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Mercury mass flow in iron and steel production process and its implications for mercury emission control

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ABSTRACT

The iron and steel production process is one of the predominant anthropogenic sources of atmospheric mercury emissions worldwide. In this study, field tests were conducted to study mercury emission characteristics and mass flows at two iron and steel plants in China. It was found that low-sulfur flue gas from sintering machines could contribute up to 41% of the total atmospheric mercury emissions, and desulfurization devices could remarkably help reduce the emissions. Coal gas burning accounted for 17%–49% of the total mercury emissions, and therefore the mercury control of coal gas burning, specifically for the power plant burning coal gas to generate electricity, was significantly important. The emissions from limestone and dolomite production and electric furnaces can contribute 29.3% and 4.2% of the total mercury emissions from iron and steel production. More attention should be paid to mercury emissions from these two processes. Blast furnace dust accounted for 27%–36% of the total mercury output for the whole iron and steel production process. The recycling of blast furnace dust could greatly increase the atmospheric mercury emissions and should not be conducted. The mercury emission factors for the coke oven, sintering machine and blast furnace were 0.039–0.047 g Hg/ton steel, and for the electric furnace it was 0.021 g Hg/ton steel. The predominant emission species was oxidized mercury, accounting for 59%–73% of total mercury emissions to air.

Introduction

Iron and steel production is considered to be one of the predominant anthropogenic sources of atmospheric mercury (Hg) (UNEP, 2008, 2013a). Mercury emissions from iron and steel plants have been confirmed to cause mercury exposure to not only the workers in the plant but also the residents in surrounding areas (Pervez et al., 2010). The global mercury emissions from iron and steel production were estimated to be 46 tons in 2010 (UNEP, 2013a). The mercury emissions from Chinese iron and steel plants were about 9 tons in 2003 (Pirrone and Mason, 2009; Streets et al., 2005; Wu et al., 2006). China's iron and steel production has been increasing at an average annual growth rate of approximately 15% since 2000. As the largest iron and steel producer in the world, China made 780 million tons of crude steel in 2013. Therefore, it is important to study and control the mercury emissions from iron and steel production in China (Wang et al., 2014c).

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In the complicated process of iron and steel production, mercury comes from a variety of raw materials at different stages and is emitted by dozens of stacks. Due to lack of information on the mercury emission characteristics of iron and steel plants, a single emission factor of 0.04 g Hg/ton steel has long been adopted for the emission estimate in previous emission inventories for the world and China (Feng et al., 2009; Pacyna and Pacyna, 2002; Pacyna et al., 2006, 2010; Pirrone et al., 2010; UNEP, 2013a; Wong et al., 2006). The above-mentioned single emission factor, neglecting the variations of Hg content in raw materials and the detailed production process, results in high uncertainty in emission estimates. The recently released report by the United Nations Environment Program (UNEP) employed a method based on the unabated emission factor and the mercury removal of the air pollution control devices (APCDs) (UNEP, 2013b). In this report, only the emissions from the coke oven, sintering machine and blast furnace were considered. However, other studies indicated that the mercury concentration in the flue gas of the electric furnace was comparable to that of the above three processes (Kim et al., 2010; Park et al., 2008). Knowledge on the emission characteristics and mercury mass flow in iron and steel production is imperative to improve the mercury emission inventory and useful in the development of a mercury emission control strategy.

In this study, we conducted field tests to study the mercury emission characteristics of two typical iron and steel plants in China. The mercury concentrations in the flue gas and solid samples were analyzed. Based on the test results, a mercury mass flow analysis of the production process was conducted. The mercury emissions from different stages of the iron and steel production were assessed. The implications of these results for mercury emission control were also discussed.

1. Experimental

1.1. *Iron and steel smelting plants studied*

The conventional iron and steel production process can be divided into four consecutive stages, that is, raw material preparation, sintering machine, blast furnace and convertor (as shown in Fig. 1). In the raw material preparation stage, coke used in the sintering machine and blast furnace is produced from coal in a coke oven. The limestone and dolomite ores are roasted in rotary kilns, though in some cases, the production of limestone and dolomite is not included in iron and steel plants. The prepared iron ores, coke, limestone (dolomite), and other recycled materials, including some collected dust from the sintering machine or blast furnace, are sintered in the sintering machine. Since the sintering machine is the first thermal treating process for most raw materials, the composition of its flue gas is very complicated. Generally speaking, the flue gas from the sintering machine includes three parts, the high-sulfur flue gas and low-sulfur flue gas from the machine head, and the flue gas from the machine tail. Electrostatic precipitators (ESP) and desulfurization devices are used to remove dust and SO_2 in the flue gas of the sintering machine. The sinter, coke and limestone are smelted in the blast furnace to produce pig iron, which is further smelted with limestone in the convertor to produce steel. Besides the above stages related to the production of steel, coal gas produced by the coke oven, blast furnace and convertor is eventually burned and emitted. In some plants, the coal gas is burned to generate electricity in a power plant. Additionally, the flue gases emerging from the production of pig iron, iron scrap and crude steel are collected and de-dusted before being emitted into the atmosphere. Besides the above conventional iron and steel production process, there is an individual process in some

