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Characteristics of mercury cycling in the cement production process

Fengyang Wang[a,b], Shuxiao Wang[a,b,*], Lei Zhang[a,b], Hai Yang[a,b], Qingru Wu[a,b], Jiming Hao[a,b]

[a] State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China
[b] State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, Beijing 100084, China

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].

* Corresponding author at: State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China. Fax: +86 10 62773650.
E-mail address: shxwang@tsinghua.edu.cn (S. Wang).

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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.

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