Atmospheric Environment 92 (2014) 421–428

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Mercury enrichment and its effects on atmospheric emissions in cement plants of China

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HIGHLIGHTS

- Mercury enrichment caused by particle recycling in cement plants was evaluated.
- Over 90% of mercury input is emitted into atmosphere due to particle recycling.
- Emission factors range from 0.044 to 0.072 g Hg/t clinker.
- Mercury from cement manufacturing process is mainly emitted in oxidized form.

ARTICLE INFO

Article history:
Received 19 October 2013
Received in revised form
13 April 2014
Accepted 16 April 2014
Available online 26 April 2014

Keywords:
Cement plant
Mercury enrichment
Atmospheric emissions
Mercury speciation

ABSTRACT

The cement industry is one of the most significant anthropogenic sources of atmospheric mercury emissions worldwide. In this study of three typical Chinese cement plants, mercury in kiln flue gas was sampled using the Ontario Hydro Method (OHM), and solid samples were analyzed. Particulate matter recycling, preheating of raw materials, and the use of coal and flue gas desulfurization derived gypsum contributed to emissions of Hg in the air and to accumulation in cement. Over 90% of the mercury input was emitted into the atmosphere. Mercury emission factors were 0.044–0.072 g/t clinker for the test plants. The major species emitted into the atmosphere from cement plants is oxidized mercury, accounting for 61%–91% of the total mercury in flue gas. The results of this study help improve the accuracy of the mercury emission inventory in China and provide useful information for developing mercury controls.

1. Introduction

Mercury is widely considered to be one of the most important global environmental pollutants because of its long-range transport and bioaccumulation characteristics. Cement production is the fourth largest anthropogenic source of atmospheric mercury emissions worldwide, contributing approximately 10% of global mercury emissions. The global mercury emissions from cement plants increased from 114 t in 1990 to 189 t in 2005 (Pacyna and Pacyna, 2002; Pacyna et al., 2006, 2010) and reached 236 t in 2010 (Pirrone et al., 2010). The Minamata Convention on Mercury requires reducing the atmospheric mercury emissions from cement plants in the near future.

Atmospheric mercury emissions from Chinese cement plants were estimated to be 23 t in 1999 and increased at an annual growth rate of 7.4% from 1995 to 2003 (Streets et al., 2005; Wu et al., 2006). However, the Chinese cement production and manufacturing processes have experienced a significant change since 2000. China's cement production has rapidly increased since 2000, reaching 2 billion tons in 2011, accounting for more than half of the global production (National Bureau of Statistic of China, 2011). The proportion of cement production using a precalciner process also increased from 10% in 2000 to 85% in 2011 (Chinese Building Materials Federation Ministry of information, 2012). Thus, accurately estimating the mercury emissions from Chinese cement plants will help to improve the global mercury emission inventory and to control the atmospheric mercury emissions.

In previous studies, an emission factor of 0.065–0.1 g Hg/t cement was used to calculate the mercury emissions from cement plants (Pacyna and Pacyna, 2002; Pacyna et al., 2006, 2010). Other

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http://dx.doi.org/10.1016/j.atmosenv.2014.04.029
1352-2310/

studies used an emission factor of 0.04 g Hg/t cement, which excluded the contribution of coal combustion in cement plants (Streets et al., 2005; Wu et al., 2006). However, recently Won and Lee estimated the emission factor for a precalciner process to be 0.026–0.034 g/t clinker, much lower than the previous values (Won and Lee, 2012). In China, the mercury emission factor for rotary kiln and precalciner processes were reported to be 0.012 g/t cement and 0.0138 g/t cement, respectively (Li, 2011; Zhang, 2007). Large uncertainties exist in the mercury emission factors of cement production. A more accurate mercury emission estimate should be based on the mercury mass balance in the cement manufacturing process and the mercury content distribution in raw materials. Therefore, it is necessary to investigate the mercury emission characteristics and behavior in Chinese cement plants.

The complex precalciner cement manufacturing process results in a more complicated mercury behavior compared with other industries such as coal-fired power plants. Mercury behavior in the precalciner process is affected by the recycling of the collected particulate matter (PM) and the use of flue gas preheating raw materials and fuel (Renzoni et al., 2010; Senior et al., 2009, 2003). These cycles include three stages: mercury stripping, sorbing, and recycling (Sikkema et al., 2011). The mercury mass distribution in the cement manufacturing process and the removal efficiencies of the different facilities were affected by these cycles (Mlakar et al., 2010). Rare field measurements were conducted to evaluate the mercury enrichment in the cement manufacturing process and its effects on the emissions (Zheng et al., 2012).

Information on mercury speciation emitted from cement plants is also limited. Only 15% of mercury was oxidized mercury (Hg^{2+}) and approximately 85% was elementary mercury (Hg^0) in a previous study (Won and Lee, 2012). Mlakar et al. (2010) indicated that Hg^{2+} accounted for 51% of mercury when a raw mill was on (operation mode) and 83% when raw mill was shut down (direct mode). A higher proportion of 70% (operation mode) and 95% (direct mode) were also reported in other studies (Schneider and Oerter, 2000; Verein Deutscher Zementwerke, 2006). Therefore, more field measurements on mercury speciation in the precalciner process are needed.