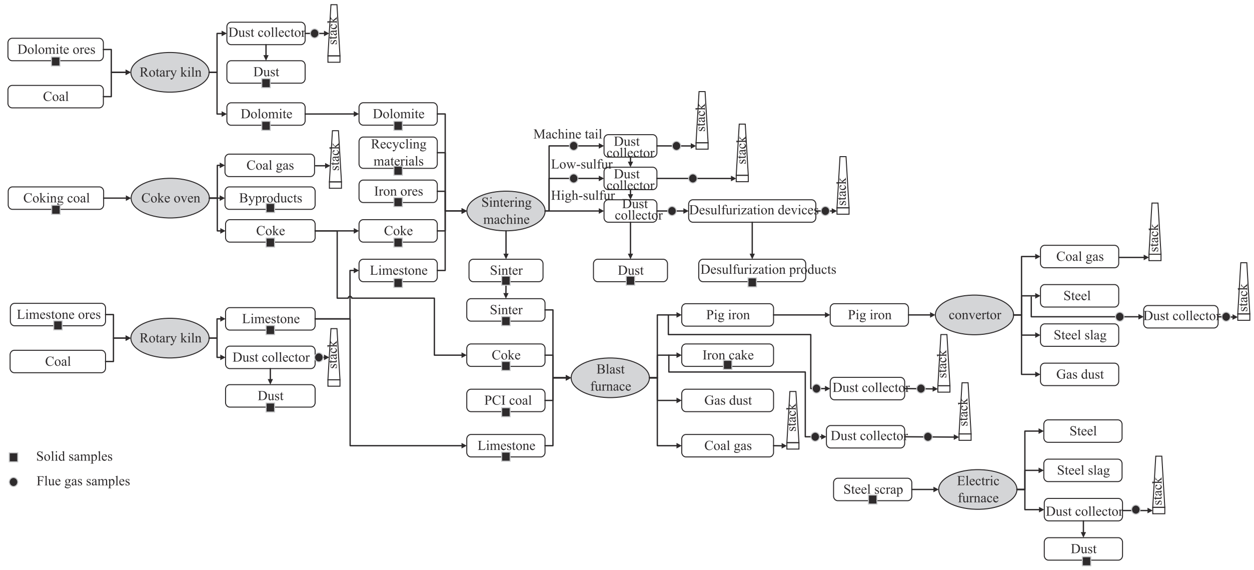

Fig. 1 – Schematic diagram of iron and steel smelting process and sampling sites. PCI coal: pulverized coal injection of the blast furnace.

plants called the electric furnace, in which the scrap steel is directly used to produce steel without any fuel.

In this study, Plant 1 includes a coke-oven, rotary kilns for limestone and dolomite, sintering machine, blast furnace, convertor, power plant and electric furnace; Plant 2 does not have rotary kilns or electric furnace. Thus, the two typical plants tested in this study covered both of the two conventional steel production processes. The sampling locations for flue gas and solid samples are presented in Fig. 1. In order to systematically investigate the mercury emission characteristics in the iron and steel production process, the flue gases from all stacks were sampled in Plants 1 and 2. The raw materials, products and by-products of different facilities were also sampled to help understand the mercury mass flows in the iron and steel production process.

1.2. Sampling and analyzing methods

The Ontario Hydro Method (OHM) was adopted to determine the concentration and speciation of Hg in the flue gas (ASTM, 2002). The flue gas was iso-kinetically pumped out from the duct and stack through a probe. The particle-bound mercury (Hg^p) was collected on a quartz filter with the particulate matters in the flue gas. The filtered flue gas successively flowed through a series of impingers. The first three impingers filled with KCl solution were used to absorb oxidized mercury (Hg^{2+}). The fourth impinger with $H_2O_2 + HNO_3$ and the three subsequent impingers with $H_2SO_4 + KMnO_4$ oxidized and absorbed the elemental mercury (Hg^0). The moisture in the flue gas was removed in the last impinger with silica gel. The probe and the filter were both heated to 120°C to avoid mercury adsorption. The impingers were put in an ice bath to promote mercury absorption. The impinger solutions after sampling were recovered using $SnCl_2$ and the mercury content was detected by a cold vapor atomic absorption spectrophotometry (CVAAS) mercury analyzer (F732-V, Shuangxu Inc., China) with a detection limit of 0.05 μg/L. The solid samples collected in the two plants were analyzed according to the United States Environment Protection Agency (US EPA) Method 7473 (RA915+, Lumex Inc., Russia), with a detection limit of 0.5 μg/kg.

