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# Characteristics of mercury cycling in the cement production process

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## HIGHLIGHTS

- Hg is enriched 3–9 times the mercury input from raw materials and fuel.
- Hg mass flows in raw mill system account for 57–73% of Hg output of kiln system.
- Hg enrichment is affected by the proportion of mercury cycled back.
- Dust treatment can reduce the atmospheric mercury emissions by 31–70%.

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## ABSTRACT

The mercury cycling caused by dust shuttling significantly increases the atmospheric emissions from cement production. A comprehensive understanding of this mercury cycling can promote the development of mercury emission control technologies. In this study, the characteristics of mercury cycling in the cement production process were first investigated. Furthermore, the mercury enrichment and effects of dust treatment were evaluated based on the field tests conducted in two Chinese cement plants. The mercury cycling between the kiln system and the raw mill system was the most important aspect and contributed 57–73% to the total amount of mercury emitted from the kiln system. Mercury emitted from the kiln system with flue gas was enriched as high as 3.4–8.8 times in the two tested plants compared to the amount of mercury in the raw materials and coal due to mercury cycling. The mercury enrichment can be significantly affected by the proportion of mercury cycled back to the kiln system. The effects of dust treatment were evaluated, and dust treatment can efficiently reduce approximately 31–70% of atmospheric mercury emissions in the two plants. The reduction proportion approximately linearly decreased with the proportion of mercury removed from the collected dust.



## 1. Introduction

Mercury has become one of the most important global pollutants due to its toxicity, long-distance transport, persistence and bio-accumulation [1]. Atmospheric mercury emissions from anthropogenic sources have caused wide concerns in recent years. The atmospheric mercury emissions from different sources have been estimated in a number of global inventories [1–6]. The predominant anthropogenic sources include coal combustion, nonferrous smelting and cement production [1]. Cement production was estimated to contribute approximately 10% to the global mercury emission inventory in 2010 [1] and was therefore listed as a priority for atmospheric mercury emission control at the Minamata Convention on Mercury [7]. As the largest cement producer in the world, China produced approximately 2.4 billion tons of cement in 2013, accounting for more than half of the world's production [8]. The atmospheric mercury emissions from Chinese cement plants were estimated to increase at an annual growth rate of 7.4% from 1995 to 2003 [9,10]. A recent study indicated that mercury emissions from Chinese cement plants increased from 16 tons in 2000 to 98.3 tons in 2010 [11]. In 2010, over 85% of Chinese cement production adopted the precalciner process, and the proportion is still rising [12]. Therefore, a comprehensive understanding of mercury behavior in the precalciner process for cement production is important for accurately estimating the mercury emissions and developing control strategies [13–16].

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In the precalciner process, the milled raw materials are preheated, pre-decomposed, and roasted in a rotary kiln system with coal as the fuel to produce clinker. The clinker is then milled with some other additives (mainly gypsum) to obtain cement. Mercury is vaporized into the flue gas in high-temperature rotary kiln systems and captured in low-temperature facilities, including raw mill, coal mill and dust collectors. The captured mercury is subsequently cycled back to the rotary kiln system with solid materials, especially the collected cement kiln dust (CKD) because all of the dust is shuttled to the rotary kiln in a cement production process (dust shuttling). Therefore, the mercury mass flows (the total amount of mercury in the flue gas or solid materials) between the high-temperature rotary kiln system and the low-temperature facilities can cause mercury cycling in the cement production process. Previous studies have confirmed this mercury cycling [17–21]. In a tested plant, the internal mercury mass flows were found to reach 20 g/h, which was 10 times as high as the emitted mercury mass flows of 0.1–2.4 g/h [17]. Another study found that the mercury concentration in the flue gas emitted from the kiln system reached 15 and 4 times as high as the equivalent mercury concentration based on mercury input from raw materials and coal, respectively [22]. The mercury concentration in a stack will experience a high peak when the raw mill is shut off because less mercury in the flue gas is captured in low-temperature facilities [23]. Therefore, understanding the mercury cycling characteristics is crucial to obtain a comprehensive knowledge of mercury enrichment in cement production. Over 90% of mercury input from raw materials and coal is eventually emitted into the atmosphere due to mercury cycling [22]. Based on mercury cycling, it may be feasible to reduce the atmospheric mercury emissions from the cement production process through dust treatment, in which the collected dust is treated outside the process and not directly shuttled [18]. However, the quantitative effects of dust treatment on atmospheric mercury emission reductions are currently unclear.

In this study, the mercury mass flows in mercury cycling and the overall process were systematically analyzed based on the field test results conducted in two Chinese cement plants using the precalciner process. For the first time, an evaluation index was established to assess the mercury enrichment in the precalciner cement production process. The influencing factors of mercury enrichment were also quantitatively discussed. The theoretic effects of dust treatment on atmospheric emission reduction were finally evaluated quantitatively.

## 2. Experiment

### 2.1. Field tests description and mercury flow analysis

Field tests in this study were conducted on the 5000 t/d precalciner production line in two Chinese cement plants, both of which were located in Sichuan Province. The detailed description of the tested plants (Plants 1 and 2), sampling procedures, analysis methods and quality assurance and quality control (QA/QC) were presented in our previous study and also in the supporting information [22]. The mercury emissions and speciation have been discussed through the mass balance for the whole cement production process in the previous study. The atmospheric mercury emissions from the two plants were 181 g/d and 156 g/d, respectively, which were dominantly composed of the oxidized mercury. The mercury was highly enriched in the flue gas emitted from the rotary kiln, and over 90% of the mercury input was emitted into the atmosphere due to mercury cycling. Therefore, this study will further systematically analyze the mercury enrichment and quantitatively assess the reduction effects of dust treatment based on a thorough investigation of mercury cycling.

