



## Mercury Speciation and Mass Distribution of Cement Production Process in Taiwan

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### ABSTRACT

In this study, the mercury (Hg) speciation and mass distribution at two cement plants located in northern and eastern Taiwan were investigated. Gaseous Hg in the kiln flue gas was sampled by the Ontario Hydro method, and the solid samples were collected to analyze the Hg mass balance. The total Hg concentrations in the raw mill electrostatic precipitator (ESP) input of the two plants were 155.70 and 64.62  $\mu\text{g Nm}^{-3}$ , respectively, which were higher than those at any other sampling point. Approximately 97.5 and 86.5% of the Hg in the raw mill ESP input at Plants 1 and 2, respectively, was particle-bound. Elemental Hg was the major gaseous Hg species emitted into the atmosphere from these two cement plants, accounting for 56.4 to 98.2% of the total Hg in the flue gas. The total Hg mass output was calculated to be 61.374 and 204.596 mg-Hg per metric ton-clinker ( $\text{mg ton}^{-1}$ ) for cement Plants 1 and 2, respectively. The Hg emission factors for Plants 1 and 2 were thus 0.059 and 0.196 g-Hg per metric ton-cement ( $\text{g ton}^{-1}$ ), respectively. These results improve our understanding of Hg emissions from cement plants in Taiwan and provide useful information for selecting Hg control technology.

**Keywords:** Cement plant; Precalciner production; Mercury speciation; Mercury distribution; Atmospheric mercury.

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### INTRODUCTION

Mercury (Hg) has been recognized as a global pollutant due to its high toxicity, long-distance transport, persistence, and bioaccumulability in the environment. It is well known that Hg could cause adverse effects to human body and animals. Therefore, atmospheric Hg emissions from anthropogenic sources have caused great concerns in recent years (Chen *et al.*, 2016; Maruszczak *et al.*, 2016). Atmospheric Hg could be contributed from different sources such as coal combustion, non-ferrous smelting, and cement production (UNEP, 2013a; Guo *et al.*, 2016). Utilization of Hg-containing fly ash in construction materials, agriculture, absorbents, smelting industries, and geotechnical engineering with heat treatment such as drying, roasting, and calcining could also lead to Hg reemission (Wang *et al.*, 2016b).

Notably, studies have indicated that global anthropogenic Hg emissions from cement plants increased from 114  $\text{ton year}^{-1}$  in 1990 to 189  $\text{ton year}^{-1}$  in 2005 and reached 236  $\text{ton year}^{-1}$  in 2010 (Pacyna *et al.*, 2006 2010; Pirrone *et al.*, 2010; Wang *et al.*, 2014). The Minamata Convention on Mercury delivered in March 19, 2013, addressed the necessity of prevention and abatement of Hg emission and release via global and legally-binding agreements between countries (UNEP, 2013b). The Minamata Convention also indicated that reducing the atmospheric Hg emissions from cement plants should be implemented.

Cement production could contribute 10% of the global Hg emissions (Wang *et al.*, 2014). The cement and mineral production was also considered as the second largest anthropogenic source of Hg emissions (Zheng *et al.*, 2012). China is the largest cement producer in the world, accounting for more than half of the world's production, which was approximately 2.4 billion ton of cement in 2013 (NBS, 2015; Wang *et al.*, 2016a). In China, industrial coal combustion, coal-fired power plants, non-ferrous metal smelting, and cement production were identified to be the major Hg emission sources; a study also indicated that Hg emissions increased from 16 ton in 2000 to 98.3 ton in 2010 from

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Chinese cement plants (Zhang *et al.*, 2015). Therefore, obtaining a better understanding of Hg distribution and speciation in the cement production process is critical, which would greatly help in improvement of comprehending the global Hg emission inventory and control of the atmospheric Hg emissions.

In the cement production process, particulate matter recycling, preheating of the raw materials, and coal use and flue gas desulfurization derived gypsum caused Hg to be emitted to the atmosphere and accumulated in cement products (Wang *et al.*, 2014). Atmospheric Hg is generally present in three major forms, including gaseous elemental Hg (GEM or Hg<sup>0</sup>), reactive gaseous Hg (RGM or Hg<sup>II</sup>), and particle-bound Hg (PBM or PHg) (Schroeder and Munthe, 1998; Zhang *et al.*, 2015, 2017). Over 90% of the Hg input from raw material was emitted into the atmosphere due to Hg cycling (Wang *et al.*, 2014). Won and Lee indicated that Hg<sup>0</sup> was the major Hg speciation (i.e., approximately 85%); only 15% oxidized Hg (Hg<sup>2+</sup>) was in the cement plants' flue gas (Won and Lee, 2012). However, the study further implied that oxidized Hg was the major species in the atmosphere emitted from cement plants, accounting for 61 to 91% of the total Hg (Wang *et al.*, 2014). Research conducted by Zhang *et al.* (2016) indicated that a greater fraction (29–90%) of Hg from non-ferrous metal smelting, cement, and iron and/or steel production (Zhang *et al.*, 2016). Gaseous Hg from the cement production process is very difficult to remove with conventional air pollution control devices because of its high volatility and low concentration. Those studies also suggested that information on Hg speciation emitted from cement plants is still limited. Thus, more field measurements on Hg speciation and distribution in the cement production process are of importance.

Hg could be present in different forms with various emission factors within the cement clinker production process because the raw materials could be greatly different. Cement plants receive Hg from both fuels and raw materials used in the production process. The Hg fate could be in three stages including vaporization, adsorption, and recycling in cement production process (Sikkema *et al.*, 2011). A study indicated that the Hg emission factors were 0.044–0.072 g ton<sup>-1</sup> clinker in three tested cement plants (Wang *et al.*, 2014). Zhang *et al.* (2015) also showed that the Hg emission factor of cement production increased from 0.027 in 2000 to 0.052 g-Hg ton<sup>-1</sup> in 2010. Dahai *et al.* (2015) exhibited that the annual Hg emission was estimated in the range of 8.6–52 ton of cement production based on data in China in 2013.

Compared to the previous studies of Hg measurements and control technology employed in coal-fired power plants (Tsai *et al.*, 2017; Song *et al.*, 2018), there is still a lack of experience related to characteristics of Hg cycling, speciation, and mass balances for cement kilns in Taiwan. Therefore, the main objectives of this study are (1) better understanding the Hg mass flows and speciation from cement production process based on the field samplings conducted in two cement plants using the precalciner process in Taiwan, (2) obtaining the emission factors of these two cement

plants, and (3) estimating the annual operating costs if an adequate control technology is applied to these two cement plants. We analyzed the Hg concentrations of gaseous and solid samples, including different types of raw materials, fuel, raw meal, and the particulate matter to understand Hg mass flows and speciation. Finally, the Hg mass balance, speciation distribution, and the Hg concentration emitted into the atmosphere were comprehended.