1.3. Quality assurance and quality control (QA/QC)

The flue gas at each test site was sampled at least three times to reduce the measurement error and increase the representativeness of tests. The mercury concentrations in all of the reagents were guaranteed to be under the detection limit. The impinger solutions were individually recovered and detected. The mercury mass in the last impinger accounted for less than 15% of the total mercury mass of oxidized mercury and elemental mercury, indicating that the mercury in the flue gas had been fully absorbed. The analysis error was less than 5%. The solid samples were collected simultaneously with the flue gas, and the number of each sample is listed in Table 1. The solid samples were dried at 40°C and the loss of mercury could be ignored. Each solid sample was analyzed at least three times. The standard reference materials from the National Institute of Standards and Technology (NIST), USA (1632c, coal, NIST, Gaithersburg, USA) and National Research Center for Certified Reference Materials (NRCCRM), China (GSS-5, soil, NRCCRM, Beijing, China) were used in this study. The average values of the mercury concentrations in flue gas and solid samples were adopted. The recovery rates of mass balance for the two plants were 116% and 103%, respectively, which are acceptable for field tests (Fukuda et al., 2011; Wang et al., 2010).

Table 1 – Hg concentration in solid samples.

Mercury concentration (ppb)		Plant 1	Plant 2
Raw materials preparation	Coking coal	450 ± 269 (10)	30 ± 11 (20)
	Coke	178 ± 54 (28)	4 ± 2 (5)
	Coking byproducts	7603 ± 3019 (7)	13923 ± 1490 (2)
	Limestone ore	139 ± 60 (11)	–
	Limestone dust	176 ± 70 (8)	–
	Limestone	18 ± 4 (4)	124 ± 90 (3)
	Dolomite ore	144 ± 51 (5)	–
	Dolomite dust	130 ± 58 (6)	–
	Dolomite	56 ± 18 (6)	–
Sintering machine	Iron ore	66 ± 31 (15)	23 ± 2 (4)
	Recycling materials	247 ± 76 (5)	37 ± 3 (6)
	Sintering mixture	106 ± 13 (6)	–
	Sinter	44 ± 27 (13)	3 ± 1 (13)
	Dust	3206 ± 676 (16)	441 ± 93 (4)
	Gypsum	7408 ± 2043 (12)	1055 ± 70 (20)
Blast furnace	PCI coal	–	40 ± 9 (13)
	Iron cake	–	0 ± 0 (2)
Electric furnace	Steel scrap	122 ± 119 (7)	–
	Dust	869 ± 472 (6)	–

PCI coal: pulverized coal injection of the blast furnace; "–" means no sampling at this site or no such materials.
The number in the brackets indicates the number of samples.

Though a series of measurements were taken to guarantee the accuracy of test results in the sampling and analysis process, there could still be several factors causing biases in the test results. The fly ashes captured by the filter are assumed not to be capable of adsorbing the gaseous mercury in the standard method. This has been confirmed to be true when the concentration of fly ashes is quite low, especially in the stack (Laudal, 1999). Therefore, the test results of mercury concentration and speciation at the outlets of the stacks are accurate. A high concentration of fly ashes might cause adsorption when flue gas flows through the filter, and would increase the proportion of Hg^p. The adsorption of gaseous mercury on fly ashes has been proved by previous studies. Fly ashes impregnated with Fe_2O_3 had a stronger ability for adsorbing mercury, and this is especially important considering that the fly ashes in iron and steel plants have a high proportion of iron (Kostova et al., 2011; Wang et al., 2014b). However, this situation has no effect on the concentration of total mercury detected. Only the mercury speciation in flue gas before the dust collector may be changed for a high concentration of fly ashes. The acid gases in flue gas, such as HCl and SO_2, have been confirmed to be beneficial for the absorption of oxidized mercury because they lower the pH (Sun et al., 2003). However, some of the elemental mercury may be lost when the $KMnO_4$ has been excessively reacted. Therefore a sufficient amount of $KMnO_4$ was assured in the whole test process.

2. Results and discussion

The mercury concentrations of solid samples in Plants 1 and 2 are presented in Table 1, while the mercury concentrations and speciation in the flue gas of the two plants are shown in Table 2. All the test results for flue gas have been normalized to the standard conditions (273.15 K, 1 atm). The mercury mass flows of the coke oven, sintering machine and blast furnace based on these test results are illustrated in Figs. 2 and 3.

2.1. Mercury mass flows in iron and steel production process

2.1.1. Mercury mass flows in coking stage

The mercury concentrations of coking coal, the input material for the coke oven, were 450 and 30 ppb in Plants 1 and 2, respectively. Part of the mercury contributed by the coking coal was vaporized into the coal gas, and the proportion reached about 70% and 90% for Plants 1 and 2. However, a large proportion of the vaporized mercury, >99% in Plant 1 and 93% in Plant 2, was subsequently removed into the byproducts when purifying the coal gas from the coke oven, and entered the byproducts including tar, tar residue and wastewater. The mercury concentrations of the byproducts were as high as 7603 and 13,923 ppb. Therefore the mercury emissions and pollution from these byproducts should be attentively considered during the application and treatment process. The mercury remaining in the coal gas only accounted for a small proportion, 0.6% in Plant 1 and 6.5% in Plant 2. The coal gas was eventually used as fuel, and all the mercury was emitted into the atmosphere with the burning of the coal gas. Only about 30% of mercury input from the coking coal in Plant 1 and 10% in Plant 2 remained in the product of the coke oven, and the mercury concentrations of coke were 178 and 4 ppb respectively. Since the amount of coke used in the blast furnace can reach ten times that for the sintering machine, around 90% of the mercury remaining in coke flowed into the blast furnace in both the two plants.

