the cement plant operator to be able to apply any of the methodologies for control discussed in this Guidance.

Materials sampling is required to establish a mass balance for mercury in the cement plant. Although emissions compliance may be demonstrated through the use of continuous monitoring systems as described in section 5, it is important for the plant operator to know which materials are contributing mercury to the process and in what amounts. The establishment of a proper mercury mass balance begins with the sampling program and ends when the analyses are completed and the balance created.

4.1 Sampling program

The sampling process needs to be extremely well executed in order to avoid errors in the results of the flow analysis and mass balance calculations. The fundamental goal of all sampling activities is to collect samples that are representative of the materials from which they were collected. Of equal importance is sampling precision to ensure consistency both within a single sampling event and between sampling events conducted over time. Sampling imprecision can rival analytical imprecision as a source of measurement error.

High-quality field practices are therefore necessary to generate representative samples consistently. A plant-specific quality assurance plan should be developed that includes data quality objectives and the generation of field-quality control samples, including equipment rinsates, trip blanks and field duplicates where necessary. Regardless of the specific program needs, the documentation of all relevant field and sample information is an essential component. This documentation provides evidence that proper procedures and quality assurance were performed during sample collection. The use of inadequate field procedures and documentation can jeopardize an entire sampling program. Third party laboratories often require chain of custody documents that follow samples from origin to analysis in order to certify compliance.

4.1.1 Time frame for mass balance

It is recommended to establish the initial mass balance over a 30-day period. The mass balance should be accomplished by collecting daily samples of all material streams. These streams include each individual raw material and fuel, as well as clinker and any solid stream being removed from the system (e.g. filter dust, bypass dust, spray tower dust, etc.). The daily samples can be composited at the end of the collection period for analysis. Accurate records are also needed for the mass flow rates and moisture content of each material stream. The mercury emissions for the period are calculated based on the mass balance equations given in section 2.2. Essentially, stack mercury equals the sum of the mercury inputs less any mercury outputs. It is important to keep in mind that mercury concentrations are usually on a dry basis so material mass flows need to be corrected to a dry basis as well.

Stack emissions can be verified using a sorbent trap system during the mass balance period or through stack sampling. Sorbent traps would be more accurate as they measure the emissions over the entire balance period. Stack sampling would provide one data point that may be influenced by process conditions at the time of sampling.

After an initial mass balance has been established it should be revisited when any part of the process is modified. These modifications can include, operating parameter changes, raw material or fuel changes, and/or changes in material output streams. It is recommended to continue to analyze all inputs on a regular basis to maintain awareness of any changes in mercury concentration. The number of samples and frequency of sampling should be adapted according to the observed variability of the material (Kline and Schreiber 2013).

4.1.2 Sampling locations

Different sampling points should be used for different purposes. The calculation of a mass balance to estimate mercury emissions requires measuring all solid material streams into and out of the kiln system. It is suggested to measure each raw material and fuel individually to have an accurate picture of individual mercury inputs. However, combined raw material and fuel streams can also be analyzed as long as the samples are representative. Mercury cycles can increase the quantity of mercury recirculating in the kiln system. Therefore the sampling of material streams that are in contact with kiln exit gases, meaning raw mill product, should be avoided for mass balances. For a summary of sampling inputs and outputs, see Appendix 3: Example of sampling inputs and outputs for mass balance.

4.2 Limits of detection

Mercury is found in minute amounts in all raw materials and fuels. The recommended limits of quantification for mercury are 1 ppb, which can be achieved using specific purpose-built mercury analyzers. Most mercury analyses are carried out by third party laboratories. It is therefore important to ensure that the selected laboratory can provide the required accuracy. Many jurisdictions utilize the detection limit of the test as the quantity of mercury in the material when a non-detect is indicated. In this situation, limestone with an actual content of 2 ppb of mercury might be classified as having 10 ppb of mercury if this was the detection limit of the equipment being used. The CSI recommendation is to use half of the detection limit for the mercury concentration when a non-detect is indicated, but some jurisdictions require a different treatment for non-detect readings.

4.3 Analytical methods

Specific purpose-built mercury analyzers typically combine thermal decomposition of the sample, catalytic conversion, amalgamation, and an atomic absorption spectrophotometer. Controlled heating stages are implemented to first dry and then thermally decompose the sample which is introduced into a quartz tube. A continuous flow of oxygen carries the decomposition products through a catalyst bed where interference elements are trapped. All mercury species are reduced to elemental Hg and are then carried along to a gold amalgamator where the mercury is selectively trapped. The system is purged and the amalgamator is subsequently heated, which releases all mercury vapors to a single beam, fixed wavelength atomic absorption spectrophotometer. The absorbance measured at 253.7 nm is proportional to the mercury content in the sample.