## EXPERIMENTAL SECTION

### *Mercury Concentration in Raw Material and Solid Product*

Field tests in this study were conducted on precalciner production lines in two cement plants located at northern (Plant 1) and eastern Taiwan (Plant 2). The sampling campaigns were conducted between July 1 and 29, 2014; duplicated samplings were done on both Plants 1 and 2. The cement clinker production processes are presented in Figs. 1–2. These diagrams also show the sampling points of solid/fuel gas samples and materials of analysis. Three fundamental stages contain preparation of feedstock, production of clinker, and preparation of cement in the cement production process. Thus, various solid samples were obtained from the entire cement manufacturing process presenting in several major forms, namely fuel ash, limestone, clay, silica sand, fly ash, waste, cement products, raw materials and solid product. Total Hg concentration in solid samples was analyzed by combustion atomic absorption spectrometry with gold amalgamation (MA-2000, Nippon Instruments Corporation). The method was described in details in EPA-NIEA M318.01C and USEPA-Method 7473 (U.S. EPA, 2007). The advantage of this method is that sample pretreatment is not needed, with a lower limit of detection (LOD) compared to the method using acid digestion and measurement by cold vapor atomic absorption spectrometry (CVAAS; NIEA M317.03B). Controlled heating in an oxygenated decomposition furnace was used to liberate Hg from solid samples in the instrument. The sample was dried and then thermally and chemically decomposed within the decomposition furnace. The decomposition products were then carried to an amalgamator that selectively trapped Hg; then the amalgamator was rapidly heated, releasing Hg vapor. The absorbance (peak height or peak area) of Hg concentration was determined at 253.7 nm as a function (USEPA, 2007). The LOD for the determination of total Hg was 0.01 ng and the method LOD for determination of total Hg was 0.002 µg g<sup>-1</sup>.

### *Mercury Speciation in Exhausted Flue Gas*

Flue gas samples from the entire cement production processes were collected and analyzed. Figs. 1–2 also show the sampling points of flue gas in Plants 1 and 2, respectively. The Hg speciation in exhausted flue gas was analyzed by the standard test method for elemental, oxidized, particle-bound and total Hg in flue gas generated from coal-fired stationary sources (i.e., D6784-02, Ontario Hydro Method; ASTM, 2002), by which the Hg speciation of elementary Hg (Hg<sup>0</sup>), oxidized Hg (Hg<sup>2+</sup>) and particle-bound Hg (PHg) in flue gas was investigated. The quartz

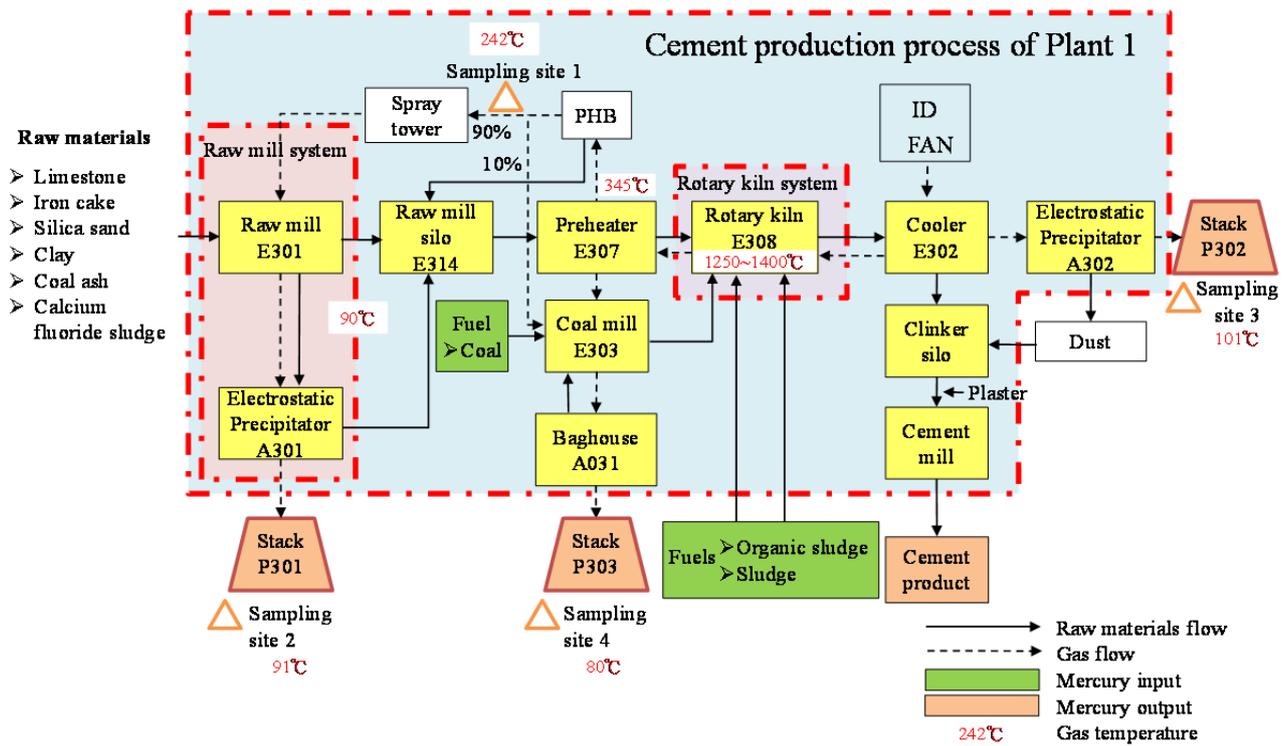


Fig. 1. Material and gas flows and sampling points in cement production process (Plant 1).