2.1.2. Mercury mass flows in sintering stage

For the sintering stage, iron ores were the main input materials besides the coke and limestone (dolomite). Recycled materials such as blast furnace dust were also added into the sintering machine. The iron ores and recycling materials contributed 52% and 42% of the mercury input in Plant 1, respectively. In Plant 2, iron ores and limestone accounted for 53% and 41%, respectively. The large proportion of iron ores was attributed to the large use amount, while the contributions of recycled materials and limestone were mainly due to their relatively high mercury concentrations. As shown in Table 1, the mercury concentrations of iron ores were 66 and 23 ppb in Plant 1 and 2, similar to the results in a previous study (Fukuda et al., 2011). The mercury concentration of

Table 2 – Hg concentration in flue gas of Plants 1 and 2.

Mercury concentration (μg/m³)		Hg^0	Hg^{2+}	Hg^P	Hg^t
Plant 1					
Raw material preparation	After ESP of rotary kiln for limestone	4.5 ± 0.9	17.3 ± 9.7	N.A	21.9 ± 9.9
	After ESP of rotary kiln for dolomite	5.9 ± 3.6	67.2 ± 37.8	N.A	73.1 ± 41.4
Sintering machine process	Before WFGD	1.8 ± 1.6	44.5 ± 26.5	N.A	46.3 ± 27.4
	After WFGD	4.8 ± 2.0	10.2 ± 3.6	N.A	15.0 ± 3.5
Electric furnace process	After FF of electric furnace	2.2 ± 1.2	0.2 ± 0.2	N.A	2.4 ± 1.3
Power plant	Power plant	0.4 ± 0.2	2.2 ± 2.2	N.A	2.6 ± 2.3
Plant 2					
Sintering machine process	Before ESP of high-sulfur flue gas	0.3 ± 0.3	15.0 ± 13.5	0.8 ± 0.8	16.0 ± 14.0
	Before CFB of high-sulfur flue gas	0.3 ± 0.2	4.0 ± 2.7	N.A	4.3 ± 3.0
	After CFB of high-sulfur flue gas	0.0 ± 0.0	0.9 ± 0.5	N.A	0.9 ± 0.5
	Before ESP of low-sulfur flue gas	0.2 ± 0.2	19.5 ± 5.5	0.5 ± 0.2	20.2 ± 5.6
	After ESP of low-sulfur flue gas	0.1 ± 0.2	15.3 ± 15.2	N.A	15.4 ± 15.4
	Before ILCA of high-sulfur flue gas	1.7 ± 2.8	14.0 ± 5.5	N.A	15.8 ± 3.2
	After ILCA of high-sulfur flue gas	1.8 ± 1.9	1.8 ± 1.3	N.A	3.5 ± 3.2
	Before ESP at machine tail	0.7 ± 0.4	0.8 ± 0.3	1.7 ± 1.1	3.2 ± 1.1
	After ESP at machine tail	0.2 ± 0.1	0.9 ± 0.5	N.A	1.1 ± 0.6
Blast furnace process	Before ESP of pig iron	0.1 ± 0.1	1.2 ± 0.4	3.1 ± 0.8	4.5 ± 0.6
	After ESP of pig iron	0.3 ± 0.5	0.4 ± 0.4	N.A	0.7 ± 0.8
	Before ESP of iron scrap	1.8 ± 0.9	0.3 ± 0.1	2.6 ± 4.3	4.8 ± 3.9
	After ESP of iron scrap	1.5 ± 0.9	1.4 ± 1.6	N.A	2.9 ± 2.4
Convertor process	Before ESP of crude steel	0.5 ± 0.5	0.5 ± 0.5	N.A	0.9 ± 0.8
	After ESP of crude steel	0.4 ± 0.4	0.3 ± 0.4	N.A	0.7 ± 0.7
Power plant	Power plant	2.0 ± 2.3	0.6 ± 0.7	N.A	2.5 ± 2.5

N.A: under detection limit; ESP: electrostatic precipitator; FF: fabric filter; WFGD: wet flue gas desulfurization device; CFB: circulating fluid bed flue gas desulfurization device; ILCA: ionic liquid circulation absorption flue gas desulfurization device; Hg^P: particle-bound mercury; Hg^t: total mercury concentration in flue gas.

