MERCURY IN THE CEMENT INDUSTRY

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1. ACRONYMS AND ABBREVIATIONS

ACI	Activated Carbon Injection
AFR	Alternative Fuels and Raw materials, often waste or secondary products from other industries, used to substitute conventional fossil fuels and raw materials.
APCD	Air Pollution Control Device
AGSM	Artisanal Small-scale Gold Mining
BAT	Best Available Technology
BATAEL	Best Available Technology Associated Emission Levels

BF	Bag Filter
BEP	Best Environmental Practice
CEM	Continuous Emission Monitor
CKD	Cement Kiln Dust
CSI	Cement Sustainability Initiative
CVAAS	Cold Vapour Atomic Adsorption Spectroscopy
CVAFS	Cold Vapour Atomic Fluorescence Spectroscopy
ECRA	European Cement Research Academy
ESP	Electrostatic Precipitator
ELV	Emission Limit Value
FF	Fabric Filter
FGD	Flue Gas Desulphurization System
GTZ	Deutsche Gesellschaft für Technische Zusammenarbeit GmbH
IPPC	Integrated Pollution Prevention and Control
LOI	Loss Of Ignition
MWC	Municipal Waste Combustor
PCA	Portland Cement Association
VDZ	Verein Deutscher Zementwerke e.V.
SNCR	Selective Non Catalytic Reduction
US EPA	United States Environmental Protection Agency
WID	Waste Incineration Directive

nm	Nanometre
°C	Degree Celsius
dscm	Dry standard cubic meter
g	Gram
K	(Degree) Kelvin
kJ	Kilojoules (1 kJ = 0.24 kcal)
lb	Pound
Nm^3	Normal cubic meter (101.3 kPa, 273 K)
ppm	Parts per million
t	Tonne (metric) = 1.10231 short tons
$\mu g/m^3$	Micrograms per cubic meter

2. GLOSSARY

BAT AEL	If not otherwise mentioned, emission levels given are expressed on a daily average basis and standard conditions. The following definitions regarding the standard conditions apply for volume flows and concentrations of kiln exhaust gases.

Nm^3/h	volume flow: if not otherwise mentioned, the volume flows refer to 10 vol-% oxygen and standard state
mg/Nm^3	concentration: if not otherwise mentioned, the concentration of gaseous substances or mixtures of substances refer to dry flue-gas at 10 vol-% oxygen and standard statel
standard state	refers to a temperature of 273 K, a pressure of 1013 hPa and dry gas

Compound operation	Kiln exhaust gases, which have a relatively high temperature and low humidity, can be utilised for the drying of raw materials in the raw mill during “**compound operation**”, i.e. when the raw mill is in operation.
Direct operation	During “**direct operation**” (raw mill off), the exhaust gases are directly led to the dust collector and the chimney.
Elemental mercury	Mercury present in its elemental state
Kiln inlet/outlet	Where the raw meal enters the kiln system/ where the clinker leaves the kiln system.
Limonite	Limonite is an ore consisting in a mixture of hydrated iron(III) oxide-hydroxide of varying composition.
Oxidised mercury	Mercury in its mercurous or mercuric oxidation states
Particle bound mercury	Mercury associated with particulate matter
Petcoke	**Petroleum coke** (often abbreviated **petcoke**) is a carbonaceous solid derived from oil refinery coker units or other cracking processes

3. EXECUTIVE SUMMARY

During the first half of 2008, CEMBUREAU, the European Cement Association and the WBCSD Cement Sustainability Initiative (CSI) launched a study with the aim of:

- compiling worldwide data on the status of mercury emissions from cement kilns,
- sharing state of the art knowledge about mercury and its derivates behaviour in cement production processes,
- and defining best environmental practices in order to control and minimise mercury emissions from cement kilns through the use of integrated process optimisation (primary measures).

The present report is based on technical and scientific literature, on an exhaustive worldwide inventory of mercury emissions in the cement industry and on the analysis of case studies provided by cement companies which are members of the CSI.

Regulatory framework

Mercury is regulated under national clean air acts and/or waste management standards in many countries. More information on legislation can be found under Chapter 5 of this report.

Mercury inventory

Worldwide cement kiln mercury emissions data were collected through CEMBUREAU and the CSI member companies. The enquiry was launched in spring 2008 and data collection took place from summer 2008 until mid 2009. The enquiry was very general as the main objective was to collect as much data as possible. The questionnaire covered 2005, 2006 and 2007. 1681 emission values were obtained from 62 different countries from all continents, with 62 companies taking part.

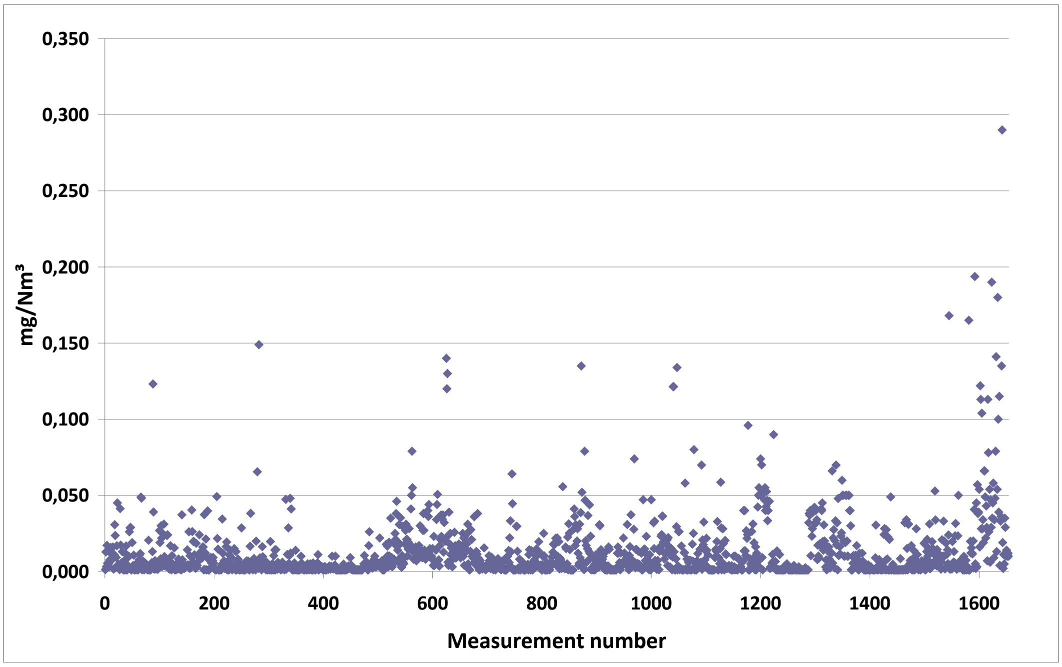


Figure 1: *CEMBUREAU/CSI enquiry: total of 1654 mercury spot measurements.*

Other cement industry mercury emission inventories available were also analysed. On the basis of the different data bases available, the present report proposes an average emission of 0.02 mg/Nm³ for further reference and mercury emission inventories. This corresponds to an emission factor of around 0.035 g/t cement which should be used instead of the factor of 0,1 g/t cement usually found in literature.

Mercury and cement kilns

Mercury enters in the cement manufacturing process as a trace element with the raw materials and the fuels. The mercury content of natural raw materials varies between individual raw material deposits and even within the same deposit. In fuels, the amount of mercury can vary in a similar way, depending on the fuel type and the fuel source. Depending on their origin, alternative raw materials and fuels may have a higher or a lower mercury content than the ordinary materials they replace.

Mass balance tests were conducted on several cement kilns and described in the literature. Moreover, CEMBUREAU and CSI members collected and provided several unpublished case studies. The information and data presented in this report and other studies demonstrate that mercury does not simply volatilise from the fuel and raw materials and directly leave the system through the stack. There are mechanisms and operating conditions that allow cement kilns to capture mercury. There is very low (if any) retention of mercury in the clinker. Mercury and its compounds form an external cycle when the dust, together with the condensed volatile compounds, precipitate on the feedstock in cool areas of the kiln system or when it is separated in dedusting devices and returned to the raw meal and subsequently to the kiln.

In a nutshell, cement kiln systems have a significant inherent ability to control mercury stack emissions. The present report and case studies largely confirm the experience and the key control factors for mercury abatement in cement kiln systems, as referenced in the available literature.

The key control factors and best environmental practices can be summarised as follow:

- ✓ In most cases, the major contributors to total mercury input into the kiln system are the natural raw materials, and not the fuels.
- ✓ Mercury input control is the most important measure for the responsible operation of a kiln. Best environmental practice is to conduct a careful selection and control of all substances entering the kiln in order to avoid too high a mercury input. A dedicated quality assurance system is recommended.
- ✓ Selective mining may be an option in order to control and avoid mercury input peaks into the kiln system.
- ✓ Mercury emissions are typically higher in kiln operations with the raw mill-off (“direct” operation) due to the missing adsorption capacity of the freshly ground particles in the raw mill.
- ✓ Periodic purging (bleeding) of cement kiln dust from the system is an efficient way to control and reduce mercury emissions. Adsorption of mercury is favoured due to the very high dust loadings present in the raw gas streams from preheater-precalciner kilns. This purging process is more efficient in the mill-off mode than in the mill-on mode due

to the higher mercury concentrations in the dust. The efficiency of this measure depends, in part, on the quantity of dust removed from the system, and on the temperature prevailing in the air pollution control device.

- ✓ Other techniques to reduce mercury air emissions are available in other industries such as waste incinerators and coal-fired power stations. Some, such as carbon adsorption, are well proven, whilst others are at laboratory or pilot stage. However, most of the test programs completed in those industries cannot be extrapolated to the cement industry. Therefore, those techniques cannot be considered as best environmental practice in the cement industry.

4. INTRODUCTION

An exhaustive analysis of mercury emissions in the cement industry was conducted. This was followed by the gathering of various cement industry case studies related to mercury, provided by several cement companies (via the CSI and CEMBUREAU). Whilst currently unpublished, this information proved to be useful in drafting this report, and is fully described in the “case studies” section under Annex B. It enabled a complete understanding of where the mercury originates from, how it behaves in the installations and which are the emissions. Some of the case studies also include mass balance studies.

Technical and scientific literature forms the basis of this report. Many studies on mercury emissions have been produced, however these have focussed mainly on waste incinerators and coal-fired boilers and not on cement plants. Nevertheless, the Portland Cement Association (PCA - US) and the Verein Deutscher Zementwerke e.V (VDZ - Research Institute of the Cement Industry, Germany) have published several studies in recent years on different issues related to mercury in the cement industry.

“Best environmental practices”, were subsequently elaborated to verify, control and reduce mercury emissions where necessary. They are described under chapter 13.

5. REGULATORY FRAMEWORK

5.1. MERCURY EMISSION LIMIT VALUES FOR CEMENT KILNS IN EUROPE

In the European Union, cement plants are essentially regulated according two Directives.

1) Directive 96/61/EC on Integrated Pollution Prevention and Control (IPPC). Industrial installations are covered under Annex I of the IPPC Directive namely: "3.1. Installations for the production of cement clinker in rotary kilns with a production capacity exceeding 500 tonnes per day" are required to obtain authorisation (environmental permit) from the EU Member States.

The IPPC Directive is based on several principles, namely (1) an integrated approach, (2) best available techniques, (3) flexibility and (4) public participation.

1. The **integrated approach** means that the permits must take into account the whole environmental performance of the plant.
2. The permit conditions, including emission limit values (ELVs), must be based on **Best Available Techniques (BAT),** as defined under the IPPC Directive. To assist the licensing authorities and companies in determining BAT, the European Commission organises an exchange of information between experts from the EU Member States, industry and environmental organisations. This results in the adoption and publication by the Commission of the BAT Reference Documents (the so-called **BREFs**).
   The Cement and Lime BREF has recently been revised and finally approved on 1 April 2009. In relation to mercury, the following is considered as BAT:
   - Emissions of metals from the flue-gases of the kiln firing processes shall be controlled by applying the measures/techniques which are listed in the BAT Reference Document individually or in combination. The BAT-AELs for metals are given in **Table 5-1**.

***Table 5-1**: BAT-AELs for Heavy Metals.*

Metals	**Unit**	**BAT-AEL** (average over the sampling period (spot measurements, for at least half an hour))
Hg	mg/Nm^3	<0.05^{2})
∑ (Cd, Tl)	mg/Nm^3	<0.05^{1})
∑ (As, Sb, Pb, Cr, Co, Cu, Mn, Ni, V)	mg/Nm^3	<0.5^{1})

$^{1)}$ Low levels have been reported.

$^{2)}$ Low levels have been reported. Values higher than 0.03 mg/Nm^3 have to be further investigated. Values close to 0.05 mg/Nm^3 require consideration of additional measures/techniques.

3. The IPPC Directive contains elements of **flexibility** by allowing the licensing authorities, when determining permit conditions, to take into account: the technical characteristics of the installation, its geographical location, and the local environmental conditions.

4. The Directive ensures that the **public has the right to participate** in the decision making process, and to be informed of its consequences.

2) Directive 2000/76/EC on the Incineration of Waste, the aim of which is to prevent or to limit as far as practicable negative effects on the environment, in particular emission pollution to air, soil, surface water and groundwater. For cement kilns co-incinerating waste, it sets, amongst others, emission limit values (0.05 mg/Nm³) for mercury and its compounds, expressed as mercury (Hg)

On 21 December 2007 the Commission adopted a Proposal for a Directive on Industrial Emissions. The Proposal recasts seven existing Directives related to industrial emissions into a single, clear and coherent legislative instrument. The recast includes, in particular, the IPPC Directive and the Incineration of Waste Directive. At the time of publication of the present report, the proposal does not propose any changes related to mercury emission limit values in the cement industry.

5.2. MERCURY EMISSION STANDARDS IN NORTH AMERICA

Mercury emission limits are currently applied to certain categories of combustion sources, including facilities burning hazardous waste. These (**Table 5-2**) have been set in the NESHAP (National Emissions Standards for Hazardous Air Pollutants*)* Final Rule (October 2005) for Hazardous Waste Combustors (which includes cement kilns).

***Table 5-2** : North American ELVs for mercury emissions from the kiln stack for cement manufacturing with the use of waste.*

	Unit	**Hg**
USA	µg/dscm	120 (1)
Canada	mg/Sm^3	0,15 (2)

(1) in µg per dry standard cubic meter in µg/dscm at 7% O_2

(2) mg/Sm^{3,} 10% O_2 for Hazardous Waste only.

Cement kilns that do not burn hazardous waste are not subject to mercury emission standards. However, the US Environmental Protection Agency (EPA) is currently reviewing the need for mercury emission standards for cement kilns. A court order obliges the US EPA to propose new limits for mercury, organics and possibly HCl by 31 March 2009 for completion by 31 March 2010.

On 21 April 2009, the US EPA proposed a new rule (which was subject to a period for comments), including a proposed cement kiln mercury emission limit of 43 lb/million tonnes clinker (21.5 mg/tonne) for existing sources and 14 lb/million tonnes clinker (7 mg/tonne) for new sources. Both proposed limits are based on a 30 day rolling average. This corresponds, more or less, to a concentration of 0.012 mg/Nm³ for existing facilities and 0.004 mg/Nm³ for new ones which would be challenging from a technico-economical point of view.

The rules would cover 163 kilns in 35 states. Around 24 other kilns, which burn hazardous waste, would be regulated separately.

5.3. MERCURY EMISSION STANDARDS IN OTHER COUNTRIES

National Emission Limit Values (ELV) for mercury emissions to air are given in **Table 5-3** to **Table 5-6**. The values relate to Hg emissions from the kiln stack. Information has been essentially collected by CSI members. The application of the data (averaging time, reference conditions, measurements techniques, compliance criteria, etc.) could differ from one country to another. In principle, emissions should be monitored. The range of ELVs is quite broad.

***Table 5-3** : African national ELVs for mercury emissions from the kiln stack for cement manufacturing without or with the use of waste.*

Country	**Hg (mg/Nm^3)** **Without the use of waste**	**Hg (mg/Nm^3)** **Using waste**
Morocco (1)	0,10	0,10

(1) 11% O_2

***Table 5-4** : Latin American national ELVs for mercury emissions from the kiln stack for cement manufacturing using waste.*

Country	Hg (mg/Nm³) Using waste
Mexico	0.07 (2)
El Salvador	0.05 (3)
Costa Rica	0.24 (4)
Colombia	0.05 (7)
Venezuela	0.05 (6)
Ecuador	-- (5)
Brazil	0.05 (8)
Argentina	No limit
Chile	0.109 (9)

(2) at 7% O_2
(3) at 10% O_2
(4) Sum of Hg and Cd; at 10% O_2
(5) under review; reference value: 0.05 mg/Nm3 at 10% O_2.
(6) at 10% O_2.
(7) at 11% O_2.
(8) Sum of Cd, Hg, and Tl: 0.2 or 0.28 (at 7% O_2).
(9) at 10% O_2

***Table 5-5** : Asian national ELVs for mercury emissions from the kiln stack for cement manufacturing without or with the use of waste.*

Country	Hg (mg/Nm³) Without the use of waste	Hg (mg/Nm³) Using waste
Bangladesh	0.2	
India	0.2	
Indonesia	5 (2)	0.2
Korea	0.1 (4)	
Malaysia	10 (3)	
Philippines	5	
Thailand		0,10 (2)
Vietnam		0.5 (5)

(2) 7% O_2
(3) 12% CO_2
(4) 13% O_2
(5) (for waste incinerators)

***Table 5-6** : Oceania national ELVs for mercury emissions from the kiln stack for cement manufacturing without or with the use of waste.*

Country	Hg (mg/Nm³) Without the use of waste
Australia	1.0 mg/Nm³ (permit limit)

6. OCCURRENCE, PROPERTIES, SPECIATION AND TOXICOLOGY OF MERCURY

6.1. OCCURRENCE

Mercury is an extremely rare element of the Earth's crust with an average abundance by mass of only 0.08 ppm (parts per million). However, it can be extremely concentrated as it does not blend geochemically with other crust elements. Mercury geochemical belts where mercury concentrations in the upper layer are higher than the average value (Schlüter, 2000) exist. The richest mercury ores contain up to 2.5% mercury by mass and the leanest concentrated deposits are at least 0.1% mercury (UNEP, 2002).

Mercury has a high mobility and diffuses to the surface as a result of the high temperature in the Earth's mantle. Regions with high surface rock mercury concentrations indicate high mercury emissions to the atmosphere.

Mercury can be found as a native metal (rarely) or in cinnabar and other possible host minerals. Cinnabar (HgS) is the most common ore.

Natural sources of mercury include volcanoes, evaporation from soil and water surfaces, degradation of minerals and forest fires.

Releases of mercury from soil and water surfaces are natural but can also be influenced by anthropogenic sources (AMAP/UNEP, 2008).

In 1998, mercury was found in crust and rocks at the concentrations given in **Table 6-1**. These estimations depend on the source of information.

***Table 6-1**: Concentrations of Mercury in Crust/Rocks (mg/kg) (Reimann and de_Caritat, 1998)*

Concentrations in Crust / Rocks (mg/kg)	**Wedepohl (1995)**	**Lide (1996)**	**Taylor and McLennan (1995)**	**Koljonen (1992)**	**Tauber (1988)**
Bulk continental crust	0,04	0,085	/		
Upper continental crust	0,056		0,02		
Ultramafic rock				0,004	
Ocean ridge basalt				0,01	
Gabbro, basalt				0,01	
Granite, granodiorite				0,03	
Sandstone				0,01	
Shale, schist				0,18	
Limestone				0,02	
Coal					0,1

6.2. MERCURY SPECIES

Mercury is a heavy metal which can exist in the environment in a large number of forms (Reimann and de_Caritat, 1998; UNEP, 2002; Johansen and Hawkins, 2003a; Richards, 2005; Schreiber et al., 2005).

Mercury can exist in three different oxidation states:

- metallic-Hg(0) or Hg^0,
- mercurous-Hg(I) or Hg^+,
- mercuric-Hg(II) or Hg^{2+}.

Mercurous and mercuric mercury form numerous inorganic and organic chemical compounds, but Hg^+ mercury is rarely stable under ordinary environmental conditions.

The main groups of mercury species (the different forms in which mercury exists) are elemental or metallic mercury, inorganic and organic mercury forms.

Speciation plays an important role in toxicity and exposure of mercury to living organisms. It also influences the transportation of mercury within and between environmental compartments, including the atmosphere and oceans. Moreover, the controllability of mercury emissions to air depends on the speciation.

Metallic mercury (or elemental mercury) is a heavy, silvery-white liquid metal at typical ambient temperatures and pressures, which vaporises under such conditions. It is rarely found in nature as a pure liquid metal but rather within compounds and inorganic salts. The melting point of mercury is -38.9°C, and the boiling point is 357°C.

The most important inorganic mercuric compounds (or mercury salts) regroup mercuric sulphide (HgS), mercuric oxide (HgO), mercuric chloride ($HgCl_2$), mercury sulphates ($HgSO_4$, Hg_2SO_4.) and mercury silicates ($HgSiO_3$, $Hg_6Si_2O_7$, etc.). **Table 6-2** gives data for different mercury compounds of interest.

- Mercuric sulphide is the compound present in cinnabar ore. It is red in colour, turning black after exposure to light.

- Mercuric oxide is formed by heating mercury in the air to below its boiling point. However, at higher temperatures (about 500°C) the oxide decomposes.

- Mercuric chloride can be formed by reacting HgO with hydrochloric acid (HCl) or Hg with chlorine gas (Cl_2). Gas-phase equilibrium calculations suggest that $HgCl_2$ is the dominant oxidised species in flue gas at temperatures below 480-590°C.

- Mercurous sulphate is a solid that forms white granules or crystalline powder. When heated at approximately 450°C, it decomposes and forms elementary mercury and sulphur oxides.

- Mercury silicates : some recent studies (Owens et al., 1995; Schreiber et al., 2005) suggest that a number of silicate compounds (i.e., $HgSiO_3$, $Hg_6Si_2O_7$, etc.) could possibly form within cement kiln systems and could exit the system with the clinker. However, there is no analytical evidence that mercury is present in the clinker.

***Table 6-2**: Characteristics of Selected Inorganic Mercury Compounds (CRC, 1976)*

Chemical name	**Metallic mercury**	**Mercury sulphide**	**Mercury sulphate**	**Mercury bromide**	**Mercury chloride**	**Mercury fluoride**	**Mercury oxide**
Chemical formula	Hg^0	HgS	Hg_2SO_4	$HgBr_2$	$HgCl_2$	HgF_2	HgO
Melting point, °C	-38,87	sublimates at 583,5	d.	236	276	d. at 645	d. at 500
Boiling point, °C	356,58	-	d.	322	302	-	-
Occurrence in nature	-	as cinnabar	-	-	-	-	-

d.: decomposes

Organic mercury compounds (or organomercurials) are the compounds formed when mercury combines with organic molecules. They are of type R_2Hg and RHgX, where X represents atoms or groups such as chlorine, bromine, iodine, cyanide, and hydroxyl, and R represents a simple alkyl group, such as methyl (CH_3^-). Depending on their properties, these compounds will be primarily soluble in organic liquids or in water. Two of the organic compounds are methyl mercury halide, CH_3HgX, and dimethyl mercury, $(CH_3)_2Hg$, the most important chemical form of mercury with respect to environmental impact assessments.

6.3. VAPOUR PRESSURE

The vapour pressure of non-adsorbed elemental mercury and non-adsorbed mercuric compounds is quite high. At a prevailing concentration of less than .010 milligram per cubic meter (mg/m^3), and when the gas temperatures exceed approximately 30ºC (**Figure 6-1**), non-adsorbed elemental mercury is primarily in its vapour form. At a temperature range of 50ºC (wet scrubber outlet) to 100ºC (electrostatic precipitator outlet), virtually all of the non-adsorbed elemental mercury is its vapour form. As with most chloride compounds, non-adsorbed mercuric chloride is even more volatile at high temperatures (i.e. >100ºC) than elemental mercury.

As shown in **Figure 6-1**, both non-absorbed elemental mercury and mercuric chloride have high volatile characteristics. For this reason, mercury in the gas stream can only form a liquid phase or a solid which is adsorbed on the surfaces of particles to become particle-bound mercury. Any mercury remaining on the surfaces or in the bulk volume of particles must be physically or chemically bound as part of a non-volatile compound.

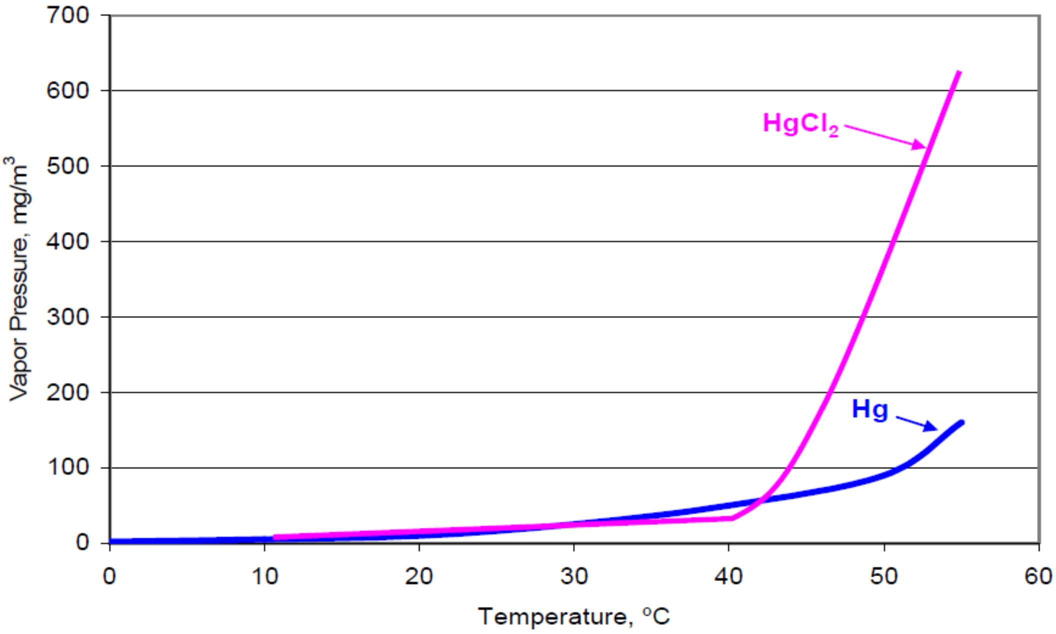


Figure 6-1: *Equilibrium concentration in vapour phase (mg/Nm³) for elemental mercury and mercuric chloride (Richards, 2005).*

6.4. SOLUBILITY IN AQUEOUS SOLVENTS

The solubility of mercury compounds can vary considerably according to their composition and oxidation state. Elemental mercury is almost completely insoluble (Richards, 2005). Mercuric hydroxide ($Hg[OH]_2$) and mercuric oxide (HgO) are insoluble in water. Mercurous oxide is only soluble to a minimal extent. Other mercurous compounds also have very limited solubility.