It is important to know the lab techniques to be used in analyzing mercury samples as detection limits and testing errors can have significant impacts. As mentioned previously, detection limits for samples with low mercury content should be in the 1ppb range.

5. Stack analysis methods

The Minamata Protocol requires the monitoring of mercury emissions on a yearly basis. This can either be done by a mass balance approach or by an appropriate stack measurement. The mass balance method as described in section 2.2 is well known in the cement industry. Continuous emission monitoring is a more recent method and is used in just a few countries worldwide (mainly Germany and the US). It requires a high degree of expertise in terms of maintenance and operational control; their support comes mostly from European and US analyzer suppliers.

Some jurisdictions will accept a mass balance approach to calculating mercury emissions. Other jurisdictions require actual stack gas measurements. It is important to understand the plant-specific regulatory requirements for mercury sampling and analysis. These can be required on a periodic basis, such as annually or quarterly, or on a continuous basis. When periodic measurements are called for, the work is usually performed by independent contractors who have the specialized equipment.

5.1 Isokinetic sampling

There is one single point in the cement line that is used for gaseous sampling: the stack. The isokinetic method is applied when collecting stack samples for analysis.

The isokinetic collector is equipment used for stationary source sampling that is designed to sample both the gas and the airborne particles in the gaseous flow without doing a mechanical separation. There are several applicable methods that can be used for mercury. In isokinetic sampling, the particle bound mercury is captured with the dust. Gaseous mercury is condensed and captured in liquid reagents and both oxidized and elemental mercury can often be measured independently.

Selected contractors should have the proper equipment and experience to perform the analyses. References should be requested and past experience reviewed before entering into a contract. Field-level quality control is important as trace elements are being measured. Plant personnel should observe all test equipment set-up, operation and tear-down.

It is important to keep in mind that periodic stack sampling provides data points that may or may not be representative of total mercury emissions. As mentioned previously, mercury emissions can vary greatly depending on process conditions, especially in plants with inline raw mills. Therefore, stack sampling and analysis should be performed during periods of stable operation. Sampling should be postponed if the kiln system becomes unstable. All operating parameters should be captured at the time of the tests, such as gas flow rates, materials used, and system temperatures. This data could be crucial in explaining any anomalies or unexpected results.

5.2 Continuous emissions monitors

There are two types of continuous mercury stack measuring equipment in use today. One is a continuous mercury measuring monitor (mercury CEM) and the other is a mercury adsorbing device where the mercury adsorbed is measured at a later time (sorbent trap). Deciding on the appropriate mercury stack measuring system will depend primarily on two issues: the consistency of mercury emissions and the compliance timeframe.

For variable mercury emissions, a mercury CEM is preferable. A mercury CEM will allow nearly instantaneous mercury emission readings for the reporting of hourly or daily mercury emission limits. Some mercury CEMs can provide both elemental and oxidized mercury outputs. If sorbent injection is used to achieve lower mercury emissions, sorbent injection rates can be optimized. However, mercury CEMs are more expensive to purchase, install and operate. They also require skilled technicians to maintain them and communications with the vendor for troubleshooting. Quality assurance required by the United States Environmental Protection Agency (US EPA) includes daily calibration, a weekly integrity check, quarterly linearity checks, and annual relative accuracy audits. In summary, mercury CEMs require an abundant amount of care to continuously meet measuring accuracy requirements.

In Europe, the BREF document (Schorcht et al. 2013) mentions that CEMs are installed in Germany and Austria due to legal requirements. Here, it was generally found that additional maintenance had to be carried out. In some other cases, it was necessary, in accordance with the competent authority, to modify the commercially available devices to make them suitable for specific individual applications. There are only a few cases (less than 10%) where CEMs cannot be used properly. Furthermore, the proper calibration of CEMs according to European standard EN 14181 requires greater effort than CEMs for other emissions, such as dust or NOx. Periodic quality assurance procedures should be carried out by experienced personnel.

Under the new National Emission Standards for Hazardous Air Pollutants (NESHAP) regulation, the US EPA requires that all operating cement plants utilize continuous emissions monitoring for mercury. The regulation allows the use of either CEMs or sorbent traps. The US EPA publishes a list of mercury CEMs that have been demonstrated to meet their requirements.