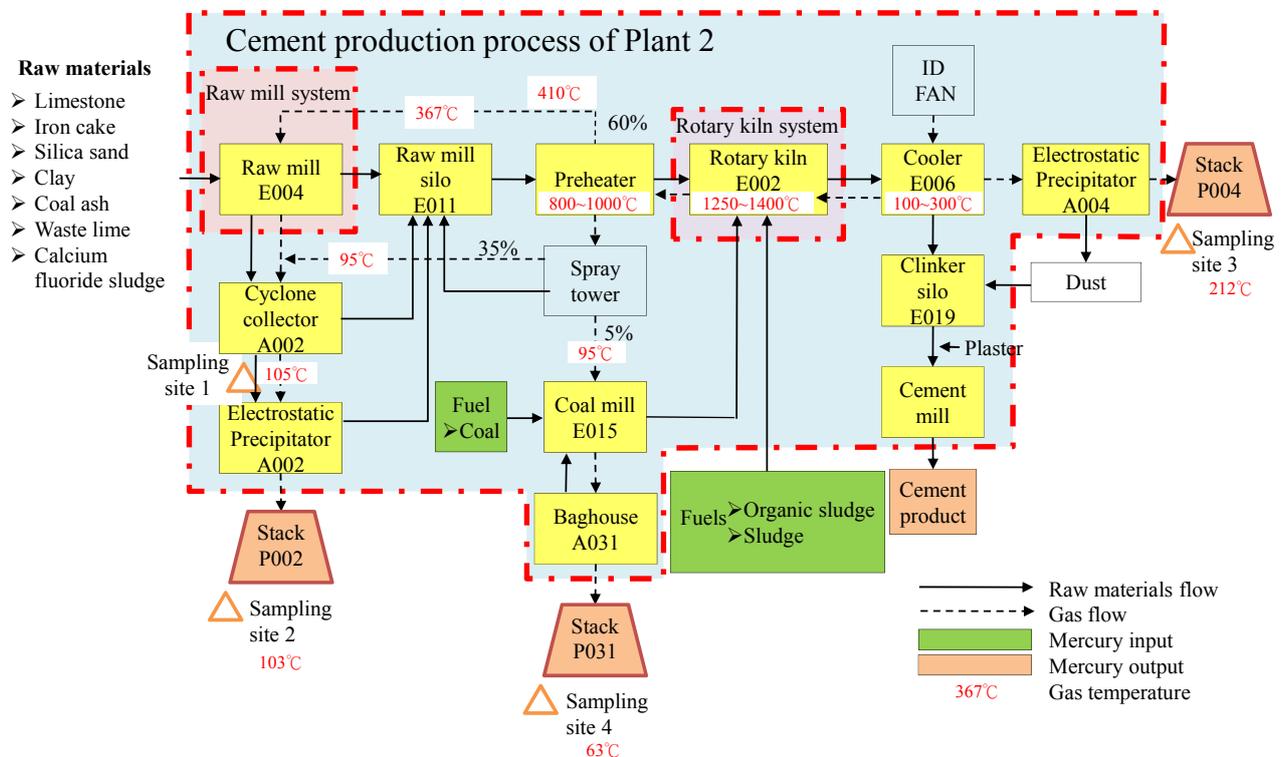


Fig. 2. Material and gas flows and sampling points in cement production process (Plant 2).

fiber filter was used to collect PHg; Hg<sup>2+</sup> was captured by impingers with KCl solution. Then, Hg<sup>0</sup> was oxidized and absorbed by impingers with H<sub>2</sub>O<sub>2</sub> + HNO<sub>3</sub> solution and H<sub>2</sub>SO<sub>4</sub> + KMnO<sub>4</sub> solution. In order to ensure full absorption

of Hg, all of the impingers were put in an ice bath. Silica gel was used to remove moisture in the flue gas. The samplers (probe and filters) were heated to 120°C to prevent water and acid condensation. After sampling, the Hg concentration

was analyzed by CVAAS (RA3320, Nippon Instruments Corporation), by which the detection range of concentration was 0.5–100  $\mu\text{g Nm}^{-3}$ .

### Quality Assurance and Quality Control

To ensure the representativeness of the experimental results and to decrease the experimental error, one measurement at each sampling site was conducted for 2 h, and the measurements at each sampling site were duplicated. The solid samples were collected every day during the entire test period. Each of the seven impingers in the sampling train of the OHM was recovered and analyzed separately. Each solid sample was analyzed at least three times to obtain an average result.

Solid samples were first dried at room temperature to a constant weight. Then, homogenization and pulverization were performed. In this study, each solid sample was analyzed at least twice to obtain an average result. Standard reference materials from the National Institute of Standards and Technology, USA (1632c, coal) were used to guarantee the analytical quality. The Hg mass balance was conducted according to the Hg concentration of flue gas and solid samples, and the Hg recovery rate was found to be in the range of 85.3–96.2%, which is acceptable for field tests (Mlakar *et al.*, 2010).

## RESULTS AND DISCUSSION

### Mercury Concentration in Different Solid Samples

Table 1 shows the Hg concentrations in different solid samples. Limestone was the main raw material in the cement production process and the Hg concentration in limestone was 0.013  $\text{mg kg}^{-1}$  in Plant 1 and 0.051  $\text{mg kg}^{-1}$  in Plant 2, respectively. Other materials including iron cake, silica sand, and clay had Hg concentrations from 0.007 to 0.408  $\text{mg kg}^{-1}$ , which are comparable to that in the limestone. Notably, that iron cake in Plant 2 had the greatest Hg concentration (0.408  $\text{mg kg}^{-1}$ ) as compared to those in the other raw materials and the iron cake used in Plant 1 showed great variation in the Hg content. These experimental results are similar with those reported in previous research examining Hg concentrations in raw materials (Wang *et al.*, 2014;

Paone, 2010). Moreover, the coal ash, a raw material from waste, had Hg concentration as high as 0.399  $\text{mg kg}^{-1}$  in Plant 1 and 0.396  $\text{mg kg}^{-1}$  in Plant 2, respectively. Compared with the coal ash, calcium fluoride sludge and waste lime had lower Hg concentrations in Plants 1 and 2. Bituminous coal was the only fuel used in these two cement plants. The Hg concentration in bituminous coal was 0.285  $\text{mg kg}^{-1}$  in Plant 1 and 0.335  $\text{mg kg}^{-1}$  in Plant 2. A study indicated that the average Hg concentration in Chinese coal was 0.335  $\text{mg kg}^{-1}$  with a range of 0.206 to 0.541  $\text{mg kg}^{-1}$  in Sichuan Province (Zhang *et al.*, 2012). The sludge in Plant 1 had higher Hg concentration (0.412  $\text{mg kg}^{-1}$ ) as compared to Plant 2 (0.098  $\text{mg kg}^{-1}$ ). Note that waste lime and oil sludge were not used in the manufacturing process of Plant 1; additionally, Hg concentration in the oil sludge of Plant 2 was under the detection limit.