The precalciner cement production process includes 4 parts: kiln system (preheater, precalciner and rotary kiln), raw mill system (raw mill and fabric filter (FF)), coal mill system (coal mill and FF), and kiln head system (electrostatic precipitator (ESP)). In the raw mill system, different raw materials are milled and preheated in the raw mill, and the dust in the flue gas is removed by the FF before the stack. Coal is prepared in the coal mill system with a similar process. The prepared raw materials are roasted in the kiln system to produce clinker with coal as fuel. The flue gas from the kiln system and emitted from the kiln tail (the end of the rotary kiln where the raw materials enter the kiln system) is used to preheat raw materials in the raw mill and coal in the coal mill. The flue gas emitted from the kiln head (the end of the rotary kiln where combustion air enters the kiln system) flows through an ESP to remove the dust. All of the dust collected at the kiln tail and kiln head in the production process are shuttled to the kiln system. Some additives (mainly gypsum) and clinker are finally milled to produce cement. Based on this production process, mercury in raw meal (the mixture of preheated raw materials and dust from FF in the raw mill system and ESP at the kiln head) and coal vaporizes in the kiln system and is then partly captured in the raw mill system, coal mill system and kiln head system. The captured mercury is finally recirculated into the kiln system along with the raw materials, coal and dust. Therefore, three so-called mercury cycling are established between the kiln system and each of the raw mill system, coal mill system and kiln head system. More information can be found in the supporting information.

The flue gas was sampled and analyzed with the Ontario Hydro Method (OH method) [24]. According to the OH method, particle-bound mercury ($Hg^p$) is first captured by a quartz filter. Oxidized mercury ($Hg^{2+}$) is then absorbed by KCl in 3 impingers. Elementary mercury ($Hg^0$) is finally oxidized and absorbed in a subsequent impinger with $H_2O_2 + HNO_3$ and three impingers with $H_2SO_4 + KMnO_4$. All of the solutions after sampling are recovered by $SnCl_2$ and detected by a cold vapor atomic absorption spectrophotometry (CVAAS) mercury analyzer. The mercury concentrations in the solid samples were detected with the United States Environment Protection Agency (US EPA) Method 7473 (Lumex RA915+, Russia). The mercury concentration was detected by cold vapor atomic fluorescent spectrophotometry (CVAFS) after decomposition. The mercury concentrations of the solid samples and most of the flue gas were also listed in our previous study. Based on the test results and flow amounts of solid materials and flue gas, the mercury mass flows in the cement production process could be calculated. The mercury mass flows in the four parts were investigated through the mass balance method. The mercury recovery rates were in the range of 71–128%, which are acceptable for field tests [17,25]. The overall mercury mass flows in the two plants were also calculated to provide an overall picture of the mercury behaviors in the cement production process.

### 2.2. Mercury enrichment evaluation

Because of the mercury cycling, the mercury mass flows in the precalciner process (the mercury mass flows in the flue gas or solid materials) are much larger than that added by the raw materials and coal, which means that the mercury is enriched in the production process (mercury enrichment). The ratio of the amount of mercury emitted from the kiln system ($T$) to the total mercury input from raw materials ($R$) and coal ($C$) can be used to evaluate the mercury enrichment in the cement production process, which is defined by the following equation.

$$\text{Enrichment Ratio(ER)} = \frac{T}{R + C} \quad (1)$$

$T$: the total amount of mercury emitted from the kiln system; $R$, $C$: the total mercury input from the raw materials, coal.

To investigate the factors affecting the mercury enrichment, the enrichment ratio (ER) should be further analyzed. According to the mass balance method (the raw mill is operating), the mercury input from raw materials and coal equals the mercury output from the flue gas through three stacks and the clinker, as expressed in Eq. (2). The mercury output through flue gas is expressed by the mercury mass flows entering the raw mill system ($TR_1$), coal mill system ($TR_2$) and kiln head system ($TR_3$) and the removal efficiency of each system (the first three items). The mercury output through the clinker is the mercury mass flows remaining in the clinker ($TR_4$, the fourth item). The mercury mass flows in the above four items are expressed by the total mercury output of the kiln system (T) and the proportion entering each system and the clinker ($R_1$, $R_2$, $R_3$, $R_4$). Therefore, the sum of the proportions of mercury output through flue gas and clinker should be 100%, as shown in Eq. (3). Considering that the mercury flows through the raw mill and FF in the raw mill system and through the coal mill and FF in the coal mill system, the removal efficiencies of the two systems ($\alpha$, $\beta$) can be calculated with the removal efficiencies of the two facilities in series. The removal efficiency of the raw mill system is expressed in Eq. (4), and that for the coal mill system is shown in Eq. (5). Substituting Eqs. (2) and (3) into Eq. (1), the enrichment ratio can be expressed by Eq. (6).

$$R + C = TR_1(1-\alpha) + TR_2(1-\beta) + TR_3(1-\gamma) + TR_4 \quad (2)$$

$$R_1 + R_2 + R_3 + R_4 = 1 \quad (3)$$

$$\alpha = \alpha_1 + (1-\alpha_1)\alpha_2 \quad (4)$$

$$\beta = \beta_1 + (1-\beta_1)\beta_2 \quad (5)$$

$$ER = \frac{1}{1 - R_1\alpha - R_2\beta - R_3\gamma} \quad (6)$$

$R_1$, $R_2$, $R_3$, $R_4$: the proportion of mercury in the flue gas entering the raw mill system, coal mill system, kiln head system and in the clinker, respectively, based on the total amount of mercury emitted from the kiln system;

$\alpha$, $\alpha_1$, $\alpha_2$, $\beta$, $\beta_1$, $\beta_2$, $\gamma$: the removal efficiency of the raw mill system, raw mill, FF after raw mill, coal mill system, coal mill, FF after coal mill and ESP at kiln head, respectively.