5.3 Sorbent traps

Sorbent traps pull a small, measured quantity of representative gas through a sorbent filter system (or trap) over a specified time period. At the end of the time period the trap is removed for analysis and a new trap is installed. The sorbent filter is designed for the specific emissions. For mercury measurement, the sorbent traps are designed to capture all of the mercury in the gas stream. The mercury content of the sorbents from the trap is measured with specialized equipment. The emissions are calculated based on the amount of mercury captured and the relationship of sorbent trap gas flow to total exhaust gas flow during the period the trap was in use.

Sorbent traps are best used for kiln systems with a low and consistent mercury input and a long-term compliance timeframe (weekly, monthly, annually). They require low capital costs and little maintenance, and are accurate and easy to certify; however, the mercury emissions will not be known instantaneously. Sorbent traps are typically designed to measure total mercury but can be designed to measure mercury types (oxidized and elemental). Due to the time delay in analysis, it may be difficult to use a mercury sorbent trap system for the control of sorbent additions or to comply with hourly or daily mercury emission limits.

Sorbent traps are typically paired in the test equipment when being used for compliance. The traps need to be extracted from the metering device for analysis. This analysis can be performed in the plant's laboratory if the proper equipment is available for analysis and certified. The traps are often sent to a third party lab for analysis. The two traps need to demonstrate similar mercury capture in order for the test to be valid. One difference between mercury traps and CEMs is that the traps capture particle-bound mercury as well. CEMs are typically designed not to measure particle-bound mercury. The differences should not be significant unless there is a large amount of dust in the gases.

When certifying a mercury sorbent trap it is recommended that the same sorbent cartridges and same laboratory be used for sampling and analysis. Since mercury is measured in low quantities, any difference in test or analysis methods can lead to inaccuracies.

Experience from US plants shows that sorbent traps provide after-the-fact analysis and can be more accurate than CEMs. Some plants use a mercury CEM for process control and sorbent traps for compliance demonstration. This requires operating both systems in parallel; however, it overcomes some of the weaknesses of each system. The mercury CEM no longer needs the extensive calibration and maintenance program but can be used for the immediate tracking of mercury emissions and process control and the traps demonstrate compliance.

5.3.1 Stack emissions over time

In section 2.3, it was noted that the cement kiln system can be subject to wide variations in emissions over time. To get a true assessment of emissions, measurements must be taken over a time period at least as long as the time period of the process variations; for some kiln systems where the raw mill is stopped only on a weekly or monthly basis, the emissions due to these infrequent stops must be captured. This can be done through a number of methods, including using a mass balance approach, CEMs, sorbent traps, or spot testing under the various process conditions and then using a weighted average of the tested emissions and the time of such process conditions. All of these alternatives have their own challenges that may be influenced by the type of materials used, the kiln process, and the location of the plant; the cement plant operator must therefore determine which methodology is best suited for its operations. Emission control strategies should be developed using robust data and it is incumbent on the cement kiln operator to understand the full range of their mercury emissions, whether due to process conditions or the use of different raw materials and fuels over time.

Figure 5: Sorbent traps and analyzer

6. Summary and conclusions

Mercury is an element of global concern due to its negative health impacts. The cement industry is the third largest source of mercury emissions after artisanal gold mining and coal fired power plants. The cement industry accounts for some 10% of global anthropogenic emissions, or 190 metric tonnes per year of mercury emitted. The Minimata Convention is a global treaty aimed at reducing mercury emissions worldwide.

Mercury enters into the cement manufacturing process via minute quantities in raw materials and fuels. The exact amount of mercury depends on the nature and source of the raw materials and fuels. The high temperatures required to produce clinker drive out practically all of the mercury, which leaves the kiln system with the exhaust gases. Therefore the first approach to minimizing mercury emissions is to select raw materials and fuels that limit the mercury introduced into the cement kiln system.

Mercury can be adsorbed on the raw materials and dust at various points in the manufacturing process. The adsorbed mercury can be returned to the process with the raw materials and dust, thus forming a mercury cycle. This cycle can build until an equilibrium is reached; but more likely than not, the cycle will be disrupted. Disruptions occur when process parameters are changed, such as temperature changes, raw mills taken off line, or material removed from the system, etc. Mercury emissions will change with these operating parameters and in particular with temperature and exposure to the raw material and dust.

Mercury emissions can be estimated for a specific facility by preparing a mass balance. These mass balances assume that all of the mercury that is not accounted for in a material stream exits through the stack. Mass balances are recommended for all plants as a means of knowing the mercury inputs. Representative sampling and good analytical practices are crucial to establishing a good material balance.