The measurement of Hg concentration in the different solid samples shows the large variation in the characteristics of Hg in the cement production process, which could be greatly different, plant to plant, and case-specific. Typically, the semi-finished product is called raw meal and finished product is called clinker. The experimental results indicated that the Hg concentrations of raw meal were 0.326  $\text{mg kg}^{-1}$  and 0.203  $\text{mg kg}^{-1}$  in Plants 1 and 2, respectively. The sampling results also suggest that different processes of Hg enrichment may lead to difference between the Hg concentration in the raw meal in Plants 1 and 2. The Hg concentration of clinker was < 0.003  $\text{mg kg}^{-1}$  for Plant 1 and the Hg concentration of clinker was under the detection limit in Plant 2. The raw meal had higher Hg concentration as compared to that in clinker because raw meal was a mixture of different raw materials. The raw meal having elevated Hg concentration may also stem from the waste gas dust recycling in the cement manufacturing process. The Hg present in the finished products (clinker) in cement production process, on the contrary, was in a low level and can be ignored for mass balance calculation.

### Mercury Concentration in Flue Gas Exhaust

Table 2 shows the concentration of Hg species at different sampling points in the two cement plants. The Hg concentrations of different species in cement kiln flue

**Table 1.** Hg concentration of solid materials in cement manufacturing process.

Materials for/produced from the process		Plant 1 ( $\text{mg kg}^{-1}$ )	Plant 2 ( $\text{mg kg}^{-1}$ )
Raw material	Limestone	0.013 $\pm$ 0.006	0.051 $\pm$ 0.009
	Iron cake	0.007 $\pm$ 0.003	0.408 $\pm$ 0.117
	Silica sand	0.011 $\pm$ 0.001	0.036 $\pm$ 0.008
	Clay	0.059 $\pm$ 0.001	0.094 $\pm$ 0.001
Raw material from waste	Coal ash	0.399 $\pm$ 0.047	0.396 $\pm$ 0.027
	Calcium fluoride sludge	0.009 $\pm$ 0.006	0.045 $\pm$ 0.005
	Waste lime	—*	0.069 $\pm$ 0.025
Fuel	Bituminous coal	0.285 $\pm$ 0.057	0.335 $\pm$ 0.113
Fuel from waste	Sludge (Organic sludge)	0.412 $\pm$ 0.071	0.098 $\pm$ 0.037
	Oil sludge	—*	0.000
Semi-finished products	Raw meal	0.326 $\pm$ 0.016	0.203 $\pm$ 0.007
Finished products	Clinker	0.003 $\pm$ 0.001	0.000

\*Waste lime (i.e., Raw materials from waste) and oil sludge (i.e., fuel from waste) were not used in Plant 1.

**Table 2.** Concentration of Hg species in flue gas of two cement plants.

Hg species concentration ( $\mu\text{g Nm}^{-3}$ )		Raw mill ESP input	Raw mill stack (P301/P002)	Cooler stack (P302/P004)	Coal mill stack (P303/P031)
Plant 1	GEM	3.79	23.31	0.07	6.15
	RGM	0.12	0.29	0.05	0.22
	PHg	151.79	0.34	0.01	0.22
	Hg <sub>total</sub>	155.70	23.94	0.13	6.59
Plant 2	GEM	8.39	47.80	0.18	1.68
	RGM	0.33	0.59	0.006	0.03
	PHg	55.90	0.54	0.002	0.01
	Hg <sub>total</sub>	64.62	48.93	0.19	1.72

gases are also shown in Fig. 3 for clarity. The total Hg concentration in the raw mill ESP input in Plants 1 and 2 was 155.70 and 64.62  $\mu\text{g Nm}^{-3}$ , respectively. The raw mill ESP input had the largest Hg concentration as compared to those in other sampling points such as raw mill stack, cooler stack, and coal mill stack. The gaseous elemental Hg (GEM) was the main species in three stack sampling points. Notably, the experimental results for Hg enrichment in flue gas were consistent with the discussion on Hg concentration in solid sample (mill meal). As shown in Table 2, the particle-bound Hg (PHg) concentration in the flue gas from the raw mill ESP input was the highest in both Plants 1 and 2, with the concentration of 151.79 and 55.90  $\mu\text{g Nm}^{-3}$ , respectively; however, the PHg concentration at the cooler stack was only 0.01 and 0.002  $\mu\text{g Nm}^{-3}$ , respectively. Notably, the GEM concentration at the raw mill stack reached 23.31 (Plant 1) and 47.80  $\mu\text{g Nm}^{-3}$  (Plant 2), greater than that at cooler stack and coal mill stack of Plants 1 and 2. The variation in the concentration and speciation of flue gas Hg at different sampling points was thus shown highly influenced by the condition of the sampling points such as temperature, the enrichment effects occurring in the raw mill system due to recirculation of the flue gas (Figs. 1–2), and the removal efficiency of the particulate removal device such as ESP. A study also indicated that temperature and oxidative atmosphere greatly affected the Hg speciation and higher shares of Hg<sub>(g)</sub> and Hg<sup>0</sup> are expected at higher temperatures (Mlakar *et al.*, 2010). In addition, the results also indicated that condensation of Hg<sup>0</sup> on particulates or walls is expected to be significant under 200°C. If the temperature falls to about 100°C, Hg in the flue gas from the mill consists mostly of Hg<sub>(p)</sub>. In addition, the temperature decreases in the direction of flue gas flows. Therefore, the largest concentration of Hg<sub>(g)</sub> was measured in the gas from the preheater and that temperature was about 300°C. In the same direction the share of Hg<sup>0</sup> was falling and that of Hg<sup>2+</sup> was increasing (Mlakar *et al.*, 2010).

Table 3 shows the proportion of Hg species in the flue gas of the select sampling points in Plants 1 and 2. The experimental results indicated that approximately 97.5 and 86.5% of Hg in the raw mill ESP input from Plants 1 and 2, respectively, were particle-bound Hg (PHg); GEM accounted for approximately 2.4 and 13.0% in Plants 1 and 2, respectively. Reactive gaseous Hg (RGM) only contributed a very small part of the total Hg (Hg<sub>total</sub>) in flue gas at the raw mill ESP input. On the other hand, other sampling

points including raw mill stack, cooler stack, and coal mill stack had GEM from 56.4 to 97.4% and 95.8 to 98.2%, respectively, which showed highly different characteristics of Hg speciation as compared to those in the raw mill ESP input because ESP removed significant amounts of particulate matter. A high proportion of PHg also suggest stronger adsorption ability on the surface of raw materials or fly ashes, then PHg can be removed by air pollution control devices. Fig. 3 also shows the Hg transformation and speciation and concentration change in cement kiln flue gases in Plants 1 and 2, respectively. Notably, the sampling points of cooler stack in Plant 1 had higher percentage of RGM (39.4%) than that in Plant 2 (i.e., 3.1%) (Table 3), suggesting that the compositions of the flue gas and fly ashes and the cooling rate of flue gas may lead to the variation in the percentage of RGM of different plants.