### 2.3. Evaluation of dust treatment effects

The mercury output of the cement production process only includes the flue gas through three stacks and clinker because of dust shuttling. Dust treatment before shuttling or dust disposal can reduce atmospheric mercury emissions. Because the byproduct of FF after the coal mill is actually coal powder, dust treatment refers to the dust of FF after the raw mill and ESP at the kiln head. The proportion of atmospheric mercury emissions based on the mercury input from raw materials ($R$) and coal ($C$) when dust is shuttled is shown by Eq. (7). This is another expression of Eq. (2) . When the dust is treated before shuttling or disposal (all of the mercury in the dust is removed), the proportion of the atmospheric mercury emissions can be calculated by Eq. (8). $T'R'_1(1\text{-}\alpha_1)\alpha_2$ is the mercury mass flow entering the dust of FF in the raw mill system. $T'R'_3\gamma$ is the mercury mass flow entering the dust of ESP in the kiln head system. Therefore, the proportion of atmospheric mercury emission should be one minus the proportion of mercury output through the solid materials, including the mercury in the dust of FF in the raw mill system and ESP in the kiln head system and the mercury mass flows remaining in the clinker. The reduction efficiency of dust treatment can be expressed by the difference of the two proportions, as shown in Eq. (9) . Dust treatment can actually be regarded as the removal efficiencies of FF after the raw mill ($\alpha_2$) and ESP at the kiln head ($\gamma$) are zero when calculating the enrichment ratio.

$$\text{Proportion of atmospheric emissions (dust shuttling)} = 1 - \frac{TR_4}{R + C} \quad (7)$$

$$\text{Proportion of atmospheric emissions (dust treatment)} = 1 - \frac{TR'_1(1-\alpha_1)\alpha_2\delta + TR'_3\gamma\delta + TR'_4}{R + C} \quad (8)$$

$$\text{Reduction efficiency} = ER[R'_1(1-\alpha_1)\alpha_1\delta + R'_3\gamma\delta + R'_4] - ERR_4 \quad (9)$$

$\delta$: dust treatment efficiency (the proportion of mercury removed from the collected dust through dust treatment).

The parameters with a single quote indicate the value in dust treatment.

## 3. Results and discussion

### 3.1. Mercury mass flows in the cement production process

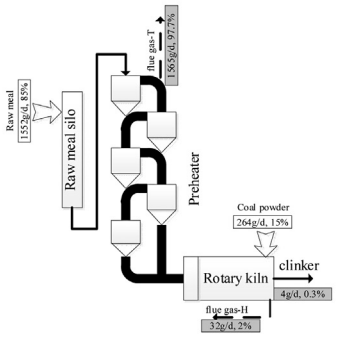
#### 3.1.1. Mercury release from the kiln system

The mercury release and distribution (the proportion of mercury mass flows entering different systems, including the raw mill system, coal mill system, kiln head system and clinker) from the kiln system are calculated in Table 1. The raw meal contributed 85.4% and 79.1% to the total mercury input for the kiln system in Plants 1 and 2, respectively, while the rest of the mercury input was from coal powder. The larger proportion of raw meal was attributed not only to the larger amount of raw materials than coal used in the cement production process but also a larger amount of mercury removed by the raw mill system than the coal mill system and cycled back with raw meal and coal (discussed in the next two sections). Almost all of the mercury in the raw materials and fuel were released into the flue gas of the kiln system, and only less than 3% of the mercury remained in the clinker. The vaporized mercury was mainly emitted with the flue gas from the kiln tail, accounting for 97.7% and 68.8% of the total mercury output in Plants 1 and 2, respectively. The flue gas emerged from the kiln tail flowed through either the raw mill system or the coal mill system before being emitting into the atmosphere, while the flue gas from the kiln head only went through an ESP. As will be discussed in Section 3.3, the removal efficiency of the raw mill system or coal mill system was higher than that of the EPS at the kiln head. Therefore, the proportion of mercury emitted from the kiln tail significantly influenced the mercury mass flows in the cement production process.

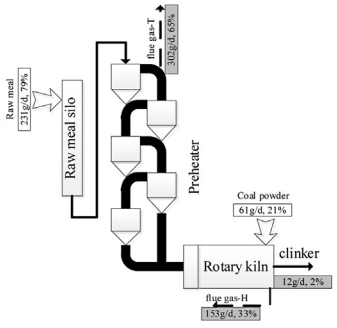
#### 3.1.2. Mercury mass flows in the raw mill system

The mercury concentrations in the flue gas after the raw mill and before FF of the raw mill in Plant 2 were tested to be $16.7 \pm 12.2$ and $22.3 \pm 5.6$ μg/m$^3$, respectively. The mercury mass flows in the raw mill system are given in Table 2. The proportions of mercury input from flue gas emitted from the kiln tail reached 83.7% and 68.5%, much higher than that of the raw materials, which were 12.5% and 30.4% in Plants 1 and 2, respectively. The main reason for this difference was the high concentration of mercury in the flue gas caused by mercury enrichment. Only less than 1% of the mercury input was from dust collected by ESP at the kiln head due to the smaller proportion of mercury emitted with the flue gas from the kiln head and the lower mercury removal efficiency of ESP at the kiln head. The results indicated that only 9.8% and 14.8% of the mercury was eventually emitted into the atmosphere in Plants 1 and 2, respectively. Approximately 90% of the mercury input entered in the raw