Mercury emissions can be measured on a periodic or continuous basis. Mercury monitors or sorbent traps can be used for continuous or semi-continuous monitoring of mercury emissions. Isokinetic sampling techniques that are specifically designed for mercury analysis can be used on a spot basis. Qualified experts should be used when sampling and analysis is subcontracted. Spot analyses may not be representative of actual mercury emissions due to the influences of operating parameters and mercury cycles.

Mercury emissions can be reduced through several methods (listed in order of preference):

- Raw material and/or fuel substitution;
- Dust shuttling;
- Sorbent usage; and
- As a co-benefit of air pollution control technologies such as SCR or wet scrubbers designed to mitigate other pollutants.

Mercury emissions are a serious global issue. The cement industry will continue to reduce mercury emissions, which are already being monitored and controlled in several countries around the world today. It should be noted that the vast majority of cement kiln systems emit relatively low levels of mercury and that a disproportionate quantity of emissions are generated from a few kilns with raw materials that have naturally high mercury levels. It is therefore necessary for all cement kiln operators to measure and take appropriate steps to control emissions, especially those from high emitting kilns.

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8. Appendices

Appendix 1: Sample mercury feed tracking form

	Mercury concentration mg/Kg (ppm_dry)											
Example of inputs	Jan	Feb	Mar	Apr	May	June	Jul	Aug	Sep	Oct	Nov	Dec
Limestone												
Sand												
Iron ore												
Fly ash												
HCFA												
Coal												
Alt. fuel material (feeder comp)												
	% Dry solids (external / internal lab results)											
Limestone												
Sand												
Iron ore												
Fly ash												
High-carbon fly ash												
Coal												
Alt. fuel material (feeder comp)												

If below the method detection limit, the assumed detection limit (or estimated value) is used.

		Consumption (tonnes_wet)											
Example of inputs		Jan	Feb	Mar	Apr	May	June	Jul	Aug	Sep	Oct	Nov	Dec
Raw meal consumption	Feed rate (tonnes)												
Limestone feeder	(%) of feed												
	Feed rate (tonnes)												
Sand / clay feeder	(%) of feed												
	Feed rate (tonnes)												
Iron source feeder	(%) of feed												
	Feed rate (tonnes)												
Fly ash feeder	(%) of feed												
	Feed rate (tonnes)												
High-carbon fly ash	Feed rate (tonnes)												
Coal / pet coke feed	Feed rate (tonnes)												
Alt. fuel feed	Feed rate (tonnes)												

	Total mercury input (lbs), If exceeds x lbs in any month then continue quarterly or if any raw material source is changed.											
Example of inputs	Jan	Feb	Mar	Apr	May	June	Jul	Aug	Sep	Oct	Nov	Dec
Kiln feed												
Limestone												
Sand												
Iron ore												
Fly ash												
High-carbon fly ash												
Coal												
Alternative fuel												
Monthly total (from individual feeds)												
12-month running total (from individual feeds)												

Appendix 2: Raw material and fuel qualification form

A. Source of material (supplier information or quarry)

Source: ....
Source address: ....

Phone: ....
Fax: ....
ID number: ....
Technical contact: ....

Address : ....

Phone : ....
Fax : ....
Contact name : ....

Customer (bill to) (cement plant and/or supplier): ....

B. Material identification

1. Material / fuel name (common name used by the source): ....

2. Category :

☐ biomass ☐ hydrocarbons/ other fossils ☐ impregnated sawdust ☐ animal meal ☐ waste water ☐ other chemicals products ☐ used oils

☐ others (specify) ☐ sewage sludge ☐ solid shredded waste ☐ solvents ☐ tyres ☐ alternative raw materials (specify) ☐ conventional material/ fuel

3. Activity producing the material: information on process ....

4. Was the material pre-treated? if yes, specify ....

5. Waste code (if applicable, for example EPA code or EC) ....

6. If waste:

☐ hazardous ☐ non hazardous ☐ not concerned

C. Flow and shipping

1. Quantity of material / fuel available per year (identify unit) : ....

2. Regularity of supply ☐ continuous (/month ....) ☐ one-off ☐ intermittent ☐ seasonal

3. Shipment method ☐ train ☐ truck ☐ others (specify) ☐ bulk ☐ big-bag ☐ drum ☐ others (specify)

D. Material / fuel characteristics

1. Physical description ☐ smelly ☐ liquid ☐ gas ☐ slurry ☐ paste

☐ homogeneous ☐ non homogeneous ☐ solid ☐ powdery ☐ non powdery

ash .... (%) density .... (kg/m3) low heat value .... (kJ/kg) pH ....

