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Research article

Mercury emission from sintering process in the iron and steel industry of China

Wenqing Xu [a,b], Mingpan Shao [a], Yang Yang [a,c], Ruihui Liu [a], Yinghong Wu [a,c], Tingyu Zhu [a,b,*]

[a] Research Center of Process Pollution Control, National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[b] Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China
[c] University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

Iron and steel production is one of the most significant anthropogenic sources of atmospheric mercury emission. However, there is little information about this source in China. In this study, we focused on three typical Chinese sintering furnace processes. Mercury in flue gas was sampled using the EPA Method 30B and Ontario Hydro Method, and solid samples were also analyzed. We found that 1.12–4.66% of mercury input in sintering furnace processes was emitted into the atmosphere. The total mercury concentrations in the sintering furnace flue gas were 17.773, 31.765 and 18.275 μg/m^3; the major mercury species was oxidized form, which accounted for 73.4– 94.7% of the total mercury. The mercury concentrations in the stack flue gas were 0.373, 0.533 and 0.465 μg/m^3, while its removal efficiencies by air pollution control devices (APCDs) were 97.5%, 81.1% and 96.8%, and its emission factors were 2.49, 2.71 and 1.28 mg/t sinter. The main mercury inputs were iron ore, coal, coke and lime, where the iron ore input was 74.84– 92.22% of the total mercury quantity. Moreover, mercury was distributed in fly ash (19.22– 81.54%), gypsum (13.29– 46.00%), iron ore sinter (0– 11.45%), and flue gas (1.12– 4.66%). An approximate mercury mass balance could be obtained from various samples in this study.

1. Introduction

Mercury (Hg) is one of the most important environmental contaminants that has attracted global concern because of its toxicity, long-range transport, persistence and bioaccumulation in the environment [1]. China plays a key role in both current and future atmosphere mercury emissions and significantly affects global mercury cycle. It is estimated that the atmospheric mercury emission in China accounts for 25– 40% of global mercury emissions. China is one of the largest steel producers: its crude steel production reached 822.7 million tons in 2014 and accounted for 49.5% of the global production. Iron and steel production emits 43 t mercury into the air and contributes approximately 5% to the global mercury emissions [2]. However, there is little information on the mercury emissions in the iron and steel manufacturing processes in China.

The iron and steel manufacturing process is notably complicated, in which more emission points are contained than other industrial processes. Iron and steel production is classified into two major types: converter furnace processes and electric furnace processes. The crude steel production of converter furnace processes accounts for more than 90% of production in China. Converter furnace processes include the coke-oven process, sintering furnace process, pelletizing process, blast furnace process, and converter procedure. The flue gas generated in sintering is approximately 4000–6000 m^3/t iron ore sinter and contains a large amount of dust, acid gases (SO_x, NO_x, and HF), volatile organic chemicals (VOCs) and other pollutants. Thus, the sintering furnace process is the main exhaust gas emission source in the converter furnace process. In this process, the iron ore sinter is produced by sintering iron ore and limestone, and the flue gas from the sintering furnace is emitted after passing through air pollution control devices (APCDs), such as the electrostatic precipitator (ESP), fabric filter (FF), or a desulfurization unit. In China, more than 80% of particulate matter collectors are ESPs. Thus, sintering furnaces that installed ESPs and desulfurization units were investigated in this study.

The emission factor is an important parameter to calculate mercury emissions. In previous studies, an emission factor of 0.0488 g/t steel was reported to calculate mercury emissions from iron and steel production [3]. This value was close to the technical background report of the global atmospheric mercury assessment by United Nations Environment Programme (UNEP), which claimed that the emission factor was 0.04 g/t steel [4]. However, driven by the application of advanced manufacturing and emission control technologies, particularly the growth of mechanized coking ovens, Zhao et al. recently reported that the estimated

* Corresponding author at: Research Center of Process Pollution Control, National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China.
E-mail address: tyzhu@ipe.ac.cn (T. Zhu).

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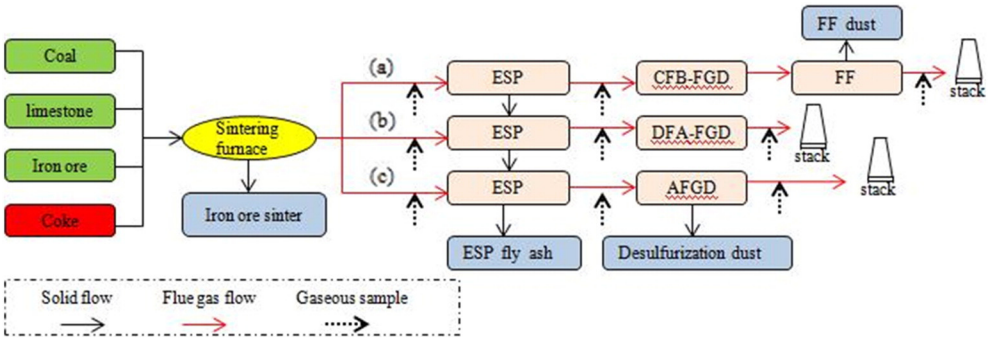