**Table 1**
Mercury release in the kiln system.




| Mercury release from kiln system in plant 1 | | | | | | | |
|---|---|---|---|---|---|---|---|
| Input | concentration | unit | flow | unit | Hg flow | unit | Percentage (%) |
| Raw meal | 296 | ppb | 5250 | t/d | 1552 | g/d | 85.4 |
| Coal powder | 544 | ppb | 486 | t/d | 265 | g/d | 14.6 |
| Hg total input | | | 1816.0 | | | g/d | 100 |
| output | concentration | unit | flow | unit | Hg flow | unit | Percentage (%) |
| Flue gas-H | 5.1 | μg/m$^3$ | 6320 | km$^3$/d | 32 | g/d | 2.0 |
| Flue gas-T | 195.6 | μg/m$^3$ | 8000 | km$^3$/d | 1565 | g/d | 97.7 |
| clinker | 1 | ppb | 3425 | t/d | 4 | g/d | 0.3 |
| Hg total output | | | 1601.1 | | | g/d | 88 |




| Mercury release from kiln system in plant 2 | | | | | | | |
|---|---|---|---|---|---|---|---|
| Input | concentration | unit | flow | unit | Hg flow | unit | Percentage (%) |
| Raw meal | - | - | - | - | 468[a] | g/d | 79.1 |
| Coal powder | 113 | ppb | 540 | t/d | 61 | g/d | 20.9 |
| Hg total input | | | 529.2 | | | g/d | 100 |
| output | concentration | unit | flow | unit | Hg flow | unit | Percentage (%) |
| Flue gas-H | 31.9[b] | μg/m$^3$ | 4800 | km$^3$/d | 153 | g/d | 28.9 |
| Flue gas-T | 43.4 | μg/m$^3$ | 8400 | km$^3$/d | 364 | g/d | 68.8 |
| clinker | 3 | ppb | 4200 | t/d | 12 | g/d | 2.3 |
| Hg total output | | | 529.2 | | | g/d | 100 |

Note: Flue gas-H: flue gas at the kiln head;
Flue gas-T: flue gas at the kiln tail;
Flue gas-R: flue gas through the raw mill;
Flue gas-C: flue gas through the coal mill;
a: calculated results assuming the recovery rate equals 100%;
b: calculated results as shown in Table 4.

materials and was cycled into the kiln system. The high proportion of mercury cycled in the raw mill and fabric filter significantly contributed to the mercury enrichment in the cement production process.

### 3.1.3. Mercury mass flows in the coal mill system

The mercury mass flows of the coal mill system are presented in Table 3. Similar to that for the raw mill system, the dominant mercury input of the flue gas from the kiln tail contributed 97.0% and 74.1% of the mercury for the coal mill system, much larger than the proportions of mercury input from coal, which were 3% and 25.9% in Plants 1 and 2, respectively. However, the mercury mass flow in the raw mill system was much larger than that in the coal mill system. The main reason is that the amount of flue gas for the raw mill is 3–5 times larger than that of the coal mill, although the flue gas used to preheat coal in the coal mill is the same as that used in the raw mill. The proportions of mercury emitted into the atmosphere accounted for 7.0% and 5.9% in Plants 1 and 2, respectively. Approximately 95% of the mercury was captured and cycled back into the kiln system in both of the two plants. Therefore, over 90% of the mercury emitted with the flue gas from the kiln tail was removed and cycled into the kiln system in both the raw mill system and the coal mill system.

### 3.1.4. Mercury mass flows in the kiln head system

The mercury concentration in the flue gas before ESP at the kiln head in Plant 1 was tested to be 5.1 ± 3.1 μg/m$^3$. The mercury mass flows at the kiln head are analyzed in Table 4. The mercury input was attributed to the flue gas emitted from the kiln head, and 92.7% and 97.3% of the mercury was eventually emitted into the atmosphere in Plants 1 and 2, respectively. The mercury removal efficiency of ESP is generally thought to be lower than that of FF [26–28]. In addition, the contact between the flue gas and raw materials or coal can also contribute a large proportion of the mercury removal efficiency. Therefore, the proportion of mercury captured and cycled into the kiln system was much lower for mercury emitted from the kiln head than that from the kiln tail. Considering that the amount of mercury emitted from the kiln tail was much larger than that from the kiln head, the mercury mass flows at the kiln tail were much more important for mercury cycling than that at the kiln head.