flash point .... (°C) water .... (%) viscosity .... (at 20°C) T.O.C .... (g/kg)

total hydrocarbons .... (ppm) fat content .... (%) particle size distribution .... (max) auto ignition temperature .... (°C°)

2. List and give approximate concentrations for main constituents entering the waste :

Constituents	%	Constituents	%

3. Chemical compounds (give average concentrations) (*analysis after calcination)

Chlorine (%)
Lead (ppm)
Antimony (ppm)
Copper (ppm)
Phosphorous (%)
* Na_2O (%)

F, Br, I (%)
Arsenic (ppm)
Cobalt (ppm)
Other metals (ppm)
* CaO (%)
* K_2O (%)

Mercury (ppm)
Cadmium (ppm)
Nickel (ppm)
Sulfur (%)
* Fe_2O_3(%)
* SiO_2 (%)

Chromium (ppm)
Thallium (ppm)
Vanadium (ppm)
Nitrogen (%)
* Al_2O_3 (%)
* MgO (%)

4. Does the material contain any of the following? Give the average concentrations :

☐ radioactive elements
☐ biologically active material
☐ reactive matter (e.g. peroxides, anhydrides…)

☐ pesticides / herbicides
☐ explosives

☐ phenols
☐ PCB / PCT

☐ benzene
☐ other organic matter (specify)

E. Safety features

1. Hazards identification / toxicological information (list and give the potential health effects)

2. Information about stability and reactivity (do not use with.., do not expose to…)

3. Handling and storage

4. Personal protection

5. First aid / accidental release measures

F. Sample

1. Date of sampling:

2. Is the sample representative of the waste stream? If not, explain why not

To the best of my knowledge, I certify that the waste delivered conforms to the above description, and that all information represented by the supplier in this profile is accurate and complete.

Supplier signature Title Date

Appendix 3: Example of sampling inputs and outputs for mass balance

Inputs	Outputs
Primary raw materials	**Products**
Limestone	Clinker
Secondary raw materials	
Shale / clay	Residues
Sand	Filter dust
Iron ore	Bypass dust
Bauxite	Spray tower dust
Alternatives	
Fuels	**Emissions**
Coal	Main stack
Coke	Bypass stack
Alternatives	

Appendix 4: Material sampling for mass balances

Materials required

- Non-powdered safety gloves
- Safety boots
- Safety googles
- Auricular protector
- Safety helmet
- Other plant-specific personal protective equipment, as required
- Non-metallic sampling containers (vermiculate free) – wide-mouth fluorinated polythene (FLPE) jars
- Non-metallic ladle or sample collector
- Homogenizing bucket / bag (vermiculate free)

Sampling techniques

Stock piles

If the sample is to be collected from a storage pile, a random spot should be selected on the downwind side. Approximately six inches of the surface material should be scooped away with a clean, gloved hand to expose the material underneath. The sample is then collected from the deeper material directly into the sample jar and capped tightly to minimize exposure to the air. The sampler is advised not to breathe directly into the samples. Samples should be taken at least one (1) meter above grade.

Belt conveyors

If possible, the sample should be taken in free fall with a cut across the entire material stream. If not possible, then the belt conveyor should be stopped and a horizontal cut of material taken off the belt. Size segregation can be an issue for belt conveyor loading and it is important to be sure that the sample is representative of the sizes on the belt.

Weigh feeders

The sample should be taken as the material falls off the weigh feeder belt. A non-metallic ladle should be used to capture the material from the belt, with samples being taken in the center and on both sides of the belt. Additional samples should be taken across the face of very wide belts.

Clinker samples

The sample should be taken from the clinker transport equipment after the clinker exits the cooler. If possible, the sample should be taken in free fall with a cut across the entire material stream. If not possible, then the transport device should be stopped and a horizontal cut of material taken off the device (similar to a belt conveyor sampling). It is important to be sure that the sample contains both clinker from the cooler and the dust from the cooler vent. If the clinker and dust cannot be sampled together, they should be sampled independently and mixed according to the weight proportions of each stream.

Air slides

The sample should be taken in free fall conditions whenever possible. Free fall indicates that the material is falling though a vertical shaft. Samples should be taken across the entire width of the shaft. For fine materials, this can often be accomplished by using a pipe with slots cut in the top side. Care must be taken to collect representative samples when they cannot be taken in free fall conditions. For example, when extracting a sample from an air slide, a non-metallic ladle should be used to collect samples from the fabric surface in the center and at both sides of the air slide.