#### **Mercury Mass Balances and Cycles in Cement Plant**

The Hg mass balance calculation results of cement production processes, raw mill system, and rotary kiln system in the two cement plants are presented in Tables 4–6. The Hg flows are also shown in Figs. 4–5. Firstly, the calculated Hg recovery was 85.3 and 96.2% in Plants 1 and 2, respectively, indicating that we may underestimate the Hg mass in the output flow for Plant 1, but the high accuracy in the Hg sampling and measurement for Plant 2 was validated. For raw materials, the Hg input from limestone accounted for high proportion of approximately 24.9 and 26.6% for Plants 1 and 2, respectively, as compared to other input sources, whereas the contributions of other Hg input sources varied with plants. Clay and coal ash contributed significant percentages, 8.7 and 10.8%, respectively, in Plant 1 and 9.3 and 30.6%, respectively, in Plant 2. Other material contributions together accounted for < 6% of Hg input in the two cement plants (Table 6). The fuels include bituminous coal, organic sludge, and oil sludge. Notably, bituminous coal was the major source of Hg input with a percentage of 54.2 and 19.3%, respectively, in Plants 1 and 2. On the other hand, organic sludge and oil sludge played a small role in Hg input in the two cement plants. The Hg outputs included the release from clinker and emissions from the three stacks. The results suggested that < 3.5% of Hg was retained in clinker, and > 85% of Hg was emitted into atmosphere by the three stacks. These experimental results are consistent with that reported in previous research (Wang *et al.*, 2014).

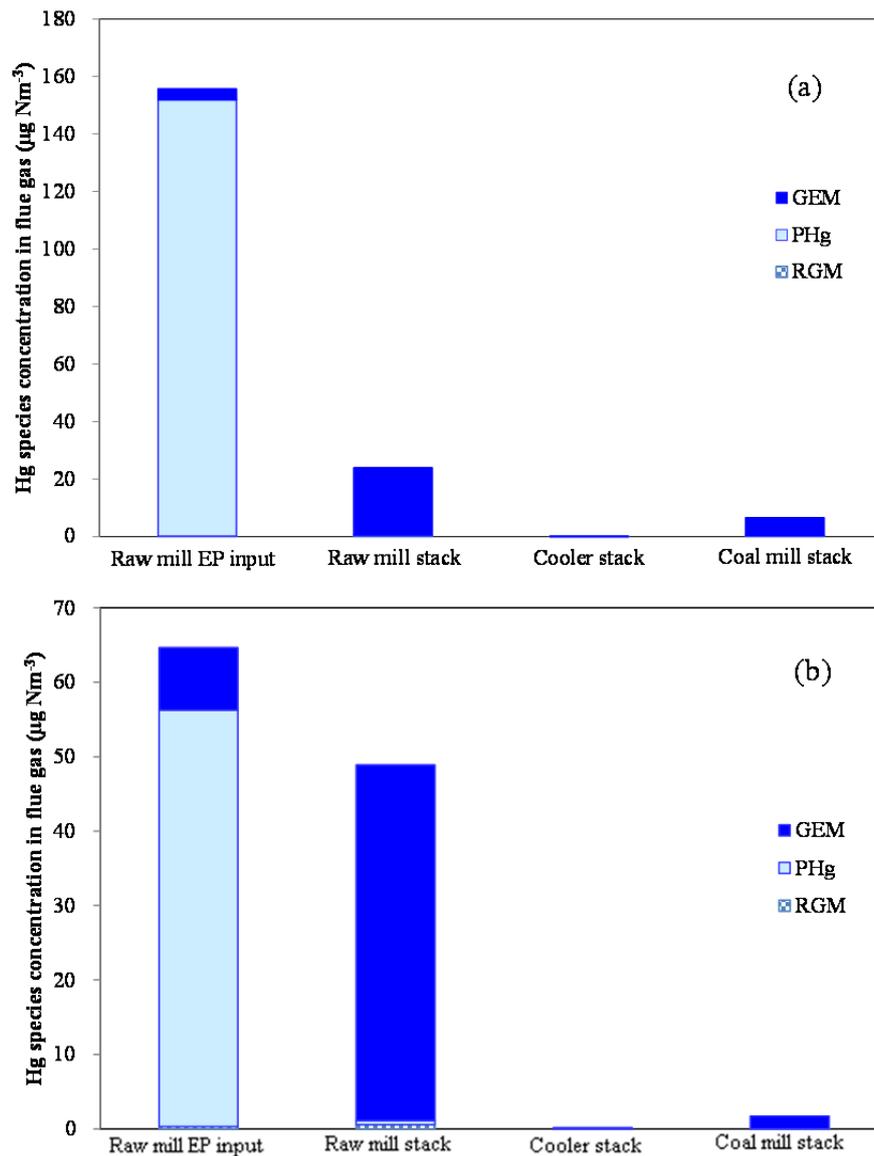


Fig. 3. Mercury concentration and speciation in cement kiln flue gases in (a) Plant 1 and (b) Plant 2.

Table 3. Proportion of Hg speciation in flue gas of select sampling points for Plants 1 and 2.

Sample points in Plant 1	Mercury species percentage (%)		
	GEM	RGM	PHg
Raw mill ESP input	2.4	0.1	97.5
Raw mill stack (P301)	97.4	1.2	1.4
Cooler stack (P302)	56.4	39.4	4.2
Coal mill stack (P303)	93.3	3.3	3.3
Sample points in Plant 2	Mercury species percentage (%)		
	GEM	RGM	PHg
Raw mill ESP input	13.0	0.5	86.5
Raw mill stack (P002)	97.7	1.2	1.1
Cooler stack (P004)	95.8	3.1	1.1
Coal mill stack (P301)	98.2	1.4	0.4

The experimental results also indicate that cooler stack and coal mill stack play a small role in Hg emission into the atmosphere; < 3% of Hg was emitted from cooler stack

and coal mill stack in the tested two plants, which is greatly affected by the operation conditions of the cement plants. Importantly, approximately 78.9 and 96.0% of Hg