## 3.2. Mercury cycling in the cement production process

The mercury mass flows in the whole cement production process for the two plants are presented in Figs. 1 and 2. The recovery rates of the above four systems were assumed to be 100% based on the mercury input of the kiln system. There were 3 mercury cycling between the kiln system and the raw mill system, coal mill system

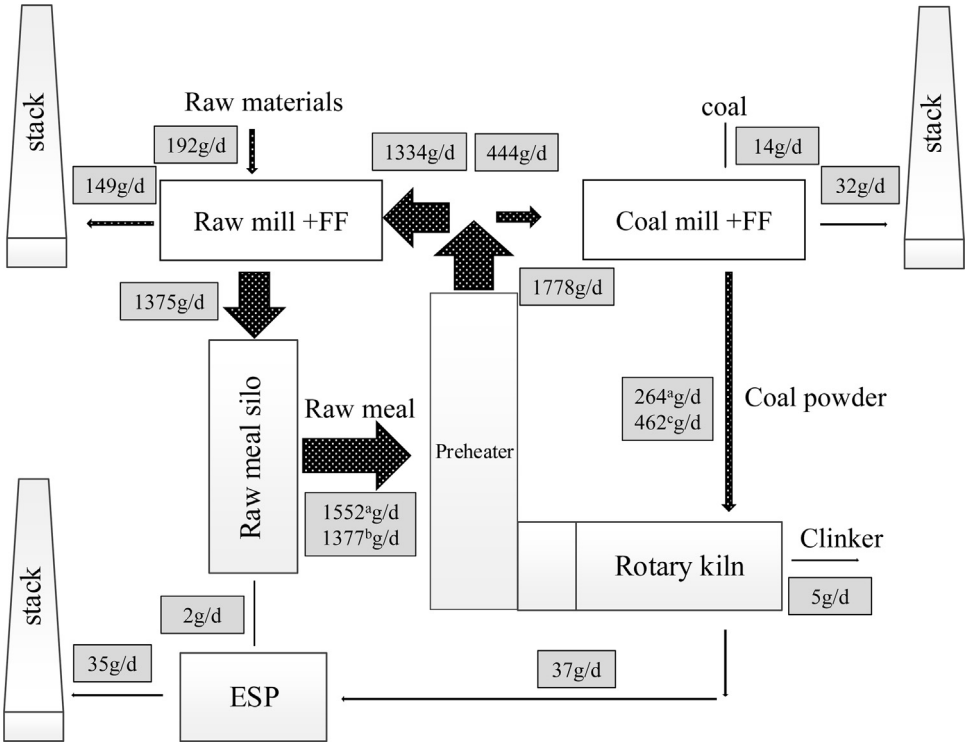



**Fig. 1.** Mercury mass flows in Plant 1.
Note: the width of the arrows indicates the relative amount of the mercury mass flows; a—calculated results for kiln system; b—calculated results for raw mill system; c—calculated results for coal mill system.

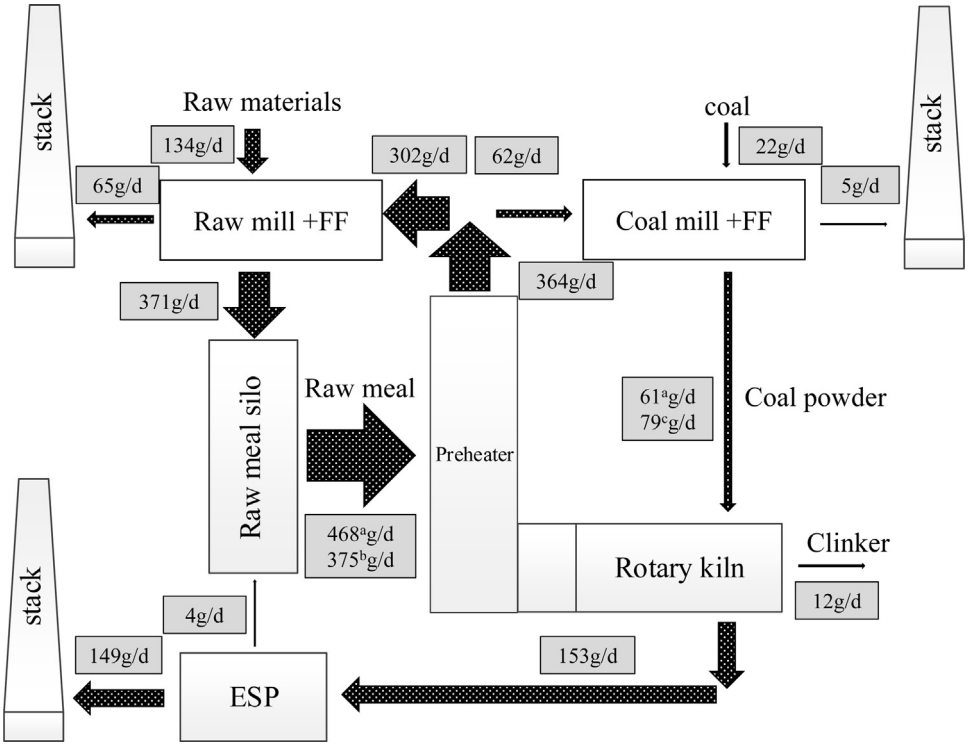
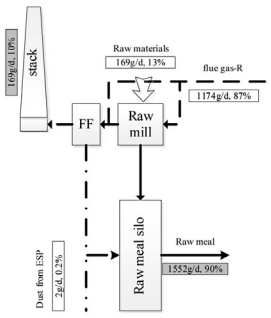
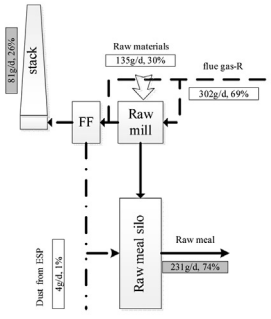



**Fig. 2.** Mercury mass flows in Plant 2.
Note: the width of the arrows indicates the relative amount of mercury mass flows; a—calculated results for kiln system; b—calculated results for raw mill system; c—calculated results for coal mill system.