Conversely, mercuric chloride is essentially completely soluble at the concentrations that can exist in the gas streams which pass through wet scrubbers and impinger solutions in the sampling train. The solubility of mercuric chloride increases with liquid temperature. Mercurous chloride (HgCl) is considerably less soluble than mercuric chloride.

Reactions that result in the oxidation of elemental mercury to oxidised mercury provide an opportunity to scrub mercury from the gas stream. Reactions that result in the reduction of oxidised mercury to elemental mercury result in the rapid release of mercury back into the gas stream in contact with the liquid.

6.5. PHYSICAL CHARACTERISTICS - UV ABSORPTION

Mercury has strong absorption peaks at 254 nanometres (nm), 313 nm, and 365 nm. There are a number of other weaker absorption peaks at a number of wavelengths ranging from 265 to 300 nm, 400 nm and 410 nm. The absorption band at 254 nm is especially important in mercury monitoring. The absorption peaks at 313 nm and 365 nm are of interest for possible photochemical control applications.

6.6. EQUILIBRIUM CONDITIONS

Thermodynamic equilibrium calculations indicate that, at temperatures exceeding 700ºC, more than 99% of the mercury should be in the form of Hg^0. The elemental mercury released with the fuel in the burner flame in the kiln or precalciner consists primarily of elemental mercury. The thermodynamically favoured chemical forms of mercury as a function of temperature are summarised in **Figure 6-2**.

As the gas temperature decreases below 500ºC, the favoured form of mercury is oxidised mercury ($HgCl_2$ or HgO). If the thermodynamic equilibrium limits were to control the partitioning between elemental and oxidised forms of mercury, elemental mercury concentrations would be low in most types of combustion systems and industrial furnaces (e.g. cement kilns). In practice, elemental mercury can form 10% to 90% of the total mercury found in coal fired boiler effluent gas streams. This indicates that kinetic factors limit the conversion of elemental mercury to mercuric chloride or oxide. The fast temperature reduction which occurs in the heat exchange sections of the boiler is probably responsible for the quenched elemental mercury reactions. A similar condition could occur in the preheater tower and in the preheater-precalciner cement kilns.

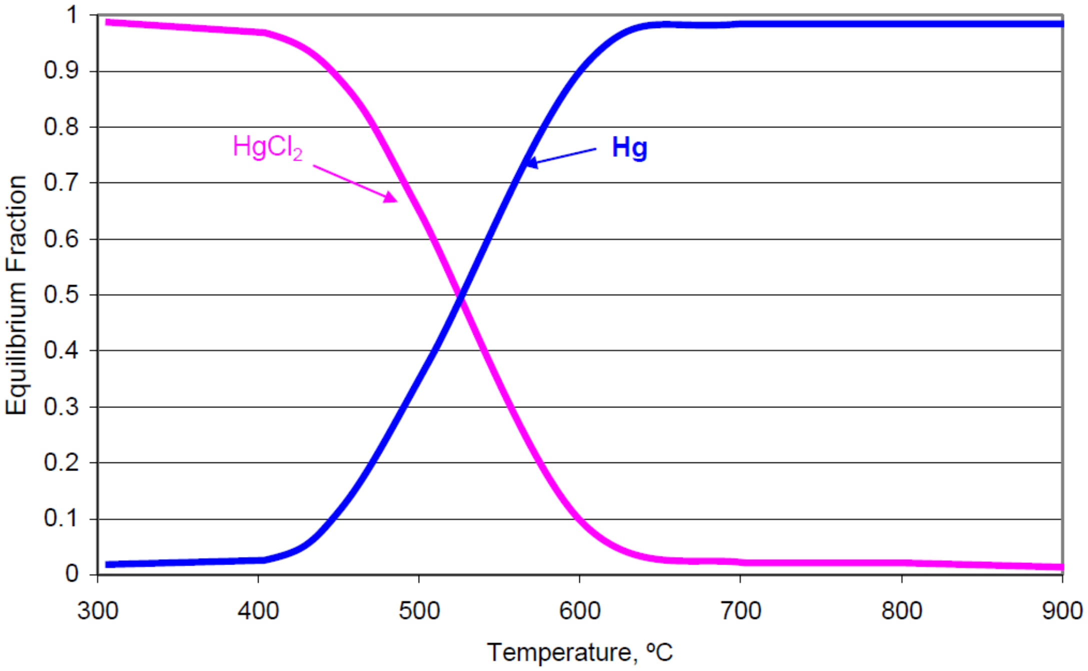


***Figure 6-2**: Thermodynamically favoured forms of mercury (Richards, 2005)*

The temperature at which mercury is released from the kiln feed is not accurately known. A major fraction of the mercury input could probably be released at a temperature of less than 500ºC. At this temperature, most- of the mercury should be in the form of oxidised mercury (Hg^{2+}).

The results from a limited number of mercury speciation tests conducted to date are consistent with these general observations (Richards, 2005). Mercury is primarily present in its oxidised form, probably due to the dominance of the feed stream in the mass balance. Elemental mercury levels in the 10% to 50% range have been observed, probably due to the quenching of reactions that result in the conversion of elemental mercury to the more thermodynamically favoured oxidised mercury form.

6.7. CHEMICAL REACTION RATES

The mercury reactions have been summarised based on several mercury chemistry compilations (Richards, 2005). Most of the data is available from experiments conducted in coal fired power plants. Conditions in cement kilns differ slightly. Due to the low mercury concentration and the large number of potential reaction mechanisms, a certain number of important mercury reactions may not have been identified as yet or not properly evaluated.

$$\mathbf{Hg^0\,(g) + O_3\,(g) \leftrightarrow HgO\,(g) + O_2\,(g)} \qquad \text{R1}$$

$$\mathbf{Hg^0\,(g) + Cl_2\,(g) \rightarrow HgCl_2\,(g)} \qquad \text{R2}$$

Elemental mercury reacts rapidly with the ozone in ambient air and/or electrostatic precipitators to form Hg^{2+} as shown in reaction R1.

Ozone levels in the ambient air range from 0.01 to 0.1 ppm depending on the ambient temperature, the solar irradiation rate and the nitrogen oxide and hydrocarbon concentrations.

In electrostatic precipitators, the ozone concentrations can be 1 to 5 ppm depending on the electrical discharge corona intensities on the discharge electrodes and on the oxygen concentration in the gas stream. This reaction may be one of the reasons why moderate-to-high fractions of the total mercury can be in the form of oxidised mercury in kiln gas streams controlled by electrostatic precipitators.

The reaction of elemental mercury with chlorine (R2) is especially important and the rate constant suggests that this reaction is fast. There are indications that the conversion of HCl into Cl_2 followed by the reaction of Hg with Cl molecules is one of the primary mechanisms for the conversion of elemental mercury to $HgCl_2$.

The following two general reactions for the gas phase conversion of elemental mercury to oxidised mercury are proposed. These reactions are considered to be possible in the temperature range of 500ºC to 800ºC.

$$\mathbf{Hg + 2HCl \rightarrow HgCl_2 + H_2} \qquad \text{R3}$$

$$\mathbf{Hg + 4HCl + O_2 \rightarrow 2HgCl_2 + 2H_2O} \qquad \text{R4}$$

Other authors have suggested that the elemental mercury reactions include a two-step reaction sequence involving chlorine atoms (Reactions R5 and R6).

$$\mathbf{Hg + Cl \rightarrow HgCl} \qquad \text{R5}$$

$HgCl + Cl \rightarrow HgCl_2$ R6

According to these authors, these reactions would be most effective at high temperatures, such as those existing in the heat exchange areas in the boiler of a power plant and in the preheater tower of a cement kiln. In this case, the question of chlorine availability is important.

It has been found that the formation of oxidised mercury from elemental mercury increases from a range of 0% to 15% at very low coal chlorine levels to more than 95% when chlorine levels exceed 0.4% by weight. This indicates that chlorine is a limiting reactant for the oxidation of elemental mercury. Available chlorine is generally low in cement kilns.

A heterogeneous reaction mechanism is supposed to occur on the surface of unburned carbonaceous ash. The heterogeneous oxidation mechanism is especially sensitive to the presence of combustion gases. Hydrogen chloride, nitric oxide, and nitrogen dioxide favour the heterogeneous conversion of elemental mercury to oxidised mercury. The presence of moderate concentrations of both sulphur dioxide and nitrogen dioxide appears to enhance the oxidation of mercury. Presumably, these effects are highly temperature sensitive and involve some adsorption or molecular complex formation on the surface of the carbonaceous material.

Reactions 7 to 13 address the aqueous phase chemistry of mercury and mercuric chloride. These reactions indicate that important interactions between dissolved sulphur dioxide and various forms of mercury in solution exist.

$Hg_2^{2+}\ (g) \leftrightarrow Hg^0\ (aq) + Hg^{2+}$ R7

$Hg^{2+} + SO_3^{2-} \leftrightarrow HgSO_3\ (aq)$ R8

$HgSO_3\ (aq) + SO_3^{2-} \leftrightarrow Hg(SO_3)_2^{2-}$ R9

$Hg(SO_3)_2^{2-} + H_2O \rightarrow Hg^0\ (aq) + H_2SO_4 + SO_3^{2-}$ R10

$HgSO_3 + H_2O \rightarrow Hg^0\ (aq) + H_2SO_4$ R11

$Hg^0\ (aq) + O_3\ (aq) \rightarrow Hg^{2+}\ (aq) + O_2\ (aq)$ R12

$Hg(OH)_2\ (aq) \leftrightarrow Hg^{2+} + 2OH^-$ R13

In some cases, gas phase SO_2 can act as a reducing agent and convert oxidised mercury to elemental mercury. Very little information is available concerning the rate of this reaction or the SO_2 concentration needed to cause a significant conversion of oxidised mercury to elemental mercury.

6.8. ADSORPTION

Elemental and oxidised mercury can readily adsorb on surfaces of solid particles containing organic compounds, alkali compounds, and silica compounds. In terms of the first two compounds (organic and alkali), adsorption is due to physisorption, which involves a relatively weak bond. Accordingly, adsorption is favoured when the temperature is low and the mercury can be released when the solid temperature increases.

The extent of adsorption due to physisorption (also called physical adsorption) also relates to the solids mass loadings, the surface area of the solids, and the residence time for mass transfer. The removal of cement kiln dust (CKD) to control alkali levels could contribute to the overall removal of mercury from the pyroprocessing system, and thereby minimise mercury emissions.

In the cement industry, elemental or oxidised mercury can probably be adsorbed due to chemisorption into silica particles (Richards, 2005). In chemisorption, the adsorbent is strongly bound and is not released unless the adsorbing material or the chemical reaction causes a thermal breakdown. The mercury could react with silica compounds to form $HgSiO_3$ or $Hg_6Si_2O_7$. Both of these compounds are probably stable at temperatures prevailing in air pollution control systems.

6.9. TOXICOLOGY

All forms of mercury are toxic but, as mentioned previously, this toxicity will depend on the speciation and on the chemical form. Mercury has different properties which make it a potential environmental toxin (Edbon et al., 2001; UNEP, 2002).

These properties are:
- the strong affinity of Hg(II) and organomercurials for thiol groups;
- a tendency to form covalent bonds with organic molecules;
- the high stability of the Hg-C bond that results from a low affinity for oxygen;
- a strong tendency to maximise bonding to two ligands in linear stereochemistry.

Symptoms and signs are rather different in exposure to elemental mercury, inorganic mercury compounds and organic mercury compounds.

Elemental mercury

Liquid metallic mercury is poorly absorbed by ingestion and skin contact but mercury vapours are hazardous. In fact, inhaled mercury is absorbed in the lungs and enters the blood stream. It can easily cross blood-brain placenta barriers due to its high lipid solubility. Intestinal absorption of elemental mercury is low. Dissolved mercury is oxidised into the inorganic divalent form in body tissues (red cells, brain, liver, lung and other tissues) where it may inhibit the activity of some enzymes with thiol groups. It can denature proteins and damage cell membranes. At high concentrations it causes cell death and destruction of tissues, however at low concentrations damage is reversible.

Organic mercury compounds

All alkylmercury compounds are thought to be rather similar with respect to toxicity, while other organic mercury compounds (e.g. phenylmercury) have similar toxicity levels as inorganic mercury compounds. The most dangerous mercury compounds are alkylmercury and, more particularly, dimethylmercury. The latter compound can be found in the food chain through bioaccumulation, reaching high concentrations among some species, especially in fish such as tuna or swordfish. It causes impairment of the central nervous system. Methylmercury is distributed in all tissues, including the brain, and it is more dangerous for pregnant women, as prenatal damage occurs in all parts of the brain unlike in adults where the damage is local.

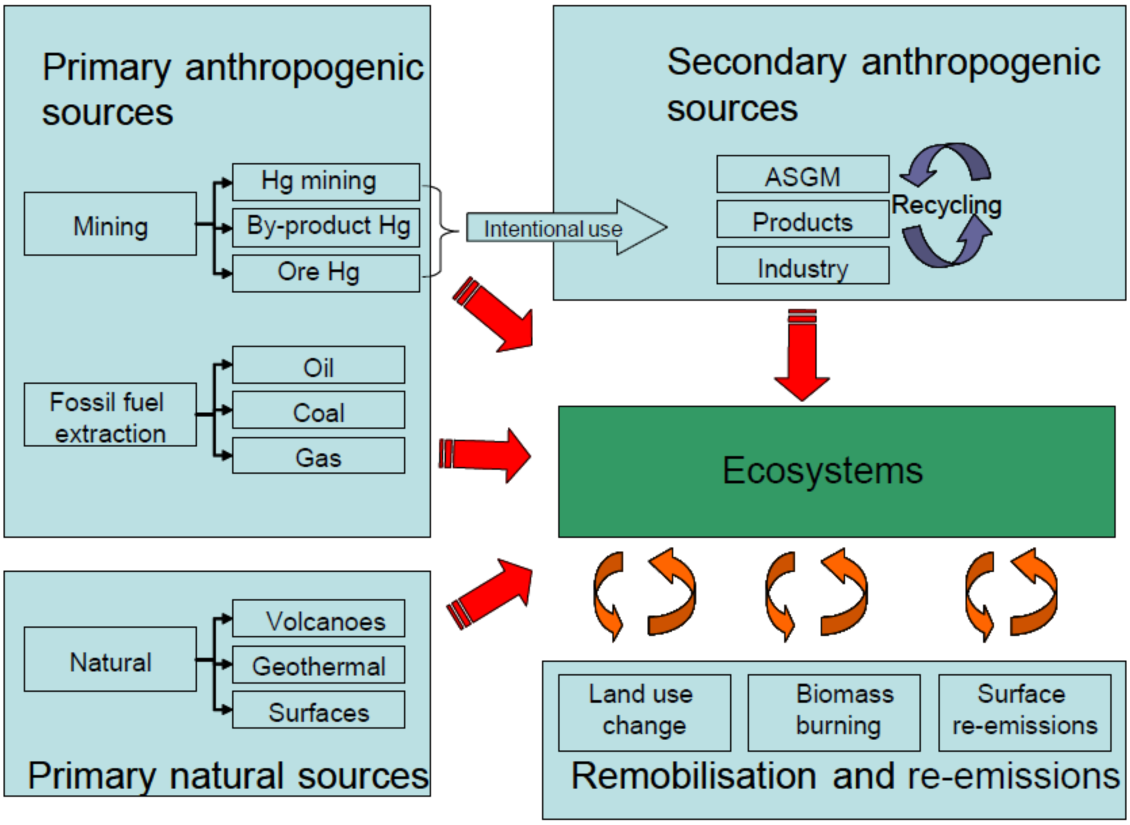
Inorganic mercury compounds

Inorganic mercury compounds, such as salts, primarily affect the gastro-intestinal tract. Kidneys are a target tissue for retention of this form of mercury. This form cannot pass the blood-brain barrier easily. Mercury salts occur in both mercury forms (Hg_2^{2+} and Hg^{2+}) with both oxidation states. Mercuric salts are usually more toxic than their mercurous counterparts because their solubility in water is greater. The inorganic mercury compounds are principally excreted in urine.

6.10. MERCURY IN THE ENVIRONMENT – EXTRACT FROM THE UNEP REPORT "TECHNICAL BACKGROUND REPORT TO THE GLOBAL ATMOSPHERIC MERCURY ASSESSMENT"

In **Figure 6-3** a schematic description of the main source types is presented. The *primary anthropogenic sources* are those where mercury of geological origin is mobilised and released to the environment. The two main source categories of this type are mining (either for mercury or where mercury is a by-product or contaminant in the mining of other minerals) and extraction of fossil fuels where mercury is present as a trace contaminant. The *secondary anthropogenic sources* are those whose emissions occur from the intentional use of mercury e.g., industry, products or for artisanal gold mining. In both these source types, emissions to the environment can occur via direct exchanges of exhaust gases and effluents, although the generation of mercury containing waste also contributes. *Primary natural sources*, are those where mercury of geological origin is released via natural processes such as volcanoes or geothermal processes or evasion from natural surfaces geologically enriched in mercury. In addition to these source types, the distribution of mercury is affected by its *remobilisation and re-emission pathways*. In the latter case, the mercury released can be of either natural or anthropogenic origin and it is currently not possible to experimentally distinguish between the two. Anthropogenic activities such as biomass burning and land use changes will affect the magnitude and location of the mercury releases.

Figure 6-3 Schematic description of emission source types and remobilisation processes affecting mercury distribution in the environment. The red arrows represent the release of mercury and subsequent transport and input to the ecosystems.



7. CEMENT PRODUCTION PROCESS

There is extensive literature on the cement production process, with the following, easily available, documents providing a good overview:

- CEMBUREAU "Best available techniques for the cement industry" (CEMBUREAU, 1999).
- European Integrated Pollution Prevention and Control document "Reference document on Best Available Techniques in the Cement and Lime Manufacturing Industries" (IPPC, 2001).
- European Integrated Pollution Prevention and Control document "Reference document on Best Available Techniques in the Cement and Lime Manufacturing Industries" Draft (IPPC, 2009).
- Formation and Release of POPs in the Cement Industry (Second Edition), (SINTEF, 2006).
- "Cement Sustainability Initiative (CSI)" website.

Hereafter, a summary is provided with a special focus on mercury.

7.1. CEMENT PRODUCTION

A. PRINCIPLE

Portland cement clinker is produced from a mixture of raw materials, the main elements of which are calcium, silica, aluminium, and iron. The prepared raw material ("kiln feed") is fed into the kiln system where it is subjected to a thermal treatment process consisting of drying/preheating, calcination (e.g. release of CO_2 from limestone), and sintering (or "clinkerisation", e.g. formation of clinker minerals at temperatures of up to 1450 °C).

The resulting product, "clinker", is cooled to 100-200°C with air and is transported for intermediate storage. Portland cement is produced by grinding clinker with a percentage of gypsum (or anhydrite) in a cement mill. Blended cements contain other additional constituents.

B. RAW MATERIALS

Natural ("primary") raw materials such as limestone/chalk, marl, and clay/shale are extracted from quarries which, in most cases, are located close to the cement plant. After extraction, these raw materials are crushed at the quarry site and transported to the cement plant for intermediate storage, homogenisation and further preparation.

"Corrective" materials such as bauxite, iron ore or sand may be required to adapt the chemical composition of the raw mix to the requirements of the process and product specifications. The quantities of these corrective materials are usually low compared to the huge mass flow of the main raw materials.

Depending on availability and chemical composition, both main and corrective raw mix components may also originate from industrial sources ("alternative" raw materials). Examples include coal fly ash from power stations, steel slag, foundry sand, lime sludge and many others.

After intermediate storage and pre-homogenisation, the raw materials are dried and ground together in defined and well-controlled proportions in a raw mill to produce a raw meal for the dry (and semi-dry) process. In the wet (and semi-wet) process, the raw materials are slurried and ground with the addition of sufficient water to produce a raw slurry.

C. KILN PROCESSING

The kiln systems commonly applied are rotary kilns with or without so-called "suspension preheaters" (and, in more advanced systems, "precalciners"), depending on the main process design selected.

In all processes the kiln feed is first dried, then calcined by dissociation of carbon dioxide (CO_2) from the $CaCO_3$ in the feed material, and finally sintered to clinker at temperatures ranging between 1400 and 1450 ºC. During this process the feed loses approximately one third of its original dry mass. The hot clinker is cooled to 100-200ºC with air in a clinker cooler. The heated air is used as secondary combustion air in the kiln.

The rotary kiln itself is an inclined steel tube with a length to diameter ratio of between 10 and 40. The slight inclination (2.5 to 4.5%), together with the slow rotation (0.5–4.5 revolutions per minute), allows for a material transport which is sufficiently long in order to achieve the thermal conversion processes required.

Exhaust heat from the kiln system is utilised to dry the raw materials, solid fuels or mineral additions in the mills. Exhaust gases are dedusted using either electrostatic precipitators or bag filter systems before being released into the atmosphere.

The clinker formation process can be divided into 4 steps:

- Drying and preheating (20–900 °C): release of free and chemically bound water;
- Calcination (600–1050 °C): release of CO_2: initial reactions with formation of clinker minerals and intermediate phases;
- Sintering or clinkerisation (1050–1450 °C): formation of calcium silicates and liquid phase;
- Kiln internal cooling (1350–1200 °C): crystallisation of calcium aluminate and calcium ferrite.

Minor mineral constituents in the cement clinker include unbound calcium oxide ("free lime") and magnesium oxide, as well as alkali sulphates. Additional chemical elements present in the raw materials, such as manganese, phosphorus, titanium or heavy metals, are mainly incorporated into the mineral structure of the major clinker phases.

The clinker properties (and thus, of the cement produced) are mainly determined by its mineral composition and its structure. Some elements in the raw materials, such as the alkalis, sulfur and chlorides, are volatilised at the high temperatures of the kiln system resulting in a permanent internal cycle of vaporisation and condensation (“circulating elements”). A large part of these elements will remain in the kiln system and will finally leave the kiln with the clinker. A small part will be carried out with the kiln exhaust gases and will be mainly precipitated with the particulates in the dedusting system.

If there is a high surplus of volatile elements, the installation of a preheater “bypass” may become necessary where part of the dust laden exhaust gases of the rotary kiln are extracted from the system. Both filter dust and bypass dust can be partially or totally used in the cement manufacturing process.

a) The four main process routes

Historically, the development of the clinker manufacturing process was characterised by the change from “wet” to “dry” systems, with the intermediate steps of the “semi-wet” and “semi-dry” process routes. The first rotary kilns – introduced in around 1895 – were long wet kilns.

The four different basic processes can be briefly characterised as follows:

- **Dry process**: Dry raw meal is fed into a cyclone preheater or precalciner kiln or, in some cases, into a long dry kiln with an internal chain preheater.
- **Semi-dry process**: Dry raw meal is pelletised with water and fed into a travelling grate preheater prior to the rotary kiln or, in some cases, to a long kiln equipped with internal cross preheaters.
- **Semi-wet process**: Raw slurry is first dewatered in filter presses. The resulting filter cake is either extruded into pellets and fed into a travelling grate preheater or fed directly into a filter cake drier for (dry) raw meal production prior to a preheater/precalciner kiln.
- **Wet process**: The raw slurry is fed either directly into a long rotary kiln equipped with an internal drying/preheating system (conventional wet process) or into a slurry drier prior to a preheater/precalciner kiln (modern wet process).

