Environmental Pollution 171 (2012) 109–117

Contents lists available at SciVerse ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Were mercury emission factors for Chinese non-ferrous metal smelters overestimated? Evidence from onsite measurements in six smelters

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ARTICLE INFO

Article history:
Received 5 June 2012
Received in revised form
19 July 2012
Accepted 21 July 2012

Keywords:
Mercury emission
Non-ferrous metal smelting
Onsite measurements
China

ABSTRACT

Non-ferrous metal smelting takes up a large proportion of the anthropogenic mercury emission inventory in China. Zinc, lead and copper smelting are three leading sources. Onsite measurements of mercury emissions were conducted for six smelters. The mercury emission factors were 0.09–2.98 g Hg/t metal produced. Acid plants with the double-conversion double-absorption process had mercury removal efficiency of over 99%. In the flue gas after acid plants, 45–88% was oxidized mercury which can be easily scavenged in the flue gas scrubber. 70–97% of the mercury was removed from the flue gas to the waste water and 1–17% to the sulfuric acid product. Totally 0.3–13.5% of the mercury in the metal concentrate was emitted to the atmosphere. Therefore, acid plants in non-ferrous metal smelters have significant co-benefit on mercury removal, and the mercury emission factors from Chinese non-ferrous metal smelters were probably overestimated in previous studies.

1. Introduction

Mercury, bound with non-ferrous metal concentrate, would be released to the flue gas during the smelting process, and has significant impact on the local and regional environment. Based on previous study, non-ferrous metal smelting contributed 46% of the total mercury emission in China in 2003 (Wu et al., 2006). Zinc, lead and copper smelting accounted for 86% of the mercury emissions from non-ferrous metal smelting sector. However, the mercury emission factors for zinc, lead and copper smelting still suffer from large uncertainties. Nriagu and Pacyna (1988) reported that the mercury emission factors for zinc smelter are in the range of 8–45 g/t and those for lead smelter are in the range of 2–4 g/t. Pirrone et al. (1996) hypothesized the mercury emission factors for zinc and lead smelting to be 25 g/t and 3 g/t, respectively. However, in Streets et al. (2005) and Wu et al. (2006), values as high as 86.6 g/t, 43.6 g/t and 9.6 g/t were used for zinc, lead and copper smelting respectively. Pacyna et al. (2006) indicated that the mercury emission factors are 7.5–8 g/t for zinc smelter, 3 g/t for lead smelter, and 5–6 g/t for copper smelter. Hylander and Herbert (2008) summarized all the existing studies and got 12.09 g/t, 15.71 g/t and 5.81 g/t for zinc, lead and copper smelting respectively.

A recent study in a Chinese zinc smelter (Wang et al., 2010a) showed that the acid plant had high mercury removal efficiency and the mercury emission factor for the smelter was only 0.5 g/t. Only 0.8% of the mercury in the zinc concentrate was emitted to the atmosphere. The flue gas scrubber and the electrostatic demister in the tested acid plant can remove 17% and 30% of the total mercury. The conversion and absorption process in the acid plant has an average mercury removal efficiency of as high as 97.4%. The conversion tower is used to convert SO_2 to SO_3 with the existence of catalyst. The catalytic mercury oxidation process takes place simultaneously (Kamata et al., 2008; Lee and Bae, 2009). The oxidized mercury can easily be absorbed into the sulfuric acid inside the absorption tower. The high mercury removal efficiency in the acid plant indicates that the mercury emission factor was probably overestimated in the past. In this paper, onsite measurements were conducted in six non-ferrous metal smelters, the mercury removal efficiencies of all the air pollution control devices (APCDs) in non-ferrous smelters were comprehensively discussed, and the behavior of mercury in flue gas and the fate of mercury inside the smelters were systematically analyzed.