**Table 2**
Mercury cycling at the raw mill + FF system (kiln tail).




| plant 1 | | | | | | | |
|---|---|---|---|---|---|---|---|
| Input | concentration | unit | flow | unit | Hg flow | Unit | Percentage (%) |
| limestone | 16 | ppb | 4681 | t/d | 76 | g/d | 5.6 |
| sandstone | 19 | ppb | 381 | t/d | 7 | g/d | 0.5 |
| shale | 35 | ppb | 669 | t/d | 23 | g/d | 1.7 |
| Iron-rich materials | 402 | ppb | 157 | t/d | 63 | g/d | 4.7 |
| Dust at kiln head | 572 | ppb | 3 | t/d | 2 | g/d | 0.2 |
| Flue gas before raw mill | 195.6 | ppb | 6000 | $km^3/d$ | 1174 | g/d | 87.3 |
| Hg total input | | | 1345 | | | g/d | 100 |
| output | concentration | unit | flow | unit | Hg flow | unit | Percentage (%) |
| Flue gas-T | 28.1 | $\mu g/m^3$ | 6000 | $km^3/d$ | 169 | g/d | 9.8 |
| Raw meal | 296 | ppb | 5250 | t/d | 1552 | g/d | 90.2 |
| Hg total output | | | 1720 | | | g/d | 128 |




| plant 2 | | | | | | | |
|---|---|---|---|---|---|---|---|
| Input | concentration | unit | flow | unit | Hg flow | unit | Percentage (%) |
| limestone | 18 | ppb | 5200 | t/d | 94 | g/d | 21.3 |
| sandstone | 47 | ppb | 700 | t/d | 33 | g/d | 7.5 |
| clay | 14 | ppb | 150 | t/d | 2 | g/d | 0.5 |
| Iron-rich materials | 27 | ppb | 180 | t/d | 5 | g/d | 1.1 |
| Nickel-rich materials | 10 | ppb | 90 | t/d | 1 | g/d | 0.2 |
| Dust at kiln head | 14 | ppb | 300 | t/d | 4 | g/d | 0.9 |
| Flue gas before raw mill | 43.4 | ppb | 6960 | $km^3/d$ | 302 | g/d | 68.5 |
| Hg total input | | | 440 | | | g/d | 100 |
| output | concentration | unit | flow | unit | Hg flow | unit | Percentage (%) |
| Flue gas-T | 11.7 | $\mu g/m^3$ | 6960 | $km^3/d$ | 81 | g/d | 14.8 |
| Raw meal | - | - | - | - | 468 | g/d | 85.2 |
| Hg total output | | | 549.3 | | | g/d | 125 |

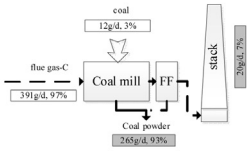
Note: Flue gas-T: flue gas at the kiln tail.

and kiln head system. The distribution of mercury emitted from the kiln system determines the amount of mercury mass flows in the 3 cycling. The mercury mass flows in the raw mill system was the largest in both of the two plants, accounting for 73% and 57% of the total mercury mass flows in Plants 1 and 2, respectively. Therefore, it is obviously important to focus on the mercury cycling in the raw mill system for mercury emission control of cement plants.

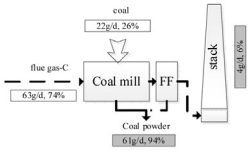
Compared to the amount of mercury input from raw materials and coal (206 g/d and 156 g/d in the two plants, respectively), the mercury mass flows were obviously enriched in the cement production process, especially for the mercury cycling between the kiln system and the raw mill system (1334 g/d and 302 g/d, respectively). The mercury enrichment primarily depended on the high proportions of mercury captured and cycled in the raw mill system. In the two plants, only approximately 11% and 22%, respectively, of the mercury brought into the raw mill system with flue gas was eventually emitted into the atmosphere. Atmospheric mercury emissions can be significantly affected by the mercury enrichment in the cement production process, especially when the raw mill starts to operate or shut off. The mercury concentration in the flue gas emitted from the stacks will experience a peak when the raw mill shuts off. Therefore, the mercury enrichment makes it quite difficult to accurately estimate the mercury emissions from the cement production process based on the mercury concentration tests in the stacks. As analyzed in the previous study, over 90% of the mercury contributed by the raw materials and coal was emitted into the atmosphere [22], meaning that the atmospheric mercury emissions can be calculated based on the mercury input from raw materials and coal.

The mercury mass flows in the another two cement plants were investigated in previous studies [17,21]. The basic characteristics of the mercury behavior are similar to those in this study. In one study, the mercury mass flows in the raw mill system accounted for approximately 93% of the total amount of mercury emitted from the kiln system. Only 11% of the mercury entering the raw mill system was emitted into the atmosphere. The mercury mass flows in the raw mill system reached 0.453 g/t clinker, which was much higher than that in the raw materials (0.106 g/t clinker) and fuel (0.01 g/t clinker) [21]. In the other study, the proportion of mercury emissions only accounted for 1% of the mercury entering FF after the raw mill. The mercury mass flows emitted from the kiln system were more than 10 times greater than that in the raw materials and fuel [17].