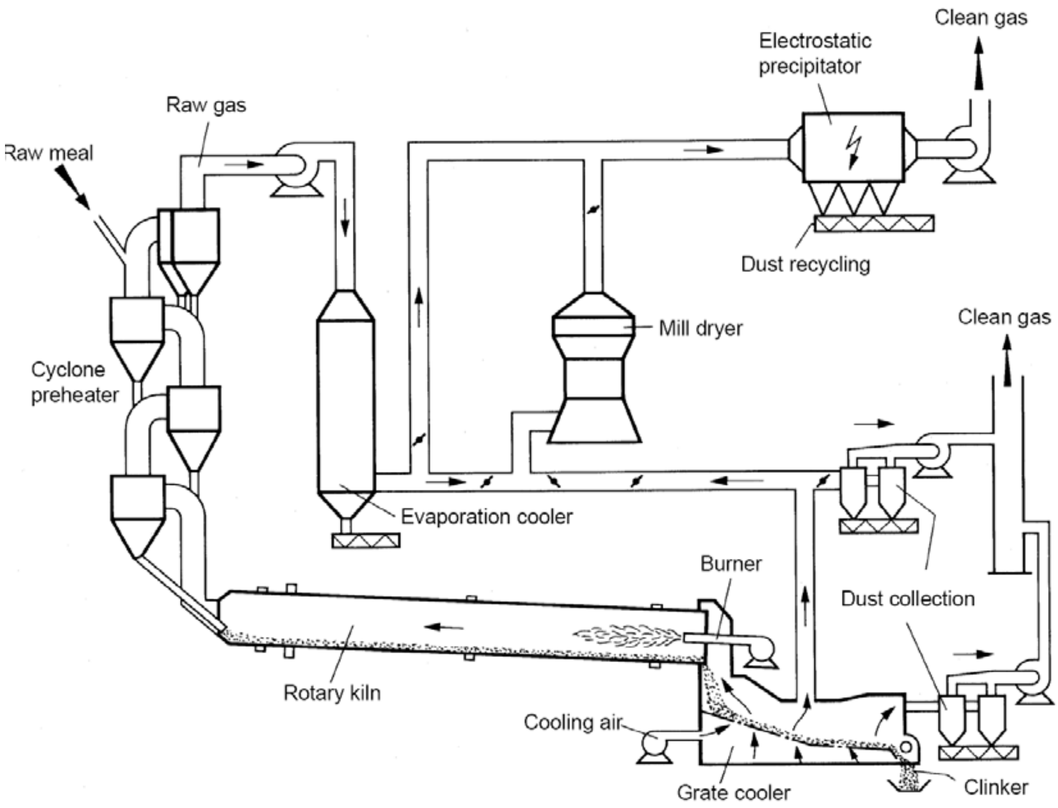


***Figure 7-1** : Rotary kiln with cyclone preheater and gas dust collection (IPPC, 2009).*

D. FUELS

The main fossil fuels (“primary” fuels) used in the cement industry are coal, petcoke, heavy fuel oil, and – to a lesser extent – natural gas. “Alternative” fuels such as tyres, waste oil, plastics, and solvents are increasingly used today. The chemical components of the ash of solid fuels combine with the raw materials and are fully incorporated into the clinker produced. Thus, the chemical composition of the ash has to be considered in the raw mix design.

E. CEMENT GRINDING

Portland cement is produced by grinding clinker with natural or industrial gypsum or anhydrite (calcium sulphate), which acts as a set regulator, and major other constituents such as slag and fly ashes or natural pozzolana (see e.g. EN 197-1 in Europe).

7.2. KILN EXHAUST GASES

In all kiln systems, the exhaust gases are finally passed through an air pollution control device for separation of the dust before being released into the atmosphere via stacks. Today, two types of dust separators are commonly used in the cement industry, namely electrostatic precipitators and bag filters.

Electrostatic precipitators use electrostatic forces to separate the dust from the exhaust gas. By means of discharge electrodes, the dust particles are negatively charged and can be separated onto corresponding collecting electrodes. The particles are then discharged from the collecting electrodes to dust hoppers by electrode rapping.

Bag filters make use of a fabric filter system, the “bags” which separate the dust particles from the exhaust gas. The dust particles are captured on the bag surface while the gas passes through the bag tissue.

With a **dedusting efficiency** of up to 99.99% in modern control devices, it is possible to achieve a dust emission level at the stack of below 20 mg/Nm^3.

In the dry process, the kiln exhaust gases have a relatively high temperature and low humidity. Therefore, they can be utilised for the drying of raw materials in the **raw mill** during “compound operation”, i.e. when the raw mill is in operation. During “**direct operation**” (with the raw mill off), the hot exhaust gases have to be cooled down to a temperature suitable for the dust collector by means of water injection before the filter.

The dust collected in the filter devices can be fed back into the process, by reintroducing it into the raw material preparation system (dry process), by insufflations into the sintering zone (wet kilns), or by feeding the dust into the cement mill (if allowed by the cement standards).

7.3. ENVIRONMENTAL IMPACTS OF CEMENT PRODUCTION

The main environmental impacts of cement manufacturing relate to the following:

- Dust from stack emissions and other sources;
- Emissions of NO_x, SO_2, CO_2;
- Emissions of trace elements;
- Resource consumption of energy and raw materials.

7.3.1. Dust

Historically, the dust emissions – particularly from kiln stacks – have been the main environmental concern in terms of cement manufacturing. “Point source” dust emissions originate mainly from the raw mills, the kiln system, the clinker cooler, and the cement mills. A general feature of these process steps is that hot exhaust gas or exhaust air pass through pulverised material resulting in an intimately dispersed mixture of gas and particulates. Primary reduction measures are therefore rarely available. The nature of the particulates generated is linked to the source material itself, i.e. the raw materials (partly calcined), clinker or cement.

Dust emissions in the cement industry have been reduced considerably over the last 20 years. The state-of-the-art abatement techniques now available (electrostatic precipitators and bag filters) result in stack emissions which are insignificant in a modern and well managed cement plant.

7.3.2. Gaseous atmospheric emissions

Gaseous emissions from the kiln system released into the atmosphere are the primary environmental concern in cement manufacturing today. Major gaseous emissions are NO_x and SO_2. In addition, cement kilns are particularly CO_2 intensive.

Other less significant emissions are VOCs (volatile organic compounds), CO, ammonia, and heavy metals.

Other gaseous emissions, such as hydrochloric acid or hydrofluoric acid, are nearly completely captured by the inherent and efficient alkaline scrubber effect of the cement kiln system.

7.3.3. Trace elements

During the clinker burning process, all mineral inputs derived from the raw materials – be it natural or alternative raw material sources – are converted into the clinker phases at the high temperatures which prevail in the sintering zone of the rotary kiln.

Trace elements, such as heavy metals, are naturally present in low concentrations in the raw materials and fuels used for the manufacture of cement clinker. The behaviour of these metals in the burning process depends largely on their volatility and the volatility of their compounds.

- **Non-volatile metals** remain completely within the product and leave the kiln system fully incorporated into the mineral structure of the clinker (similar to the main elements). Most of the common metals are non-volatile.
- **Semi-volatile elements,** such as cadmium or lead, may, in part, be volatilised with the high temperature conditions in the sintering zone of the kiln system. They condense on the raw materials in cooler parts of the kiln system and are reintroduced into the hot zone once again. A major part of the cadmium and lead will be incorporated into clinker. The remaining part will precipitate with the kiln dust and be collected in the filter systems.
- **Volatile metals,** such as mercury and thallium, are more easily volatilised and condense on raw material particles at lower temperatures in the kiln system (thallium at approximately 300-350°C, mercury at 120-150°C). Whereas thallium is nearly completely precipitated onto the kiln dust particles, not all of the mercury will be collected within the filter system. Volatile metals are only retained in the clinker minerals to a very small extent.

7.3.4. Resources consumption

Cement manufacturing is a “high volume process”. As a result, it requires adequate quantities of resources, i.e. raw materials, fuels and electrical power.

A “medium-sized” plant with a clinker production of 3000 tonnes per day or 1 million tonnes per year corresponds to a cement production of 1.23 million tonnes per year (based on average figures for the clinker content of cements in Europe).

Cement manufacturing is also an energy intensive process. The specific thermal energy consumption of a cement kiln varies between 3000 and 7500 MJ per tonne of clinker, depending on the basic process design of the plant.

7.4. WORLD CEMENT PRODUCTION

According to the following table, world cement production was approximately 2 776 million tonnes in 2007. This represents an increase of approximately 8.18% (210 millions of tonnes) compared to the previous year and a continuation of the annual basic expansion which has seen year-on-year growth since 2000. A substantial fraction of cement production is located in Asia, with China accounting for a large and increasing share of global cement production (about 44% in 2006) (MNP, 2008).

***Table 7-1**: Cement production in different world regions (1000 tonnes)(from CEMBUREAU).*

Year	Africa	America	Asia	Oceania	Europe	CIS	Total
2007	121 578	265 966	1 947 778	11 030	335 743	94 741	2 776 836
2006	110 532	253 623	1 774 446	10 619	329 762	87 777	2 566 759
2005	98 458	240 599	1 552 451	10 508	312 173	78 125	2 292 314
2004	88 932	231 407	1 451 779	10 118	299 956	71 889	2 154 081
2003	85 977	218 810	1 311 733	9 391	286 176	63 537	1 975 624
2002	78 713	216 523	1 180 796	8 983	277 289	57 532	1 819 836
2001	75 956	217 878	1 076 077	7 798	274 062	50 590	1 702 361
2000	69 326	220 891	1 023 961	8 549	283 174	45 770	1 651 671

8. THE BEHAVIOUR OF MERCURY IN THE CLINKER KILN SYSTEM

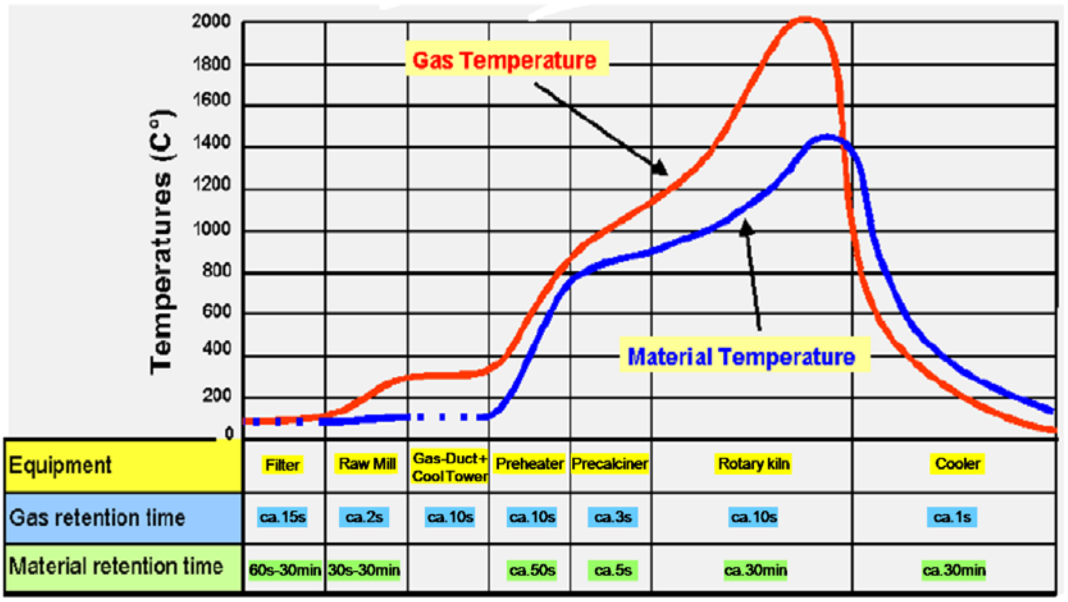
8.1. THE BEHAVIOUR OF HEAVY METALS IN THE CLINKER KILN SYSTEM

The following factors determine the emission behaviour of individual heavy metals:

- the input,
- their physico-chemical characteristics (i.e. volatility)
- the efficiency of the gas cleaning devices

During the burning of cement clinker it is necessary to maintain material temperatures of up to 1450°C in order to ensure the required sintering reactions. This is achieved by applying peak combustion temperatures of about 2000°C with the main burner flame.

Figure 8-1 illustrates the temperature profiles for the combustion gases and the material for a preheater/precalciner rotary kiln system. While the temperature profiles may be different for the various kiln types, the peak gas and material temperatures described above have to be maintained in any case.



Equipment	Filter	Raw Mill	Gas-Duct+ Cool Tower	Preheater	Precalciner	Rotary kiln	Cooler
Gas retention time	ca.15s	ca.2s	ca.10s	ca.10s	ca.3s	ca.10s	ca.1s
Material retention time	60s-30min	30s-30min		ca.50s	ca.5s	ca.30min	ca.30min

Figure 8-1 : Gas and Materials Profile in a cyclone Preheater/precalciner System (Lafarge)

Depending on their volatility, the heavy metals which enter the clinker burning process with the raw materials and fuels may be completely or partly vaporised in the high-temperature zones of the preheater and/or the kiln, react with the gas-phase components in the kiln and preheater and condense on the kiln charge in the colder zones of the kiln system. If the heavy metals are largely condensed in the preheater area, they will be returned to the kiln with the kiln charge. This results in an internal heavy metal cycle, the so-called kiln/preheater cycle.

A distinction is made between an internal and an external balance to describe the general behaviour of heavy metals in rotary kiln systems and the heavy metal cycles that may form. The proportion of volatile compounds carried out of the preheater with the raw gas is either separated in the dust collectors together with the raw gas dust and/or the dust from the grinding-drying unit, or precipitates on the raw meal. If this dust is once again added to the raw material, an external heavy metal cycle or kiln/grinding-drying unit cycle will be established.

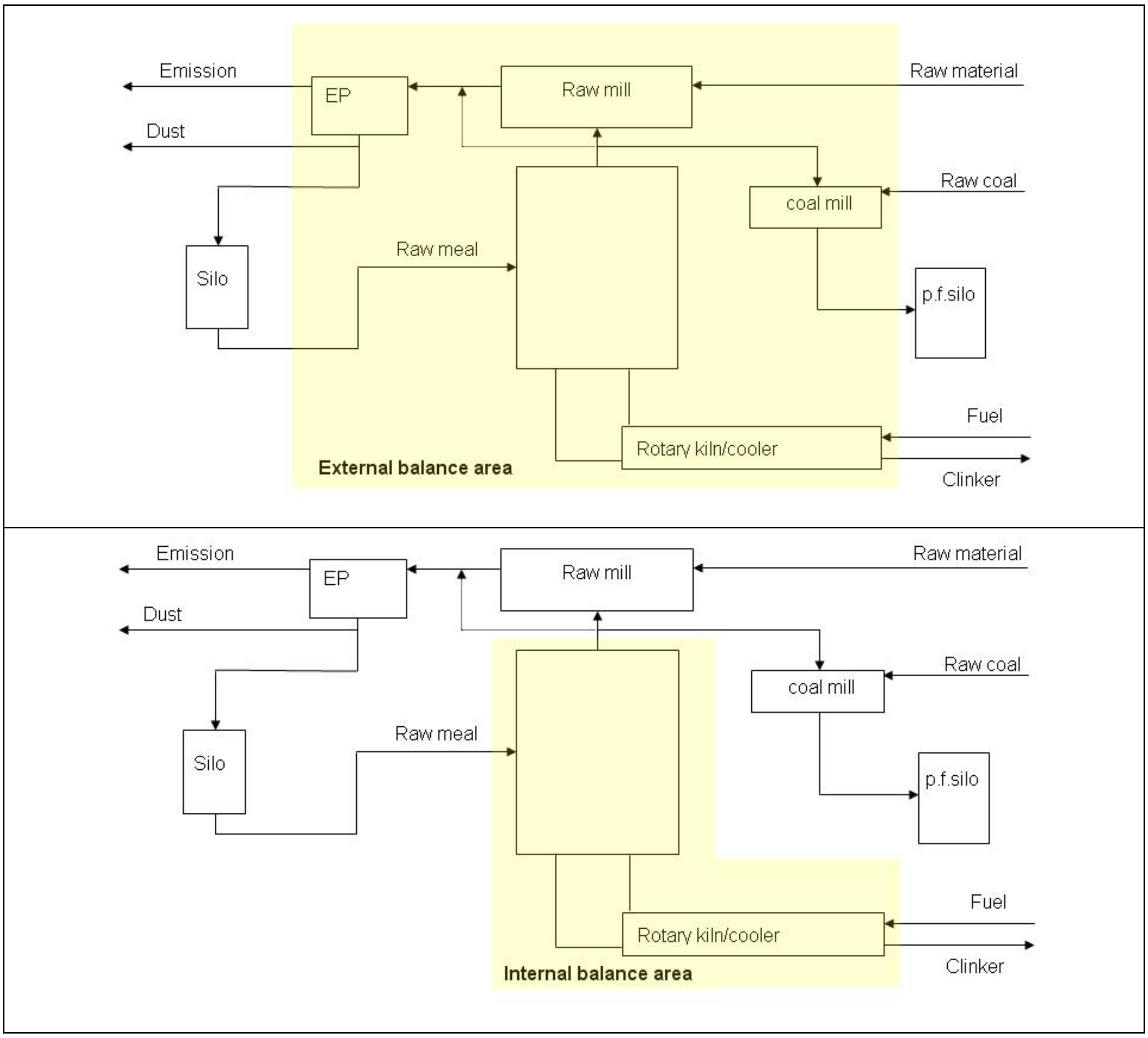


***Figure 8-2**: Internal and external balance in cement kiln system.(Schäfer and Hoening, 2001).*

8.2. MERCURY STREAMS AND KILN SYSTEM TEMPERATURE PROFILES

Due to its high volatility, mercury forms gaseous compounds which are not retained in the rotary kiln and preheater area. Instead, gaseous mercury compounds condense on the raw material particles in the dust collector area, with the dust particles acting as condensation nuclei. This means that mercury may only become enriched in the external cycle.

As the combustion gases move toward the raw material feed end of the kiln system, the temperature decreases from approximately 2 200°C to 90-300°C depending on the type of equipment installed, the operation mode and the moisture of the raw materials. In addition, some of the mercury released from the raw materials as they heat up reacts with the chlorine to form $HgCl_2$.

Some of the mercury reacts to form HgO as flue gas temperatures continue to cool down to the boiling point of mercury (approximately 350°C). The formed oxide may further react with chlorine to form $HgCl_2$. At gas temperatures below approximately 325°C, some of the mercury may react with sulfur to form mercury sulphate ($HgSO_4$) (Schreiber et al., 2005).

Very few analyses of mercury concentration have been conducted in alkali bypass streams. The mercury levels in these streams should be lower than in the main kiln gas stream, because mercury entering the pyroprocessing system with the raw materials is assumed to have volatilised within the preheater tower or precalciner vessel. Therefore, fuel mercury is the only significant source of mercury in the kiln gas stream. Finally, there is no concentration loop that can recycle mercury into the alkali bypass system. The rapid quench that is characteristic of alkali bypass systems could be especially effective in reducing the rate of elemental mercury conversion to mercuric chloride.

As the raw feed is heated to temperatures of between 225°C and 325°C, the formation of mercury silicates is possible. However, experimentation did not demonstrate whether $HgSiO_3$ is thermodynamically stable at the high temperatures of the clinker as it exits the kiln.

As the flue gas passes through the dedusting device, temperatures continue to drop until reaching 100°C. This decrease permits some of the elemental mercury to condense onto the dust particles. Some of the oxidised mercury compounds (i.e., $HgCl_2$, HgO, and $HgSO_4$) can also adsorb and condense onto the dust particles. The remaining mercury compounds pass through the stack.

The possible reactions mentioned above are summarised in **Table 8-1** and in **Figure 8-3**.

***Table 8-1** : Potential mercury transformation within cement kiln systems (Schreiber et al., 2005).*

System temperature (°C)	Chemical species influencing reactions	Resulting mercury compounds
2200	**-**	Hg (elemental, vapor)
<480-590	Chlorine	$HgCl_2$
<350	Oxygen, Chlorine	HgO, $HgCl_2$
<325	Sulphur	$HgSO_4$
225-325	Silica	$HgSiO_3$

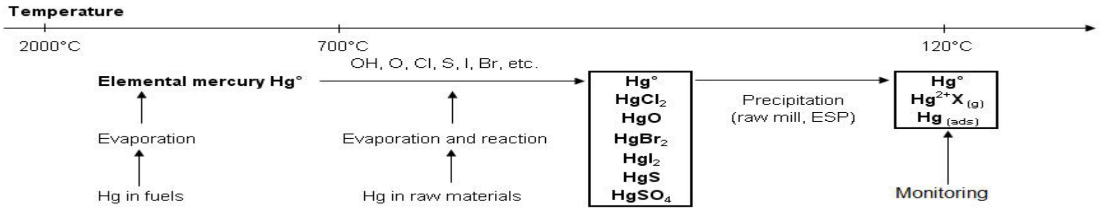


***Figure 8-3**: Potential mercury reactions within cement kiln systems*

Typical material and gas temperature profiles for dry kilns are shown in **Figure 8-1**. From the temperature profiles, it is likely that for kilns with preheaters, many of the reactions involving mercury are initiated in the preheater section of the systems.

For a dry kiln system with an operating in-line raw mill, the raw materials in the mill and the dust in the air pollution control device remove mercury compounds. Stack temperatures and ambient mercury emissions are usually lower during operations when the raw mill is on-line, due to the combined effects of raw mill exit temperatures and the scrubbing effect of the raw feed.

The concentration level of this cycle and the emissions are mainly determined by the exhaust gas conditions. In this regard, adsorption of mercury compounds on cold exhaust gas particles plays a key role. Condensation and, hence, mercury removal increases with decreasing exhaust gas temperature.

To prevent a long-cycle increase in mercury emissions, it may become necessary to limit the concentration of the external cycle by, for example, continuously or intermittently bleeding part of the dust collected in the electrostatic precipitator from the system. The dust bleed stream is fed into the cement mill as raw material.

9. KILN INPUT: FUELS AND RAW MATERIALS IN CEMENT PRODUCTION

Mercury enters the cement manufacturing process as a trace element in the raw materials and the fuels.

9.1. RAW MATERIALS

Mercury concentrations can vary significantly from one raw material to another and even within a single quarry. Limestone and clay are the main kiln feed constituents with fly ash capable of substituting up to 20% of these raw materials.

Table 9-1 (compiled using different sources) shows the mercury content of different raw materials extracted from quarries as well as other raw materials which are usually used in cement manufacturing, such as fly ash or other alternative materials.

Table 9-1 *: Mercury content of materials used for cement production*

Mercury content	**Range mg/kg**	**Reference**
Limestone, lime marl, chalk	<0.005 - 0.40	(Schneider and Oerter, 2000); (Sprung, 1985); (BUWAL, 1997); (Johansen and Hawkins, 2003b); (VDZ, 2008b) (CSI, 2008) (Cement_Company_A, 2008) (Hills and Stevenson, 2006)
Clay	0.002 - 0.45	(Schneider and Oerter, 2000) (CSI, 2008) (Hills and Stevenson, 2006) (Sprung, 1985) (Cement_Company_J, 2007)
Sand	< 0.005 – 0.55	(Cement_Company_A, 2008) (Hills and Stevenson, 2006)
Fly ash	< 0.002 – 0.8	(VDZ, 2008b) Adriano in (Johansen and Hawkins, 2003b) (Hills and Stevenson, 2006)
Iron ore	0.001 – 0.68	(Cement_Company_A, 2008)
Blast furnace slag	< 0.005 – 0.2	(Cement_Company_A, 2008)
Pouzzolana	< 0.01 – 0.1	(VDZ, 2008b)
Burned oil shale	0.05 – 0.3	(VDZ, 2008b)
Shale	0.002 – 3.25	(Hills and Stevenson, 2006) (Johansen and Hawkins, 2003b)
$CaSO_4$	< 0.005 – 0,02	(VDZ, 2008b)
Gypsum (natural)	< 0.005 – 0.08	(VDZ, 2008b)
Gypsum (artificial)	0.03 – 1.3	(VDZ, 2008b)
Aggregates	< 0.01 – 0.1	(VDZ, 2008b)

The mercury content of limestone is highly variable. The variability within a single quarry is illustrated in the case studies (**Section 12.2**). Compiled data indicates that mercury concentrations range from <0.001 to about 0.4 mg/kg. Overall, there is an important variation in the reported values.

Clay and shale have a mercury content ranging from 0.002 to 3.25 mg/kg, which is even more variable than the mercury content of limestone.

The mercury content of fly ash is linked to the dedusting of coal fired power plant air emissions. The presence of carbon on particle surfaces may provide some adsorptive removal of mercury. Capture efficiency for mercury suggests that fly ash mercury levels are slightly higher than those of coal (Richards and Holder, 2005). Fly ash can be divided into two categories: high and low loss on ignition fly ash. The mercury content of fly ash with high loss on ignition (LOI) (i.e. 10% to 20% carbonaceous LOI) might be higher than that of low carbonaceous LOI fly ash.

No information on mercury speciation was available.

***Table 9-2** : Mercury content of intermediary materials in clinker production*

Mercury content	**Range mg/kg**	**Reference**
Raw meal	0.01 - 1	(Schneider and Oerter, 2000) (CSI, 2008) (Schäfer and Hoenig, 2001) (BUWAL, 1997) *(Johansen and Hawkins, 2003b)*

9.2. FUELS

Both fossil fuels (coal, petcoke, etc.) and alternative fuels (tyres, animal meal, waste-derived fuels, etc.) are used in the cement manufacturing process. Not only do mercury concentrations vary among fuel types, but they may also vary significantly amongst a particular fuel type obtained from different sources. Alternative fuels are regularly analysed (including their mercury content).

The data collected shows that the mercury content of fossil fuels ranges from 0.001 (below detection limit) to mg/kg, and that of alternative fuels from 0.005 (below detection limit) to about 10mg/kg. No information on mercury speciation was available.

Table 9-3 *: Concentration of mercury in fossil fuels used for clinker production.*

Mercury content	**Range mg/kg**	**Reference**
Coal	0.1 – 13	(Schneider and Oerter, 2000) (BUWAL, 1997) (Johansen and Hawkins, 2003b) (Hills, 2006)
Lignite	0.03 – 0.11	(Johansen and Hawkins, 2003b)
Petcoke	0.01 – 0.71	USEPA in (Hills, 2006) (Cement_Company_J, 2007)
Heavy oil	0.006	(Johansen and Hawkins, 2003b)

Table 9-4 *: Concentration of mercury in alternative fuels used for clinker production.*

Mercury content	**Range mg/kg**	**Sources**
Liquid-waste derived fuel	<0.06 – 0.22	Pers. Comm. in (Hills, 2006)
Solid-waste derived fuel	< 0.07 – 2.77	Pers. Comm. in (Hills, 2006)
Sewage sludge	0.31 – 1.45	(Cement_Company_A, 2008) (Cement_Company_J, 2007)
Secondary fuel	0.04 – 10	(Johansen and Hawkins, 2003b) (Hills, 2006)
Tyre-derived fuel	0.01 – 0.4	(Hills, 2006) (Sprung and Rechenberg, 1994)

10. STACK MEASUREMENT METHODS OF MERCURY

Mercury is present at extremely low levels in cement plant emissions. Mercury can be considered as a micro-pollutant as emissions are typically expressed in milligrams per normal cubic meter. Emission monitoring is, therefore, technically challenging and expensive.