**Table 4.** Mercury balances in cement plant (Plant 1).**(a) Cement production process**

Sample			Flow rate (g h <sup>-1</sup> )			Flow rate/input (%)
			Run 1	Run 2	Average	
Input	Raw material	Limestone	4.22	2.36	3.29	24.9%
		Iron cake	0.04	0.08	0.06	0.5%
		Silica sand	0.09	0.12	0.11	0.8%
		Clay	1.16	1.14	1.15	8.7%
	Raw material from waste	Coal ash	1.25	1.61	1.43	10.8%
		Calcium fluoride sludge	0.004	0.01	0.01	0.1%
	Fuel	Bituminous coal	8.16	6.17	7.17	54.2%
	Fuel from waste	Sludge	0.00	0.00	0.00	0.0%
	Input total		14.92	11.50	13.21	100.0%
Output	Product	Clinker	0.37	0.55	0.46	3.5%
		Raw mill (P301)	10.33	10.53	10.43	78.9%
	Stack	Cooler stack (P302)	0.08	0.03	0.05	0.4%
		Coal mill (P303)	0.37	0.27	0.32	2.4%
Output total		11.14	11.39	11.26	85.3%	

**(b) Raw mill system**

Sample			Flow rate (g h <sup>-1</sup> )			Flow rate/input (%)
			Run 1	Run 2	Average	
Input	Raw material	Limestone	4.22	2.36	3.29	3.1%
		Silica sand	0.09	0.12	0.11	0.1%
		Iron cake	0.04	0.08	0.06	0.1%
		Clay	1.16	1.14	1.15	1.1%
	Raw material from waste	Coal ash	1.25	1.61	1.43	1.4%
		Sludge	0.00	0.00	0.00	0.0%
		Calcium fluoride	0.00	0.01	0.01	0.0%
	Stack	Preheater exhaust (estimated)	96.30	102.70	99.50	94.3%
	Input total		103.07	108.02	105.54	100.0%
Output	Product	Silo	92.70	97.66	95.18	90.1%
	Stack	Raw mill stack (P301)	10.33	10.53	10.43	9.9%
Output total		103.03	108.19	105.61	100.1%	

**(c) Rotary kiln system**

Sample			Flow rate (g h <sup>-1</sup> )			Flow rate/input (%)
			Run 1	Run 2	Average	
Input	Raw material	Silo	92.70	97.66	95.18	93.0%
	Fuel	Coal ash	8.16	6.17	7.17	7.0%
Input total			100.86	103.84	102.35	100.0%
Output	Product	Clinker	0.37	0.55	0.46	0.4%
		Preheater exhaust (estimated)	107.00	114.11	110.56	108.0%
	Stack	Cooler stack (P302)	0.08	0.03	0.05	0.1%
		Coal mill (P303)	0.37	0.27	0.32	0.3%
Output total			107.81	114.97	111.39	108.8%

were emitted through the raw mill stack. The Hg removal efficiency of the ESP before the raw mill in Plants 1 and 2 may determine the difference in Hg concentration in the raw mill stack. The high removal efficiency of the ESP or baghouse and a stronger adsorption of Hg in the raw mill/coal mill are the main cause of a high Hg enrichment in the production process. In other words, if the particulate control devices remove less Hg, resulting in a decrease in the Hg enrichment in the raw mill region, then the distribution of Hg in the cement production process will be perturbed and redistributed. Then, the Hg emissions from

cooler stack and coal mill stack may accordingly increase. The total Hg output mass was calculated to be 61.374 and 204.596 mg ton<sup>-1</sup> clinker for cement Plants 1 and 2, respectively (Table 6). Based on an empirical equation that clinker to cement ratio = 0.96, which was provided by the cement company, the Hg emission factors for Plants 1 and 2 were 0.059 and 0.196 g ton<sup>-1</sup> cement, respectively. Compared to the average emission factor of 0.105 g ton<sup>-1</sup> cement, with a range between 0.01 and 1.5 g ton<sup>-1</sup>, the factors obtained in this study are comparable to those obtained in previous research (AMAP/UNEP, 2013). Plant 2

**Table 5.** Mercury balances in cement plant (Plant 2).**(a) Cement production process**

Sample			Flow rate (g h <sup>-1</sup> )			Flow rate/input (%)
			Run 1	Run 2	Average	
Input	Raw material	Limestone	7.07	5.47	6.27	26.6%
		Iron cake	1.72	1.11	1.41	6.0%
		Silica sand	0.68	0.50	0.59	2.5%
		Clay	2.18	2.22	2.20	9.3%
	Raw material from waste	Coal ash	7.55	6.89	7.22	30.6%
		Waste lime	1.13	0.68	0.90	3.8%
		Calcium fluoride	0.30	0.25	0.28	1.2%
	Fuel	Bituminous coal	3.48	5.63	4.55	19.3%
	Fuel from waste	Organic sludge	0.10	0.18	0.14	0.6%
		Oil sludge	0.00	0.00	0.00	0.0%
Input total			24.21	22.92	23.56	100.0%
Output	Product Stack	Clinker	0.00	0.00	0.00	0.0%
		Raw mill (P301)	24.03	21.20	22.62	96.0%
		Cooler stack (P302)	0.04	0.03	0.04	0.2%
		Coal mill (P303)	0.03	0.005	0.02	0.1%
Output total			24.10	21.24	22.67	96.2%

**(b) Raw mill system**

Sample			Flow rate (g h <sup>-1</sup> )			Flow rate/input (%)	
			Run 1	Run 2	Average		
Input	Raw material	Limestone	7.07	5.47	6.27	9.9%	
		Iron cake	1.72	1.11	1.41	2.2%	
		Silica sand	0.68	0.50	0.59	0.9%	
		Clay	2.18	2.22	2.20	3.5%	
	Raw material (waste)	Coal ash	7.55	6.89	7.22	11.5%	
		Waste lime	1.13	0.68	0.90	1.4%	
		Stack	Preheater exhaust (estimated)	45.07	43.77	44.42	70.5%
	Input total			65.39	60.63	63.01	100.0%
	Output	Product Stack	Silo	41.36	39.43	40.40	64.1%
			Raw mill stack (P301)	24.03	21.20	22.62	35.9%
Output total			65.40	60.63	63.01	100.0%	