In this study, the Ontario Hydro Method (OHM) was used to sample the mercury in flue gases at the outlet of the kiln system and in stacks of three cement plants. The solid samples, including different types of raw materials, fuel, raw meal, and the particulate matter, were simultaneously collected by fabric filter (FF) and electrostatic precipitator (ESP) and analyzed for their mercury concentrations. Based on the monitoring results, the removal efficiencies of two typical combinations of facilities, raw-mill + FF (RF combination) and coal-mill + FF (CF combination), were determined, and the enrichment of mercury in the cement manufacturing process was evaluated. Finally, the mercury mass balance, the emission factor, and the speciation of mercury emitted into the atmosphere were calculated.

2. Experimental

2.1. Cement plants tested

Onsite tests were performed in three typical cement plants employing the precalciner process. Two of the plants are located in Sichuan Province, and the third one is in Shandong Province. In 2011, Shandong Province and Sichuan Province had the first and third largest cement production in China, respectively, both producing over 100 million tons of cement. Fig. S1 in Supporting Information shows the locations of the cement plants tested in this work. All of the tests were performed on the production line with a capacity of 5000 t/d cement production. The 5000 t/d production lines contributed over half of the cement production using the precalciner process in China.

A schematic diagram of the cement manufacturing process is shown in Fig. 1. The raw materials, including limestone, clay, sandstone, and slag, are ground in the raw mill and then homogenized to produce the raw meal in the raw meal silo. The raw meal goes through a preheater and a precalciner and is heated by coal in a rotary kiln to produce clinker. Finally, the gypsum, usually from power plants, is added to the clinker to produce the cement. In this study, the preheater, precalciner, and rotary kiln compose the kiln system. The combustion air enters the rotary kiln and flows in the opposite direction of the raw meal in the kiln system. The kiln end where the combustion air enters is called the kiln head and the other end is called the kiln tail. Flue gas is emitted from the kiln tail and head. To increase the fuel utilization efficiency, the high-temperature flue gas from the kiln tail is separated into two flows and used to dry and preheat raw materials and coal. FF is installed after the raw mill and the coal mill to collect PM in the flue gas. Two modes of the cement manufacturing process that are dependent on the raw mill operation affect mercury emissions. When the raw mill is operating (operation mode), the flue gas flows through the raw mill into the FF before entering the stack. However, when the raw mill is shut off (direct mode), the flue gas goes directly into the FF. The operation mode accounts for 80%–90% of all production. Therefore, all of the mercury emission tests in this study are conducted under the operation mode. The flue gas from the kiln head is emitted into the atmosphere after flowing through an ESP. The PM from the FF after the raw mill and the ESP at the kiln head is recycled into the raw meal silo and mixed with raw materials. The PM from the FF after the coal mill enters the rotary kiln after mixing with coal powder from the coal mill.

2.2. Mercury cycles in the cement manufacturing process

The flue gas from the kiln tail preheats the raw materials in the raw mill and the coal in the coal mill. The high-temperature flue gas is therefore cooled down in the raw and coal mills. The raw materials and coal absorb some mercury in the flue gas, which is then cycled back to the kiln system. The remaining mercury in the flue gas flowing out of the raw mill or coal mill still has to go through the adjacent FF. Over 70% of the mercury in the flue gas is collected with PM in the FF. The PM collected by the FF is recycled back to the kiln system, including the mercury on the collected PM. Therefore, the mercury in the flue gas is cycled back to the kiln system twice. The flue gas at the kiln head flows through an ESP, and the collected PM is also recycled back to the kiln system. The PM recycling significantly affects the mercury in atmospheric emissions and clinker. Generally, the mercury concentration in clinker is extremely low and the atmospheric emissions account for more than 90% of mercury output. Overall, the mercury is cycled in the cement manufacturing process and the amount of mercury flow is much higher than the mercury input from raw materials and coal.

2.3. Sampling and measurement methods

In this study, flue gas samples and solid samples from the entire cement manufacturing process were collected and analyzed. The sampling sites of the flue gas and solid samples are presented in Fig. 1.

The OHM was used in this study to investigate mercury speciation, including elementary mercury (Hg^0), oxidized mercury (Hg^{2+}) and particle-bound mercury (Hg^p) in flue gas (ASTM International, 2002). Hg^p is first collected by a Teflon filter. Then, three impingers with KCl solution are used to capture Hg^{2+}. An