recycled materials was 247 ppb in Plant 1. In Plant 2, limestone was purchased outside, with a mercury concentration of 124 ppb. The mercury output of the sintering machine was composed of the sinter, the byproducts of APCDs and the flue gas. The sinter accounted for different proportions, 38.7% in Plant 1 and 8.9% in Plant 2, and flowed into the blast furnace. Therefore most of the remaining mercury in the coke and sinter entered the blast furnace, and higher proportions of mercury remaining in coke or sinter actually increased the mercury emissions from the blast furnace. The mercury entering the flue gas experienced different fates according to the APCDs installed. In Plant 1, both the high-sulfur and low-sulfur flue gas were desulfurized, while in Plant 2, only the high-sulfur flue gas flowed through the desulfurization device. The mercury concentrations in the high-sulfur flue gas and low-sulfur flue gas that emerged in the sintering machine head were 16 and 20.2 μg/m^3 in Plant 2 (Table 2). It can be seen that there is no remarkable difference in mercury concentrations in the two flue gases from the sintering machine head. Since the predominant species in the flue gas was Hg^{2+} (discussed in Section 2.3), the mercury emissions from the sintering machine largely depended on the desulfurization devices. Therefore the un-desulfurized low-sulfur flue gas from the sintering machine head can be a significant contributor to mercury emissions. Though the proportions of mercury entering the collected dust and byproducts of desulfurization devices varied with the plants, the emitted mercury happened to account for about 30% in the two plants. Different from Plant 1, the mercury emissions in Plant 2 were mainly contributed by the low-sulfur flue gas because of the lack of a desulfurization device. It is very essential to desulfurize the low-sulfur flue gas together with the

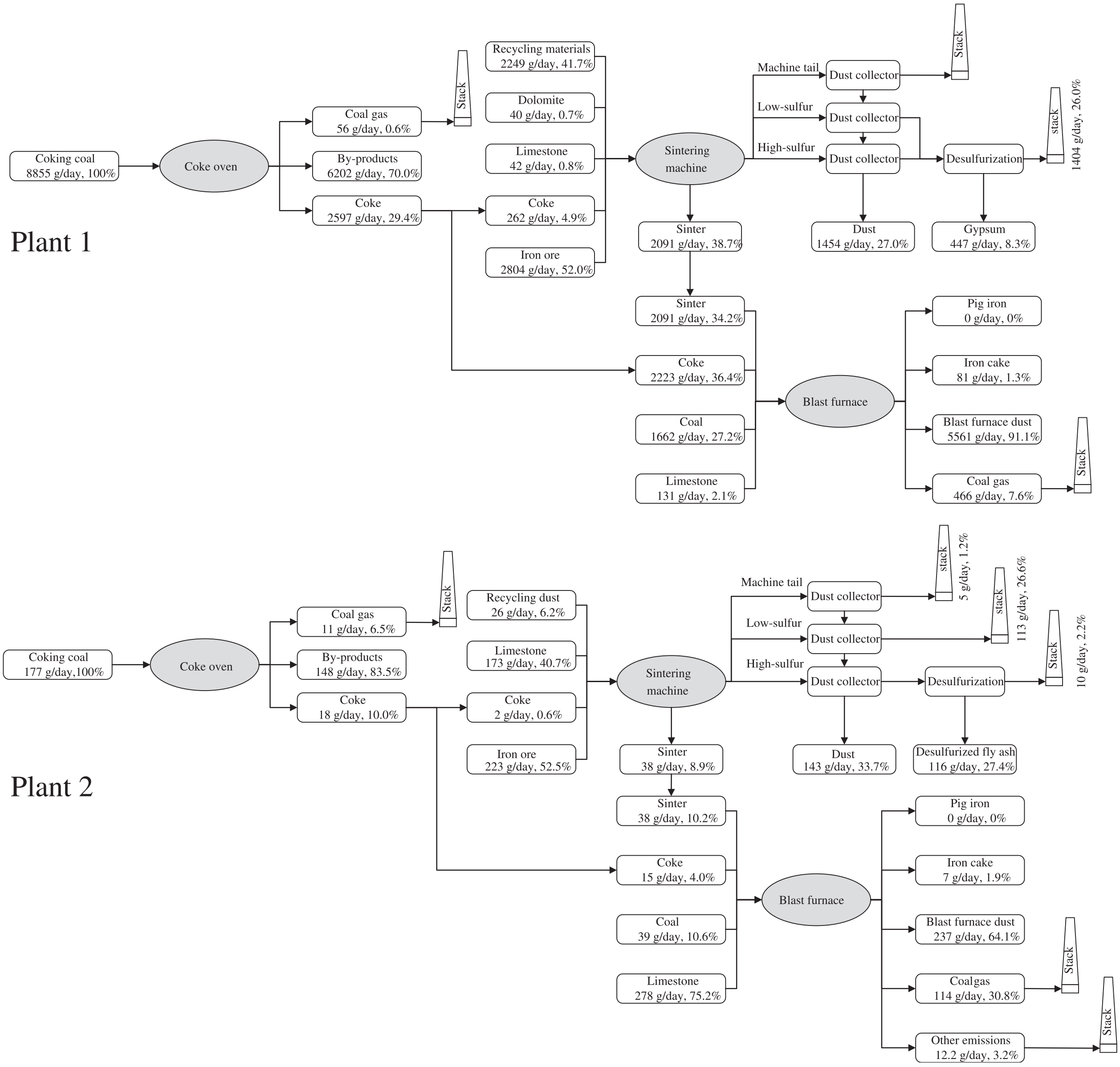

Fig. 2 – Mercury mass flows in Plants 1 and 2. Other emissions: mercury emissions when producing pig iron and iron cake.