Mercury is present in cement kiln effluent gas, primarily in the form of elemental and oxidised mercury. The physical and chemical characteristics of mercury (see Chapter 6) have a considerable impact on the measurement methods.

10.1. MANUAL METHODS FOR MERCURY SPOT MEASUREMENT IN STACK EMISSIONS

Numerous measurements test methods have been developed to measure mercury in stack emissions. A general description of the methods and standards is given in Annex. The most relevant standards are:

- EN 13211:2001-2005
- EN 14385:2004
- VDI 3868, page 2, E
- US EPA Method 29
- US EPA Method 101A
- US EPA Method 101B
- Ontario Hydro Method - ASTM 6784-02
- US EPA Method 324

The majority of these methods have been validated in waste incinerators or coal-fired sources flue gases.

EN 13211 was largely validated in incineration plants. However, the method for cement plants is validated as a result of the limited differences with the typical composition of the exhaust gas of cement plants. EN 13211, US EPA Methods 101A, 101B, ASTM 6784-02 (Ontario Hydro), and USEPA Method 324 are the test methods available for the measurement of cement kiln mercury emissions. Methods 101A and 101B are only useful for the measurement of total mercury emissions. EN 13211 is also normally only used for the measurement of total mercury emissions but can be associated with EN 14385 to measure other metals. The Ontario Hydro Method provides total and speciated mercury emissions. Nevertheless, the Ontario Hydro speciated mercury data should be evaluated with caution in relation to tests conducted in cement kilns involving potential catalytic reactions to convert Hg^0 to Hg^{2+}.

The sample recovery procedures in Method 29 are more difficult than in other North American methods. Method 29 is useful for total mercury measurements primarily when emission data for other metals is also necessary. Method 324 is useful for vapour phase mercury emission tests involving long sampling periods from two to twenty-four hours.

The Research Institute of the Cement Industry (VDZ, 2001a) estimated the mercury detection limit to be between 0.003 and 0.006 mg Hg/Nm³ when taking into account the whole procedure. Detection limits depend on sampling, sample preparation and analysis methods and are thus not identical for all measurements. In some cases, measurement reports give significantly lower detection limits, however, these generally refer to the analytical part of the measuring method only.

10.2. CONTINUOUS MEASUREMENT OF MERCURY EMISSIONS

Mercury is present in the exhaust gas in different forms. A distinction can be made between elemental gaseous mercury and combined gaseous mercury. Instruments for continuous mercury measurements have to be capable of detecting all forms of mercury.

Two types of measuring devices are used for continuous measurement.

1. Thermo-catalytic devices: the mercury compounds in the sampled gas are reduced with the aid of a heated fixed catalyst.
2. Wet chemical devices which comprise a reaction stage with a liquid reducing agent (usually tin(II) chloride).

Photometers (UV detection) are used in all instrument types and can only detect elemental, fully reduced mercury.

Continuous measurement of mercury emissions from waste incinerators and co-combustion plants is mandatory in several countries.

Since 2000, continuous monitoring of mercury emissions in cement kilns which use alternative fuels in Germany is mandatory. Problems were faced in the application of the mercury CEMs (Continuous Emission Monitors) from the very beginning. As such, the cement industry endeavoured to identify the reasons for these problems and failures and, as a result, discovered that many additional maintenance steps have to be conducted. In addition, many of the commercially available devices had to be modified to make them suitable for individual application. In general, the performance of the CEMs improved, but even now instances remain whereby the devices cannot be used properly.

34 mercury CEMs are currently operated in the German cement industry. So far, in about 10 % of the cases it has not been possible to find a satisfactory solution even though several devices have been checked and modified to make them suitable for the respective kilns. Furthermore, the long term stability of the devices as such is still questionable. Periodic maintenance intervals will have to be fixed based upon future experience.

A further challenge is the proper calibration of the devices according to the European standard EN 14181. Calibration consists of determining the functional relation between the values measured by the automatic measuring instrument and an independent reference measuring method. In case of the mercury CEMs this procedure requires more effort than other CEMs (e.g. for dust or NO_x). In this context, it has to be highlighted that reference standards are still lacking. This is the reason why the periodic quality assurance procedures have so far had to be carried out by external institutes.

Taking the German experience into consideration, the continuous monitoring of mercury emissions cannot, as yet, be considered as an available technology for the cement industry such as, for example, the continuous monitoring of dust or NO_x.

11. MERCURY RELEASES FROM CEMENT PRODUCTION

11.1. AIR EMISSIONS DATA

The University of Liège has collected worldwide cement kiln mercury emissions data through CEMBUREAU and CSI member companies. The enquiry was launched in spring 2008 and data collection took place from summer 2008 until autumn 2008.

The enquiry was very general as the main objective was to collect as much data as possible. For obvious practical reasons, the enquiry did not encompass review of original measurements reports; data were provided directly by the companies.

Nevertheless, as described here below, additional information (such as information on dedusting devices, operational mode and thermal substitution rate) was made available.

The questionnaire covered 2005, 2006 and 2007. 1681 emission values were obtained from 62 different countries in all continents. 62 companies took part in the investigation. Only 27 of the measurements relate to continuous mercury measurements. The remainder (1654) are spot measurements obtained by manual methods.

The following methods were reported as being used:

- **EN 13211 in** Croatia, Denmark, Egypt, Finland, France, Germany, Greece, Italy, , Luxembourg, Poland, Portugal, Slovenia, Spain and UK (485 values),
- **EPA 29 in** Belgium, Brazil, Greece, Israel, Portugal, Spain and Turkey (150 values),
- **VDI 3868 in** Croatia, Italy and Switzerland (14 values).

It should be noted that EN 14385 was reportedly (approximately 15 measurements) used in one European country. EN 14385 has been designed to measure other metals and not only mercury (as in the case of EN 13211). There is, however, the possibility of measuring other metals according to standard EN 14385 and referring to standard EN 13211 for mercury, given that the later must be implemented in EN 14385.

11.1.1. Measurement data analysis

Figure 11-1 displays spot data ranged by concentration (in mg/Nm³). The values are expressed in dry gas and reported at 10% oxygen. Many of values (314) are under 0.001 mg/Nm³, lower than the detection limit. For the statistical analysis, these values have been processed as equal to 0.001 mg/Nm³.

Very few values are higher than the 0.05 mg/Nm³ value, which is the limit value defined by the European Directive for the Co-incineration of Waste. The value spread appears to follow a log-normal distribution (this distribution is illustrated in **Figure 11-2**) whereby the values are classified on a logarithmic scale).

The arithmetic average is 0.012 mg/Nm³, the geometric average is 0.005 mg/Nm³ and the 98 percentile (which means that 2% of values are greater than) is 0.07 mg/Nm³.

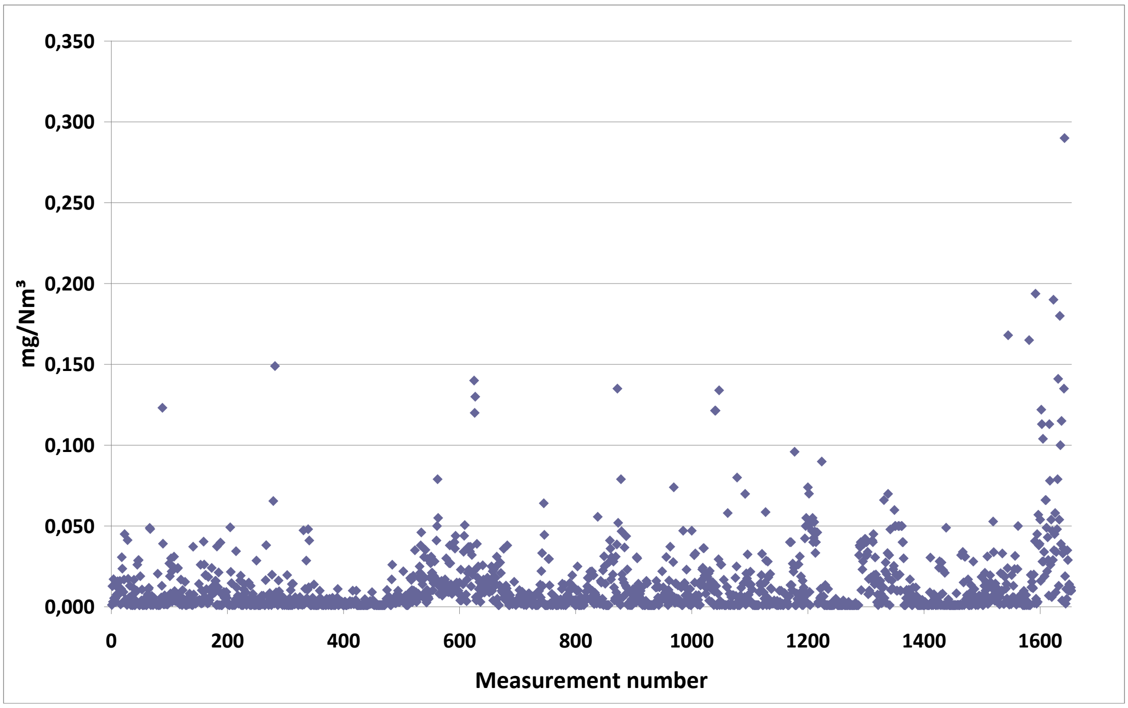


***Figure 11-1** : CEMBUREAU/CSI enquiry: total of 1654 mercury spot measurements. The highest values (0.36, 0.911, 1.26, 1.44 mg/Nm³) were reported in plants identified as using raw materials with high concentrations of mercury; they were measured in direct operation and are consequently not typical of the whole functioning time.*

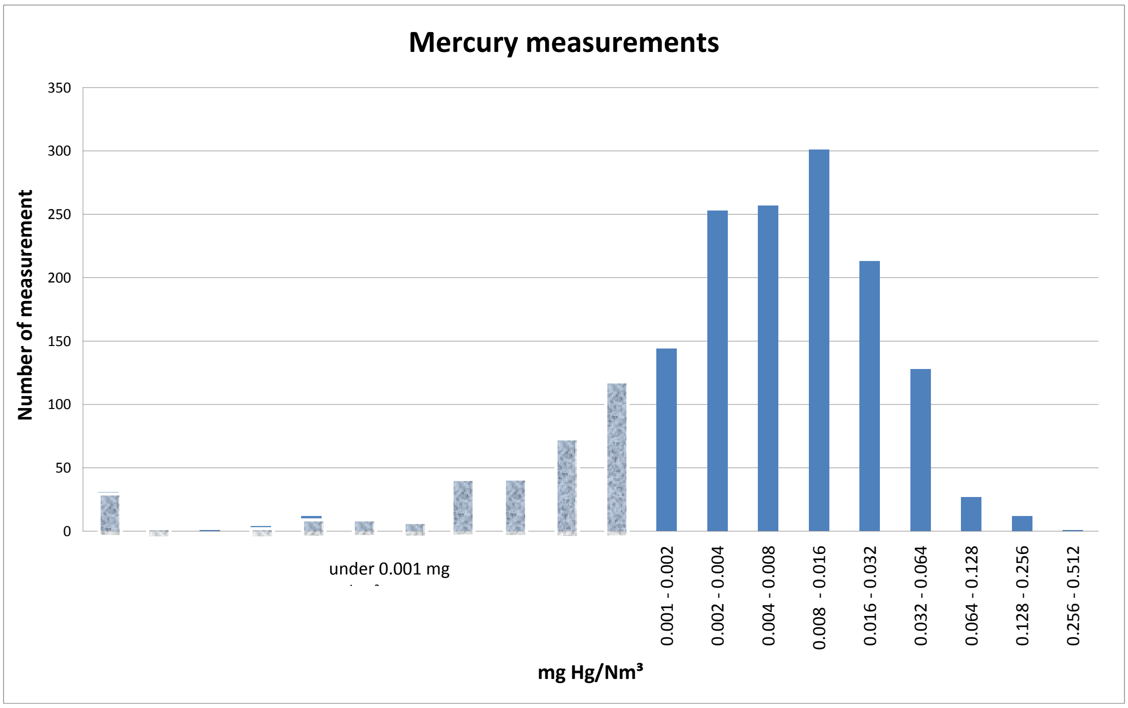


***Figure 11-2**: Mercury measurements classified on a logarithmic scale. Values are, for the most part, between 0.002 and 0.032 mg/Nm³.*

Although the majority (70%) of the data has been collected in Europe (**Table 11-1)**, worldwide information has also been obtained.

***Table 11-1**: Regional distribution of mercury spot measurements; CEMBUREAU/CSI inquiry.*

	Number of values
Africa Egypt, Morocco, Namibia, South Africa, Tanzania	80
Asia Azerbaijan, India, Indonesia, Israel, Japan, Lebanon, Philippines, South Korea, Sri Lanka, Thailand, Vietnam	182
Europe Austria, Belgium, Bosnia, Bulgaria, Croatia, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Italy, Latvia Luxembourg , Moldavia, Netherlands, Norway, Poland, Portugal, Romania, Serbia, Slovak Republic, Slovenia, Spain, Sweden, Switzerland, Turkey, Ukraine, United Kingdom	1159
Of which in European Union	1044
North America Canada, Mexico, USA	130
Oceania Australia, Malaysia, New Zealand	24
South and Central America Argentina, Brazil, Chile, Colombia, Costa, Rica Ecuador, El Salvador, Honduras, Venezuela	80

The type of dust abatement device related to the mercury emission value was reported for a limited number of measurements (around one third of the total data from the CEMBUREAU – CSI inquiry).

Some studies have shown that mercury speciation changes with an increasing oxidised portion through the electrostatic precipitator (Lee et al., 2006). The electrostatic precipitator ozone concentrations can range from 1 to 5 ppm, depending on the electrical discharge corona intensities on the discharge electrodes and on the oxygen concentration in the gas stream. This reaction is one of the reasons why moderate-to-high concentrations of oxidised mercury can be present in kilns controlled by electrostatic precipitators (Richards and Holder, 2005). Such a change in speciation could enhance mercury removal.

Studies (Richards and Holder, 2005) suggest that, in cement plants, mercury emissions are lower in kilns equipped with an ESP device rather than with a fabric filter. Based on the US EPA program for coal-fired power plants, others (Pavlish et al., 2003; Senior et al., 2003; Wang et al., 2008) suggest that fabric filters have demonstrated to be as capable of removing significant percentages of gaseous mercury, owing to the oxidation and capture that occurs because of excellent gas-solid contact across the dust-cake on the material.

The CEMBUREAU-CSI dataset shows that kilns equipped with ESP (285 values) have higher mercury emission values than those with bag filters (272 values). The arithmetic mean values are 0.015 mg/Nm³ for ESP and 0.009 mg/Nm³ for bag filter (BF). To test the validity of this difference, a t-test was applied[1], with the Student t-test confirming the difference. The means of mercury emissions for dust abatement techniques are statistically different.

The lowest temperatures in the bag filter do not appear to provide a valid explanation as the average temperatures do not differ. Besides the better contact in fabric filters, there are numerous other explanations, such as the fact that modern kilns are often equipped with bag filters or, more simply, the scope of the enquiry. The question therefore remains open and no conclusions can be drawn on the possible difference in removal efficiency between fabric filters and ESP.

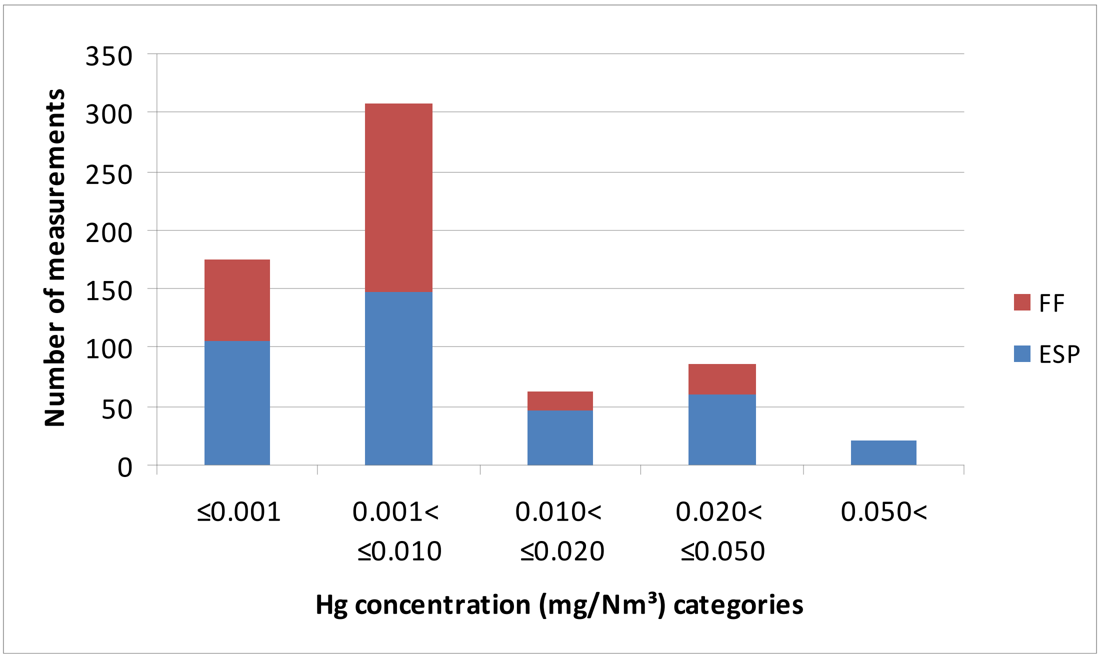


Figure 11-3 *: Number of mercury measurements (CEMBUREAU-CSI inquiry) ranged by concentration categories for fabric filters (FF) and electrostatic precipitator (ESP).*

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Only a few values (46) related to raw mill off lines were reported in the CEMBUREAU-CSI inquiry. Although many indications and case studies show that mercury emissions are correlated to raw mill operation and that lower emissions are expected when the raw mill is operating in line, the limited present data set is not correlated.

Other mercury emission inventories in the cement industry are available. The Portland Cement Association (PCA) compiled 122 emission reports (data from 1989 and 1996) from cement kiln operations at cement plants (Johansen and Hawkins, 2003a). Out of 35 reports, 50 mercury

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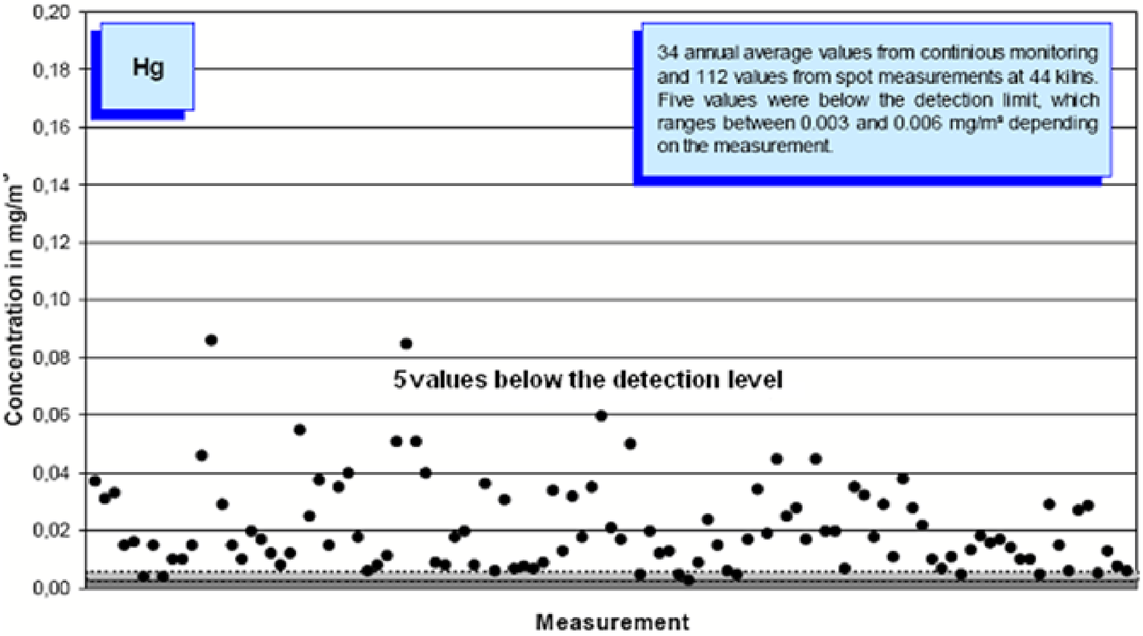
[1] A t-test is any statistical hypothesis test in which the test statistic has a Student's t distribution if the null hypothesis is true. A test of the null hypothesis is that the means of two normally distributed populations are equal. Given two data sets, each characterised by its mean, standard deviation and number of data points, we can use some kind of t-test to determine whether the means are distinct, provided that the underlying distributions can be assumed to be normal. All such tests are usually called Student t tests.

emission concentration tests were identified, with all of the mercury emission data essentially obtained with the raw mill operating in-line. The emission data only covers plants not burning hazardous waste. The average stack gas mercury concentration was 0.02 mg/Nm³. The mercury emission concentrations varied from <0.002 mg/Nm³ to 0.3 mg/Nm³.

The Research Institute of the Cement Industry reported mercury emission results from 216 measurements obtained from 44 cement plant kilns in Germany (VDZ, 2001a). Most of the measurements were between the detection limit and 0.04 mg/Nm³. Twenty of the results were below the detection limit and only six of the results were 0.06 mg/Nm³ or higher, with one maximum value registered at 0.18 mg/Nm³.

The same Institute also reported (VDZ, 2006; VDZ, 2007; VDZ, 2008a) mercury emission results for 2005, 2006 and 2007. The 2007 data presented in **Figure 11-4** shows 34 annual average values from continuous monitoring and 112 values from spot measurements on 44 kilns at German cement plants. Five values were below the detection limit. The data is very similar to that of the aforementioned report.



34 annual average values from continious monitoring and 112 values from spot measurements at 44 kilns. Five values were below the detection limit, which ranges between 0.003 and 0.006 mg/m³ depending on the measurement.

***Figure 11-4**: Mercury concentration values (year 2007) measured in the clean gas of 44 rotary kilns (VDZ, 2008a).*

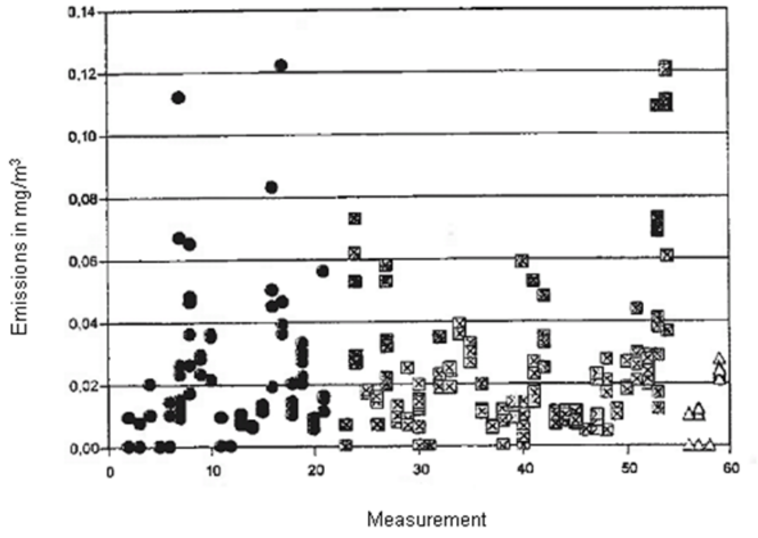
CEMBUREAU collected mercury emission data from approximately 200 kilns in 2003 and 2004. Figure 11-6) was around 0.02 mg/Nm³.

On the basis of the analysis of the different data bases available, an average emission of 0.02 mg/Nm³ is proposed for further reference and mercury emission inventories.

11.1.2. Impact of the use of waste as an alternative fuel on emissions

Before presenting the results collected through the CEMBUREAU-CSI inquiry, information on previous and more limited research on the same issue is provided below.

The German Research Institute of the Cement industry (VDZ) carried out 58 test series in the period from 1996 to 1998 (Schneider and Oerter, 2000). The results show that the individual values of the measured mercury concentrations are quite strongly scattered, which can be attributed to the different levels of mercury in the materials used and to the respective operating conditions. The study compares the results obtained when using alternative fuels and raw materials, and shows that the use of alternative materials has no relevant effect on the level of mercury emissions.



● Normal fuels
■ Replacement fuels
▲ Replacement raw materials

Figure 11-5: *Mercury emissions measured by the Research Institute of the Cement Industry with and without the use of secondary materials (Schneider and Oerter, 2000).*

In relation to the draft BREF (IPPC, 2009), which reports information on mercury emissions measurements collected by CEMBUREAU in 2004, measurements were taken from different plants located in Europe. The pollutant figures reported from each kiln were clustered into four categories relating to the fossil fuel substitution rate: 0% (indicating no fuel substitution), 0 - 10%, 10 – 40% and > 40%.