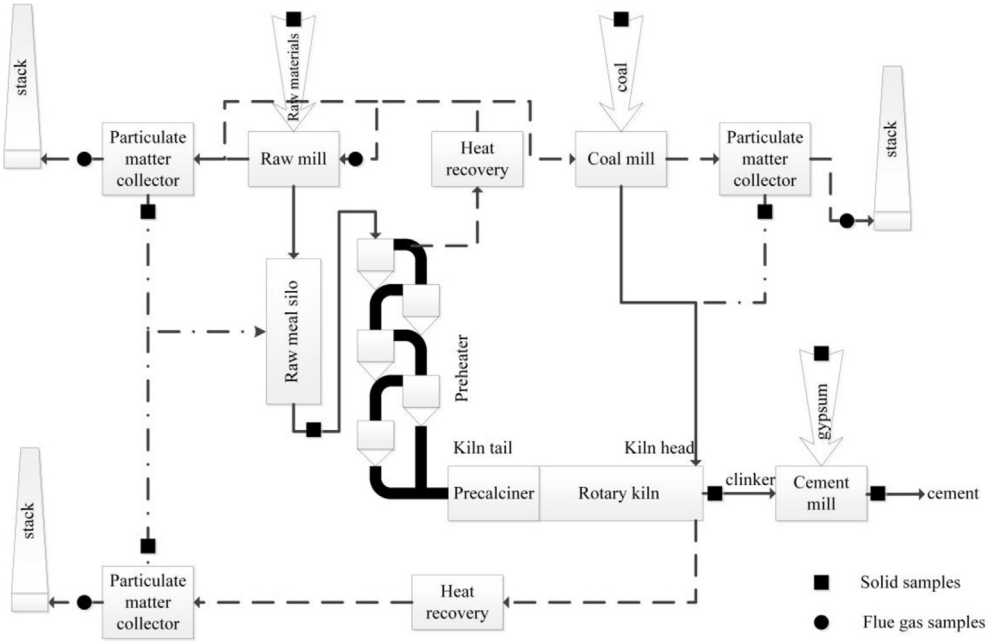

Fig. 1. A schematic representation of cement manufacturing process.

impinger with H_2O_2 + HNO_3 and three impingers with H_2SO_4 + $KMnO_4$ solution oxidize and absorb Hg^0. At the end, an impinger with silica gel removes the moisture in the flue gas. All of the impingers are put in an ice bath to ensure full absorption of mercury. Both the probe used to sample the flue gas and the filters are heated to 130 °C to avoid the adsorption of mercury. After sampling, the mercury in each impinger is recovered by $SnCl_2$ and measured by cold vapor atomic absorption spectrophotometry (CVAAS), which has a detection limit of 0.05 μg/L.

Solid materials were sampled simultaneously with the sampling of flue gas, and the United States Environment Protection Agency (US EPA) Method 7473 (Lumex RA915+, Russia) was adopted to determine the mercury concentrations in the solid samples. The solid samples were thermally and chemically decomposed, followed by the amalgamation and detection by Cold Vapor Atomic Fluorescent Spectrophotometry (CVAFS) with a detection limit of 0.5 μg/kg.

2.4. Quality assurance and quality control

To improve the representativeness of the test results and to reduce the measurement error, one measurement at each sampling site was taken over 1–2 h, and the measurements at each sampling site were repeated at least three times. Most solid samples were collected every two days during the entire test period, and the number of all solid samples collected was more than three, as presented in Supporting Information. The details about the representativeness of the cement plants, mode, and sampling process are discussed in Supporting Information. Because mercury emissions are dependent on the mercury concentrations in raw materials and fuel, the emission factors vary with cement plants. Large uncertainty exists in the emission factor because of limited samples. However, over 90% of mercury input from raw materials and fuel is emitted into the atmosphere due to the PM recycling as indicated by this study, therefore the results of this study help to improve the accuracy of the emission inventory estimated from the mass balance method.

Each of the seven impingers in the sampling train of the OHM was recovered and analyzed separately. The mercury concentration in all of the reagents was determined and found to be under the detection limit. The error in the analytical procedure is less than 5%.

Solid samples were first dried at 40 °C to a constant weight. The loss of mercury in the samples could be ignored. Then, homogenization and pulverization were performed. In this study, each solid sample was analyzed at least three times to obtain an average result. Standard reference materials from the National Institute of Standards and Technology, USA (1632c, coal) and National Research Center for Certified Reference Materials, China (GSS-5, soil) were used to guarantee the analytical quality. The mercury mass balance was conducted according to the mercury concentration of flue gas and solid samples, and the mercury recovery rate was found to be in the range of 101%–127%, which is acceptable for field tests (Mlakar et al., 2010; Senior et al., 2003).

3. Results and discussion

3.1. Mercury concentrations in solid samples

Mercury concentrations in different solid samples are shown in Table 1. The mercury concentrations in limestone, the main raw material, were 16 ppb in Plant 1, 18 ppb in Plant 2, and 42 ppb in Plant 3. Other materials including sandstone, shale, clay, and coal gangue had mercury concentrations from 6 to 47 ppb, which are comparable with that in the limestone. Iron-containing materials had a mercury concentration as high as 402 ppb. Other researchers have obtained similar results for mercury concentrations in raw materials (Johansen and Hawkins, 2003; Paone, 2010). The results from this study also fell into the range summarized by Sikkema et al. (2011).