2. Experimental methods

2.1. Tested smelters

Hydrometallurgy, vertical retort (VR) pyrometallurgy and Imperial Smelting Process (ISP) pyrometallurgy are the three most commonly used techniques for zinc smelting in China, taking up 77%, 10% and 7% of zinc production in 2010 (MEP, 2011), respectively. ISP pyrometallurgy is a typical technique for both zinc and lead

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http://dx.doi.org/10.1016/j.envpol.2012.07.036

smelting. VR pyrometallurgy is an outdated technique which will be eliminated in the near future. For lead smelting, sintering + blast furnace technique is a traditional technique, making up 48% of lead production in 2010, while bath smelting (e.g. oxygen bottom-blowing, oxygen side-blowing, etc.) + blast furnace technique is an advanced technique, making up 47%. Bath smelting (e.g. Ausmelt smelting, Isa smelting, etc.), flash smelting and ISP smelting are the three dominant techniques for copper smelting, making up 52%, 34% and 10% of copper production in 2010, respectively. In this study, six non-ferrous metal smelters including two zinc smelters, two lead smelters, and two copper smelters, were selected for onsite measurements considering their smelting techniques and the APCDs used. Table 1 shows the basic information of the tested smelters. The two zinc smelters use hydrometallurgy and ISP pyrometallurgy, respectively. The two lead smelters use oxygen bottom-blowing + blast furnace technique and sintering + blast furnace technique, respectively. The two copper smelters use Ausmelt smelting and flash smelting, respectively.

The process flow diagram of non-ferrous metal smelting is illustrated as Fig. 1. Primary smelting is the key procedure in the smelting technique. Roasting, sintering, bath smelting and flash smelting are the main options for primary smelting. The operation temperature of primary smelting is over 850 °C, and thus most of the mercury goes into the flue gas after primary smelting. The flue gas will first pass through the exhaust-heat boiler and then the particle control devices. Electrostatic precipitator (ESP) is used in all tested smelters, while some smelters also use cyclone to collect coarse particles. The flue gas after ESP with high SO_2 concentration will enter the acid plant. In the acid plant, the flue gas usually goes through the flue gas scrubber (FGS), electrostatic demister (ESD), dehydration tower (DHT), and the conversion and absorption (C&A) process successively. Double-conversion double-absorption (DCDA) process is used in all other tested smelters except for Smelter 5 which uses single-conversion single-absorption (SCSA) process.

The metal extraction procedure includes leaching, blast furnace reduction, converter, and flash converting. Except for leaching, the metal extraction procedures are usually conducted in a temperature as high as 1000 °C. The flue gas from metal extraction usually is cleaned by the fiber filter (FF) before entering into the stack. The step after extraction is reclaiming or refining. This step is usually conducted in either volatilization kiln or fuming furnace for zinc and lead smelting, and anode furnace for copper smelting. The reclaiming/refining flue gas will also be cleaned by ESP or FF, and flue gas desulfurization device (FGD) may be applied if the SO_2 concentration exceeds the emission standard. The other three processes that will produce flue gas are dehydration kiln before smelting, overflow while smelting, and cooling for smelting residue.

2.2. Testing and analytical methods

The flue gas sampling sites were located at the inlets and outlets of APCDs. Different smelters have different sampling locations due to the operability of measurements. Nevertheless, the sampling sites in the six tested smelters have basically covered all the commonly used APCDs in non-ferrous metal smelters. Several sampling sites were located inside the acid plants in Smelter 1, Smelter 5 and Smelter 6, as shown in Fig. 2. The sampling ports, subject to test feasibility, did not completely cover all the inlets and outlets of the APCDs inside acid plants. The Ontario Hydro Method (namely, OH Method) (ASTM, 2002) was employed in the flue gas mercury measurements for the sampling sites with the SO_2 concentration less than 1000 ppm. For those sampling sites where the SO_2 concentration is over 1000 ppm, OH Method is not applicable because the large amount of SO_2 will easily deplete the H_2O_2 and $KMnO_4$ and affect the absorption of elemental mercury. Therefore, two alternative methods were introduced for high SO_2 conditions (see Table 2). Alternative Method 1 was developed based on EPA Method 29 (USEPA, 1996) to sample the total mercury in flue gas. Alternative Method 2 replaced the KCl impingers with KOH impingers to sample both oxidized mercury (Hg^{2+}) and elemental mercury (Hg^0), overcoming the impact of SO_2 in flue gas. To get a comprehensive understanding of the fate of mercury in smelters, the method of mass balancing was also adopted in this study. The input (raw materials) and the output (products) samples were collected in all the tested smelters. The mass flow data was collected to calculate the mercury flow in each smelter.