**(c) Rotary kiln system**

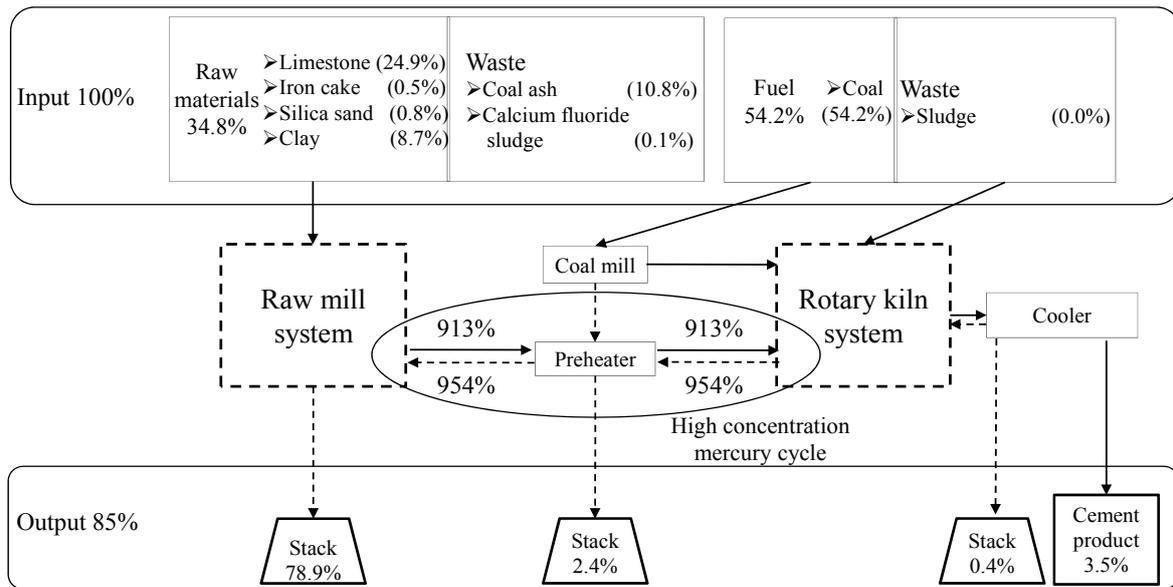
Samples			Flow rate (g h <sup>-1</sup> )			Flow rate/input (%)
			Run 1	Run 2	Average	
Input	Raw material	Silo	41.36	39.43	40.40	89.0%
		Waste addition feed	Calcium fluoride sludge	0.30	0.25	0.28
	Fuel	Bituminous coal	3.48	5.63	4.55	10.0%
		Organic sludge	0.10	0.18	0.14	0.3%
		Oil sludge	0.00	0.00	0.00	0.0%
	Input total			45.25	45.49	45.37
Output	Product Stack	Clinker	0.00	0.00	0.00	0.0%
		Preheater exhaust (estimated)	45.07	43.77	44.42	97.9%
		Cooler stack (P004)	0.04	0.03	0.02	0.1%
		Coal mill (P031)	0.03	0.005	0.02	0.0%
Output total			45.14	43.81	44.46	98.0%

had a larger Hg output mass flow as compared to Plant 1, which was attributed to the higher concentration of Hg in limestone and coal ash used in Plant 2. The annual Hg emissions from these two plants can thus be estimated. The annual cement production is approximately 2.30 and

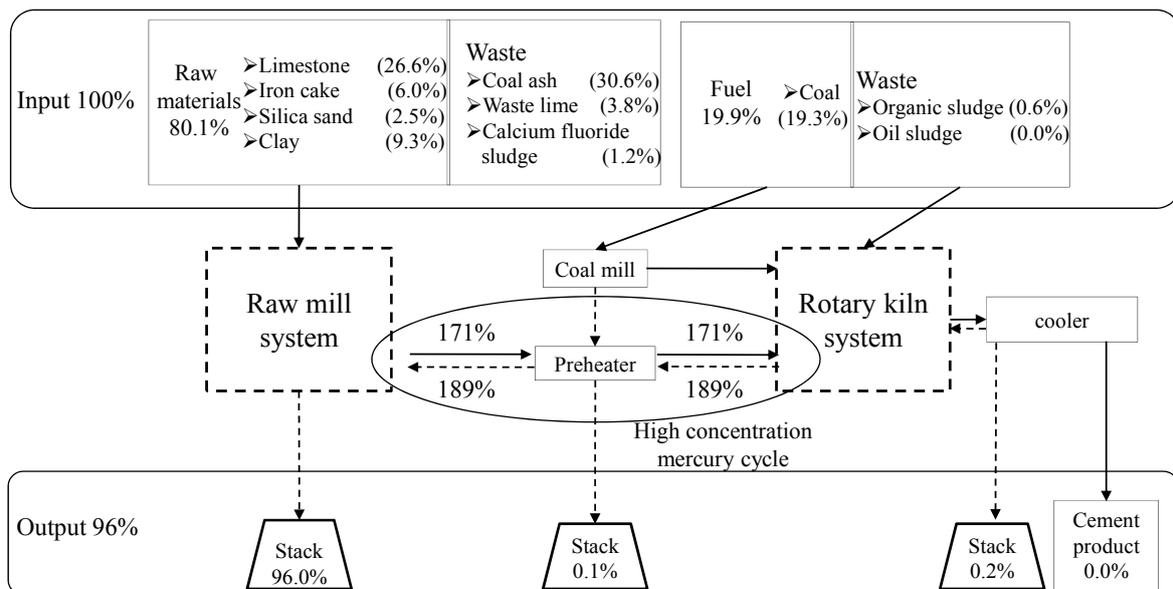
0.895 million ton year<sup>-1</sup> for Plants 1 and 2, respectively. Consequently, Hg emission from these two plants will account for 10.2% (by Plant 1) and 13.3% (by Plant 2) of the total Hg emission (1.328 ton-Hg yr<sup>-1</sup>) in Taiwan, based on year 2016 investigation by Taiwan EPA.