Coal was the only fuel used in these three cement plants. The mercury concentration in coal was in the range of 20–40 ppb. Previous studies indicated that the average mercury concentration in Chinese coal was 190 ppb (Streets et al., 2005) or 170 ppb (Zhang et al., 2012). Zhang et al. (2012) reported that the average mercury

Table 1
Hg concentration of solid samples in cement manufacturing process.

Materials from the process		Plant 1 (Sichuan Province)	Plant 2 (Sichuan Province)	Plant 3 (Shandong Province)
Raw materials (ppb)	Limestone	16 ± 3	18 ± 1	42 ± 39
	Sandstone	19 ± 0	47 ± 6	6 ± 1
	Shale	35 ± 8	–	–
	Clay	–	14 ± 4	–
	Coal gangue	–	–	49 ± 40
	Iron-rich materials	402 ± 9	27 ± 4	187 ± 80
	Nickel-rich materials	–	10 ± 1	–
Fuel (ppb)	Coal	25 ± 3	36 ± 18	26 ± 4
Samples in process (ppb)	Coal powder	544 ± 10	113 ± 4	–
	Raw meal	296 ± 3	37 ± 2	–
	Particulate matter at the kiln tail	1992 ± 951	428 ± 36	–
	Particulate matter at the kiln head	572 ± 243	14 ± 3	–
Product (ppb)	Clinker	1 ± 1	3 ± 2	3 ± 6
	Gypsum	499 ± 83	473 ± 95	–
	Cement	61 ± 0	35 ± 1	–

Note: "–"means no sample or not used in manufacturing process.

concentration was 163 ppb with a range of 51–386 ppb in Shandong Province and 335 ppb with a range of 206–541 ppb in Sichuan Province. The United States Geological Survey (USGS) reported that the average mercury concentration of coal was 131 ppb in Shandong Province and 90 ppb in Sichuan Province (United States Geological Survey, 2004). The mercury concentration in coal was affected by several factors, including the mine location and depth (Tian et al., 2013).

The mercury concentrations in the solid samples indicate the characteristics of mercury behavior in the cement manufacturing process. The input to the kiln system is called raw meal, which is a mixture of different raw materials (approximately 90% on a weight basis) and PM collected by the FF of the raw mill at the kiln tail and the ESP at the kiln head. In this study, mercury concentrations of the raw meal were 296 ppb and 37 ppb in Plant 1 and Plant 2, respectively. Mercury concentrations of the PM from the FF and ESP were 1992 ppb and 572 ppb, respectively, in Plant 1, and 428 ppb and 14 ppb, respectively, in Plant 2. Obviously, PM from the FF and ESP is the main source of mercury in raw meal and for the kiln system. The concentrated mercury in the recycled PM results in a higher mercury content in the cement manufacturing process compared with the mercury input from the raw materials. This point is also confirmed by the mercury concentration in the flue gas emitted from the kiln system, as discussed in the next section. The difference between the mercury concentrations in the raw meal in Plants 1 and 2 is mainly from the different processes of mercury enrichment, which will be discussed in Section 3.3.

The mercury concentrations in coal powder from the FF of the coal mill were also very high, 544 ppb in Plant 1 and 113 ppb in Plant 2 because of the coal preheating. The mercury concentrations of clinker were less than 4 ppb for all three cement plants. However, the cement had a relatively high mercury concentration, 61 ppb in Plant 1 and 35 ppb in Plant 2, which was mainly due to adding the gypsum from the flue gas desulfurization system (FGD) of the power plants. The mercury concentrations in gypsum were 499 ppb in Plant 1 and 473 ppb in Plant 2. The temperature of the process of adding gypsum to clinker to produce cement is usually below 100 °C. The results of temperature programmed decomposition of gypsum and fly ashes have indicated that there is little mercury emission below 100 °C (Liu et al., 2013; Lopez-Anton et al., 2011; Rallo et al., 2010). Therefore the mercury emissions from such process can be ignored.

3.2. Mercury concentration and speciation in flue gas

Table 2 gives the concentrations of different mercury species at different sampling sites in the three cement plants, which are normalized to dry flue gas in standard conditions (273.15 K, 1 atm).

3.2.1. Mercury release from the kiln system

The mercury concentrations of different chemical forms in flue gas before the raw mills in Plant 1 and Plant 2 are presented in Fig. 2. The total mercury concentrations in the two plants were 195.6 and 43.4 μg/m^3, respectively. To evaluate the mercury enrichment, we can compare the tested results with the "equivalent mercury concentration," which is the calculated mercury concentration assuming no PM recycling and preheating of raw materials and coal. With the assumption of no PM recycling, the

Table 2
Hg concentration in the flue gas.