Pipe lines

Samples should be taken across the pipe diameter, perpendicular to the flow in the pipe. The sampler should be designed to capture and hold a representative sample of material from the gas stream in the pipe.

Silos

Samples should be taken at the feed point to a silo in free fall conditions when possible. Samples from the discharge of a bin or silo are subject to segregation due to funnel flow. This is not normally an issue for mass flow designs.

Sampling preparation, preservation and storage

- Sample container materials can introduce either positive or negative errors in measurement, particularly at low or ultra-trace levels, by contributing contaminants through leaching or surface desorption, or by depleting concentrations through adsorption. Additionally, the sample containers should be compatible with the reagents used for sample preservation. Thus, the collection and containment of the sample prior to analysis requires particular attention. Sample contamination introduced through field collection activities, including sample containment and shipment, can be assessed from the analysis of equipment rinsates and trip blanks.
- Cross-contamination of samples from a sampling program can be an important issue. CKD samples can often have 1,000 to 10,000 times the mercury concentration of the limestone and other raw materials. A small amount (0.05%) of cross-contamination of CKD with limestone could double the apparent limestone mercury concentration. Therefore it is important that sample containers be sealed in the field. When lab analysis is being performed, the samples with the lowest concentrations of mercury should be analyzed first.
- Lab areas and sample containers should be scrupulously clean so as not to introduce contaminants that could interfere with mercury quantification. This is of particular importance when determining trace or ultra-trace mercury concentration levels. It is recommended to use new sample containers whenever important samples are taken, for example for compliance demonstration.

- The following cleaning sequence has been determined to be adequate to minimize contamination in the sample bottle, whether borosilicate glass, linear polyethylene, polypropylene, or polytetrafluoroethylene (PTFE):
  - Detergent
  - Tap water
  - 1:1 HNO_3
  - Tap water
  - 1:1 HCl
  - Tap water
  - Reagent water
- NOTE: Chromic acid should not be used to clean glassware, especially if chromium is to be included in the analytical scheme. Commercial, non-chromate products (e.g. nochromix) may be used in place of chromic acid if adequate cleaning is documented by an analytical quality control program. Chromic acid should also not be used with plastic bottles.
- Sample holding times, recommended collection volumes or masses and recommended digestion volumes, and preservatives are listed in Appendix 5: Materials for use in sample collection for inorganic analyte determinations. The sample collection and digestion amounts depend on the combination of digestion or extraction and determinative procedures that will be employed for a given sample as well as the sensitivity that is required for the specific analysis. Likewise, the use of alternative preservatives to those indicated in Appendix 6: Recommended sample holding times, preservation, collection quantities, and digestion volumes for selected inorganic analyte determinations in aqueous and solid samples may be necessary depending on the objectives of the analysis. In all cases, the sample quantity that is collected should be representative of the bulk material whenever feasible.

Sample preparation

- For all non-speciated digestion methods, great reductions in analytical variability can be achieved through the use of appropriate sample preparation procedures. Generally, a reduction in subsampling variance can be accomplished by reducing the sample particle size and homogeneously mixing the resulting fines. Under most circumstances, it is recommended that the sample be analyzed without drying. If it is necessary to report the analytical data on a dry-weight basis, then a separate aliquot may be analyzed for moisture content and the wet-weight data corrected accordingly.
- If the sample cannot be well-mixed and homogenized in the form in which it was received by the laboratory, then air or oven drying at 60°C or less, crushing, sieving, grinding and mixing should be performed, as needed or feasible, to homogenize the sample until the subsampling variance is less than the data quality objectives of the analysis. While proper sample preparation generally produces great reductions in analytical variability, it should be noted that in certain unusual circumstances there could be loss of volatile metals (e.g. Hg, organometallics) or irreversible chemical changes (e.g. precipitation of insoluble species, change in valence state) caused by inappropriate sample preparation procedures. Variability due to sample heterogeneity is assessed by analyzing individually prepared sample replicates. Variability inherent in the analytical determinative procedure is assessed by matrix spiking of individually digested samples.
- List of equipment required: scales, drier, crusher, grinder, sampler, sample splitter, sieves and homogenizer.
- Volume of sample required for analysis: The indicative volume and fineness of sample according to the type of analysis is given in Table 2.