All the impinger solutions obtained from flue gas sampling and the liquid samples for mass balance were analyzed according to EPA Method 7470A (USEPA, 1994). The impinger solutions were recovered and analyzed with F732-V Intelligent Mercury Analyzer using Cold Vapor Atomic Absorption Spectrophotometry (CVAAS), which has a detection limit of 0.05 μg/L. Most of the solid samples were analyzed according to EPA Method 7473 (USEPA, 1998). The solid samples were air dried and grounded into 80 meshes for subsequent analysis. DMA-80 Direct Mercury Analyzer (Milestone, Italy), with a detection limit of 0.02 ng, was used for the mercury content analysis of solid samples. Some of the solid samples, such as zinc or lead concentrates, have very high mercury content which exceeded the measuring range of DMA-80. Those samples were first digested for 30 min using aqua regia at a temperature of 95 °C in a water bath and then measured using CVAAS.

2.3. QA/QC

In order to ensure the accuracy and reliability of the results, we strictly followed the operating procedures in standard methods for sampling and analysis. Before each field test, the flue gas mercury sampling system was calibrated carefully with thoroughly cleaning of the sampling line, and a leak test was performed to ensure no leakage. To reduce the accidental error in the tests for each location, parallel samplings were conducted to ensure the validity of the results. At least three valid test results were obtained under the stable operating condition, with the relative standard deviation less than 20%. Prior to the analysis of absorption samples, the F732-V was calibrated by drawing a standard curve with a correlation coefficient over 0.995. The analysis results were all over 10 times higher than detection limit of the instrument, and the samples with high mercury concentration were diluted before analysis. The blanks of all the reagents were low and deducted in the analysis. Two or more parallels of each sample were analyzed with the relative standard deviation less than 10%.

3. Results and discussion

3.1. Mercury concentrations and speciation in smelting flue gas

The mercury content in zinc concentrate was much higher than that in lead and copper concentrate (see Table 3), leading to very high mercury concentrations in the flue gas before acid plants in Smelter 1 and Smelter 2. All the mercury concentrations in the flue gas after acid plants were lower than 100 μg/m^3 (see Table 3). Smelter 1, Smelter 3 and Smelter 5 exceeded the newly implemented mercury emission standard (50 μg/m^3) for zinc and lead smelters in China (MEP, 2010). The lowest one was found in Smelter 6, where the mercury concentration was only 8 μg/m^3. The mercury speciation in the flue gas at the outlets of the acid plants was given in Fig. 3. The mercury speciation in the primary smelting flue gas before acid plants varied a lot among different smelters, while that in the exhaust flue gas after acid plants was similar. The proportions of Hg^{2+} in the exhaust flue gas for Smelter 1 to Smelter 4 were in the range of 78–88%. The Hg^{2+} proportion for Smelter 6 was 64%. The lowest Hg^{2+} proportion occurred in Smelter 5, because it was the only smelter using the single-conversion single-absorption (SCSA) process inside the acid plant. The SCSA process has lower mercury oxidation efficiency than the double-conversion double-absorption (DCDA) process used in other smelters.