Hg concentration (μg/m^3)		Before raw mill	After FF of raw mill at kiln tail	After FF of coal mill at kiln tail	After ESP at kiln head
Plant 1	Hg^0	18.9 ± 18.1	2.4 ± 0.3	0.8 ± 0.8	0.6 ± 0.4
	Hg^{2+}	124.5 ± 18.5	25.7 ± 19.6	9.2 ± 3.9	3.4 ± 2.2
	Hg^p	52.3 ± 24.7	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Hg^t	195.6 ± 30.8	28.1 ± 19.9	9.9 ± 4.4	4.0 ± 2.0
Plant 2	Hg^0	1.5 ± 0.7	3.8 ± 1.3	1.0 ± 1.5	9.2 ± 3.2
	Hg^{2+}	33.0 ± 10.1	1.0 ± 0.4	1.7 ± 1.1	21.9 ± 5.9
	Hg^p	8.9 ± 4.4	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
	Hg^t	43.4 ± 11.5	4.8 ± 1.4	2.6 ± 1.8	31.0 ± 8.9
Plant 3	Hg^0	–	3.0 ± 2.9	7.7 ± 7.7	2.3 ± 3.1
	Hg^{2+}	–	16.6 ± 5.7	5.9 ± 5.2	0.2 ± 0.1
	Hg^p	–	0.2 ± 0.2	0.6 ± 0.7	0.2 ± 0.2
	Hg^t	–	19.8 ± 3.1	14.2 ± 11.2	2.7 ± 3.2

Note: "–"means no sampling at this site or no such facility.

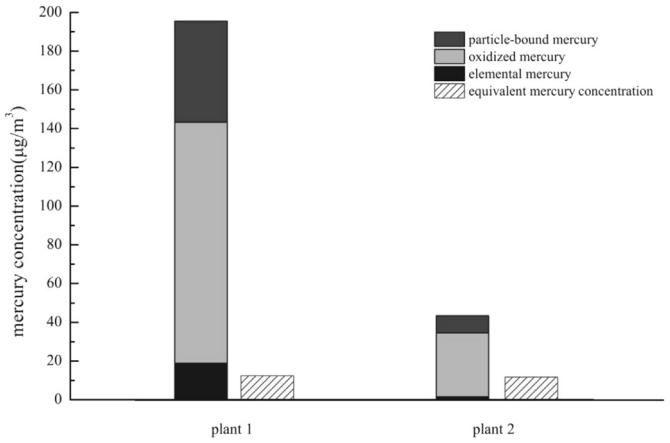

Fig. 2. Mercury speciation before raw mill and comparison with equivalent mercury concentration according to raw materials and coal.

mercury concentration in flue gas emitted from the kiln system can be calculated by dividing the mercury input from raw materials and coal by the total amount of flue gas produced by the kiln system. The equivalent mercury concentration in flue gas can be calculated with the following equation:

$$C_{Hg} = \frac{\sum C_i M_i}{\sum Q_j}$$

C_{Hg}: Equivalent mercury concentration in flue gas, μg/m^3; C_i: Mercury concentration of the i_{th} raw materials, ppb; M_i: Amount of the i_{th} raw materials, tons/d; Q_j: Amount of flue gas including that through the raw mill, coal mill and kiln head, km^3/d.

The theoretical calculation results for Plant 1 and Plant 2 were 12.6 and 11.9 μg/m^3, respectively, which indicates that the mercury is concentrated to approximate ratios of 15 and 4. This mercury enrichment in flue gas is consistent with discussions on mercury concentrations in raw meal. The mercury enrichment caused by the recycling of collected PM is the most important characteristic of mercury behavior in the precalciner process. If a component of the PM is not recycled in the cement production process and disposed of as hazardous waste, atmospheric emissions will significantly decrease (Zheng et al., 2012). The PM disposal will reduce mercury enrichment. Therefore, further quantitative studies are needed to answer the question of how the PM disposal affects the mercury emission and speciation.

The PM recycling also impacts the mercury speciation in flue gas. As shown in Fig. 2, approximately 64% and 76% of the mercury from plants 1 and 2, respectively, were in oxidized form (Hg^{2+}). Hg^p accounted for approximately 27% and 20% in plants 1 and 2, respectively. Hg^0 only contributed a very small part of the total mercury (Hg^t) in flue gas. Mercury oxidation in flue gas is mainly affected by the compositions of the flue gas and fly ashes and the cooling rate of the flue gas. The physical and chemical characteristics of flue gas in cement plants are more supportive of oxidized mercury than those in power plants. For example, the PM concentration in flue gas before the raw mill in Plant 1 is in the range of 10.2–11.6 g/Nm^3, much higher than the PM concentration in the flue gas after the boiler of power plant, which is usually lower than 1 g/Nm^3. High PM concentration in the cement manufacturing process can promote the mercury oxidation through the heterogeneous reaction occurring on the surface of fly ashes because more catalytic sites are provided. Additionally, iron-containing materials are also used as raw materials in cement plants, and Fe_2O_3 is proved to be catalytic for mercury oxidation (Dunham et al., 2003). The lower temperature at the inlet of the raw mill (approximately 200 °C) also results in a higher tendency of oxidization. The longer residence time in cement plants than that in power plants can promote the oxidation of mercury, as reviewed by Zheng et al. (2012). However, currently it is unclear about the exact mechanisms. A high proportion of Hg^{2+} indicates a strong adsorption ability on the surface of raw materials and PM. This finding was confirmed by the removal efficiency across different facilities as discussed later.