**Table 3**
Mercury cycling at the coal mill + FF system (kiln tail).

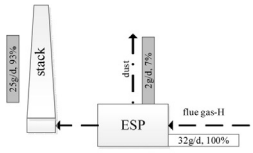



| plant 1 | | | | | | | |
|---|---|---|---|---|---|---|---|
| Input | concentration | unit | flow | unit | Hg flow | unit | Percentage (%) |
| coal | 25 | ppb | 479 | t/d | 12 | g/d | 3.0 |
| flue gas before coal mill | 195.6 | ppb | 2000 | $km^3/d$ | 391 | g/d | 97.0 |
| Hg total input | | | 403 | | | g/d | 100 |
| output | concentration | unit | flow | unit | Hg flow | unit | Percentage (%) |
| flue gas exhausted | 9.9 | $\mu g/m^3$ | 2000 | $km^3/d$ | 20 | g/d | 7.0 |
| coal powder | 544 | ppb | 486 | t/d | 264 | g/d | 93.0 |
| Hg total output | | | 284 | | | g/d | 71 |

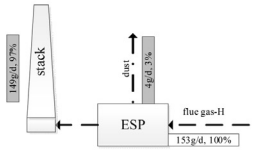



| plant 2 | | | | | | | |
|---|---|---|---|---|---|---|---|
| Input | concentration | unit | flow | unit | Hg flow | unit | Percentage (%) |
| coal | 36 | ppb | 600 | t/d | 22 | g/d | 25.9 |
| flue gas before coal mill | 43.4 | ppb | 1440 | t/d | 62 | g/d | 74.1 |
| Hg total input | | | 84 | | | g/d | 100 |
| output | concentration | unit | flow | unit | Hg flow | unit | Percentage (%) |
| flue gas exhausted | 2.6 | $\mu g/m^3$ | 1440 | $km^3/d$ | 4 | g/d | 5.9 |
| coal powder | 113 | ppb | 540 | t/d | 61 | g/d | 94.1 |
| Hg total output | | | 65 | | | g/d | 77 |

**Table 4**
Mercury cycling at the kiln head.




| plant 1 | | | | | | | |
|---|---|---|---|---|---|---|---|
| Input | concentration | unit | flow | unit | Hg flow | unit | Percentage (%) |
| flue gas before ESP | 5.1 | $\mu g/m^3$ | 6320 | $km^3/d$ | 32 | g/d | 100.0 |
| Hg total input | | | 32 | | | g/d | 100 |
| output | concentration | unit | flow | unit | Hg flow | unit | Percentage (%) |
| flue gas exhausted | 4.0 | $\mu g/m^3$ | 6320 | $km^3/d$ | 25 | g/d | 92.7 |
| dust | 572 | ppb | 3 | t/d | 2 | g/d | 7.3 |
| Hg total output | | | 27 | | | g/d | 84 |




| plant 2 | | | | | | | |
|---|---|---|---|---|---|---|---|
| Input | concentration | unit | flow | unit | Hg flow | unit | Percentage (%) |
| flue gas before ESP | 31.9[a] | $\mu g/m^3$ | 4800 | $km^3/d$ | 153 | g/d | 100.0 |
| Hg total input | | | 153 | | | g/d | 100 |
| output | concentration | unit | flow | unit | Hg flow | unit | Percentage (%) |
| flue gas exhausted | 31.0 | $\mu g/m^3$ | 4800 | $km^3/d$ | 149 | g/d | 97.3 |
| dust | 14 | ppb | 300 | t/d | 4 | g/d | 2.7 |
| Hg total output | | | 153 | | | g/d | 100 |

Note: a: calculated assuming recovery rate equals 100%.

**Table 5**
Mercury removal efficiencies of different facilities.

| Removal efficiency (%) | Raw mill | FF after raw mill | Raw mill system | Coal mill | FF after coal mill | Coal mill system | ESP at kiln head |
|---|---|---|---|---|---|---|---|
| Plant 1 | | – | 85.6 | – | – | 94.9 | 22.0 |
| Plant 2 | 61.5 | 78.3 | 88.9 | – | – | 93.9 | 2.3 |

Note: "–"means no sampling at this site.

### 3.3. Mercury enrichment in the cement production process

An appropriate evaluation index can help compare the mercury enrichment in different cement plants. Further quantitative analysis of factors affecting mercury enrichment is the basis of comprehensively understanding the mercury enrichment in the precalciner cement production process. The mercury enrichment ratios (ER) calculated according to Eq. (1) in the two plants were 8.8 and 3.4, respectively. The mercury enrichment varied between the two plants, although the configuration of the production line and the concentrations of the raw materials made no significant difference. Eq. (6) indicates that the enrichment ratio of mercury in the cement production process depends on the mercury distribution in the kiln system ($R_1$, $R_2$, $R_3$) and the removal efficiencies of the facilities in the 3 mercury cycling ($\alpha$, $\beta$, $\gamma$). The distribution of mercury in the different cycling is mainly dependent on the operation conditions of the cement production process. Generally speaking, the proportion of mercury entering the raw mill system ($R_1$) is much larger than that entering the coal mill system ($R_2$) and emitted from the kiln head ($R_3$) ($R_1$ = 73% in Plant 1 and $R_1$ = 57% in Plant 2). Therefore, the removal efficiency of the raw mill system is crucial for mercury enrichment.

Holding the mercury distribution in the kiln system constant ($R_1$, $R_2$, $R_3$), the enrichment ratio (ER) increases with the removal efficiency of each facility ($\alpha$, $\beta$, $\gamma$), following a curve similar to a power function. Therefore, the mercury enrichment increases rapidly with removal efficiency at first and then becomes slower and slower. The maximum mercury enrichment ratio of $1/R_4$ ($R_4$: the proportion of mercury in the clinker) can be obtained assuming the removal efficiencies of the raw mill systems, coal mill systems and kiln head system are all 100%, which cannot be reached in reality. Considering that the proportion of mercury remaining in the clinker is often very small ($R_4$ = 0.26% and 2.28% in Plants 1 and 2, respectively), the enrichment ratios can theoretically reach as high as 392 and 44 in the two tested plants, respectively. The mercury removal efficiencies of different facilities in the two tested plants are shown in Table 5. For the raw mill and coal mill systems, not only traditional dust control devices (FFs) but also the raw mill and coal mill have quite high mercury removal efficiencies. The high mercury enrichment can be confirmed by the high removal efficiencies of the raw mill systems and coal mill systems (>85%).