Fig. 1. Schematic diagram of the selected sintering furnace.

emission factor for iron and steel production decreased from 0.071 to 0.039 g/t steel from 2005 to 2012 [5], which indicates that the emission factor in earlier studies [6–7] might have underestimated the emissions for this sector in previous years. They suggested that the emission factor would further decrease to 0.035 g/t steel in the future. Apparently, there are large uncertainties in the mercury emission factors of iron and steel production. More accurate mercury emission estimate should be based on mercury mass balance in the iron and steel manufacturing process and mercury content distribution in raw materials. Therefore, it is necessary to investigate the mercury emission characteristics and behavior in Chinese iron and steel plants.

Mercury emission is classified as gaseous elemental mercury (Hg^0), divalent gaseous mercury (Hg^{2+}), and particulate mercury (Hg_p). Pacyna et al. [8] reported that the percentages of Hg^0, Hg^{2+} and Hg_p were 80%, 15% and 5%, respectively. This result was similar to that of a previous report [9], which suggested that the percentages of Hg^0, Hg^{2+} and Hg_p from steel-iron production were 81.2%, 14.6% and 4.2%, respectively. In addition, mercury concentrations widely varied in gas samples from iron and steel production. Yue et al. measured mercury concentration in the flue gas of sintering machine upstream, and the value was 18–100 μg/m^3 before the FGD device [10]. The reported mercury concentration in the gas from a sintering furnace in Korea was 13.27–114.05 μg/m^3 at the inlet of the ESP and 10.18–19.12 μg/m^3 at the exit [11]. Furthermore, another study reported mercury emission concentrations of 4.95 and 9.95 μg/m^3 from electric and sintering furnaces, respectively [12]. Because there is limited information on the mercury concentration and speciation emitted from the iron and steel industry, more field measurements on the mercury speciation and concentration in iron and steel production are necessary. This study will help to improve the accuracy of the mercury emission inventory in China and provide useful information to develop mercury controls.

In this study, the 30B Method was used to monitor the mercury concentration in sintering flue gas at the inlet and outlet APCDs, and the Ontario Hydro Method (OHM) was used to investigate mercury speciation. Solid samples, including different raw materials, fuels, products and byproducts, were also collected and determined. Based on the monitoring results, the removal efficiencies of APCDs, mercury mass balance and emission factors of three sintering furnace processes were calculated.

2. Material and methods

2.1. Site description and configuration

On-site tests were performed in three typical sintering furnaces from three iron and steel production enterprises. The first and second sintering furnaces are located in Hebei Province; the third furnace is located in Hubei Province. A schematic diagram of the sintering furnace process is shown in Fig. 1. The desulphurization methods of the three sintering furnaces are: circulating fluidized-bed flue gas desulphurization (CFB-FGD), dense flow absorber flue gas desulphurization (DFA-FGD), and ammonia flue gas desulphurization (AFGD). As shown, the flue gas is emitted into the atmosphere after the ESP/FF and FGD. Mercury was simultaneously tested at three sampling points: up and down stream of the ESP and outlet of the FGD, which is at the stack.

2.2. Mercury tending in the sintering process

In the sintering system, most of the mercury content is from raw materials, such as iron ore, coal, coke and limestone. Among these materials, iron ore and coal account for more than 90%. The raw materials and coal are heated, and mercury is released into the flue gas, which subsequently enters the sintering system. Mercury in the sintering flue gas flow go through the adjacent ESP, by which over 30% of the mercury content in the flue gas is collected with PM. A portion of mercury exits the ESP and enters the FGD system; then, it is captured by desulphurization: over 20% of the mercury content is collected in desulfurization dust. The remaining mercury is lost in atmospheric emission from the stack. Overall, the mercury concentration in the stack is very low (no more than 5%).

2.3. Sampling approach and mercury analysis

In this study, flue gas samples and solid samples from the entire sintering furnace process were collected and analyzed. The sampling sites of the flue gas and solid samples are presented in Fig. 1. The 30B Method was used to investigate the mercury concentration in sintering flue gas at every site; the Ontario Hydro Method (OHM) was used to investigate the mercury speciation, which included Hg^{2+}, Hg^0, and Hg_p, in the flue gas. Solid samples, which included different raw materials, fuels, products and byproducts, were simultaneously sampled with the flue gas. The United States Environment Protection Agency (US EPA) Method 7473 (Lumex RA915 +, Russia) was used to determine the mercury concentrations in solid and liquid samples.

The Hg^0 removal efficiency (η) is defined as

$$\eta = \frac{\Delta Hg^0}{Hg^0_{inlet}} = \frac{Hg^0_{inlet} - Hg^0_{outlet}}{Hg^0_{inlet}} \times 100\%$$

Where $Hg^0{}_{inlet}$ (μg/m^3) and $Hg^0{}_{outlet}$ (μg/m^3) are the concentrations of Hg^0 measured at the inlet and the outlet of the reactor, respectively.