3.2.2. *Mercury in flue gas exhaust*

As presented in Table 2, the mercury concentrations in the flue gas from the kiln tail were the highest in Plant 1 and Plant 3, with average values of 28.1 and 19.8 μg/m^3, respectively, whereas the concentrations at the kiln head were only 4.0 and 2.7 μg/m^3, respectively. However, the mercury concentration at the kiln head reached 31.0 μg/m^3, higher than that at the kiln tail of Plant 2. This might be mainly caused by the high Hg concentration in the flue gas of the kiln head, as well as poor Hg co-benefit performance of the ESP in Plant 2. Though the mercury concentration before the ESP in Plant 2 was not measured, it was calculated to be 31.9 μg/m^3 from the mercury concentration after the ESP and the mercury concentration of the PM from the ESP. The mercury removal efficiency of the ESP in Plant 2 was less than 5%. Moreover, the low mercury removal efficiency in the ESP can also reduce the mercury enrichment in mercury cycles. Although the flue gas preheating the coal was the same as that preheating the raw materials, the mercury concentration after the CF combination was lower than that after the RF combination in each plant. The mercury concentration after the CF combination was within the range of 2.6–14.2 μg/m^3.

Hg^{2+} remained the main species in exhausted flue gas, which was attributed to the high proportion of Hg^{2+} in the flue gas before the raw mill. More than 60% of the mercury was in the oxidized form except at three sampling sites in the tested cement plants: after the FF of the raw mill at the kiln tail in Plant 2, after the FF of the coal mill and after the ESP at the kiln head in Plant 3. However, the amount of flue gas from the three stacks in each plant differed greatly. Thus, the emitted mercury speciation from a cement plant should be calculated considering both the speciation of mercury and the amount of flue gas.

3.3. *Mercury removal efficiencies*

The mercury in flue gas is removed when the flue gas flows through the RF or CF combined facility. The removal efficiencies of the facility combinations are calculated according to the mercury concentrations at the inlet and outlet of these facilities. The removed mercury enters the raw meal because of the PM recycling. The removed mercury flows back to the kiln system, causing mercury enrichment in the cement manufacturing process. Therefore, the mercury enrichment is associated with the removal efficiencies of the facilities. A higher mercury removal efficiency of ESP or FF means a higher mercury enrichment. If more mercury is emitted through the stacks because of either the poor performance of the PM collector or the low mercury adsorption on the raw materials and coal, less mercury is concentrated in the cycles.

For Plant 1 and Plant 2, the removal efficiencies of the RF combination were 86% and 89%, whereas those of the CF combination were 95% and 94%, respectively. The removal efficiencies for each combination in the two cement plants were quite close. In Plant 1, all mercury species were efficiently removed from the flue gas in each combination. However, in Plant 2, only a small part of Hg^0 was removed, and Hg^0 increased in the RF combination. The increase of Hg^0 might be caused by the reductive composition in the raw materials, especially the organic compounds in the clay, as

Table 3
Mercury mass balance in the tested cement plants.

		Plant 1		Plant 2		Plant 3	
		Hg flow	Percentage (%)	Hg flow	Percentage (%)	Hg flow	Percentage (%)
Hg input (g/d)	Limestone	75.6	41.8	93.6	59.9	312.5	74.1
	Sandstone	7.2	4.0	33.1	21.1	2.1	0.5
	Shale	23.2	12.8	–	–	–	–
	Clay	–	–	2.2	1.4	–	–
	Coal gangue	–	–	–	–	49.5	11.7
	Iron-rich materials	63.0	34.8	4.8	3.1	43.1	10.2
	Nickel-rich materials	–	–	0.9	0.6	–	–
	Coal	11.9	6.6	21.8	21.8	14.8	3.5
	Total	181	100	156	100	422	100
Hg output (g/d)	Clinker	4.1	1.9	12.1	6.1	19.0	4.4
	Flue gas of kiln head	25.1	11.5	148.8	75.1	30.1	7.0
	Flue gas after raw mill	168.6	77.5	33.6	16.9	351.1	82.0
	Flue gas after coal mill	19.8	9.1	3.8	1.9	28.0	6.5
	Total	218	100	198	100	428	100
Hg output/input (%)		120		127		101	

Note: "–"means no sampling at this site or no such facility.

the two cement plants used different raw materials. The removal efficiency of the CF combination was higher than that of the RF combination in both Plant 1 and Plant 2. The property of the coal might be the main reason for the difference. In addition to the different characteristics of the raw materials and coal, the operation parameters of each facility, including residence time and cooling rate of flue gas, could also affect the removal efficiency. The high removal efficiencies of the two combinations contributed to the high mercury enrichment. However, a large difference exists between the mercury enrichment in Plant 1 and Plant 2 despite the similar mercury input from the raw materials and coal. The major reason for the difference is that the mercury removal efficiency of the ESP in Plant 2 is less than 5%. Therefore, more mercury is emitted through the stack after the ESP at the kiln head, and the mercury enrichment in Plant 2 is much lower than that in Plant 1.