Flue gas from metal extraction, dehydration kiln, reclaiming or refining only has particulate matter control devices, such as ESP or FF. The flue gases from metal extraction in the two lead smelters (Smelter 3 and Smelter 5) have mercury concentrations of 50 μg/m^3 and 38 μg/m^3, respectively, when they are emitted into the air. The mercury concentrations in reclaiming/refining flue gas of Smelter 2, Smelter 3 and Smelter 4 vary at a large range, from 0.9 to 254 μg/m^3. The mercury concentrations in the flue gas of dehydration, cooling and overflow process vary at the range of 9.47–824 μg/m^3, 8.59–72.1 μg/m^3, and 13.4–127 μg/m^3, respectively (as shown in Table 3). In comparison, the mercury emissions from primary

Table 1
Information on the tested non-ferrous metal smelters.

Testingsite	Product type	Capacity (kt/yr)	Technique type	Air pollution control devices (APCDs)
Smelter 1	Zn	150	ISP Pyrometallurgy (Blast furnace)	ESP + AP (DCDA)
Smelter 2	Zn	100	Hydrometallurgy (Roasting + Leaching)	ESP + AP (DCDA)
Smelter 3	Pb	80	Oxygen bottom-blowing + Blast furnace	ESP + AP (DCDA)
Smelter 4	Cu	200	Flash smelting + Flash converting	ESP + AP (DCDA)
Smelter 5	Pb	60	Sintering + Blast furnace	ESP + AP (SCSA)
Smelter 6	Cu	200	Ausmelt smelting furnace + Converter	ESP + AP (DCDA)

Note: ESP – electrostatic precipitator; AP – acid plant; SCSA – single-conversion single-absorption process; DCDA – double-conversion double-absorption process.