Table 2: Indicative volume and fineness of sample according to type of analysis

Type of analysis	Volume of sample to be prepared	Fineness
Chemical analysis of minor elements	100g	<90µm

- Preparation of samples:

  a) Raw materials for raw mills
  - A 1.0 kg sample with grading below 10mm and dry is provided to the lab.
  - Primary crushing: sample is crushed in a jaw crusher to grading from 8 to 10mm. Drying should be done at 60°C in order to avoid volatizing mercury.
  - Sample size reduction: sample is divided with sample splitter to 100g.
  - Secondary crushing: sample is ground in a sample preparation grinding mill with grinding vessels in tungsten carbide to grading below 90µm (about).
  - Sieving: sample is sieved to 90µm, sieve residue is reground in a sample preparation grinding mill or manually in a mortar.
  - Transfer: sample is transferred into a pillbox in polyethylene with double sealing and labeled.
  - Sample homogenization.

  b) Coal and pet-coke
  - A 1.0 kg sample with grading below 10mm is provided to the lab.
  - Drying: sample is dried, 55°c for 12 hours.
  - Sample size reduction: sample is divided with sample splitter to 100g.
  - Crushing: sample is ground in a sample preparation grinding mill with grinding vessels in tungsten carbide to grading below 200µm (about).
  - Sieving: sample is sieved to 200µm, sieve residue is reground back in the sample preparation grinding mill.
  - Transfer: sample is transferred into pillbox in polyethylene with double sealing and labeled.
  - Sample homogenization.

Appendix 5: Materials for use in sample collection for inorganic analyte determinations

Materials for use in sample collection for inorganic analyte determinations

(Source: US EPA SW-846, chapter 3 – Inorganic Analytes, https://www.epa.gov/hw-sw846)

Analyte	**Recommended container material**
Metals	PTFE, plastic, glass
Chloride	PTFE, plastic
Cyanide	PTFE, plastic
Fluoride	PTFE, plastic, glass
Nitrate	PTFE, plastic, glass
pH	PTFE, plastic, glass
Specific conductance	PTFE, plastic, glass
Sulphate	PTFE, plastic, glass
Sulfide	PTFE, plastic, glass

These recommendations are intended as guidance only. The selection of sample container should be made based on the nature of the sample, the intended end use of the data and the project data quality objectives.

Appendix 6: Recommended sample holding times,preservation, collection quantities, and digestion volumes for selected inorganic analyte determinations in aqueous and solid samples

(Source: EPA SW-846, chapter 3 – Inorganic Analytes, https://www.epa.gov/hw-sw846)

Analyte	Matrix	Fraction	Minimum collection volume / mass	Preservation[1]	Digestion volume	Holding time[2]
Metals (except Hg and Cr^{5+})	Aqueous	Total	600 mL	HNO_3 to pH<2	100mL	6 months
		Dissolved	600 mL	Filter on site; HNO_3 to pH<2	100mL	6 months
		Suspended	600 mL	Filter on site;	100mL	6 months
	Solid	Total	200 g	None	2g	6 months
Hexavalent chromium	Aqueous		400 mL	≤6˚C	100mL	24 hours
	Solid		100 g	≤6˚C		30 days to extraction
				≤6˚C	2.5g	7 days from extraction to analysis
Mercury	Aqueous	Total	400 mL	HNO_3 to pH<2	100mL	28 days
		Dissolved	400 mL	Filter HNO_3 to pH<2	100mL	28 days
	Solid	Total	200 g	≤6˚C	0.2g	28 days
Chloride	Aqueous		50 mL	≤6˚C	—	28 days
Cyanide	Aqueous		500 mL	≤6˚C NaOH to pH>12	—	14 days
	Solid		5 g	≤6˚C	—	14 days
Fluoride	Aqueous		300 mL	≤6˚C	—	28 days
Nitrate	Aqueous		1000 mL	≤6˚C	—	28 days
Hexane Extractable Material (HEM; Oil & Grease)	Aqueous		1000 mL	≤6˚C HCl or $H2SO_4$ to pH<2	—	28 days
	Solid		100g	≤6˚C HCl or $H2SO_4$ to pH<2 when practical		28 days
pH	Aqueous		25 mL	NA	—	Analyze immediately
	Solid		20g	NA	—	Analyze immediately
Specific Conductance	Aqueous		100 mL	NA	—	Analyze immediately
Sulfate	Aqueous		50 mL	≤6˚C	—	28 days
Sulfide	Aqueous		100 mL	4 drops 2N zinc acetate / 100 mL sample; NaOH to pH<9; Minimize selection; Store headspace free at ≤6˚C	—	7 days
Organic Carbon, Total (TOC)	Aqueous		200 mL	≤6˚C store in dark HCl or H_2SO_2 to pH<2;	—	28 days
	Solid		100g	≤6˚C	—	28 days

a These recommendations are intended as guidance only. The selection of samples and digestion volumes and preservation and holding times should be made on the nature of the sample the intended end use of the data quality objectives.

b Additional sample quantities may need to be collected in order to allow for the preparation and analysis of QC samples, such as matrix spikes and duplicates.