The mercury emissions cannot be calculated from the mercury input and removal efficiencies because of the existing mercury cycles. The mercury emissions in the cement plants can be estimated from the mercury input from the raw materials and coal and the mercury output from clinker. This point will be discussed in the mass balance section.

3.4. Mercury mass balance

The mass balance calculation results of the three cement plants are shown in Table 3. The mercury recovery rates ranged from 101% to 127%. The mercury input from limestone accounted for a large proportion, 41.8%–74.1%, whereas other material contributions varied with plants. Iron-containing materials and shale contributed significant percentages, 34.8% and 12.8%, respectively, in Plant 1. Sandstone was a main source of mercury input with a percentage of 21% in Plant 2. For Plant 3, coal gangue and iron-containing materials brought 11.7% and 10.2% of the mercury input. Other material contributions together accounted for less than 10% of the mercury input in each plant. Coal, the only fuel for the three cement plants, played a small role in mercury input except in Plant 2. The mercury output included atmospheric emissions from the three stacks and clinker. Our results indicated that less than 10% of mercury was retained in clinker, and more than 90% of mercury was emitted into the atmosphere. This is consistent with a previous study (Won and Lee, 2012). Therefore, the mercury emissions can be estimated based on the mercury concentrations and flow amounts of solid materials, including different raw materials, fuel, and clinker.

Among the atmospheric emissions from the three stacks after the raw mill, after the coal mill and at the kiln head, less than 10% of mercury was emitted after the coal mill in all of the three plants primarily because of the small amount of flue gas compared with the other two stacks. The proportion of mercury emitted through the left two stacks, however, was significantly affected by the operation factors. In Plant 1 and Plant 3, approximately 80% of the mercury was emitted through the stack after the raw mill, whereas in Plant 2, the flue gas at the kiln head contributed approximately 75%. This difference was mainly caused by the low mercury removal efficiency of the ESP at the kiln head in Plant 2. A stronger adsorption in the raw mill/coal mill and the higher removal efficiency of the FF/ESP can result in a higher mercury enrichment in the whole process. If any of these facilities remove less mercury, that is, more mercury flows out of the facility, the mercury enrichment will be consequently decreased and the distribution of mercury in the whole process will be changed. These results also indicate that emission tests in the cement plants should include all three stacks.

The full mercury mass flows in these three cement plants were 181 g/d, 156 g/d and 422 g/d for Plants 1, 2, and 3, respectively. The larger mercury mass flow in Plant 3 was attributed not only to the higher concentration of mercury in limestone but also to the larger clinker production in the test period.

Table 4
Mercury emissions and speciation in the exhaust gas.

Hg emissions (g/d)	Plant 1			Plant 2			Plant 3		
	Hg^0	Hg^{2+}	Hg^p	Hg^0	Hg^{2+}	Hg^p	Hg^0	Hg^{2+}	Hg^p
After raw mill	14.6	154.0	0.0	26.6	7.0	0.0	53.4	293.6	4.1
After coal mill	1.5	18.3	0.0	1.4	2.4	0.0	15.1	11.7	1.2
Kiln head	3.5	21.6	0.0	44.0	104.9	0.0	27.0	2.1	1.1
Total	19.6	193.9	0.0	72.0	114.2	0.0	95.6	307.3	6.3
Proportion (%)	9.2	90.8	0.0	38.7	61.3	0.0	23.4	75.1	1.6
Emission factor[a] (g/t clinker)	0.062			0.044			0.072		
Emission factor[b] (g/t clinker)	0.058			0.035			0.069		

[a] Including coal contribution.
[b] Excluding coal contribution.

3.5. Mercury emission and speciation

The speciated mercury emission amounts from the three stacks in each cement plant are shown in Table 4. Unlike power plants, Hg^{2+} was the main mercury species emitted from the cement plants. The percentage of Hg^{2+} was in the range of 61.3–90.8%. Hg^p

Table 5
Comparison of mercury emission factors from cement plants.

Mercury concentration in limestone (ppb)	Process	APCDs	Emission factor	Particulate matter recycle?	
–	–	–	0.065–0.1 g Hg/t cement	–	Pacyna et al. (2010)
4.9–79.1	Precalciner	FF + ESP	0.026–0.034 g Hg/t clinker	No	Won and Lee (2012)
7.9 ± 7	Precalciner	ESP (FF)[a]	0.001–0.027 g Hg/t clinker[b]	Yes	Mlakar et al. (2010)
2	Precalciner	FF	0.0138 g Hg/t clinker	Yes	Zhang (2007)
16 ± 3	Precalciner	FF & ESP[c]	0.062 g Hg/t clinker	Yes	This study
18 ± 1	Precalciner	FF & ESP[c]	0.044 g Hg/t clinker	Yes	This study
42 ± 39	Precalciner	FF & ESP[c]	0.072 g Hg/t clinker	Yes	This study
11 ± 3	Vertical kiln	FF	0.0036 g Hg/t cement	N.A	Li (2011)
–	Vertical kiln	Wet scrubber	0.15 g Hg/t clinker	Yes	Zhang (2007)
–	Vertical kiln	FF	0.0069 g Hg/t clinker	N.A	Zhang (2007)
–	Rotary kiln	ESP	0.0229 g Hg/t clinker	N.A	Zhang (2007)
–	Rotary kiln	FF	0.0033 g Hg/t cement	No	Li (2011)
28 ± 10	Rotary kiln	FF	0.012 g Hg/t cement	No	Li (2011)
–	Rotary kiln	FF	0.0087 g Hg/t cement	No	Li (2011)