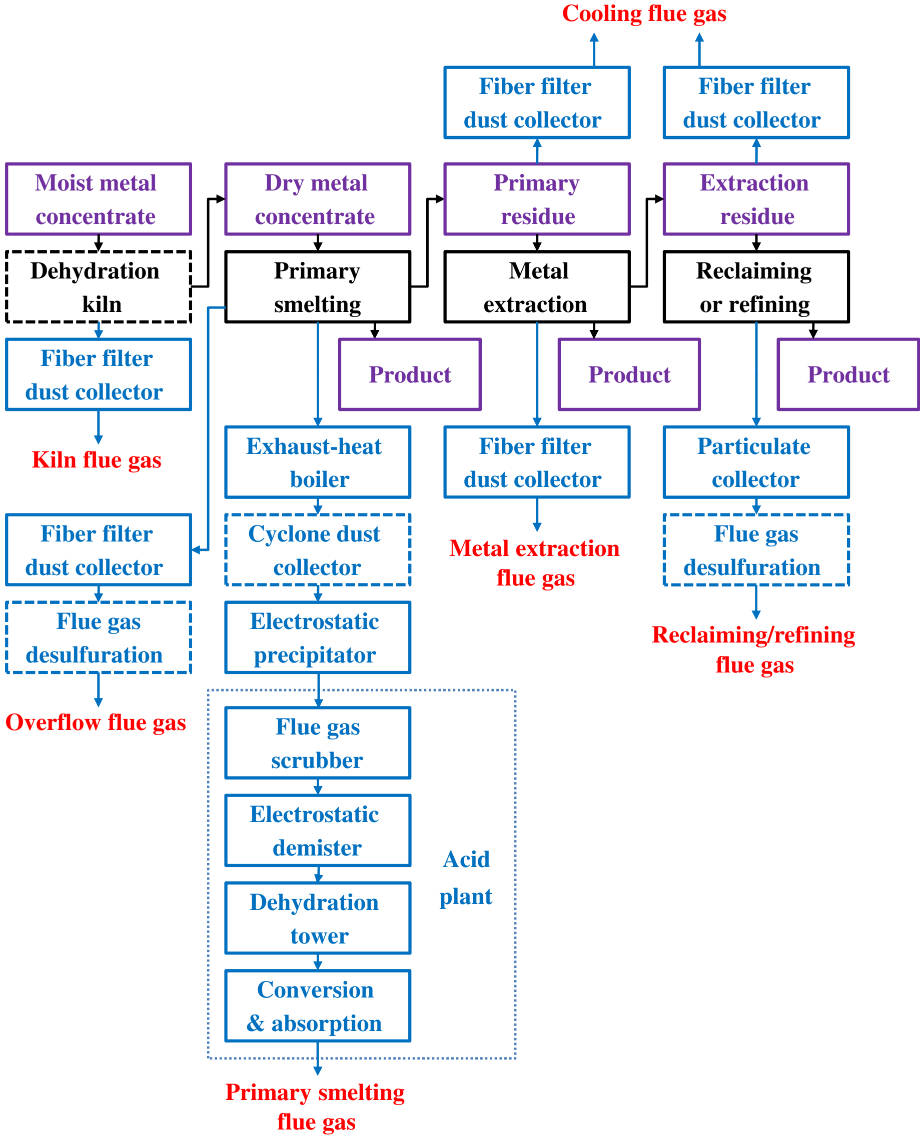

Fig. 1. Flow diagram for non-ferrous metal smelting.

smelting flue gas are much lower. The mercury concentration in flue gas is shown in Table 3.

A recent study (Kim et al., 2011) reported that the flue gas mercury concentration in zinc, lead and copper smelters in field tests in South Korea was 1.80 $\mu g/m^3$, 2.26 $\mu g/m^3$ and 0.58 $\mu g/m^3$, which was much lower than that in this study and previous studies. The possible reason is that the APCD configuration was different in their study. There is a flue gas scrubber after the acid plant in the tested smelters in Kim et al.'s study (2011), which is not present in the tested smelters of this study. Flue gas scrubber has high removal efficiency for Hg^{2+} because Hg^{2+} is water soluble (Wang et al., 2010b). It was mentioned above that the Hg^{2+} proportion in the flue gas after the acid plant is high according to results from our study. Therefore, the low mercury concentration in Kim et al.'s study is probably a result of the influence of the flue gas scrubber. Further flue gas scrubbing after the acid plant in non-ferrous metal smelters is a possible approach for mercury control in non-ferrous metal smelters.

For a certain smelter, the mercury speciation in the flue gas after the acid plant can be influenced by the SO_2 concentration in the flue gas. With the increase of SO_2 concentration, more H_2SO_4 is formed and the mercury oxidation process is enhanced, as shown by Reaction 1 (R1) and Reaction 2 (R2). However, as the SO_2 concentration further increases, the facilitation for the mercury oxidation process is overwhelmed by the reduction of $HgSO_4$, as illustrated by Reaction 3 (R3), and the proportion of oxidized mercury in flue gas gradually decreases.

$$SO_2 + (1/2)O_2 + H_2O \rightarrow H_2SO_4 \quad \text{(R1)}$$

$$Hg + (1/2)O_2 + H_2SO_4 \rightarrow HgSO_4 + H_2O \quad \text{(R2)}$$

$$HgSO_4 + SO_2 + 2H_2O \rightarrow Hg + 2H_2SO_4 \quad \text{(R3)}$$

These chemical reactions are only tentative and further studies are needed to verify the relationship between mercury speciation and SO_2 concentration in the flue gas after the acid plant. With the tightening of the SO_2 emission standard in non-ferrous metal smelters in the future, the flue gas desulfurization system would be installed at the outlet of the acid plants. Consequently the oxidized