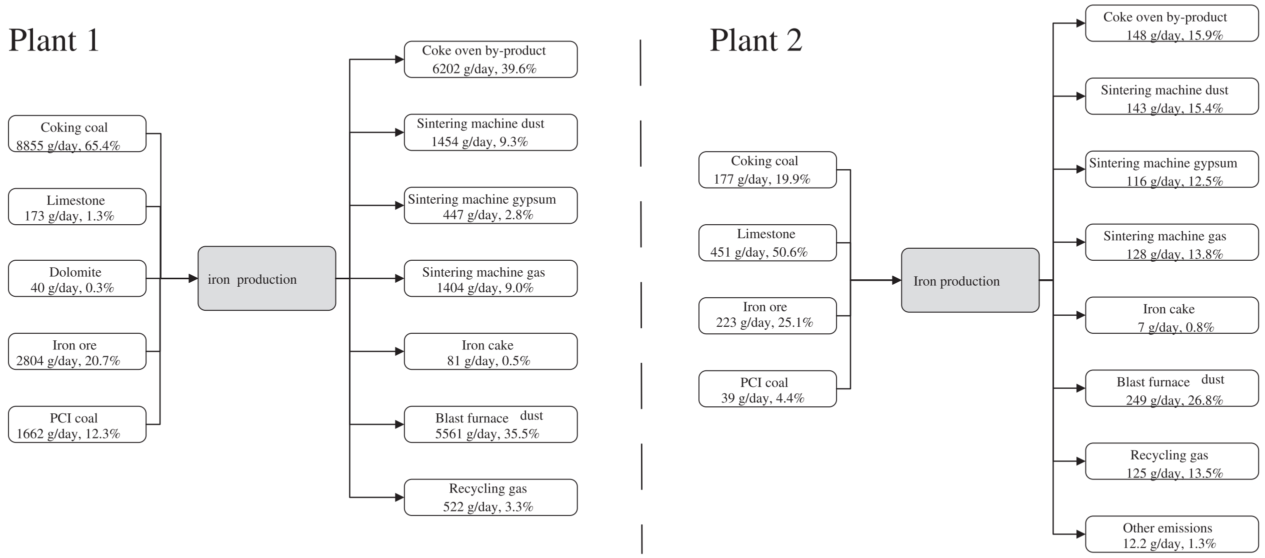

Fig. 3 – Overall mercury mass balance of Plants 1 and 2. Other emissions: mercury emissions when producing pig iron, iron cake and crude steel.

high-sulfur flue gas for mercury control. The mercury concentrations of the byproducts from APCDs were 3206 and 441 ppb for the collected dust, and 7408 and 1055 ppb for the desulfurization byproducts in Plant 1 and 2, respectively. Apparently, the mercury concentrations in both the collected dust and desulfurization byproducts were much higher than that in power plants (Wang et al., 2010).

2.1.3. Mercury mass flows in blast furnace stage

The proportions of the mercury input from sinter, coke and coal were all greater than 30%, while the contribution of limestone was only 2.1% in Plant 1. However, more than 75% of the mercury input was from limestone in Plant 2, which was mainly caused by the high mercury concentration in the limestone and less mercury remaining in the coke and sinter. Almost all the mercury was vaporized into the blast furnace gas but removed in the purification process, with efficiencies of 91% in Plant 1 and 64% in Plant 2. The blast furnace gas accounted for 7.6% of mercury in Plant 1 and 30.8% in Plant 2.

As discussed above, the iron and steel production process is composed of a series of thermal treatment processes with different temperatures. During the high-temperature processes, Hg in raw materials and fuel is released into flue gas with different release rates. It can be seen that the mercury release rates in the coke oven and sintering machine were in the range of 61%–90%, lower than that in coal boilers (>99%), since the temperature was lower than that in power plants (Fukuda et al., 2011; Wang et al., 2010; Zhang et al., 2008). The mercury release rate of the blast furnace was nearly 100%. The rotary kilns, coke oven and sintering machine are mainly used to prepare materials for the blast furnace. Their lower release rates substantially increase the mercury input to the blast furnace, and almost all the mercury is vaporized into the blast furnace gas. The mercury in the blast furnace gas is eventually emitted into the atmosphere after burning. Therefore, the lower Hg release rates of the rotary kilns, coke oven and sintering machine actually increase the mercury emissions into the atmosphere.

2.2. Overall mercury mass balance

The overall mercury mass balance results of Plant 1 and 2 are presented in Fig. 3. It can be seen that the largest mercury input for Plant 1 was from coking coal, accounting for 65%, while it was from limestone in Plant 2, with 51%. The proportions of mercury input for the whole iron and steel production process varied with the plants, since the mercury concentrations of the multitudinous materials added in different processes had large differences.