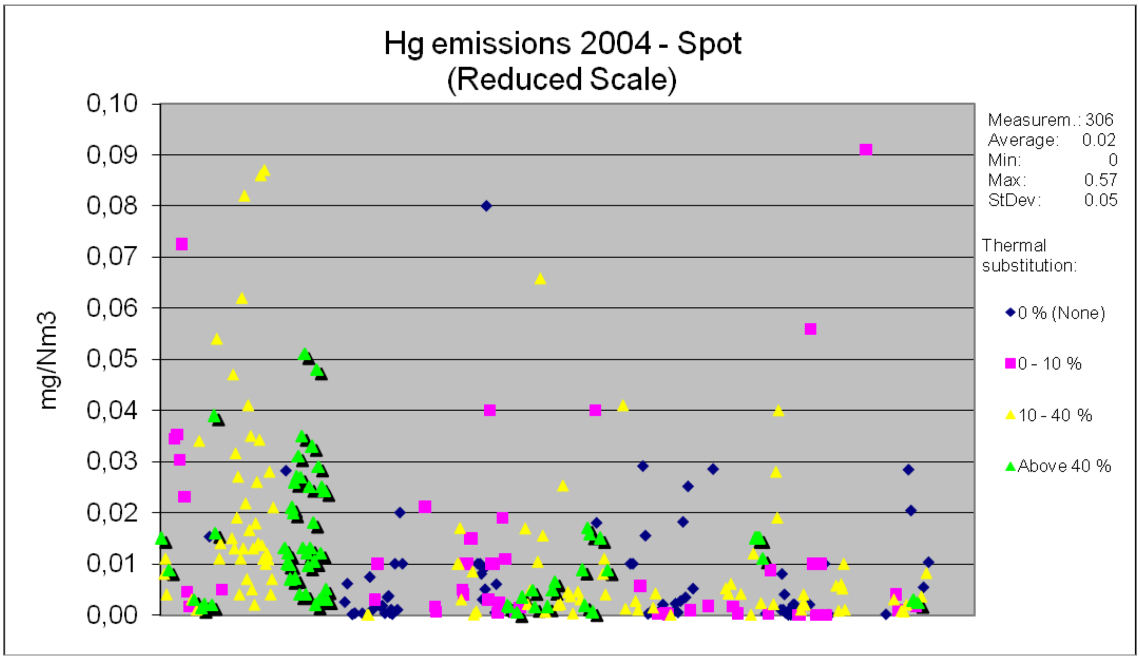


***Figure 11-6** : Mercury emission values from 306 spot Hg measurements in the clean gas of the rotary kilns in Europe (IPPC, 2009). 6 measurements are above the scale. Of these, 1 is of '0' substitution rate, 1 is '0-10', 2 are '10-40' and 2 are 'Above 40'.*

With regards to the mercury measurements (649 values for 2005, 2006 and 2007) from the CEMBUREAU–CSI inquiry, reporting the thermal substitution rate, **Figure 11-7** does not seem to show any differences between plants which have reported either a high or a low waste substitution rate.

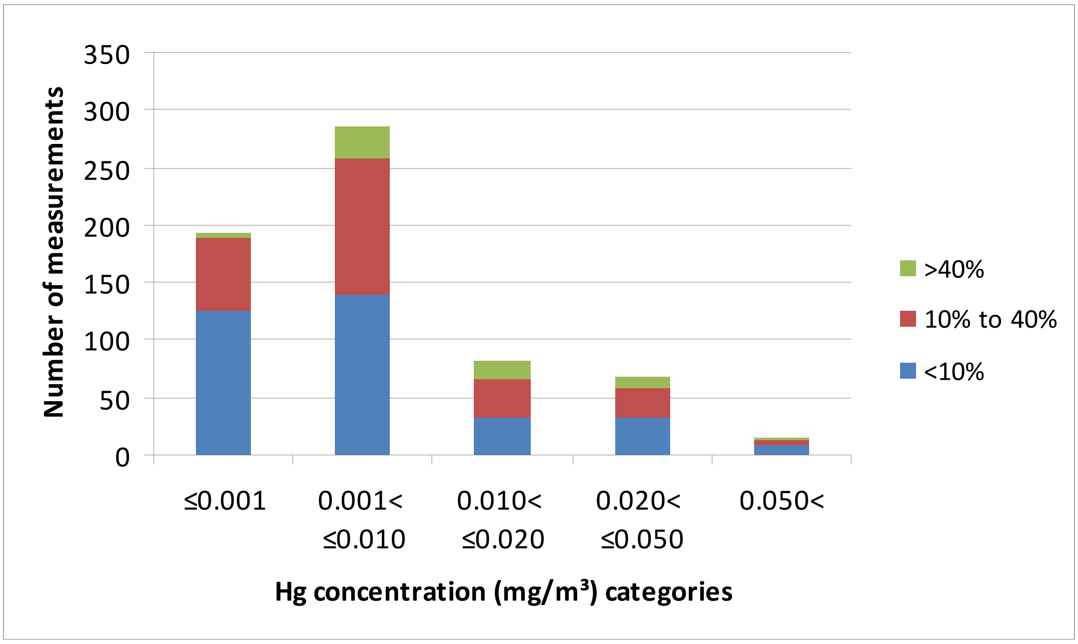


***Figure 11-7** : Mercury emission values from 649 spot Hg measurements in relation to the thermal substitution rate from the CEMBUREAU-CSI inquiry. Values are ranged by concentration (mg/Nm³) categories: below 10% of thermal substitution, between 10 and 40% and above 40% of substitution.*

Figure 11-7 displays spot data ranged by concentration (mg/Nm³) categories. Many of the values are lower than the detection limit or under 0.001 mg/Nm³. These values have been processed for statistical analysis as equivalent to 0.001 mg/Nm³. Very few values are higher than 0.05 mg/Nm³.

In this dataset, the arithmetic average is 0.009 mg/Nm³ for kilns under 10% of thermal substitution, 0.010 mgNm³ for kilns between 10 and 40% of substitution and 0.013 mg/Nm³ for kilns with more than 40% of substitution.

Although the averages show a slight increase in mercury emissions for plants burning more waste, the average mercury emissions for the different categories relating to the amount of waste used do not differ in statistical terms. In this case, the Student t-test shows that the thermal substitution rate has no influence on mercury emissions.

11.2. MERCURY EMISSIONS INVENTORIES

Estimates of global atmospheric mercury emissions from anthropogenic sources are provided in many published studies (Pacyna et al., 2006a; Pacyna et al., 2006b). The 2008 UNEP Report (AMAP/UNEP, 2008) presents an inventory for the year 2005, which indicates that the largest atmospheric mercury emissions result from the combustion of fossils fuels, mainly coal, in utility, industrial and residential boilers.

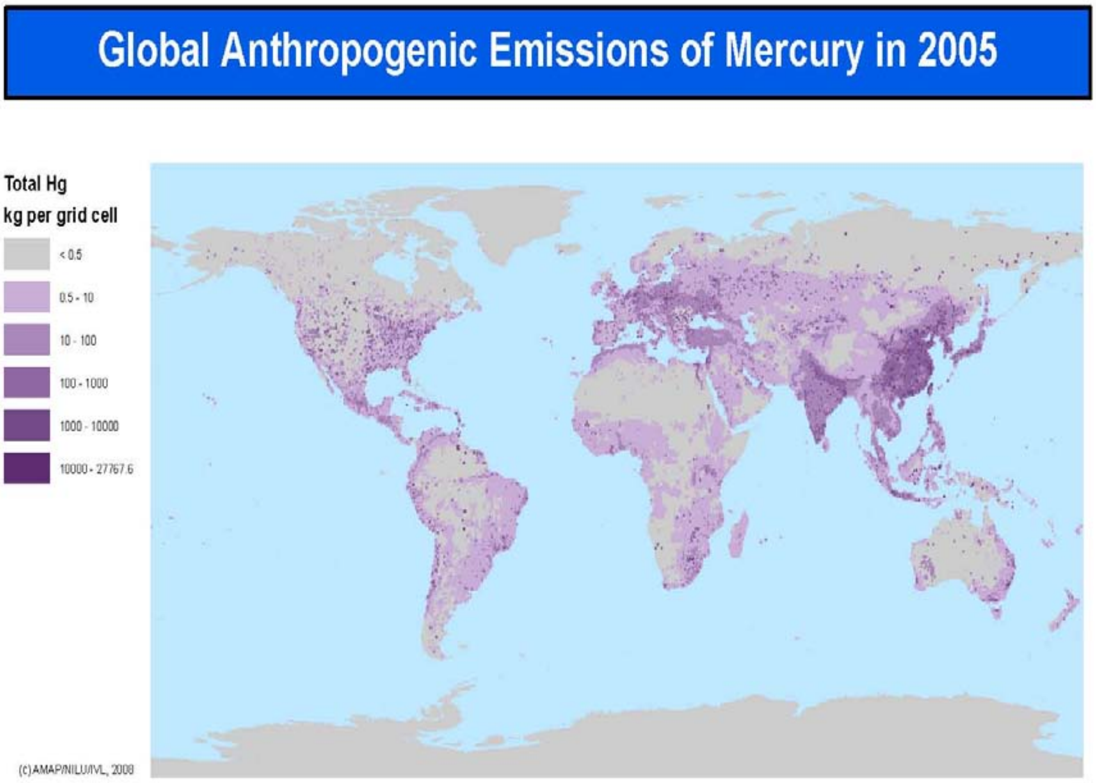


***Figure 11-8** : Spatially distributed inventories of global anthropogenic emissions of mercury to the atmosphere,2005; (AMAP/UNEP, 2008)*

Around two-thirds of the total 2005 mercury emissions emitted from all worldwide anthropogenic sources (1930 tonnes) resulted from the combustion of fossil fuels. Mercury emissions from coal combustion are between one and two orders of magnitude higher than emissions from oil combustion. Different industrial processes account for an additional 30% of mercury emissions.

The Technical Background Report (AMAP/UNEP, 2008) states: *“The fuel-firing kiln system and the clinker-cooling and handling system are responsible for emissions of mercury in the cement industry. This industry contributes about 12% to the mercury by-product emissions on a global scale. The content of mercury in fuel used in the kiln and the type and efficiency of control equipment, mostly ESPs, are the main parameters affecting the size of mercury emissions*.” Considering not only by-product emissions, world production of cement is responsible for 9.8 % of anthropogenic mercury emissions.

The calculation of anthropogenic mercury emissions was carried out by collecting emission data from countries where such data was estimated by national emission experts. For countries where reliable national estimates were not available, emission estimates were realised on the basis of emission factors and statistical data on the production of industrial goods and/or the consumption of raw materials.

The emission factor for mercury emissions in cement production is estimated at 0.1 g Hg/t cement in the UNEP report. The same emission factor is provided by the European Environment Agency (EEA, 2007) in its Emission Inventory Guidebook to support reporting under the UNECE Convention on Long-range Transboundary Air Pollution and the EU National Emission Ceilings Directive. On the basis of this emissions factor, UNEP estimates cement industry emissions at 189 tonnes.

As demonstrated here below these estimates are not accurate and lead to an overestimation of global mercury emissions from the cement industry. An emissions factor of 0.035 gram mercury per tonne cement would be a more accurate one. This represents more or less one third of the emissions calculated in the literature (Pacyna et al., 2006b; AMAP/UNEP, 2008).

- **Rough estimation of cement industry emissions**

  An empiric formula (Cemsuisse, 2008) is used to calculate total yearly emissions for the EPER-Register of Switzerland for the calculation of the specific volume of air emissions from cement kilns.

$$Vspec = \left(0.25 \times Wspec/_{1000} + 0.27\right) \times 1.91 \left[Nm^3/_{kg\ clinker}\right]$$

$$Wspec : Heat\ Consumption\ ^{(kj)}/_{kg\ clinker}$$

0.27: Factor from calcination

1.91: Normalisation factor to 10% oxygen

For a dry kiln system with a heat consumption of 3500 kJ/kg clinker, this means 2.2 Nm³/kg clinker. For wet kiln systems, the volume will be larger.

Assuming that the average clinker–cement ratio is 0.8, and the average emission of 0.02 mg/m³ as proposed in chapter 11.1.1, the emission factor is around 0.035 g/t cement. .

12. MERCURY MASS BALANCE STUDIES

As described in Chapter 8, the behaviour of some substances and metals during the clinker burning process depends on their volatility. Volatile metal compounds condense on raw material particles at lower temperatures and, if not emitted with the flue gas of the kiln, they potentially form internal or external cycles. Analysis and balance investigations allow a better understanding of the behaviour of mercury in a cement kiln system.

12.1. MASS BALANCE STUDIES IN THE LITERATURE

Tests were conducted (Denis et al., 2000) on several Belgian rotary cement kilns with varying substitution ratios of fossil fuels by waste. Mass balances were fitted over the whole plant and emission factors (defined as the total output of pollutant at the chimney divided by the total input of the considered pollutant in the process) were explained. The authors emphasised the analytical difficulties faced when evaluating the mercury but highlighted the fact that a significant amount (35.9% to 85%) of mercury is captured in the dust and in the clinker, especially in dry processes.

In its 1999-2001 Activity Report, the German Cement Works Association (VDZ, 2001a) described a four-week mass balance study that was conducted on a dry kiln in Germany with an in-line raw mill and an electrostatic precipitator. One of the main objectives of the study was to determine whether mercury stack emissions were influenced by the removal of cement kiln dust from the system. **Figure 12-1** and **Figure 12-2** illustrate the variation in mercury emissions according to raw mill operation and the bleeding or removal of dust.

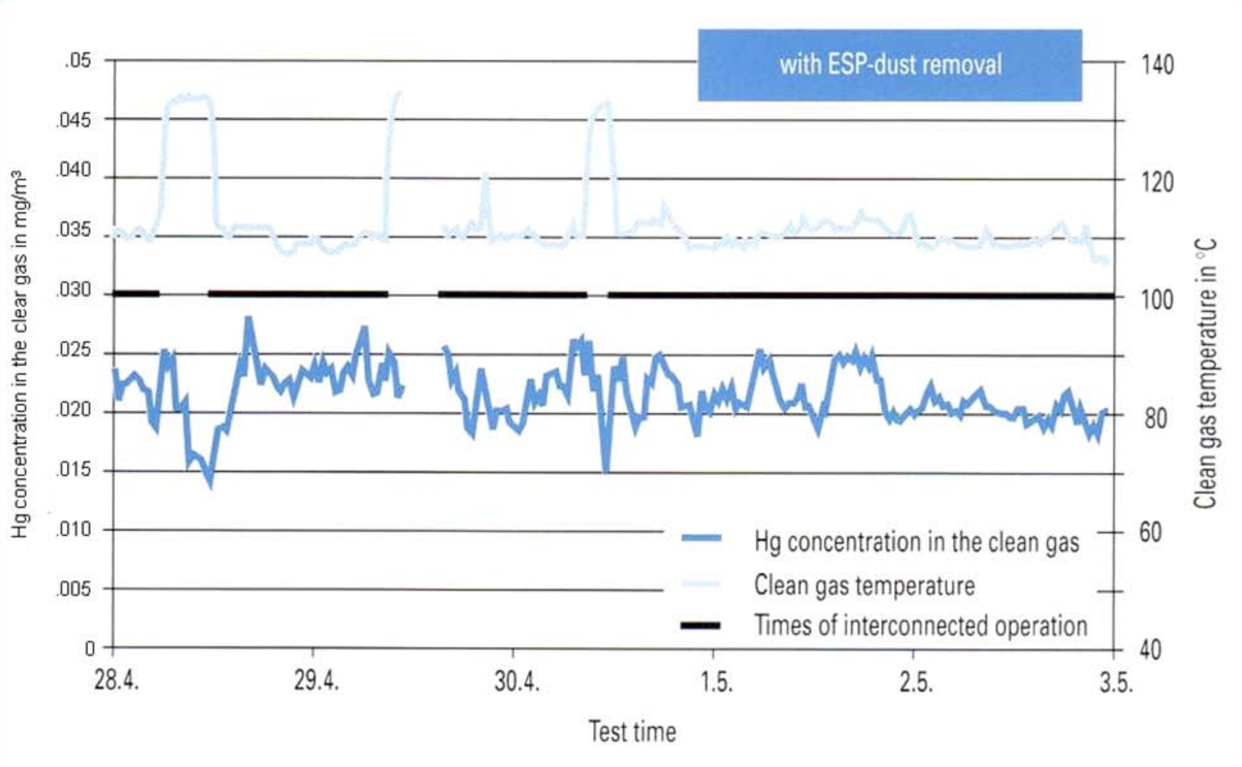


***Figure 12-1:** Curve of clean gas temperature and Hg concentration in the clean gas under removal of the dedusting device dust (VDZ, 2001a).*

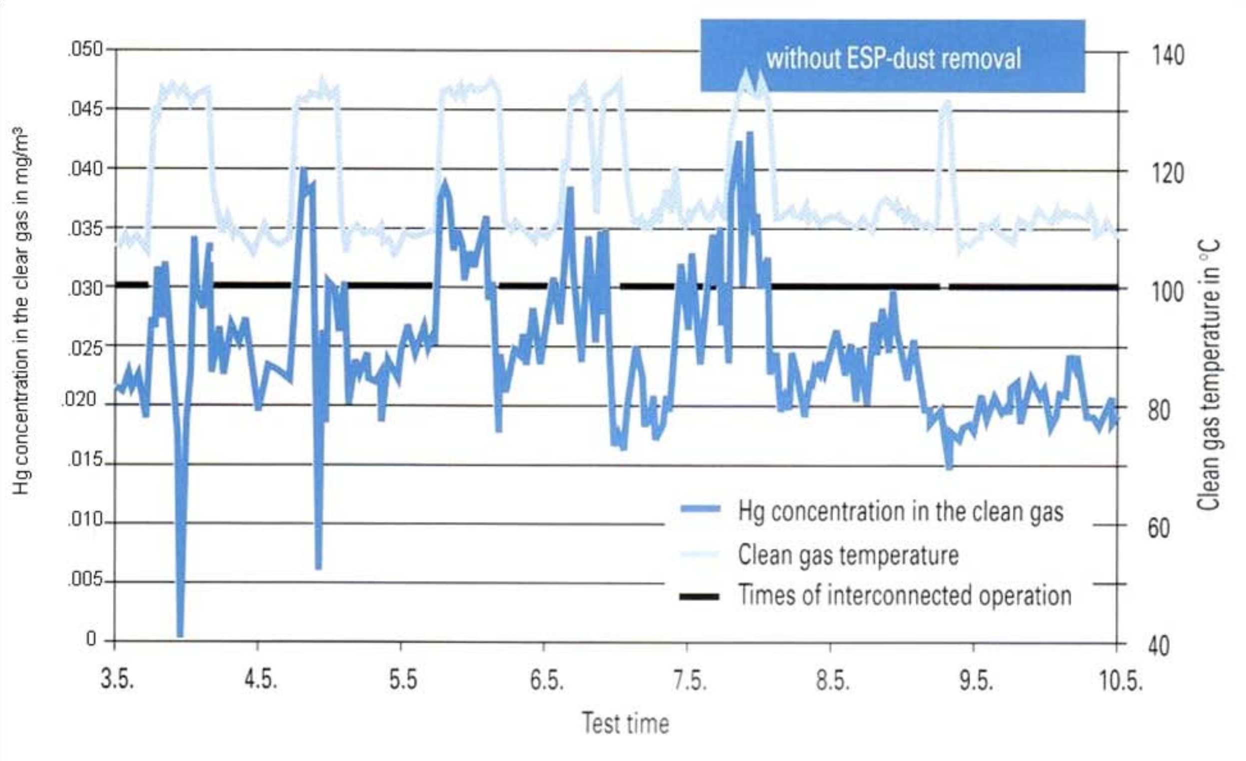


***Figure 12-2:** Curve of clean gas temperature and Hg concentration in the clean gas under recovery of the dedusting device dust (VDZ, 2001a).*

The same results were described in more detail in Zement-Kalk-Gips International (Schäfer and Hoening, 2001). In addition, results from this study indicated a weekly cycle of mercury concentrations in the kiln feed that corresponded with raw mill operations. For this study, the kilns operated with their raw mills on only during the weekend. This weekly cycle of only grinding kiln feed on weekends is not typical of operations in other countries, but it does provide an interesting example of the circulation of mercury. It was noted that after the kilns returned to direct (raw mill-off) operations, preheater feed concentrations generally increased by midweek as the raw feed that was ground during the weekend made its way into the kiln system. Preheater feed concentrations then generally decreased during the latter part of the week. This may indicate that when the raw mills were operating, the cooler temperatures at the dust control devices allowed mercury to adsorb into the particles from the raw mills and kilns. This dust was collected and stored in the raw meal silos adding to the kiln dust that was collected during the previous week's direct burn operations (thus, the older material would have lower concentrations of mercury). This weekly pattern of increasing and decreasing mercury concentrations in the preheater feed tends to indicate that the mixing systems in the meal silos may not have been blending the raw meal efficiently.

Over the course of the study, the mercury concentrations in the raw material (entering the raw mill) doubled. However, no immediate proportional increase in emissions was noted. This further demonstrates that the kiln system has the capacity to smooth or buffer the effect of a higher mercury input on a cement kiln system.

Furthermore, the mercury content of the raw material and fuel input streams was compared in order to determine which had a greater impact on the total amount of mercury in the kiln system. Almost 300 solids samples were evaluated and the results showed that the mercury input from the kiln feed was about 10 times that from the fuels.

Results also indicated that, due to relatively cold temperatures in the ESP (100°C during raw mill-on operations and 130°C during raw mill-off operations), much of the mercury precipitation that occurred in the system occurred in the ESP. As the dust was returned to the system, a circulation of mercury was created through the preheater, raw mill, and ESP. Mercury emissions during raw mill-off operations were found to be higher than during raw mill-on operations. However, when dust was removed from the system during raw mill-off operations, the mercury emissions decreased to levels comparable to those found during raw mill-on operations.

The Portland Cement Association carried out a study (Schreiber et al., 2005) in which data on mercury emissions was obtained from stack emission tests conducted since 1992 on USA cement kiln systems utilising hazardous waste-derived fuels (HWDF). These facilities have been required for more than a decade to perform mercury emission testing in order to comply with the Resource Conservation and Recovery Act (RCRA) regulations. These facilities have also collected mercury concentration data in other input and output streams as part of the testing.

Two main values were calculated:

1. System Removal Efficiencies (**SREs**) for mercury, where the calculations are based on the amount of metals emitted to air compared to the amount entering a kiln from all feed streams.
2. Mass balances (and the concept: **fractional closure** (Hg mass out/Hg mass in)) calculated from the stack data that had sufficient material input and output information.

However, the authors were disappointed by the poor quality of the clinker and CKD data as well as by the fact that the mass balance results were erratic and no conclusions could be drawn.

The data used to calculate SREs were expected to be more reliable because they were collected for regulatory compliance purposes. Results indicated that when high rates of mercury entered the systems through fuels and raw materials, SREs were greater than 90%. At low input rates, however, SREs varied significantly. Nevertheless, it is believed that when mercury concentrations in process stream samples were low, the precision of laboratory results was less reliable. The study confirms that not only are the SRE results fairly high, but that in the case of dry kilns SRE values are higher during the raw mill-on condition, as expected. This implies that mercury may be condensing on the material in the raw mill rather than exiting the stack.

The Portland Cement Association (Senior et al., 2008) has reviewed previous results and, in addition, described the modelling of mercury behaviour in the cement kiln system. The model was verified by using the dataset on the dynamic behaviour of mercury in a cement kiln reported by VDZ (Schäfer and Hoening, 2001). According to the authors, the model is able to reproduce the features of the data and therefore provides a useful tool for planning mercury control strategies by changes in the removal of dust and in the temperature of the pollution control device. It is also a means for planning experiments to take into account the long times needed to reach a steady state as a result of the internal mercury cycle.

12.2. CEMBUREAU – CSI CASE STUDIES

Within the framework of the present study, some information (case studies presented in more detail in appendix B) was provided by the CSI member companies and/or by Research Centres. The first case study provides a general outlook of the mercury balance of a cement kiln. The latter two case studies represent extreme or atypical situations: in the first instance, the mercury enters the kiln system via the fuels, and in the second, the mercury input is very limited. The three cases illustrate the accumulation of mercury in the external cycle of the cement kiln system.

A. CASE STUDY N°1

This case study (ECRA, 2008) shows the typical mercury mass balance in cement kilns. **Figure 12-3** depicts the situation whereby the mercury cycle is broken via periodic meal removal.

It has to be highlighted that the mass balance shows the typical situation whereby mercury inputs are mainly driven by the composition of the raw materials. According to research by the European Cement Research Academy (ECRA), the contribution of the fuels (primary and secondary fuels) is always very small or even negligible.

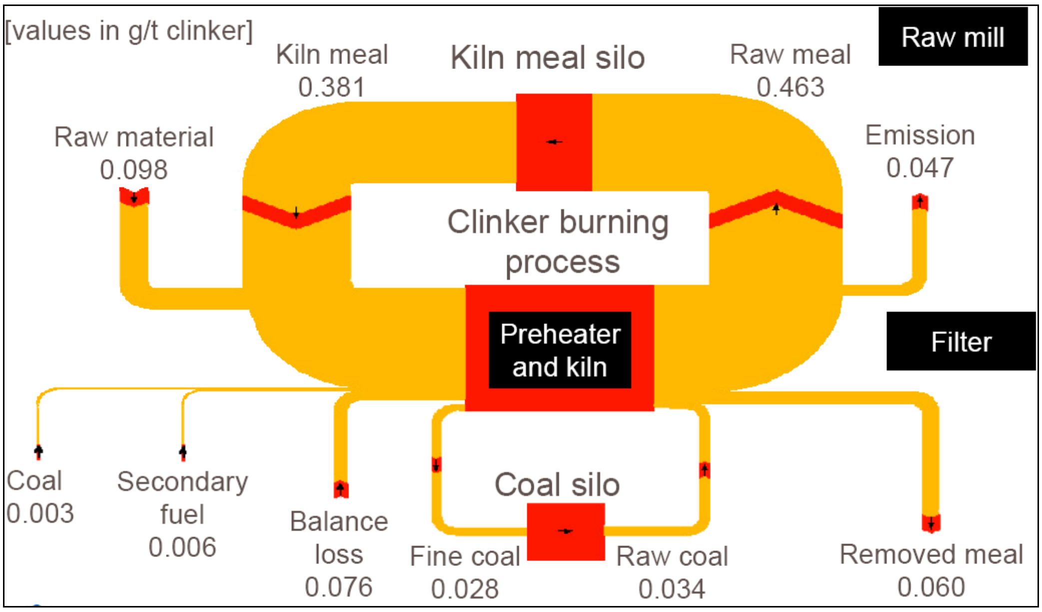


__Figure 12-3__: Mercury cycle under meal removal (ECRA, 2008).

B. CASE STUDY N°2

A study (Cement_Company_A, 2008), including mercury mass balance, was conducted in an European cement plant in 2006. The dry kiln has a precalciner and a five stage preheater. A significant amount (average 70%) of alternative fuels are used. The kiln operates interconnected with a raw mill for 90% of the functioning time. During direct operation, the filter dust is discharged and incorporated into the cement.