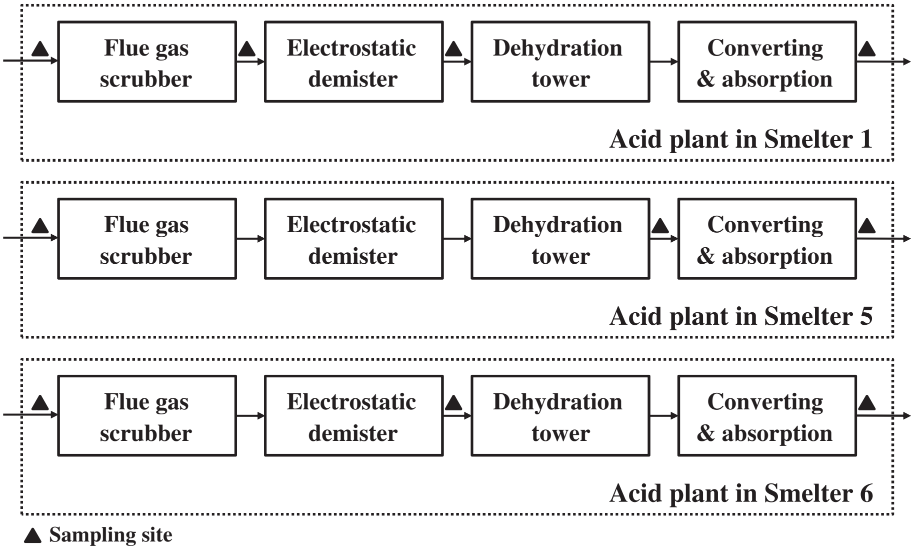

Fig. 2. Sampling sites inside acid plants.

mercury can be largely removed in wet flue gas desulfurization (WFGD) system. Therefore, the SO_2 control strategies for non-ferrous metal smelters in the future will benefit the mercury removal and the co-benefit can be further enhanced when the relationship between mercury speciation and SO_2 concentration is comprehensively identified.

3.2. *Mercury removal efficiencies of APCDs*

Table 4 listed the mercury removal efficiencies of APCDs inside non-ferrous metal smelters. The average mercury removal efficiencies of ESP and FF are 12% and 44%, respectively, while that for the acid plant with DCDA is as high as 99.6%. The acid plant in Smelter 5 with SCSA process removed 83% of the total mercury in the primary smelting flue gas. For Smelter 1, FGS and ESD process abated the mercury concentration by 49% and 24% respectively, while DHT and C&A process had a total mercury removal efficiency of 99.7%. In Smelter 5, FGS + ESD + DHT removed 51% of the total mercury in flue gas, and the total mercury concentration decreased by 65% in C&A process. In Smelter 6, FGS and ESD had a high efficiency of 99.5% for mercury removal, while DHT and C&A process only removed 43% of the total mercury in flue gas.

The mercury removal inside the acid plant can be generally divided into two stages. During the first stage, that is, FGS and ESD, mercury in the flue gas goes into the waste water. During the second stage, that is, DHT and the C&A process, mercury in the flue gas goes into the sulfuric acid product. The removal efficiency in each stage is determined by the speciation of mercury in the flue gas entering into the acid plant. The comparison between Smelter 5 and Smelter 6 provides a good example. The elemental mercury accounts for 96% of the total mercury in the flue gas entering into the acid plant in Smelter 5, which results the lower mercury removal efficiency in the first stage. In the second stage, the mercury removal efficiency is higher due to the oxidation of Hg^0 in the C&A process. In contrast, the Hg^{2+} accounts for 98% of total mercury in the flue gas entering into acid plant in Smelter 6. Therefore, most of the mercury in flue gas is removed in the first stage because Hg^{2+} can easily dissolve into the scrubbing water.

3.3. *Fate of mercury in non-ferrous metal smelters*

The mass distribution of mercury is shown in Table 5, and the fate of mercury in tested non-ferrous metal smelters is shown in Fig. 4. The mass balance recovery rates of all the tested smelters were in the range of 85–120%, which indicates that the test results are in acceptable accuracy. Less than 4% of the mercury is emitted into the air except for Smelter 5. In Smelter 5, 11% of the mercury is emitted to the air. The fractions of mercury removed via fly ash are

Table 2
Impinger trains of the two alternative methods.