**Table 6.** Mercury mass flow calculation for Plants 1 and 2.

	Plant 1					Plant 2				
	Average Hg concentration (mg kg <sup>-1</sup> (solid); µg Nm <sup>-3</sup> (gas))	Hg flow rate (g h <sup>-1</sup> )	Hg flow rate (%)	Clinker product (mg ton <sup>-1</sup> )	Average Hg concentration (mg kg <sup>-1</sup> (solid); µg Nm <sup>-3</sup> (gas))	Hg flow rate (g h <sup>-1</sup> )	Hg flow rate (%)	Clinker product (mg ton <sup>-1</sup> )		
Input										
Raw materials										
	Limestone	0.013	3.29	24.9%	17.927	6.27	26.6%	56.599		
	Iron cake	0.007	0.06	0.5%	0.329	1.41	6.0%	12.782		
	Silica sand	0.011	0.11	0.8%	0.575	0.59	2.5%	5.303		
	Clay	0.059	1.15	8.7%	6.267	2.20	9.3%	19.812		
	Coal ash	0.399	1.43	10.8%	7.799	7.22	30.6%	65.157		
Waste addition feed	Waste lime	-	-	-	-	0.90	3.8%	8.175		
	Calcium fluoride sludge	0.009	0.01	0.1%	0.051	0.28	1.2%	2.519		
Fuel	Bituminous coal	0.285	7.17	54.2%	39.063	4.55	19.3%	41.014		
	Organic sludge	0.412	0.00	0.0%	0.000	0.14	0.6%	1.262		
	Oil sludge	-	-	-	-	0.00	0.0%	0.000		
Total		-	13.21	100.0%	72.011	23.56	100.0%	212.622		
Output										
Product	Clinker	0.003	0.46	3.5%	2.500	0.00	0.0%	0.000		
Stack	Raw mill stack	23.941	10.43	78.9%	56.824	22.62	96.0%	204.107		
	Cooler stack	0.114	0.05	0.4%	0.300	0.04	0.2%	0.332		
	Coal mill stack	6.588	0.32	2.4%	1.750	0.02	0.1%	0.158		
Total		-	11.26	85.3%	61.374	22.67	96.2%	204.596		



**Fig. 4.** Mercury mass flow for cement Plant 1.



**Fig. 5.** Mercury mass flow for cement Plant 2.

### **Mercury Exhaust from Cement Plants and Control Strategy Evaluation**

The Hg emission concentrations from the raw mill stack of Plants 1 and 2 are shown in Table 7. The concentration of Hg emission was 23.94 and 48.90  $\mu\text{g Nm}^{-3}$  for Plants 1 and 2, respectively. Because of the higher concentration of Hg in limestone and coal ash and the larger clinker production in the test period for Plant 2, Plant 2 had higher Hg emission concentration than Plant 1. These results also suggest a large uncertainty in Hg emission estimates from cement production process based on the emission factors currently used. Wang *et al.* (2014) indicated that cement plant using the limestone with a relatively high Hg concentration often had a greater Hg emission as compared

to using other raw materials. In this study, however, we also noticed that various raw materials and waste could have higher Hg concentration than limestone. The type and effectiveness of several control approaches could also reduce the emission of Hg from stack. Table 7 also lists the proposed methods of Hg reduction by combination of source control or end-of-pipe Hg removal. The results suggest that activated carbon injection may be the most effective removal technology for Hg as compared to other methods of reduction; the Hg emission could be controlled to  $< 15 \mu\text{g Nm}^{-3}$  under adequate operation. The advantages of activated carbon injection include: (1) The investment cost could be low ( $< \text{USD } 3 \text{ kW}^{-1}$ ) if only a carbon injection device is installed; (2) device transformation is easy; (3) the

**Table 7.** Estimated Hg emission concentration from the raw mill stack for Plants 1 and 2 if control strategy is applied.

Reduction method*	Hg concentration emission from stack ( $\mu\text{g Nm}^{-3}$ )	
	Plant 1	Plant 2
Measured Hg emission concentration	23.94	48.90
Sample selection (Assuming reduction efficiency 20%)	19.15	39.12
No waste added	21.33	31.17
Dust not to melt down	-	23.74
No waste added and dust not to melt down	-	15.13
Activated carbon injection (If removal efficiency = 70%)	7.18	14.67

\* Information pertaining to the mercury removal efficiency of control strategy was referred to: Faizul M. Mohee, A review of the Effects and Control of the Mercury Emissions from Cement industry, EIC Climate Change Technology Conference 2013.

technology has been extensively used on bituminous coal or sub-bituminous coal combustion in boilers; and (4) high removal efficiency for Hg can be achieved (> 90%) (Zhao *et al.*, 2014). However, based on the information from another study (Sikkema *et al.*, 2011), if following the primary dust collector, an adsorbent (typically powdered activated carbon optimized for mercury control) is injected into the facility's flue gas to achieve a high percentage of Hg capture; then, a secondary dust collector is installed to capture the adsorbent, removing it from the gas stream. Based on that study, the annual operating costs of Plants 1 and 2 could be approximately \$9 million (2.3 million tons of capacity) and \$3.6 million (0.9 million tons of capacity), respectively, estimated as a capital investment of \$20 million. These results showed that activated carbon injection could be very expensive. Lowering the activated carbon cost and the capital investment will be the key to success for this Hg control technology applied in cement plants.

## CONCLUSIONS

The present study examined the behavior and emission speciation of Hg during the cement production process at two cement plants in Taiwan. The experimental results indicated that the average Hg concentration was 0.326 and 0.203  $\text{mg kg}^{-1}$  in the raw meal and < 0.003  $\text{mg kg}^{-1}$  and below the detection limit in the clinker at Plants 1 and 2, respectively. Hence, the amount of Hg released from the finished product (i.e., clinker) during the cement production process is negligible. The total Hg concentration in the raw mill ESP input was 155.70 and 64.62  $\mu\text{g Nm}^{-3}$  at Plants 1 and 2, respectively, which was higher than concentrations sampled at the other locations, viz., the raw mill stack, cooler stack, and coal mill stack. Approximately 97.5 and 86.5% of the Hg in the raw mill ESP input at Plants 1 and 2, respectively, was particle-bound (PHg). Also, a far higher percentage of reactive gaseous Hg (RGM) was measured at the cooler stack of Plant 1 (39.4%) than of Plant 2 (3.1%), suggesting that the compositions of the flue gas and fly ash and the cooling rate of the flue gas can cause the distribution of RGM to vary. The total Hg mass output was calculated to be 61.374 and 204.596  $\text{mg ton}^{-1}$  for cement Plants 1 and 2, respectively, resulting in emission factors of 0.059 and 0.196  $\text{g-Hg ton}^{-1}$ . Plant 2 exhibited a larger Hg mass flow than Plant 1, which was attributable to the

higher concentration of Hg in its limestone and coal ash feedstock. The emission concentration of Hg was 23.94 and 48.90  $\mu\text{g Nm}^{-3}$  at Plants 1 and 2, respectively. Compared to other methods, activated carbon injection may possess the highest potential for removing Hg in these two plants. The results obtained from this study help characterize Hg emissions from Taiwanese cement plants using precalciner systems.

## ACKNOWLEDGMENTS

This work was financially supported by the Environmental Protection Administration, Taiwan (EPA-103-FA12-03-A054). The opinions expressed in this paper are not necessarily those of the sponsor.

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Received for review, May 13, 2018

Revised, September 15, 2018

Accepted, October 9, 2018