In this specific case, a large proportion of the mercury inputs come from the fuels. A large quantity of mercury circulates in the kiln waste gas and in the raw meal. This case study shows that existing cement manufacturing technology allows for high mercury separation efficiency (more than 90% in mill in line operation). This leads to mercury circuits between the preheater and the filter. Mercury raw gas concentrations depend much more on mercury cycle than on mercury input.

Another significant point is the increase of mercury concentrations in the raw meal and in the filter dust after the raw mill has stopped, when the filter dust discharge is not in operation and the dust is added to the raw meal (see **Figure 12-4**). The mercury concentration in the filter dust and in the kiln meal rise rapidly. A similar increase affects mercury air emissions when the discharge of filter dusts is interrupted.

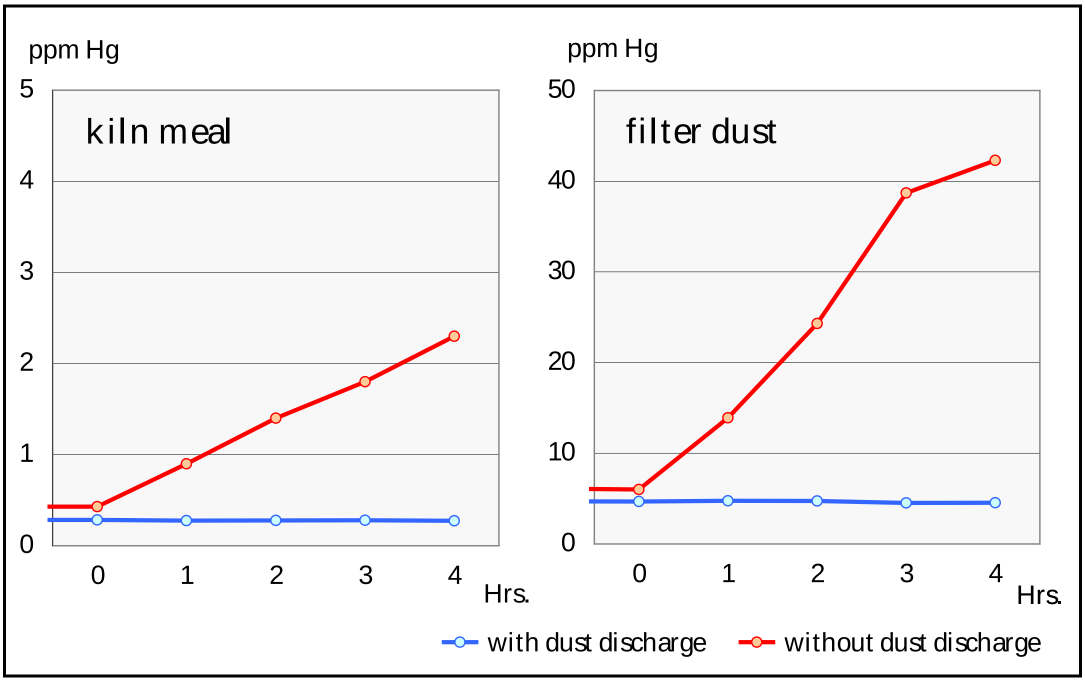


Figure 12-4 : Developments of mercury contents after raw mill stop.

C. CASE STUDY N°3

A separate study (Cement_Company_B, 2008) involving mercury mass balance was conducted in another European cement plant. In this case, the dry kiln has a precalciner and a five stage preheater, and the main fuels used are petcoke and animal meal. The kiln is interconnected with a raw mill and the dusts are recycled in the raw meal. Mercury stack emissions are low, measured at 0.0007 mg/Nm³.

In this case, the mercury mainstream input comes from raw materials. Although pyrite ashes have a higher mercury concentration according to the mass flow of each raw material, it is the limestone which has the highest mercury concentration.

Mass balance shows that a large portion (around 96%) of the mercury is captured in the dedusting device and in the raw mill. It is a global efficiency, with the raw mill probably acting in two ways, lowering the temperature and creating an accumulation of cold dust ready to adsorb mercury.

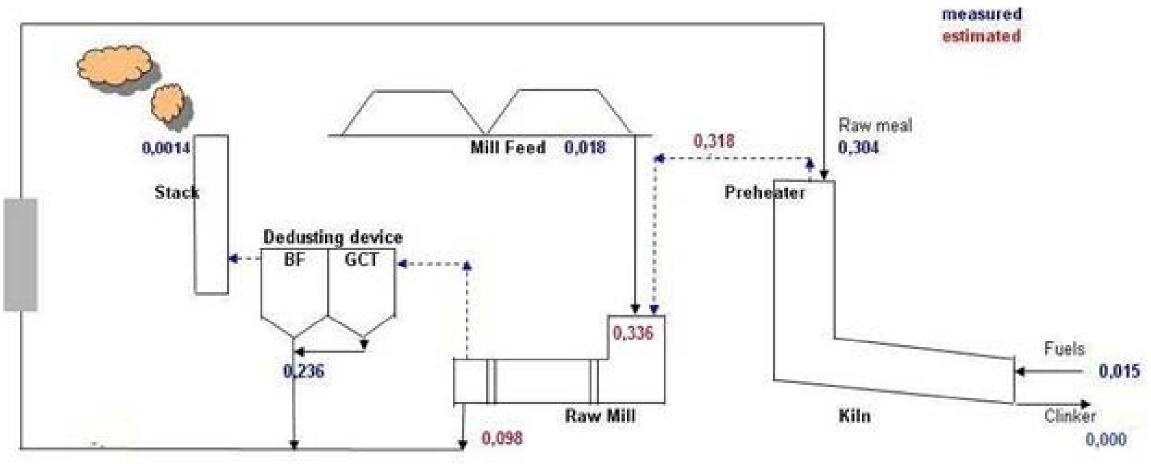


Figure 12-5 *: Diagram and mass balance; case study n°3 (values in mg Hg/kg clinker).*

12.3. MERCURY OUTPUT IN CEMENT KILN SYSTEMS

12.3.1. Clinker

Although some data provides values for the mercury concentration in clinker, the majority of the measurements are below the detection limit.

12.3.2. Cement

Total cement mercury concentrations were determined using samples from the US and Canada (PCA, 1992).

For samples above the detection limit (21/94), the average total mercury content in the cement was 0.000014 mg Hg/g with a maximum value of 0.000039 mg Hg/g. Other studies reported by Johansen (Johansen and Hawkins, 2003a) found that the mercury concentration in the cement ranged from 0.0000028 to .0012 mg Hg/g.

Figure 12-6 presents the results of extensive research (VDZ, 2001b) into the mercury content of cement performed on more than 400 spot samples taken in 2001 for the quality surveillance of standard German cements. The average is 0.00006 mg Hg/g of cement.

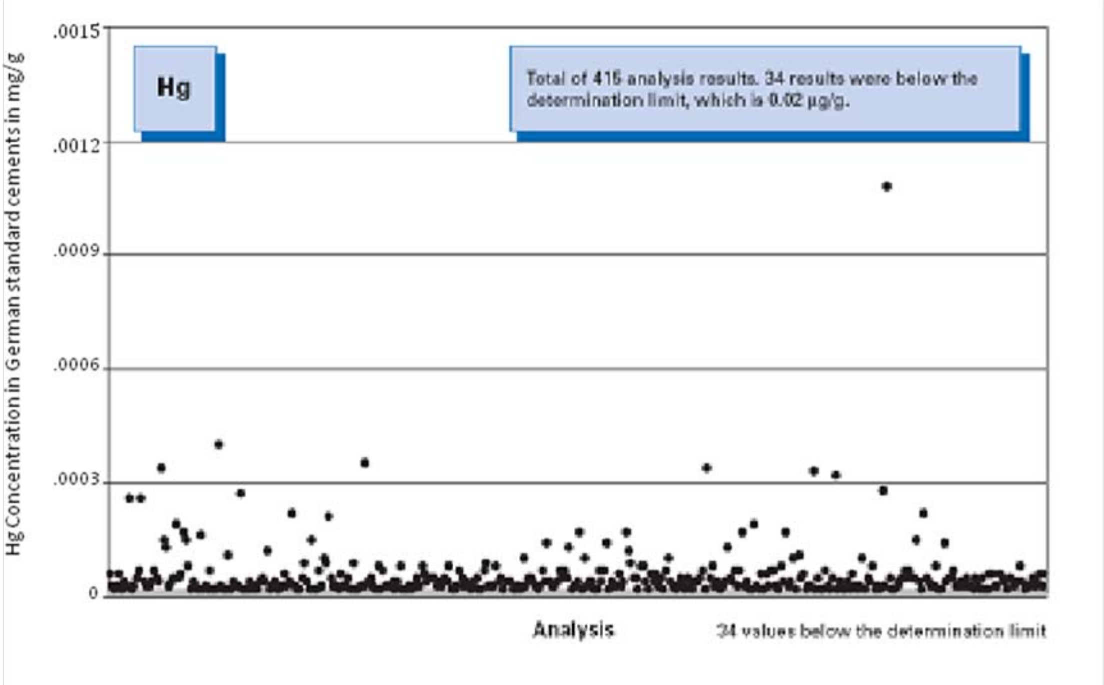


***Figure 12-6:** Mercury concentration in German standard cements; the determination limit was marked as a grey area to facilitate assessment (VDZ, 2001b).*

12.3.3. Cement Kiln Dust

A study on cement kiln dust constituents (including mercury) was conducted in 1992 (PCA, 1992). The raw data from US and Canadian cement plant dust samples resulted in an average mercury content of 0.00051 mg Hg/g with a maximum value of 0.0255 mg Hg/g. The mercury content was below the detection limit in many (27/95) of the samples analysed. The study also demonstrated that the total mercury concentration in dust does not differ statistically between plants burning waste-derived fuels and plants burning conventional fuels only.

In a study reported by Johansen (Johansen and Hawkins, 2003a), the mercury concentration ranged from 0.00013 to 0.001 mg Hg/g with an average of 0.0003 mg Hg/g. Half of the samples presented a mercury concentration below the detection limit.

CSI member companies provided some information which is shown in **Table 12-1**.

The concentrations of particle-bound mercury in cement kiln gas are generally considered to be very low - this is independent from the probable removal of a major fraction of the mercury as an adsorbed material on the surface of cement kiln dust. This is very significant as the mercury stack emissions are not very dependent on the effectiveness of the dedusting (taking into account that a normal dedusting device like ESP or FF is implemented).

For example, the kiln dust mercury concentrations reported by PCA (PCA, 1992) averaged at 0.00051 mg Hg/g. Assuming that the dust emissions from a cement kiln are 30 mg/Nm³, the average particle-bound mercury would be only 0.000015 mg/Nm³. At an average mercury emission rate of approximately 0.020 mg/Nm³, the fraction of mercury present in the particle-bound form is only 0.07 %.

Table 12-1: *Mercury concentration in cement kiln dust from case studies. (see Appendix B).*

Average	Range in ppm	Reference
1.5	0.26-3.2	(Cement_Company_A, 2008)
1.32	-	(Cement_Company_B, 2008) One value; waste gas emission low
-	1.0-3.5	(Cement_Company_F, 2008) waste gas emission high
-	3.5-6.5	(Cement_Company_F, 2008) waste gas emission high

Table 12-2 shows additional data on output and intermediate products in one cement plant. It should be highlighted that bypass dust mercury concentrations are quite low.

Table 12-2: *Mercury concentrations (ppm) in output and intermediate products (Cement_Company_A, 2008).*

	Average ppm	number of samples	Range ppm	standard deviation
Intermediate				
raw meal	0.38	13	0.23 – 0.54	0.096
hot meal	< 0.0050	6	< 0.005	0
filter dust	1.5	11	0.26 – 3.2	0.75
conditioning tower dust	3.5	8	2.53 – 5.85	1.0
bypass dust	0.039	11	0.023 – 0.056	0.010
Output				
clinker	< 0.0050	12	< 0.005	0

13. MEASURES FOR MINIMISATION AND CONTROL OF MERCURY EMISSIONS

The information and data presented in this report and other studies (Richards, 2005) demonstrate that mercury does not simply volatilise from the fuel and raw materials to directly leave the system through the stack. There are mechanisms and operating conditions that allow cement kilns to capture mercury in some form. Cement kiln systems have a significant inherent ability to control mercury stack emissions.

The present report and the case studies largely confirm the experience and the key control factors for mercury abatement in cement kiln systems, as referenced in the available literature.

- ✓ In most cases, the major contribution to the total mercury input into the kiln system is the natural raw materials, and not the fuels.
- ✓ Control of mercury input is the most common reduction measure.
- ✓ Selective mining can be an option in order to control and reduce the mercury input into the kiln system.
- ✓ Mercury emissions are typically higher in kiln operations with the raw mill-off ("direct" operation), due to the missing adsorption capacity of the freshly ground particles in the raw mill.
- ✓ To avoid accumulation of mercury in the kiln system, the primary measures to reduce mercury emissions are:
    - o Extraction of the filter dust ("bleeding") during direct kiln operation (i.e. when the dust has a high mercury concentration)
    - o Reduction of the temperature in the gas cleaning device.
- ✓ Secondary measures, such as the injection of activated carbon, may further contribute to the reduction of mercury emissions, but will impose technical solutions if the filter dust is recycled back into the kiln or into the cement mill.

In this context it has to be noted that the cement industry's conversion of existing wet kiln and long dry kilns to advanced preheater-precalciner kilns has resulted in a significant industry-wide reduction in mercury emissions. The conversion to preheater-precalciner kilns provides significant energy recovery improvements and thereby reduces the quantity of fossil fuel needed and the specific amount of exhaust flue gas.

In terms of controls, periodic measurements of mercury emissions ensure that the emission levels remain low or that modifications to kiln operation or raw material variations do not have an effect on the mercury emissions.

Continuous monitoring of mercury emissions cannot yet be considered as an available technology for the cement industry such as, for example, the continuous monitoring of dust or NO_x. However, in the event of significant mercury emissions, continuous measurement can provide precious support towards understanding the parameters which influence mercury emissions and to finding solutions in order to improve the situation.

Very low levels of global mercury emissions have been reported. Though most of values are lower than 0.03 mg/Nm³, values higher than 0.05 mg/Nm³ may require further investigation.

High dedusting efficiencies can be achieved with electrostatic precipitators and bag filters. The reduction of dust emissions is very important in terms of reducing heavy metal emissions. Fractions of many metals leave the kiln with the emitted dust particles. Nevertheless, contrary to common opinion, the upgrading of dedusting equipment does not provide an effective solution to the capture of mercury since it is mainly emitted in vapour form from the cement kiln stack.

In principle, the following methods are available to reduce mercury emissions:

- Input control,
- Process integrated measures.

Other techniques are described in order to reduce mercury air emissions, mainly for waste incinerators and coal-fired boilers.

13.1. BEST ENVIRONMENTAL PRACTICE

13.1.1. Input control

As explained, mercury enters the kiln system as a trace element naturally present in raw materials and, to a lesser extent, in fuels. **Best environmental practice** is to carry out a careful selection and control of all substances entering the kiln in order to reduce mercury input.

13.1.1.1. Raw materials

A. RAW MATERIALS FROM QUARRIES

As shown in chapter 9.1, mercury concentrations in raw materials (limestone, marl or clay) vary significantly from quarry to quarry. There are even cases where mercury concentrations vary significantly within a single deposit, thereby sometimes requiring selective mining.

In those cases, after exploration and analyses of the quarry, it is possible to define specific parts of the quarry with higher mercury concentrations and to continue exploitation in zones where the concentration is lower (selective mining) (see case study n°4 (Cement_Company_C, 2008)). It has to be highlighted that such a procedure is complex to manage and cannot always be carried out (case studies n°5 and 6 (Cement_Company_D, 2008; Cement_Company_E, 2008).

If mercury is present in all quarry layers, other options have to be considered.

B. OTHERS RAW MATERIALS AND WASTE MATERIALS

“Corrective” materials such as bauxite, iron ore or sand may be required to adapt the chemical composition of the raw mix to the requirements of the process and product specifications. To a limited extent, alternative raw materials are used to substitute natural raw materials and correctives.

Best environmental practice consists of selecting materials with a low mercury content as well as in using a quality assurance system to guarantee the characteristics of the materials used.

In cases where alternative raw materials lead to a significant increase in the mercury intake into the system they may have to be replaced by another alternative material. Fly ash, for example, can have a higher or a lower mercury content.

13.1.1.2. Fuels

The cement production process usually uses fossil fuels such as coal, petroleum coke, oil and alternative fuels (tyres, wastes derived fuels, etc.). Fuels are not usually the dominant source of mercury in cement kiln input. Nevertheless, it can be necessary, in specific cases, to also monitor the mercury content of the fuels (more particularly alternative fuels, such as sewage sludge).

In principle, for alternative fuels, best environmental practice is to apply quality assurance systems to guarantee the characteristics of the waste and to analyse and control the mercury content if necessary.

GTZ and Holcim formed a partnership with the aim of introducing, promoting and supporting acceptable guidelines for the co-processing of waste materials in cement production. The document (Holcim and GTZ, 2006) offers guiding principles and gives a general orientation concerning the conditions under which secondary materials and fuels can be used.

Analysis of alternative fuels is a crucial issue. These guidelines support the improvement of laboratory equipment which comprises a comprehensive set of state-of-the-art analytical instruments. Precision, accuracy and low detection levels are key.

In terms of alternative fuels, mercury limits are not necessarily set as it is the total input which matters. Nevertheless, in some countries mercury inputs are limited. The Holcim-GTZ guidelines provide a summary of the limit values set in different permits and regulations.

The CSI produced guidelines entitled "The responsible use of fuels and materials," which were published in 2005 and reflect the agreement of the CSI companies. These guidelines can be downloaded for free here:
http://www.wbcsdcement.org/index.php?option=com_content&task=view&id=70&Itemid=141

13.1.2. Process integrated measures

In order to avoid an undesired increase of mercury in the kiln system, the periodic purging (bleeding) of cement kiln dust from the system is an efficient way to control mercury emissions. Case studies n° 2 and 5 (Cement_Company_A, 2008; Cement_Company_D, 2008) in Appendix B illustrate this. Many preheater-precalciner kiln systems have raw mills in-line. Adsorption is favoured due to the very high dust loadings of up to several 100 g/m³ present in the raw gas streams from preheater-precalciner kilns. This purging process is more efficient in the mill-off mode than in the mill-on mode due to the higher mercury concentrations in the dust.

During the mill-on operation mode, the finely ground raw material in the raw mill retains mercury from the flue gases. This leads to lower mercury emissions in the mill-on mode compared to the operating periods without raw mill (mill-off). About 80 to 95% of the overall operating hours are carried out in the mill-on mode.

Furthermore, the temperature of the flue gas plays an important role: case studies n°5 and 6 (Cement_Company_D, 2008; Cement_Company_E, 2008). In general, the adsorption capacity for mercury increases with lower temperatures (c.f. **Figure 13-1**).

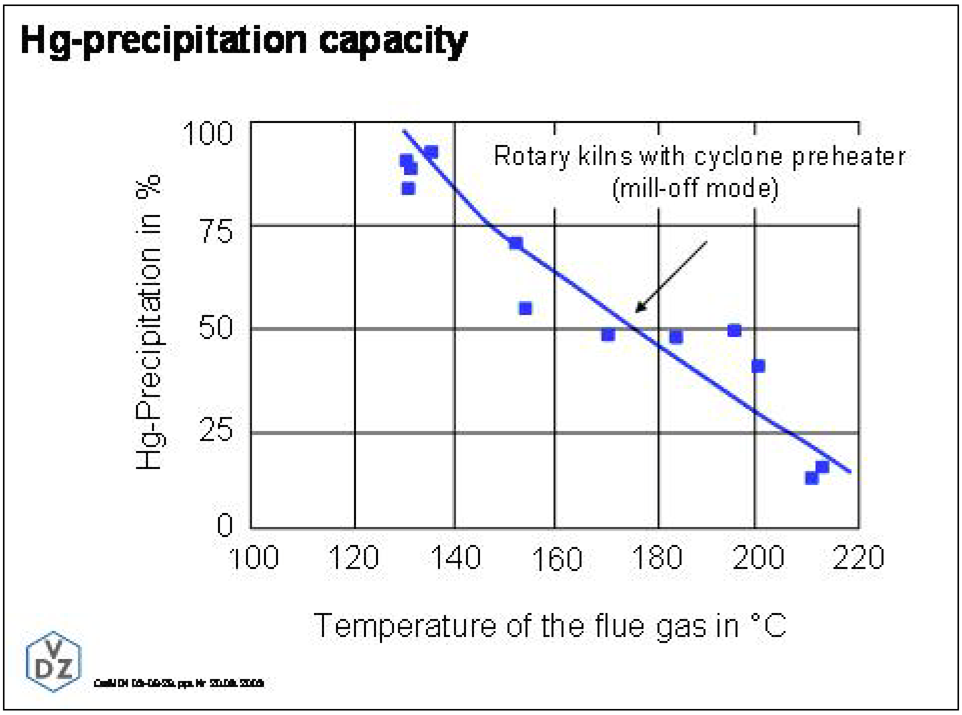


***Figure 13-1**: Graph on the temperature dependence of the precipitation (condensation or/and adsorption) capacity for mercury (VDZ, 2008b).*

Best environmental practice to lower mercury emissions is to bleed the kiln dust system as described above, whereby cement standards allow for the incorporation of the collected dust into the cement. This is a proven and safe procedure in many regions of the world: neither the environment nor the product quality is affected.

13.2. OTHER TECHNIQUES

Other techniques to reduce mercury air emissions are available in other industries such as waste incinerators and coal-fired power stations. Some, such as carbon adsorption, are well proven; others are at laboratory or pilot stage. Most of the test programs completed in these industries cannot be extrapolated to the cement industry and cannot, therefore, be considered as best environmental practice in the cement industry.

13.2.1. Other techniques tested in the cement industry

13.2.1.1. Adsorption on activated coke, Polvitec

The Polvitec system (CEMBUREAU, 1999) consists of several packed beds of activated coke. The dedusted kiln exhaust gas is passed across the activated coke whereby compounds like heavy metals (and mercury), VOC, SO_2 and NH_3 are adsorbed. The cleaned gas is then released into the atmosphere. The spent activated coke is periodically extracted to a separate silo and replaced with fresh adsorbent.

Since volatile and semi-volatile heavy metals are effectively adsorbed on activated coke and since the clean gas dust content downstream of the activated coke device is down to a few mg/Nm³, the emission of heavy metals is virtually equal to zero.

Adsorption on activated coke is not economically viable. In the case of a Polvitec system installed in a Swiss cement plant, the project was only made economically feasible through the financial contribution of the communities burning their sewage sludge in the kiln, the fees for burning other alternative fuels in the kiln and the complex problem related to different emission components.

13.2.1.2. Activated Carbon Injection

Activated carbon injection systems are well established as commercial air pollution control processes for a variety of volatile organic compounds, dioxin-furan and mercury controls in waste incinerator applications (Richards, 2005). Activated carbon injection processes are being considered in the US for widespread use in the coal-fired utility boiler industry.

For many reasons, the possible application of activated carbon injection systems in cement kilns is considerably more challenging than in the case of coal-fired power stations. Cement kilns must recycle a major portion of the collected dust. Some kilns use the fabric filter system as an integral part of the raw material processing system. The temperature of this system would have to be carefully controlled to less than 200ºC to ensure proper mercury adsorption and reduce the risk of activated carbon fires in the fabric filter or solids handling system.

As a final solution, if all other measures fail, is the possible installation of a powdered activated carbon injection system and a further dedusting device (fabric filter) downstream of the main kiln filter. This last control option would be extremely expensive. The high costs are due to the need for a second fabric filter system, a new fan and an activated carbon injection system, The operating costs depend heavily on the cost of the adsorbent. Dust management is a subsequent issue. This is the reason why, so far, there are only a few applications of such a technique in the cement industry (case study n°7 (Cement_Company_F, 2008)).

After extensive research, FLSmidth has developed a patent pending-process that fits this description. The mercury roaster concept was tested and proven on a laboratory scale to confirm the efficiency of the concept. The main filter dust acts as a natural sorbent for mercury, and it is this dust which enhances a cycle of mercury in the system. The process designed by FLSmidth removes this dust from the system for cleaning. The mercury enriched dust is fed to a “roasting” system which heats the material above the boiling points of mercury compounds in the system. The dust is then collected while hot to avoid re-adsorption of mercury and is returned to the silo. The gas stream, which is now mercury enriched, is then cooled and an adsorbent may be added to the stream to supplement the capture of mercury on any dust escaping from the initial dust collector. The sorbent and/or dust collects mercury from the gas stream and is captured in a second dust collector. The cleaned gas is vented to the atmosphere, while the sorbent is removed as a waste stream. The airflows and the sorbent flows are significantly smaller than would be seen with a full ACI system after the main baghouse. With less air and sorbent handling, the operating costs are significantly reduced. The system results in a much smaller installation than a “tail-pipe” solution and can allow for installation in locations where fitting a large baghouse would not be possible.