Method	Scope of application	Impinger trains
Ontario Hydro Method	Speciated mercury (SO_2 < 1000 ppm)	3 (1M KCl) + 1 (1% H_2O_2/5% HNO_3) + 3 (4% $KMnO_4$/10% H_2SO_4)
Alternative Method 1	Total mercury SO_2 > 1000 ppm)	3 (3% H_2O_2/5% HNO_3) + 3 (4% $KMnO_4$/10% H_2SO_4)
Alternative Method 2	Speciated mercury (SO_2 > 1000 ppm)	3 (1M KOH) + 1 (3% H_2O_2/5% HNO_3) + 3 (4% $KMnO_4$/10% H_2SO_4)

Table 3
Mercury in concentrates and flue gases.

	Smelter 1 (Zn)	Smelter 2 (Zn)	Smelter 3 (Pb)	Smelter 4 (Cu)	Smelter 5 (Pb)	Smelter 6 (Cu)
Hg content in raw material (mg/kg)						
Metal concentrate	268.2	47.58	18.66	1.48	2.15	4.23
Hg concentration in flue gas (μg/m^3)						
Before acid plant	60,985	151,34	11,720	1772	430	2631
After acid plant	74.8	34.5	50.6	16.5	72.6	7.9
Hg speciation in the primary smelting flue gas (%)						
Hg^{2+}	–	69	87	–	4	98
Hg^0	–	31	13	–	96	2
Hg concentration in flue gas emitted to the air (μg/m^3)						
Metal extraction	–	–	50.0	–	37.8	–
Reclaiming/refining	–	254	30.6	0.90	–	–
Dehydration kiln	824	–	–	9.47	–	–
Cooling	–	–	72.1	8.59	–	–
Overflow	127	–	–	–	–	13.4

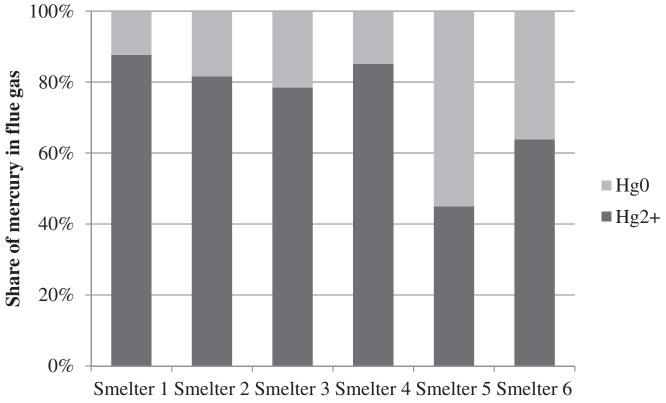

Fig. 3. Mercury speciation in the flue gas at the outlets of the acid plants.

14–20% for smelters 1, 2 and 3 but only 3% in the other smelters since fly ash is reused in the process in these plants. In total 70–97% of the mercury is removed via waste water and 1–17% via the sulfuric acid product.

The proportion of mercury entering into the waste water is significantly relevant with the proportion of Hg^{2+} in the flue gas after the acid plant (see Fig. 5). The mercury captured by the flue gas cleaning processes goes to the waste water. The Hg^{2+} in flue gas is easily scrubbed by water, while Hg^0 is not. Therefore, higher mercury retention in the waste water will lead to a significant decrease in Hg^{2+} proportion in flue gas, and thus the percentage of Hg^{2+} in the flue gas after the acid plant will become lower. Smelter 5 is not included in Fig. 5 since its C&A process is not same as those of other smelters.

Waste water and fly ash are two main byproducts from non-ferrous metal smelters. The waste water from FGS and ESD will be treated and most of the mercury will enter into the sludge. The sludge and the fly ash will be disposed as hazardous solid waste. It should be noted that these byproducts could be potential mercury emission sources to water and soil if they are not properly disposed.