Note: "N.A" and "–": not available; APCDs: air pollution control devices; ESP: electrostatic precipitator; FF: fabric filter.
[a] ESP was changed to FF between two test period.
[b] Calculated results with a production of 900,000 t/y and 1–24 kg Hg emitted because of lack of emission factor calculation.
[c] FF was installed after raw mill and coal mill, and ESP was installed at the kiln head.

was negligible in the mercury emissions because of the high removal efficiency of the FF.

The emission factors including and excluding the coal contribution are shown in Table 4. The emission factors excluding the coal contribution were calculated by multiplying the proportion of mercury input from the raw materials with the emission factors including the coal contribution to mercury because the mercury recovery rate was not always 100% in field tests. The emission factors of the three plants including the coal contribution are 0.062, 0.044 and 0.072 g/t clinker, or 0.054, 0.038, 0.063 g/t cement. The above calculation assumed that 1 t of clinker and 0.15 t of other materials such as gypsum are mixed to produce cement. The emission factor of 0.065–0.1 g/t cement for calculating the mercury emissions from cement plants in China appears to be 26–94% higher compared with the average emission factor in this study. Compared with the emission standard in the United States, the mercury emissions in our study of 97.7, 137.3, and 158.3 lb/million tons clinker are much higher than the 30-day rolling average standards for existing and new cement plants of 55 or 21 lb/million tons clinker (US EPA, 2011). However, the mercury emissions are directly dependent on the mercury concentration in raw materials and fuel. The emission factors obtained in Sichuan Province (Plant 1 and Plant 2) are lower than that in Shandong Province (Plant 3), and there is even a difference between the two plants located close to each other in the same province.

Large uncertainty in mercury emission estimates from cement plants exists in the emission factor. Table 5 summarizes the mercury emission factors in previous field test studies. To help understand the difference in emission factors, Table 5 also lists the mercury concentration in limestone as the main raw material, the process, the air pollution control devices (APCDs) and whether all of the PM is recycled. The mercury emission factor of 0.065–0.1 g Hg/t cement used in global inventories from 1995 to 2010 (Pacyna and Pacyna, 2002; Pacyna et al., 2006, 2010; Pirrone et al., 2010) was much higher than recent field test results (Mlakar et al., 2010; Won and Lee, 2012). A cement plant with a relatively high mercury concentration in limestone often has a higher mercury emission factor, although other raw materials may make a significant contribution. However, this positive relationship is affected by whether all of the PM is recycled. When there is a low mercury concentration in clinker, the mercury concentrations in raw materials and the proportion of recycled PM determine the mercury emissions. This is considered to be the main reason that the cement plant with a 28 ppb mercury concentration in limestone has a lower emission factor than that of the cement plant with a 16 ppb or 18 ppb mercury concentration. Therefore, comprehensive studies of mercury concentrations in raw materials and the percentage of cement plants with PM recycling are needed for more accurate estimates of mercury emissions.

4. Conclusions

In this study, three cement plants were tested to investigate the mercury behavior and emission speciation in the cement manufacturing process. Though the mercury concentrations in raw materials and coal are generally quite low, the mercury concentration in the flue gas generated in the kiln is high because of the PM recycling and the use of the flue gas to preheat the raw materials and coal. The raw-mill + FF and the coal-mill + FF remove 87% and 94%, respectively, of mercury in the flue gas. The mercury removed by the raw-mill + FF and the coal-mill + FF enters the kiln system again because of the PM recycling, which results in over 90% of the mercury being emitted into the atmosphere. The mercury emission factors in this study are 0.044, 0.062 and 0.072 g/t clinker for the three plants tested, which are higher than the mercury emission standard of cement plants in the United States but lower than the emission factor previously used for mercury emission estimates of Chinese cement plants. Oxidized mercury is the major species emitted from cement plants, accounting for 91%, 61%, and 75% of total Hg in the flue gas of the three plants. These results not only help improve the accuracy of mercury emission inventory in China but also have strong implications on mercury control policies.

Acknowledgments

This study was supported by the Major State Basic Research Development Program of China (973 Program) (No. 2013CB430001), the Natural Science Foundation of China (No. 21077065), and the Collaborative Innovation Center for Regional Environmental Quality. The corresponding author, Dr. Shuxiao Wang, is supported by the Program for New Century Excellent Talents in University (NCET-10-0532) and the China Scholarship Council.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2014.04.029.

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