13.2.2. Techniques considered for other industry sectors

13.2.2.1. Activated Carbon Fixed and Moving Beds

Fixed and moving bed systems for mercury and dioxin-furan control are used in several sectors. In both types of systems, contaminant-laden gas is forced through a bed of granular activated carbon.

Fixed bed and moving bed systems are commercially available. Some carbon filter systems have been installed in European power plants, primarily for the removal of SO_2. Several units have been installed in European hazardous and municipal waste incinerators to reduce organic compounds, mercury, and acid gas emissions. One of these systems has been installed in a cement kiln in Europe.

In the cement plant, the fixed and moving bed activated carbon systems could not be installed upstream of the main kiln FF or ESP. The high dust loadings in these locations would quickly blind both type of beds thereby resulting in very high activated carbon usage rates and disposal requirements.

Accordingly, it would be necessary to install these systems downstream of the main particulate matter control system. A separate vessel and connecting ductwork would be needed. The control approach would be prohibitively expensive and vulnerable to condensable particulate matter related fouling and blinding. So far, this procedure is not an available technique for the cement industry.

13.2.2.2. Flue Gas Desulphurization Systems

Flue gas desulphurization (“FGD”) systems are considered to be one of the two “mature” techniques for the control of mercury from power plants (Richards, 2005).

These are designed to reduce SO_2 emissions from 60% to 90%. The control of mercury in addition to SO_2 is considered a “co-benefit” of scrubbing technology. Wet scrubbing systems collect only oxidised mercury. When used as standalone systems, they are capable of achieving moderate-to-high removal efficiencies for oxidised mercury. They are entirely ineffective in the removal of highly insoluble non-oxidised elemental mercury(main form of Hg in emissions from a cement kiln). There are two basic types of FGD systems:

- conventional wet scrubbing systems;
- spray dryer absorbers.

Two US cement plants presently use wet scrubbing systems, and several new plants will be equipped with wet scrubbers for SO_2 reduction. The ability to retrofit a wet scrubbing system to a cement kiln must be evaluated on a site-specific basis, essentially on the basis of their SO_2 emissions.

13.2.2.3. Oxidation Pretreatment Systems

Oxidation pre-treatment systems potentially convert elemental mercury to oxidised mercury upstream of wet scrubber systems and even upstream of conventional particulate matter control systems. Once in its oxidised form, mercury is captured in these air pollution control systems. The oxidation pre-treatment systems must be able to withstand the gas stream conditions upstream of the air pollution control system used for capture of the oxidised mercury. A review of these techniques is available in the PCA publication (Richards, 2005). Some techniques have been only tested on a laboratory scale.

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15. APPENDIX A: MEASUREMENT METHODS

a) Manual method of determination of the concentration of total mercury EN 13211:2001-2005

This European Standard EN 13211 specifies a manual reference method for the determination of the mass concentration of mercury in exhaust gases from ducts orstacks. This European standard is validated for the determination of the mass concentration of total mercury in exhaust gases from the incineration of waste for the concentration range of total mercury from 0.001 mg/m³ to 0.5 mg/m³). The method may be applicable for exhaust gases from other sources with the typical composition shown in the following table. The method cannot speciate between the three forms of mercury.

***Table 15-1** : Typical composition for applicability of the EN 13211 method.*

Total Suspended Matter	from 0 to 20 mg/m³
C_xH_y	from 0 to 10 mg/m³
HCl	from 0 to 50 mg/m³
HF	from 0 to 10 mg/m³
SO_2	from 0 to 250 mg/m³
CO	from 0 to 250 mg/m³
NOx	from 0 to 500 mg/m³
CO_2	from 0 to 15 % (volume fraction)
H_2O (g)	from 2 to 25 % (volume fraction) (actual)
O_2	from 8 to 15 % (volume fraction) (dry, actual)
Temperature	from 60°C to 140°C

During the test, a sample gas stream is withdrawn isokinetically. The need for isokinetic sampling is eliminated if no vesicle is present in the gas stream and if the ratio between the highest speed of gas stream and the lowest speed is lower or equal to a factor of 1.2.

A nozzle (glass, quartz, PTFE, titanium) is used to acquire the sample gas stream. The sample gas is transported through a probe and passes through a (quartz, glass, PTFE) filter. The method can be used with an external filter or with an in-stack filter configuration. The probe and the filter located on the outside of the chimney must be maintained at a temperature of at least 20°C above that of the effluent gas. When titanium material is used, the temperature must be maintained at 180º-C degrees or more.

The sampling train has a set of minimum two absorbers for the absorption of mercury. An empty absorber can be positioned before this device as a liquid scavenger or to protect the sampling train. Either impingers or scrubbing flasks with fritted discs can be used.

The mercury content analysed in the second absorber must be lower than 5% of the total mercury content of both absorbers or else must be lower than .002 mg/m³ if this value is higher.

Two absorption solutions can be selected:

1. Acidified potassium permanganate (10% H_2SO_4 / 2% $KMnO_4$)
2. Acidified potassium dichromate (4% K_2Cr2O_7 / 20% HNO_3)

The absorption solution must not be preserved more than one week.

The method does not specify the time of test runs or a minimum sample volume.

A field blank is collected and analysed. The field blank is assembled, leak checked and heated as if to collect a gas sample, but no exhaust gases are drawn through the sample train. It is recovered in a manner that is identical to the trains used in the test runs.

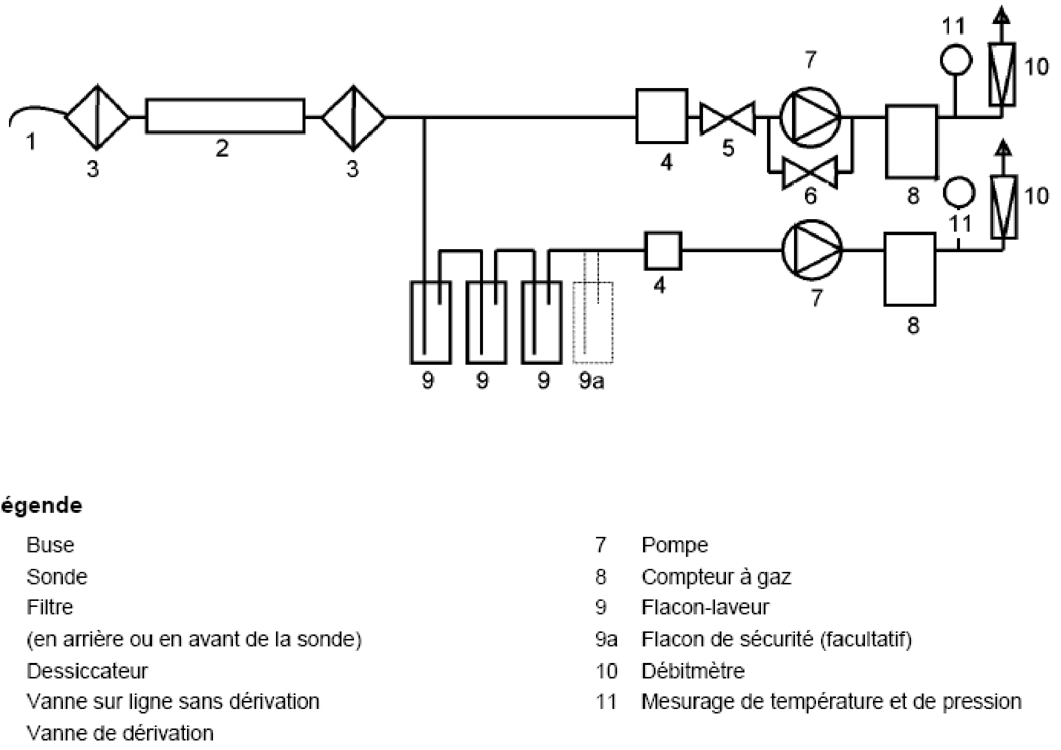

Figure 15-*1 : Sample train for EN 13211 Standard.*

b) VDI 3868, page 2, E

The VDI Guideline 3868, page 2, E; “Determination of total emission of metals, metalloids, and their compounds - Measurement of mercury - Atomic absorption spectrometry with cold vapour technique” was edited in 1995. VDI is the Association of German Engineers and the largest engineering association in Western Europe.

This VDI method is a Draft which was later withdrawn. Its presence in this document is justified by the fact that the CEMBUREAU-CSI Inquiry showed that some organisations still referred to it.

The particulate and gas mercury emissions are collected isokinetically according to the instructions of the VDI 2066 page 2. Dust is treated by an oxidising mixture (HNO_3). Gas mercury is absorbed into a solution of $KMnO_4$ and sulphuric acid. The recovered solution samples are analysed for mercury by cold vapour atomic adsorption spectroscopy (CVAAS).

c) US EPA Method 29

Method 29, “Determination of Metals Emissions from Stationary Sources”, (US_EPA, 2000a) was developed as a multi-metals sampling train. It has been validated for total mercury measurements.

During the test, a sample gas stream is withdrawn isokinetically. This is needed primarily because of the possible presence of particle-bound mercury or other metals. The need for isokinetic sampling is eliminated if the Method 29 tests are conducted strictly to measure elemental and oxidised gaseous mercury in the gas stream.

A glass (Pyrex or quartz) nozzle is used to acquire the sample gas stream. The sample gas is transported through a glass-lined probe. The use of a glass nozzle and probe is critical because of possible mercury reactions on the surfaces of the metal nozzles and probe liners. The sample gas stream passes through a quartz filter. The probe and filter are maintained in the temperature range of 120°C. All of the elemental and oxidised mercury remains in a vapour state at this temperature and, therefore, passes through the filter.

The substances are collected in a set of seven impingers maintained in an ice bath. The temperature is kept below 20°C.

Two HNO_3 – H_2O_2 impingers collect the oxidised mercury. Elemental mercury passes through these impingers and is captured in the $KMnO_4$ – H_2SO_4 impingers. These solutions were not chosen primarily because of their effectiveness with respect to the capture and speciation of mercury. Mercury is just one of more than seventeen metallic elements measured in a Method 29 sampling train. However, the ability of the method to speciate mercury was not established, with several adsorptions and chemical conversions being able to occur in the sampling train.

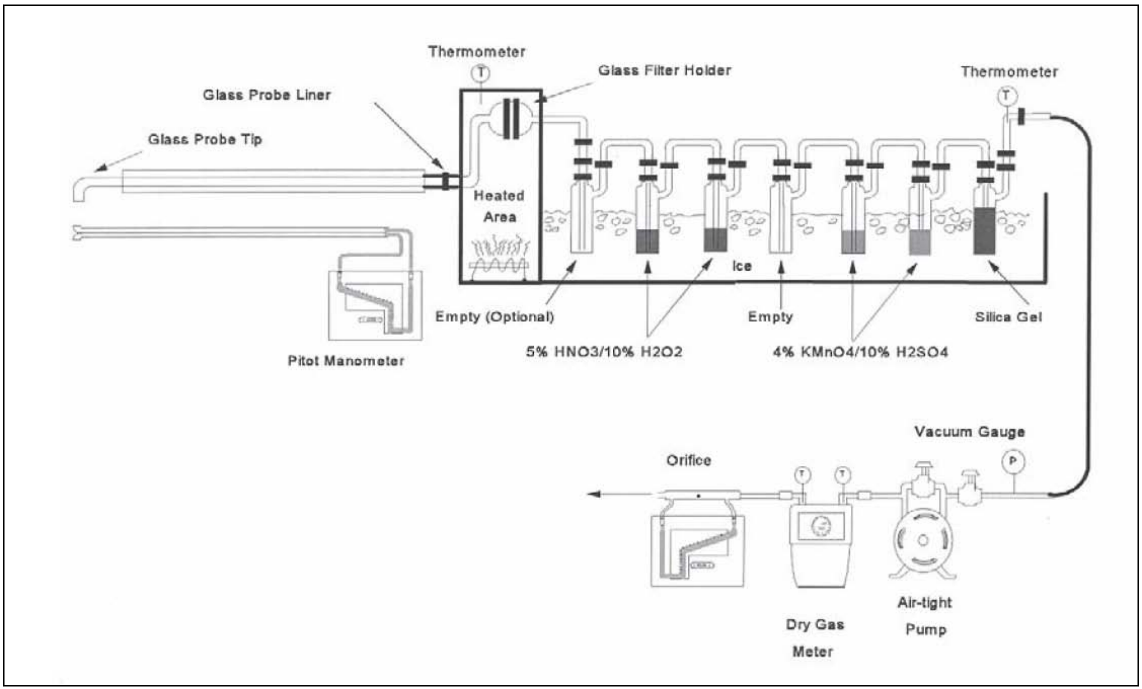

***Figure 15-2** : US EPA Method 29 sampling train.*

The $KMnO_4$ / H_2SO_4 absorbing reagent used in the rear impingers should be prepared onsite so it is fresh for each test day.

Method 29 does not specify the time of test runs or a minimum sample volume, however most test runs are 2 hours in duration. This long sampling time is needed to obtain sufficient quantities of the metals, including mercury, which can be present at low concentrations.

Following the end of the test run, the sampling train is sealed and transported to a clean recovery area. The various samples are recovered in accordance with the method.

A field blank is collected and analysed. The field blank is assembled, leak checked and heated as if to collect a gas sample, but no exhaust gases are drawn through the sample train. The sampling train is kept at the sampling location for the same duration as the sampling trains used in the test runs. It is recovered in a manner that is identical to the trains used in the test runs.

Seven samples are recovered from the sampling train. Each sample is analysed by cold vapour atomic adsorption spectroscopy (CVAAS) for mercury.

The detection limit specified in Method 29 for mercury is about 0.00056 mg/Nm^3.

US EPA Method 29 can provide valid total mercury data for cement plants (Richards and Holder, 2005). However, it is not viewed as a “user-friendly” emission measurement method; the sample recovery procedures are more difficult than these from others methods. Method 29 is useful for total mercury measurements mainly when emissions data for other metals are also needed.

d) US EPA Method 101A

US EPA Method 101A “Determination of Particulate and Gaseous Mercury Emissions from Sewage Sludge Incinerators” (US_EPA, 2000b) was developed to measure total mercury emissions from sewage sludge incinerators. It is used in a wide variety of applications, including cement kilns, coal-fired boilers, and municipal waste incinerators.

This method is similar to EPA Method 29 with the exception that no other substance is collected by this method. The nozzle and probe material are similar to Method 29. The temperatures are maintained at 120°C in both the probe and the filter. The sampling times used in Method 101A are identical to those used in Method 29.

The main difference between Method 101A and Method 29 is the arrangement of the impingers. Method 101A uses a 4% $KMnO_4$/10% H_2SO_4 solution in the impingers exclusively. These impingers are effective in the capture of elemental mercury and the conversion of any oxidised mercury to the elemental form. This simplifies the sample recovery and analysis procedures.

With respect to total mercury collection and analyses, there are no significant differences regarding the accuracy, precision, and interferences between Method 101A and Method 29. Validation of Method 29 for total mercury measurement is regarded as sufficient to validate Method 101A.

e) US EPA Method 101B

US EPA Method 101B is an adaptation of Method 101A and Method 29. The test method has been designed to reduce the effect of SO_2 on the conversion of elemental mercury to oxidised mercury in the first set of impingers by adding a set of two deionised water-filled impingers upstream of the HNO_3/ H_2O_2 impingers. This allows for the removal of oxidised mercury in the water filled impingers without excessive SO_2 absorption.

Method 101B tests are conducted for time periods identical to those used in Method 101A. The gas stream is sampled isokinetically and particle-bound mercury is captured on a glass fiber filter that is maintained at 120ºC. A method blank is obtained using a fully assembled sampling train that is heated to this temperature, leak checked, and kept at the sampling location for a time period similar to that used for the sampling trains.

Method 101B has satisfied (Richards and Holder, 2005) validation tests for total mercury. Method 101B might have an application in the relatively infrequent tests in cement plant tests involving SO_2 levels exceeding approximately 1 000 ppm.

f) Ontario Hydro Method - ASTM 6784-02

The Ontario Hydro Method, ASTM Method D6784-02, is a “Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources” (ASTM, 1999). This method has been developed under ASTM procedures primarily for coal-fired boiler applications. It has become widely used in North America, particularly when speciated mercury data is needed.

The method is similar to the US EPA Method 29. However, the sampling train and procedures are planned to improve the separation of particle-bound, oxidised, and elemental mercury.

The sample train consists of a glass nozzle and a glass-lined probe. The method can be used with an external filter or with an in-stack filter configuration. The in-stack filter configuration is the preferred arrangement because it does minimise the biases that are related directly to gas temperature such as physical adsorption and condensation.

If an external filter is used then the temperature of the probe and the filter must be maintained within ±15°C of the stack temperature and above 120°C at a minimum. The temperature specifications differ from those usually applied to prevent loss of gaseous mercury to particle-bound mercury during sampling.

The improved control of sample temperature in the Ontario Hydro sampling train does not entirely eliminate filter solid related problems. Elemental mercury can be captured in carbonaceous material on the filter surface, and both elemental and oxidised mercury can condense on the surfaces of the solids. Elemental mercury can be oxidised catalytically by materials present at a high concentration on the surface of solid particles and can also participate in reactions with SO_2 to form oxidised mercury. All of these conditions can lead to a bias to higher-than-true particle-bound mercury and/or higher-than-true oxidised mercury.

These biases are especially important in tests at cement plants upstream of kiln fabric filters and electrostatic precipitators. The solids loadings in the gas streams on the inlets to the particulate matter control devices are especially high (Richards, 2005).

The Ontario Hydro sampling train has a set of eight impingers for the sequential absorption of oxidised mercury followed by elemental mercury: three impingers containing KCl, followed by one impinger containing acidified hydrogen peroxide (5% HNO_3 / 10% H_2O_2) followed by three impingers containing acidified potassium permanganate (10% H_2SO_4 / 4% $KMnO_4$), and finally an impinger containing silica gel.

The $KMnO_4$ / H_2SO_4 absorbing reagent used in the rear impingers should be prepared onsite daily.

Impingers 1 through 3 are used to measure the concentration of oxidised mercury in the sample. Impingers 4 through 7 are used to measure the concentration of elemental mercury. The filter and rinses of the nozzle and probe are used to measure the concentration of particle-bound mercury.

A sampling train must be assembled, leak checked, and kept at the sampling location to provide a field blank.

The sample recovery procedures for the Ontario Hydro Method are somewhat more time consuming than the previously described EPA Method 29 cleanup procedures. Five sample fractions are delivered to an offsite analytical laboratory.

The recovered samples are digested in the laboratory and analysed for Hg by cold vapour atomic adsorption spectroscopy (CVAAS) or by cold-vapour atomic fluorescence spectroscopy (CVAFS). Using these techniques and with sampling times ranging from two to three hours, the minimum detectable level for all three forms of mercury is approximately 0.0005 mg/m³.

g) US EPA Method 324

US EPA Method 324 “Determination of Vapor Phase Flue Gas Mercury Emissions from Stationary Sources – Dry Sorbent Trap” was promulgated in 2004 (US_EPA, 2004). This method was designed for semi-continuous sampling of vapour phase mercury emissions representing the sum of elemental and oxidised forms of mercury in combustion flue gases using dry sorbent traps. Method 324 was developed for coal-fired boiler applications.

Known volumes of flue gas are drawn through the sorbent traps with a nominal flow rate of 0.2 to 0.6 litres per minute. Sorbent traps tubes containing activated charcoal are mounted in probes inserted into the gas stream and maintained between 200ºF (93°C) and 375ºF (191°C). Large sorbent tubes can be used to go to a maximum temperature limit of 425ºF (218°C). This temperature limits encore the use of this method for cement kilns (some long dry and wet process) having stack gas temperatures that exceed 220°C.

Each trap is leached with acid and the resulting leachate is analysed for mercury.

The method is designed for use over periods of one 1/2 hour to 48 hours. If significant amount of hydrocarbons are present, it could compete for the available adsorption sites and, in this manner, could reduce the capacity of the sorbent tubes for mercury.

When used to demonstrate compliance with regulatory requirements, Method 324 requires the use of paired sampling trains. Each of the paired trains includes a set of two sorbent tubes in series. The quantity of mercury captured in the second (back-up) tube is compared with the quantity in the first tube to confirm that no breakthrough has occurred. A field blank must be run during tests.

Analysis of the sorbent traps is by cold vapor atomic fluorescence spectroscopy (CVAFS) or cold vapor atomic adsorption spectrometry (CVAAS).

The method is intended for applications having vapour-phase mercury levels ranging from 0.80 to 0.150 mg/Nm^3.

US EPA has indicated that this method has satisfied Method 301 validation criteria. However, the validation testing did not include the 25% to 40% moisture levels possible in wet process cement kiln effluent gas streams (Richards and Holder, 2005).

16. APPENDIX B: CASE STUDIES

A. CASE STUDY N°1

The two following figures (ECRA, 2008) illustrate typical examples for a mercury balance of a cement kiln. The first diagram depicts the situation without the removal of kiln dust from the external cycle. On the contrary, the second graph shows an example for a kiln where the mercury cycle is released via a periodic dust removal.

Based upon these two examples it has to be highlighted that the mass balances show the typical situation whereby the intake of mercury is mainly influenced by the composition of the raw materials. According to the experience of the European Cement Research Academy (ECRA), the contribution of the fuels (primary and secondary fuels) is in most cases very small or even negligible.

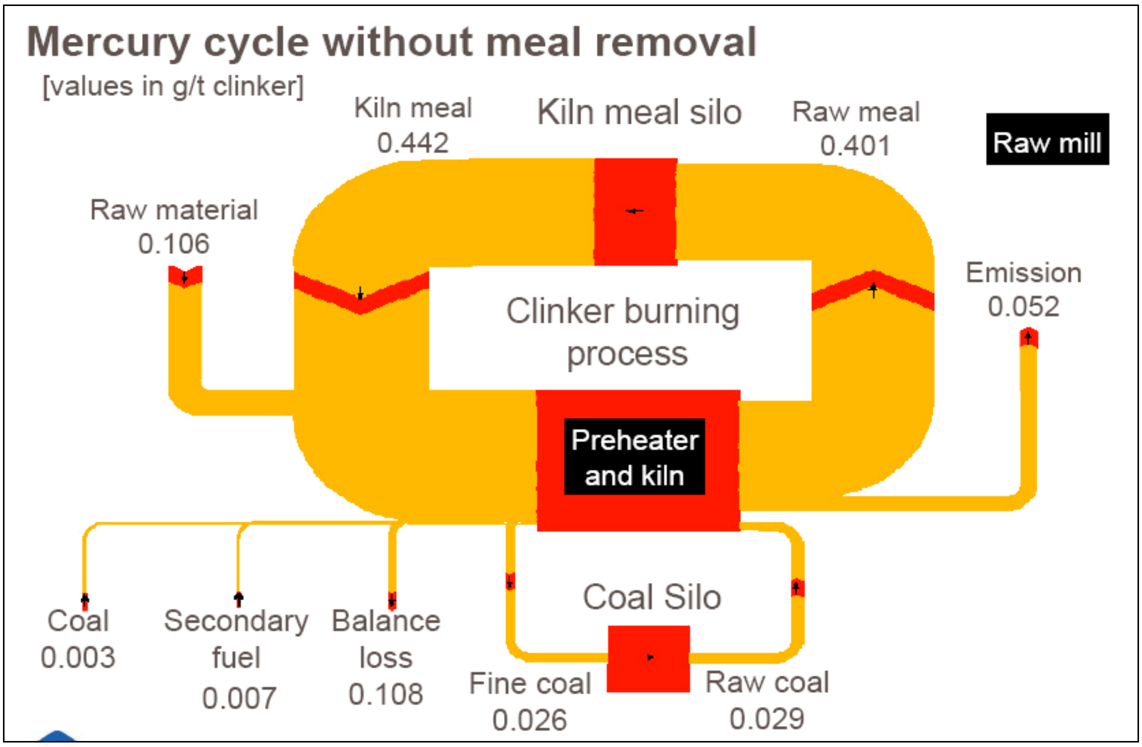

***Figure 16-1**: Mercury cycle without meal removal (ECRA, 2008)*

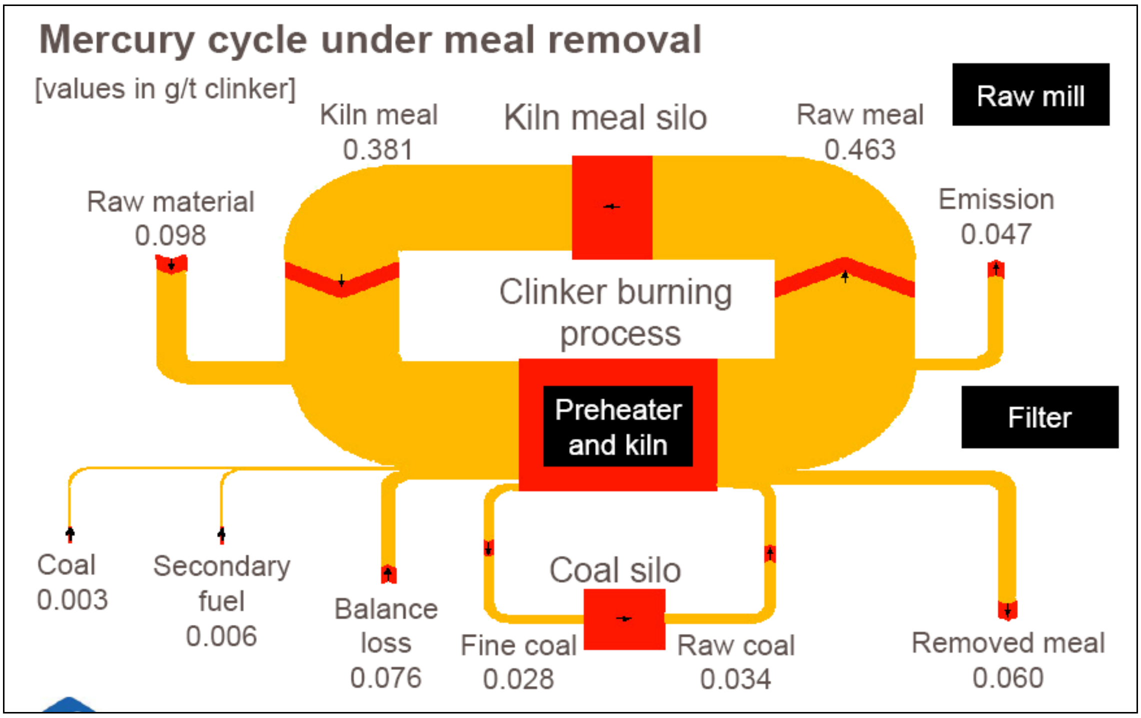

***Figure 16-2**: Mercury cycle under meal removal (ECRA, 2008)*

B. CASE STUDY N°2

A study (Cement_Company_A, 2008), involving mercury mass balances, was conducted in an European cement plant in 2006. The dry kiln has a precalciner and a five stage preheater with a capacity of about 6000 tonnes of clinker per day. A significant amount (average 70%) of secondary fuels is used for the energy needs of the kiln. The kiln operates interconnected with a raw mill for 90% of the functioning time. In direct operation, the filter dust is discharged and incorporated into the cement. The waste gas temperature varies in relation to the connection or not of the raw mill: mill in line: 90°C and mill off-line: 150°C.