1 The exact sample extract and standard storage temperature should be based on project specific requirements and or manufacturers recommendations for standards. Alternative temperatures may be appropriate based on demonstrated analysis stability within a matrix, provided the data quality objectives for a specific project are still attainable.

2 A longer holding time may be appropriate if it can be demostrated that the reported analysis concentration are not adversley affected by preservation, storage and alaysis performed outside the recommended holding times.

Appendix 7: EPA methods – hyperlinks

EPA Method 101: http://www.epa.gov/ttnemc01/promgate/m-101.pdf
EPA Method 101A: http://www.epa.gov/ttnemc01/promgate/m-101a.pdf
EPA Method 7471B: https://www.epa.gov/hw-sw846
EPA Method 29: http://www.nj.gov/dep/bts/pdffiles/Techmanuals/METHOD%2029.pdf
EPA SW-846 Chapter3: https://www.epa.gov/hw-sw846

Appendix 8: Testing the suitability of the measuring equipment

The suitability of a measuring instrument is determined by calculating the total measuring uncertainty according to EN ISO 14956 prior to installation, which refers to the following variables:

- Standard deviation
- Linearity deviation
- Reproducibility
- Drift
- Temperature dependence
- Operating voltage effects

Suitability test

- Cross sensitivities
- Response behavior
- Response times
- Measuring instrument type
- Installation / calibration testing
- Selection of the measuring location (measuring site report)
- Correct installation of the measuring instrument
- Correct selection of the measuring range
- Calibration of the device using a standard reference method, min. 15 measuring points distributed over 8-10 hours on 3 days
- Determination of the calibration curve or curves under different operating conditions (fuels, load, etc.) without manipulation of the furnace or filter systems (adjusting the burner, slitting the filter hoses or reducing the capacity of the electrostatic precipitator)
- Calibration curve either as linear regression or straight line from the zero point to the center of a point cluster
- Calculation of the fluctuation range as s at the 95% confidence interval

Test repeated at least every 5 years and more frequently if so required by legislation or authority.

Continuous monitoring

- Permanent quality assurance during plant operation through the operating personnel
- Assurance of reliable and correct operation of the measuring instrument (maintenance records)
- Regular checks, at least once per maintenance interval
- Zero point, measuring range, drift
- Determination of drift and accuracy using cumulative sum control (CUSUM) cards or with a chart
- Identification / definition of when manufacturer’s maintenance is necessary for the measuring instrument; AST – annual surveillance test
- Annual confirmation of the quality assurance level (QAL) 2 calibration curve
- Verification of the validity of the calibration curve
- Function test
- Small calibration using 5 parallel measurements
- QAL 2 is to be repeated if AST fails
- Resetting of the exceedance counter for the invalid calibration range

About the World Business Council for Sustainable Development (WBCSD)

The World Business Council for Sustainable Development (WBCSD), a CEO-led organization of some 200 forward-thinking global companies, is committed to galvanizing the global business community to create a sustainable future for business, society and the environment. Together with its members, the council applies its respected thought leadership and effective advocacy to generate constructive solutions and take shared action. Leveraging its strong relationships with stakeholders as the leading advocate for business, the council helps drive debate and policy change in favor of sustainable development solutions.

The WBCSD provides a forum for its member companies – who represent all business sectors, all continents and a combined revenue of more than $7 trillion – to share best practices on sustainable development issues and to develop innovative tools that change the status quo. The council also benefits from a network of 65+ national and regional business councils and partners organizations, a majority are based in developing countries.

www.wbcsd.org

About the Cement Sustainability Initiative (CSI)

The CSI is a global effort by 24 leading cement producers, with operations in more than 100 countries. Collectively, these companies account for around 30% of the world's cement production and range in size from very large multinationals to smaller local producers. All CSI members have integrated sustainable development into their business strategies and operations, as they seek strong financial performance with an equally strong commitment to social and environmental responsibility. The CSI is an initiative of World Business Council for Sustainable Development (WBCSD).

www.wbcsdcement.org

Disclaimer

This report is released in the name of the WBCSD. It is the result of a collaborative effort by members of the secretariat and executives from member companies participating in the Cement Sustainability Initiative (CSI). Drafts were reviewed among CSI members, so ensuring that the document broadly represents the majority view of this group. This does not mean, however, that every member company agrees with every word.

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