The main output in Plant 1 included the byproducts from the coke oven (39.6%) and blast furnace (35.5%). In Plant 2, the byproducts from the blast furnace also contributed a high proportion of 27.2%. As discussed above, the blast furnace dust was recycled to the sintering machine in the tested plants. In this situation, the mercury collected in the dust was also cycled. Similar mercury cycling in the cement production process and its effects on emissions has been explored in a previous study (Wang et al., 2014a). It was found that the dust recycling increased the mercury emissions. Considering that the mercury concentrations and mass flows of the dust were quite high, the recycling of the blast furnace dust could significantly increase the mercury emissions. The atmospheric emissions of sintering machine gas accounted for 9% and 13.8% in Plants 1 and 2, respectively. The recycled gas including the coal gas from the coke oven and blast furnace contributed 3.3% and 13.5%. Clearly, the mercury emissions from the sintering machine and recycling gas were comparable. The mercury emissions from both the sintering machine and burning of coal gas should be considered, as discussed next.

2.3. Emission and speciation of the mercury from iron and steel production process

The atmospheric mercury emissions and speciation from different processes in Plants 1 and 2 are shown in Table 3. In

Plant 1, the total mercury emissions were 2.8 kg/day. The mercury emissions from the sintering machine contributed around half of the total atmospheric mercury emissions. The rotary kilns for the limestone and dolomite and the burning of coal gas each accounted for about 15%. The emissions from the electric furnace contributed about 5%. For Plant 2, the total mercury emissions were 0.3 kg/day, much smaller than that of Plant 1 because of its smaller production level. The largest mercury emission in Plant 2 was from the burning of coal gas, accounting for 48.8%. The low-sulfur flue gas from the sintering machine contributed a high proportion of 41%. The mercury emissions from the sintering machine reached 46% of the total. It is clear that the mercury emissions from the iron and steel production were mainly from the sintering machine and coal gas burning, especially the emissions of the low-sulfur flue gas from the sintering machine.

It can also be seen that oxidized mercury (Hg^{2+}) was the predominant mercury species emitted from both of the two plants. The proportions of Hg^{2+} were 73.3% and 59.2% in Plants 1 and 2, respectively. The Hg^p was negligible since all the flue gas flew through the ESPs. The mercury speciation is affected by several factors, including the compositions of the flue gas and dust, residence time and the cooling rate of flue gas. Chlorine is confirmed to be the main oxidant in coal combustion flue gas (Krishnakumar and Helble, 2007; Niksa and Fujiwara, 2005; Senior et al., 2000). The low chlorine content in the iron ores (the main materials for the sintering machine) is usually comparable with that in the coal (Hu et al., 2007). The average chlorine content in Chinese coal is 260 ppm (Zhang et al., 2012). Therefore the high proportions of oxidized mercury should not be attributed to the chlorine content in iron ores. But there is still a lack of information on the chorine content in other kinds of materials used in the iron and steel production process. The high content of Fe_2O_3 in the dust can promote mercury oxidation in the flue gas, since Fe_2O_3 has been proved to act as a catalyst for mercury oxidation (Dunham et al., 2003). Heterogeneous mercury oxidation can also be enhanced by the high concentration of dust in the flue gas from the sintering machine, which can reach 10 g/m^3. The mercury speciation can affect the removal efficiencies of APCDs. The removal efficiencies of ESPs and desulfurization devices in the iron and steel production process are listed in Table 4. The removal efficiencies of ESPs were in the range of 24%–85%, similar to that in power plants (Wang et al., 2010; Zhang et al., 2008). However, the removal efficiencies of three different desulfurization devices were between 68% and 82%, higher than that in power plants, due to the higher proportions of oxidized mercury (Wang et al., 2010; Zhang et al., 2008).

The mercury emission factors of the two plants were also calculated. The mercury emission factor of Plant 1 was 0.068 g Hg/ton crude steel when including the emissions from the production of limestone and dolomite, or 0.047 g Hg/ton crude steel when excluding the limestone and dolomite production. The mercury emission factor of Plant 2 was 0.039 g Hg/ton crude steel, which excludes the

Table 3 – Mercury emissions and speciation from Plants 1 and 2.

Mercury emissions (g/day)	Hg^0	Hg^{2+}	Hg^p	Hg^t	Proportion to total emissions (%)
Plant 1					
Rotary kiln for limestone	95.9	366.2	N.A	462.1	16.3
Rotary kiln for dolomite	29.9	338.7	N.A	368.6	13.0
Sintering machine	450.2	953.8	N.A	1404.0	49.5
Electric furnace	109.3	9.4	N.A	118.7	4.2
Coal gas combustion	72.3	411.3	N.A	483.6	17.0
Total emissions	757.6	2079.4	N.A	2837.0	100
Proportion of each species to Hg^t (%)	26.7	73.3	N.A	100.0	
Emission factor[a] (g/ton crude steel)	0.068				
Emission factor[b] (g/ton crude steel)	0.047				
Emission factor[c] (g/ton crude steel)	0.021				
Plant 2					
Sintering machine-high-sulfur	0.0	9.6	N.A	9.6	3.5
Sintering machine-low-sulfur	0.9	112.1	N.A	113.0	41.0
Sintering machine tail	0.7	4.2	N.A	4.9	1.8
Blast furnace-pig iron	1.9	3.1	N.A	5.0	1.8
Blast furnace-iron scrap	3.6	3.5	N.A	7.2	2.6
Convertor-crude steel	0.8	0.7	N.A	1.5	0.5
Coal gas combustion	104.6	30.0	N.A	134.6	48.8
Total emissions	112.4	163.3	N.A	275.8	100.0
Proportion of each species to Hg^t (%)	40.8	59.2	N.A	100	
Emission factor[b] (g/ton crude steel)	0.039				

N.A: under detection limit; Hg^P: particle-bound mercury; Hg^t: total mercury concentration in flue gas; Hg^0: elemental mercury; Hg^{2+}: oxidized mercury.