***Table 16-1** : Balance of mercury in kg/year.*

Input		**Output**	
Raw materials:	30 kg/y	Emission:	25 kg/y
Fuel:	100 kg/y	Clinker	0 kg/y
		Bypass:	3 kg/y
		Filter dust:	102 kg/y
Total	130 kg/y	Total	130 kg/y

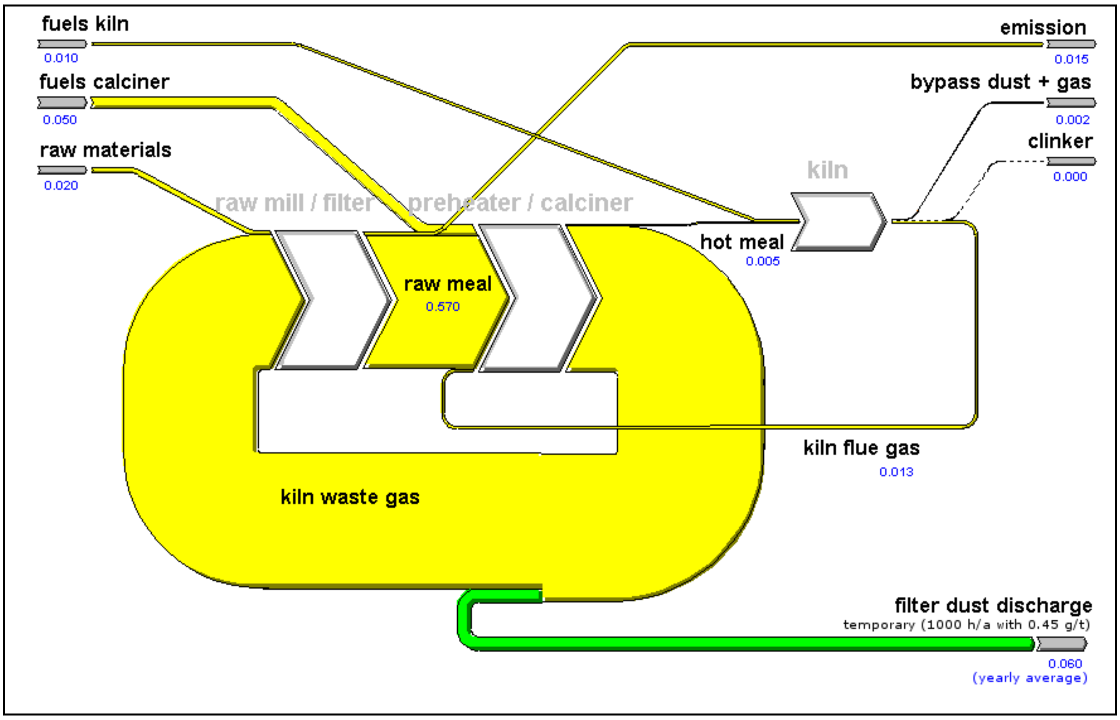

***Figure 16-3** :* **Emissions of Hg [mg/Nm^3]**

In this case, the larger proportion of mercury input is brought in by fuels. A large quantity of mercury circulates in kiln waste gas and in raw meal- this determines air emissions.

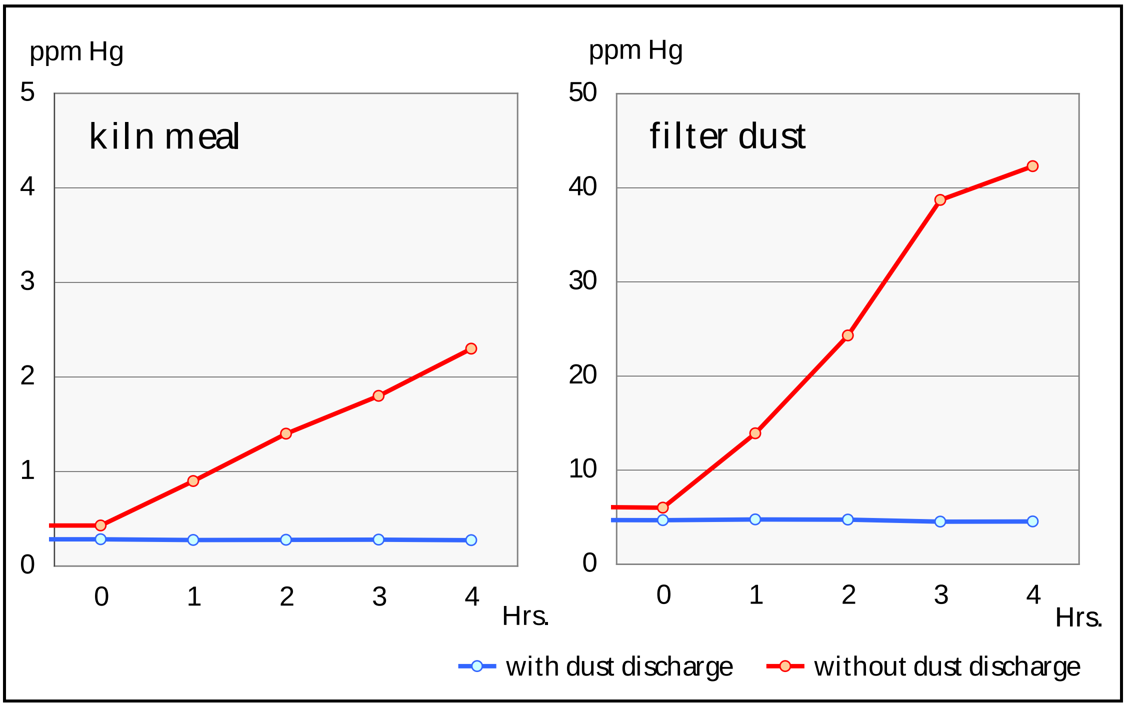

***Figure 16-4** : Developments of Hg contents after raw mill stop.*

Another significant point is the increase in the mercury contents after raw mill stop when the filter dust discharge is not in operation and the dust is added to the kiln meal as illustrated in **Figure 6-1**. The mercury concentration in filter dust and in kiln meal rises rapidly. A similar increase affects mercury air emissions when the discharge of filter dusts is interrupted.

This case study shows that existing cement technology allows high mercury separation efficiency (more than 90% in mill in line operation). This leads to Hg circuits between preheater and filter. Mercury raw gas concentration depends much more on mercury cycle than on mercury input. The control the mercury emission requires knowing the input, limiting the cycle and balancing the mass flow over a certain period of time.

C. CASE STUDY N°3

An additional study (Cement_Company_B, 2008) involving mercury mass balances was conducted in another European cement plant. The dry kiln has a precalciner and a five stage preheater with a capacity of about 3200 tonnes of clinker per day. Petcoke and “animal meal” are the usual fuels used in the kiln burner and petcoke in the precalciner. The kiln operates interconnected with a raw mill. The waste gas temperature is approximately 125°C. There is no by-pass system on this kiln and the dust abatement device is a bag filter. Dusts are recycled in raw meal.

Mercury stack emission is low, measured at 0.0007 mg/Nm³.

In this case, the mercury mainstream input (see **Table 16-2**) comes from raw materials and, although pyrite ashes have the higher mercury concentration, according to the mass flow of each raw material, the main contribution originates from the limestone.

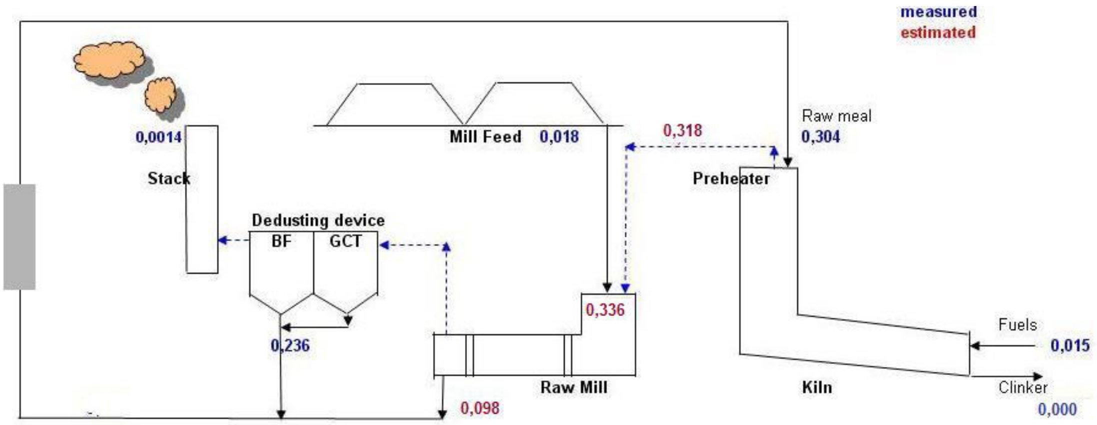

__Figure 16-5__ : Diagram and mass balance (values in mg Hg/kg clinker); case study n°3.

The content of the hot meal, collected in cyclone 4, is very low, at 0.01 ppm.

Table 16-2 *: Mercury mass balance (kiln system); case study n°3.*

	Hg ppm	Flow rate (mg Hg/kg clinker)
INPUT		
Limestone	0.01	0.015
Sand	0.00	0.000
Pyrite ashes	0.54	0.003
Total (mill feed)	**0.009**	**0.018**
Petcoke	0.12	0.011
Animal meal	0.22	0.004
Total fuels		**0.015**
RAW MEAL	0.18	0.304
OUTPUT		
Clinker	< LD *	0.000
Dust (BF + GCT)	1.32	0.236
Stack emissions		0.0014
Pre-heater outlet (estimated)		0.318
Captured mercury in raw mill (estimated)		0.098

* For calculations it will be assumed that the Hg concentration in the clinker is zero.

Mass balance shows that 0.236 mg Hg/kg clinker is captured in the dedusting device (BF+GCT) and 0.098 mg Hg/kg clinker in the raw mill. Of course, it is a global efficiency, and the raw mill probably acts in two ways, lowering temperature and creating an accumulation of cold dust ready to adsorb mercury. Overall mercury capture is around 96%.

D. CASE STUDY N°4

Mercury concentrations can vary significantly among different raw materials, and it is possible that they also vary within the stone acquired from the same quarry.

In another case study (Cement_Company_C, 2008) it appears that the mainstream of mercury in cement kiln system originated from quarry products. Quarry samples have shown the presence of mercury in some areas of the existing quarry, namely the clay area. The plant management decided to explore the quarry for mercury content. Mercury concentrations fluctuate from 0.05 to more than 2 ppm. The current quarry and a projected new quarry were mapped in 2007 for mercury content. The raw materials from the new quarry will mean a lower mercury content.

In addition to changing quarries, the plant investigated the option of removing mercury via the filter dust. The temperature at the inlet of the filter is lower than 130°C. After a test period, the plant put in place an installation for recycling dust into the cement.

In mid 2008, a sampling and analysis campaign was conducted to carry out a mercury balance and to assess the impact of both measures (new quarry and dust to cement). Only solid streams (fresh feed & recycled dust) were analysed for their mercury content. It appeared that more than 50% of the mercury input has been removed by the dust. The mercury content at the system inlet was much lower than during all previous measurement campaigns (old quarry) and with less variability. Mercury in the fresh feed was between 0.13 mg/kg to 0.23 mg/kg.

This confirms that, in the case of quarries with a high mercury content, selective mining, when feasible, is the primary option for mercury emission reduction. Bleeding and recycling dust into the cement is a good complement that could remove up to 50% of the mercury inputs.

E. CASE STUDY N°5

Another study (Cement_Company_D, 2008) was conducted in an European cement plant. The kiln is a four-stage preheater kiln (without precalciner) with a production rate of approximately 2'000 tpd, and operates interconnected with a raw mill. The fuels used are usually coal and petcoke. The dust abatement device is a bag filter. The exhaust gas temperature was approximately 170-180°C.

Two quarries feed the process, one limestone and the other clay. The mercury contents of the limestone and clay (due to ancient volcanic activity) are high (up to 2 mg/kg). Selective mining is not possible because of the widespread mercury distribution in limestone and clay samples from the quarries. The natural raw materials were identified as the main source of the elevated mercury emissions. The mercury content of the raw meal is between 0.1 and 0.4 mg/kg. The mercury emission level is illustrated in **Figure 16-7**. The plant was at risk of exceeding the (new) mercury emission limit of 0.05 mg/Nm^3.

A first decision was to extract filter dust from the kiln during direct operation mode to be incorporated in cement. For technical reasons, this measure had limited efficiency. The extraction rate of filter dust to the cement mill was 3-4% at maximum.

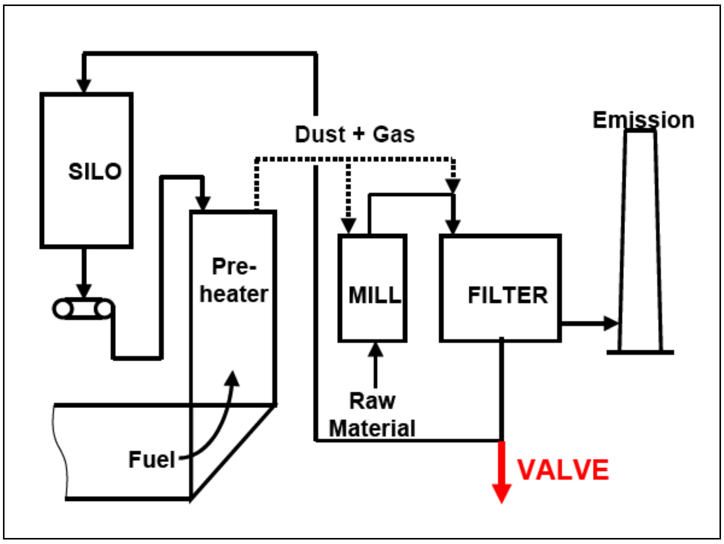

***Figure 16-6** : First action: bleeding of dust.*

A second decision was to reduce the filter temperature. Injection of water at the 4th stage of preheater section had no significant influence on mercury emissions. Reduction of the cooling tower outlet temperature from 180° to 150°C showed a positive influence on mercury emissions. However, the existing cooling tower and the exhaust fan had limited capacity.

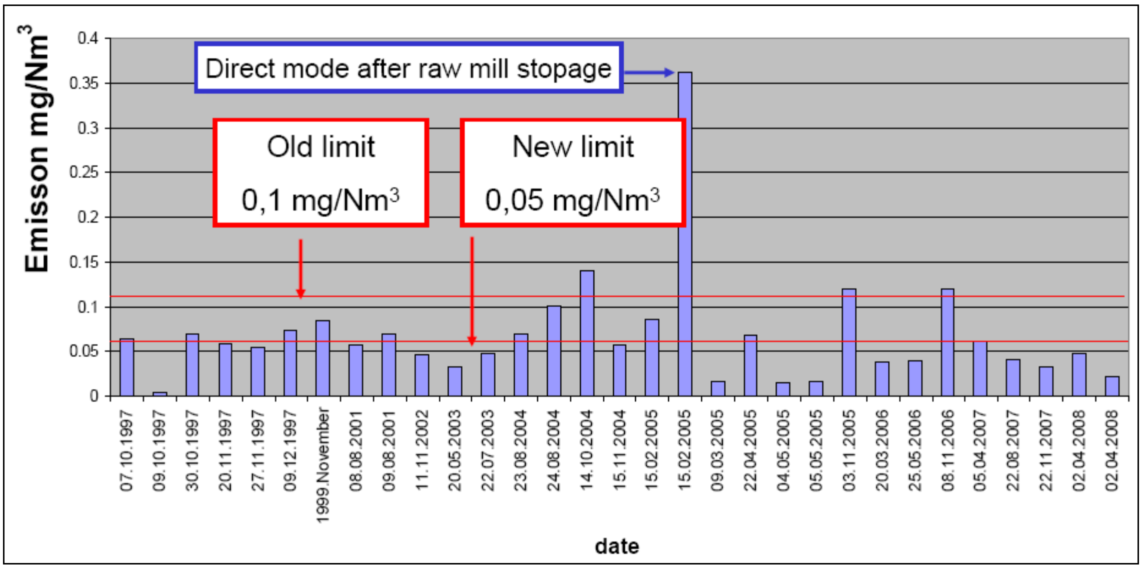

Figure 16-7 *: Hg emissions [mg/Nm^3 at 10 % O$_2$]*

This case study confirms that mercury emissions are typically significantly higher during direct kiln operation (i.e. with the raw mill off). It illustrates that natural raw materials (limestone, clay) can be the primary sources of Hg input to the kiln system. Selective mining to reduce Hg input was not a viable option on a permanent basis in this case. Primary measures such as the bleeding of filter dust to the cement mill and reduction of stack temperature had a positive effect on mercury emissions. The plant is able to meet the regulatory emission limit. However, a permanent control of the mercury input and output is needed

F. CASE STUDY N°6

Another case study (Cement_Company_E, 2008) involves a site in Latin America with two kilns (4-stage preheater kilns with a standard capacity of 1100 and 2600t clinker per day, respectively) equipped with bag filters. During regular biannual measurements, mercury emission levels were detected to be above permitted limits (0.07 mg/Nm^3), sometimes even higher than 1 mg/Nm³.

The limestone of the main quarry (main component of the raw mix) was identified as the major source (on average: 1.0 mg/kg of mercury). Unfortunately, selective mining was not an option because of the widespread distribution of high mercury limestone. The marl and clay used in the raw mix showed considerably lower concentrations, generally below 0.3 mg/kg.

Alternative limestone deposits were available, but at a distance of seven km from the plant.

Tests were carried out with the extraction of filter dust and with reduced gas temperatures at the inlet of the main filters of both kilns in order to determine the potential to reduce mercury emissions by dust bleeding and to determine the transfer coefficients.

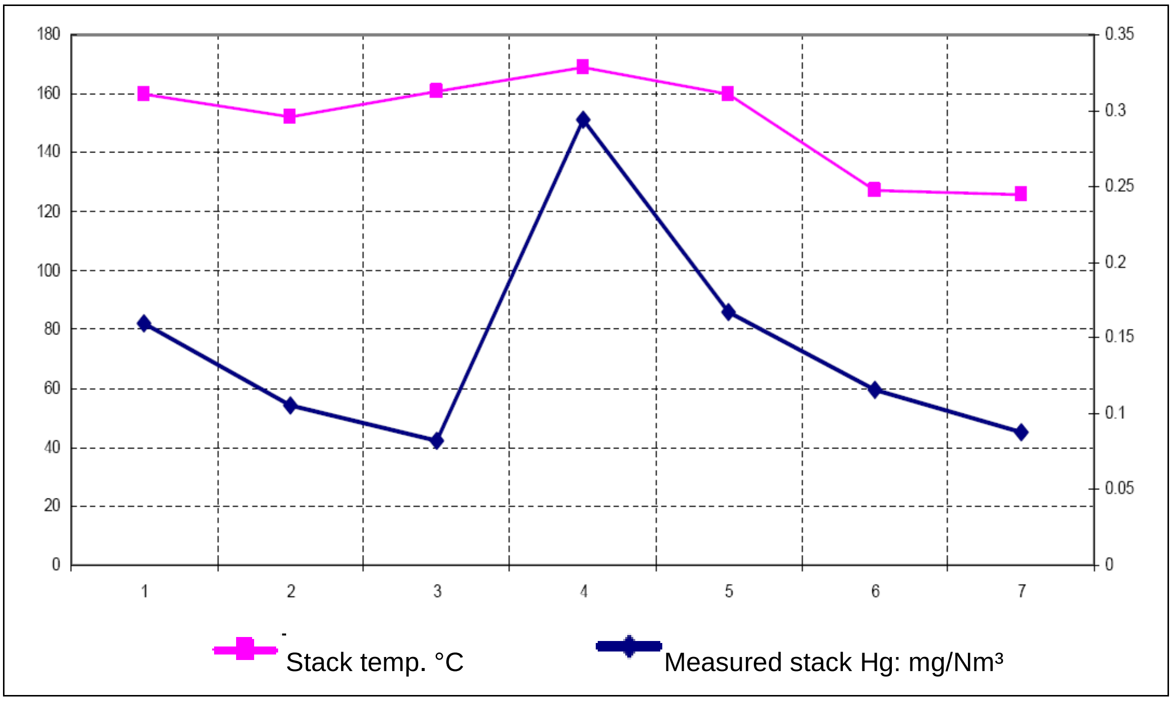

Figure 16-8 *: Impact of filter temperature on mercury emissions (case study n°6).*

Table 16-3 *: Results of investigation (case study n°6).*

Temperature at the filter inlet (kiln 1) [°C]	**Emissions of Hg [mg/Nm^3] (limit = 0.07 mg/Nm^3)**	**Hg in the filter dust [ppm]**
170	> 1.0	1.0 – 3.5
130	0.1 – 0.5	3.5 – 6.5

The Hg emissions could be significantly reduced (without changing the raw materials). However, there was still a permanent risk of exceeding the regulatory emission limit. Therefore, the limestone had to be blended with low-mercury limestone from the alternative deposit which substantially increased raw material costs for the plant. In addition, a permanent input control has been established by means of purchasing a dedicated mercury analyser in the quality control laboratory.

G. CASE STUDY N°7

Another case study (Cement_Company_F, 2008) relates to a site in Europe. The plant was subject to new emission limits (0.03 mg/Nm^3 daily average and 0.05 mg/Nm^3 half hourly average). At that time, mercury concentrations in mill-off mode exceeded the daily average limit value. The mercury content of the raw materials is between 0.1 and 0.3 ppm.

Tests were conducted to inject activated carbon between the gas conditioning tower (GCT) and the dust collector (EP) during mill off mode at different temperatures.The results of the tests show that lowering temperature offers higher removal efficiency (**Figure 6-1**).

In mill off mode, the temperature has been reduced to 125°C and all dust is extracted. With an injection of 40 to 50 kg of activated carbon per hour, the mercury emission limit (0.030 mg/Nm^3) can be maintained.

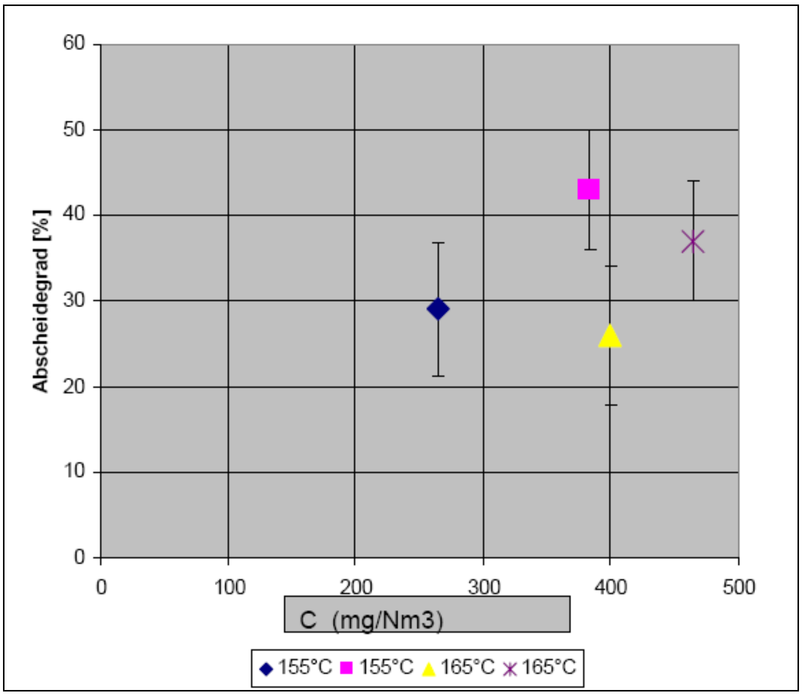

***Figure 16-9** : Mercury removal efficiency of lower temperature and activated carbon injection (in mg of carbon / Nm^3; case study n°7.*