The field tests in this study were all conducted when the raw mill was operating. The shutoff of the raw mill will cause the flue gas to directly flow through FF after the raw mill, indicating a lower mercury removal efficiency of the raw mill system. The enrichment ratio when the raw mill is shut off can also be calculated assuming the removal efficiency of raw mill is zero ($\alpha_1$ = 0). The mercury enrichment ratio of Plants 1 and 2 will significantly decrease from 8.8 and 3.4 to 5.3 and 2.3, respectively, when the raw mill is shut off based on the current mercury removal efficiencies of the facilities. The reductions (40% and 32%, respectively) in the two plants indicate that the mercury concentrations in the emitted flue gas will significantly increase when the raw mill is shut off, as observed in the field tests [23]. Once again, this result confirms that the mercury emission estimate cannot be based on the mercury concentration tests in the stacks. The operation conditions of the raw mill can significantly affect the mercury mass flows and emissions in cement plants. Therefore, more studies should be conducted to obtain more comprehensive knowledge of mercury behavior in the precalciner cement production process.

### 3.4. Effects of dust treatment on atmospheric mercury emissions

Eq. (9) shows that the atmospheric mercury emission reduction efficiency is related not only to the mercury distribution ($R_1$, $R_3$, $R_4$) and removal efficiencies of different facilities ($\alpha_1$, $\alpha_2$, $\gamma$) but also to the dust treatment efficiency ($\delta$). The dust treatment efficiency indicates the proportion of mercury removed from the collected dust through treatment, such as dust roasting or partial dust removal. The maximum reduction efficiency can be obtained when the dust treatment efficiency is 100%. According to Eq. (9), the maximum reduction efficiencies were 70% and 31% for Plants 1 and 2, respectively, based on the measurement results in the plants (holding all of the parameters constant, and using the removal efficiencies of raw mill and FF of Plant 2 in Plant 1). This result means that the dust treatment can efficiently contribute up to 70% and 31% of atmospheric mercury emission reductions, respectively. The large difference between the two plants is mainly caused by the large proportion of mercury emitted from the kiln head and the low removal efficiency of ESP at the kiln head.

The reduction efficiency is approximately linearly correlated with the dust treatment efficiency ($\delta$). When the dust treatment efficiency ($\delta$) decreases from 100% to 50% or 30%, the reduction efficiency also decreases from 70% to 34% or 20% in Plant 1 and from 31% to 15% or 8% in Plant 2, respectively. However, the mercury removal efficiency is related to the mercury concentrations in the flue gas, and the mercury concentration will change with the mercury enrichment ratio. The mercury enrichment ratio discussed in the last section indicates that a lower mercury removal efficiency can cause less mercury enrichment in the cement production process. The mercury enrichment ratio in the cement production process will be smaller if dust is not all shuttled but treated instead. The smaller enrichment ratio indicates a lower mercury concentration in the flue gas, which will also affect the mercury removal efficiency of other facilities, including raw mill, coal mill and FF after coal mill. Therefore, the calculated reduction efficiency is actually overestimated. The effects of mercury concentration in the flue gas on the removal efficiencies of different facilities should be investigated in further studies. Above all, the dust treatment can reduce the atmospheric emissions, but the effect varies with the mercury removal efficiencies of facilities in the cement production process. This result is confirmed in a previous study [29]. Currently, dust removal and dust roasting (in which CKD is heated to remove mercury before shuttling) have been under development as dust treatment technologies to reduce mercury emissions. The reduction efficiency of dust removal was estimated to be less than 35% and could reach 75% for dust roasting in pilot scale testing [29] . Therefore, the reduction efficiency should be specifically evaluated when dust treatment is used in a cement plant.

## 4. Conclusions

In this study, the characteristics of mercury cycling in the cement production process were systematically investigated based on field tests in two Chinese cement plants. For the first time, an evaluation index was established to assess the mercury enrichment in the cement production process. The factors affecting mercury enrichment were quantitatively discussed. The theoretical effects of dust treatment were also quantitatively evaluated. Three mercury cycling were found between the high- temperature kiln system and each of the low-temperature raw mill system, coal mill system and kiln head system. The mercury mass flow analysis indicated that the mercury cycling between the kiln system and raw mill system contributed 57–73% to the total mercury mass flows emitted from the kiln system. Based on the assessment method established in this study, mercury was enriched up to 8.8 and 3.4 times in the two tested plants, respectively. The mercury enrichment was dependent on the proportion of mercury cycled back to the rotary kiln system in the cement production process. The mercury enrichment ratio increased with the removal efficiencies following a power function. Dust treatment could efficiently reduce

the atmospheric mercury emissions from the cement production process, and the proportions of atmospheric emissions reduction could reach up to 31-70% in the two tested plants. The reduction efficiency approximately linearly decreased with the dust treatment efficiency. The methodology and results can not only help further understand the mercury cycling in cement production process, but also theoretically predict the efficiency of this technology.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2015.09.042.

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