[a] Including mercury emissions from rotary kiln for limestone and dolomite (without electric furnace).

[b] Excluding mercury emissions from rotary kiln for limestone and dolomite (without electric furnace).

[c] Mercury emission factor for the electric furnace.

Table 4 – Mercury removal efficiencies of the air pollution control devices (APCDs).

		Removal efficiency (%)
Electrostatic precipitator (ESP)	Low-sulfur flue gas from sintering machine head	23.6
	Sintering machine tail	66.6
	Pig iron production	84.9
	Iron scrap production	39.0
	Crude steel production	28.9
Desulfurization devices	Wet flue gas desulfurization device (WFGD)	67.6
	Circulating fluid bed flue gas desulfurization device (CFB)	79.8
	Ionic liquid circulation absorption flue gas desulfurization device (ILCA)	77.5

contributions of limestone and dolomite production. The emission factor of the electric furnace was 0.021 g Hg/ton crude steel in Plant 1. Our test results indicate that the mercury emission factor will significantly increase when including the mercury emissions from the production of limestone and dolomite, and the electric furnace.

2.4. Implications for mercury emission control

The above investigation of mercury mass flows and emission characteristics for the iron and steel production process can have important implications for mercury emission control. Firstly, it is crucial to reduce the mercury emissions of low-sulfur flue gas from the sintering machine. As discussed above, the low-sulfur flue gas could contribute more than 40% of atmospheric mercury emissions in Plant 2. It was also found that the proportions of oxidized mercury in low-sulfur flue gas can reach more than 90%. Therefore desulfurization devices can significantly help reduce the mercury emissions. Secondly, coal gas burning can greatly affect the mercury emissions from iron and steel plants. The coal gas is generated from the coke oven, blast furnace and convertor in the iron and steel production process. The proportions of the amount of coal gas from these three processes are typically 42%, 50% and 8%, respectively (Tao, 2011). The coal gas from the blast furnace is the main source of coal gas generated in the iron and steel production process. The mercury mass flows and emissions in the convertor are usually thought to be very low (UNEP, 2013b). Therefore the removal of mercury in the coal gas from the blast furnace should receive more attention. If the coal gas is mainly burned to generate electricity in the power plant as in the two tested plants of this study, the mercury emission control of the power plant will be important for the whole iron and steel plant. Thirdly, the recycled materials for the sintering machine can cause elevated mercury emissions from the iron and steel plant. The recycled materials consist mainly of the blast furnace dust. It can be seen that the blast furnace dust constitutes the dominant mercury output in both the blast furnace and the whole iron and steel production process. The recycling of the blast furnace dust can remarkably raise the mercury emissions, and therefore should not be conducted. Finally, the emissions from the electric furnace should be considered. In this study, the mercury concentration in the flue gas from the electric furnace was 2.4 μg/m^3, comparable with another study finding 0.75–1.04 μg/m^3 (Park et al., 2008). The mercury concentrations in the steel scrap and collected dust were 122 and 869 ppb, respectively (Table 1). Clearly the mercury emission from the electric furnace is significant. The steel production using an electric furnace in China made up only about 10% of all the steel production in 2010, while the average proportion was 30% worldwide (Lu and Zhang, 2012). It can be foreseen that steel production using electric furnaces in China may increase significantly in the future. Therefore mercury emission control for the electric furnace can be predicted to become more important and should not be neglected.

3. Conclusions

To systematically investigate the mercury mass flows and emission characteristics of iron and steel plants, field tests were conducted in two typical Chinese plants. It was found that the mercury emissions from the sintering machine and coal gas burning were largest, accounting for 46%–50% and 17%–49% of the total mercury emissions from the iron and steel plants. The mercury emissions from the production of limestone and dolomite and the electric furnace were also significant. The mercury emission factors for the two tested plants were 0.047–0.039 g Hg/ton steel, including emissions from the coke oven, sintering machine and blast furnace. The mercury emission factor for the electric furnace was 0.021 g Hg/ton steel. The oxidized mercury was the predominant emitted species, accounting for 73% and 59% of total Hg. The mercury emission estimate indicated that mercury emission control of low-sulfur flue gas from the sintering machine is crucial for the whole iron and steel plant. Desulfurization of the low-sulfur flue gas can remarkably help reduce the mercury emissions. Mercury control of coal gas burning, specifically for the power plant burning coal gas to generate electricity, is also important. More attention should be paid to the mercury emissions from the electric furnace, in view of the anticipated increase of the proportion of steel production using electric furnace in China. Additionally, the mercury mass flows indicated that the recycling of blast furnace dust could greatly increase the atmospheric mercury emissions and should not be conducted.

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