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

	Electrostatic precipitator (η_{ESP})	Fiber filter (η_{FF})	Acid plant (DCDA) ($\eta_{AP\text{-}DCDA}$)	Acid plant (SCSA) ($\eta_{AP\text{-}SCSA}$)
Mercury removal efficiency (%)	11.6	43.7	99.6	83.1
Number of tested APCDs	5	6	5	1

3.4. Mercury emission factors for non-ferrous metal smelting

To get a comprehensive understanding of mercury emission from non-ferrous metal smelters, we applied a mass balance method to calculate the mercury emission factor for various non-ferrous metal smelting processes.

$$EF_{overall} = \sum_i EF_i \cdot \lambda_i \tag{E1}$$

$$EF = EF_{DHK} + EF_{OF} + EF_{PS} + EF_{ME} + EF_{RR} + EF_{RC} \tag{E2}$$

$$EF_{DHK} = M\varepsilon_{DHK}(1 - \eta_{DHK\text{-}FF}) \tag{E3}$$

$$EF_{OF} = M(1 - \varepsilon_{DHK})\varepsilon_{OF}(1 - \eta_{OF\text{-}FF})(1 - \eta_{OF\text{-}FGD}) \tag{E4}$$

$$EF_{PS} = M(1 - \varepsilon_{DHK})(1 - \varepsilon_{OF})r_{PS}(1 - \eta_{PS\text{-}ESP})(1 - \eta_{PS\text{-}AP}) \tag{E5}$$

$$EF_{ME} = M(1 - \varepsilon_{DHK})(1 - \varepsilon_{OF})(1 - r_{PS})r_{ME}(1 - \eta_{ME\text{-}FF}) \tag{E6}$$

$$\begin{aligned} EF_{RR} = M(1 - \varepsilon_{DHK})(1 - \varepsilon_{OF})(1 - r_{PS})(1 - r_{ME})r_{RR} \\ (1 - \eta_{RR\text{-}ESP})(1 - \eta_{RR\text{-}FGD}) \end{aligned} \tag{E7}$$

$$\begin{aligned} EF_{RC} = M(1 - \varepsilon_{DHK})(1 - \varepsilon_{OF})(1 - r_{PS})[1 \\ + (1 - r_{ME})]\varepsilon_{RC}(1 - \eta_{RC\text{-}FF}) \end{aligned} \tag{E8}$$

Table 5
Mass distribution of mercury inside the tested smelters (%).

	Smelter 1	Smelter 2	Smelter 3	Smelter 4	Smelter 5	Smelter 6
Primary smelting flue gas	**98.84**	**99.25**	**96.00**	**96.95**	**97.96**	**99.52**
Smelting product	–	–	0.02	0.82	1.31	1.46
Fly ash	19.81	13.77	13.21	–	2.31	–
Waste water from scrubber	69.74	84.63	82.23	78.08	72.92	97.06
Sulfuric acid	9.22	0.68	0.17	17.16	11.88	0.69
Flue gas to the air	0.07	0.17	0.37	0.90	9.56	0.32
Metal extraction flue gas	–	–	**1.57**	**0.16**	**2.04**	**0.35**
Extraction product	–	–	0.06	0.16	0.70	0.35
Fly ash	–	–	0.85	–	0.05	–
Flue gas to the air	–	–	0.66	–	1.29	–
Reclaiming/refining flue gas	–	**0.75**	**1.14**	–	–	–
Reclaiming/refining product	–	0.19	0.07	–	–	–
Fly ash	–	0.05	0.55	–	–	–
Flue gas to the air	–	0.52	0.52	–	–	–
Dehydration kiln flue gas	**0.13**	–	–	**0.90**	–	–
Flue gas to the air	0.13	–	–	0.90	–	–
Cooling flue gas	–	–	**1.28**	**1.99**	–	–
Fly ash	–	–	0.33	0.68	–	–
Flue gas to the air	–	–	0.96	1.31	–	–
Overflow flue gas	**1.03**	–	–	–	–	**0.12**
Fly ash	0.98	–	–	–	–	–
Desulfurization gypsum	0.02	–	–	–	–	–
Flue gas to the air	0.04	–	–	–	–	0.12
Recovery rate	**118**	**85**	**106**	**105**	**102**	**105**

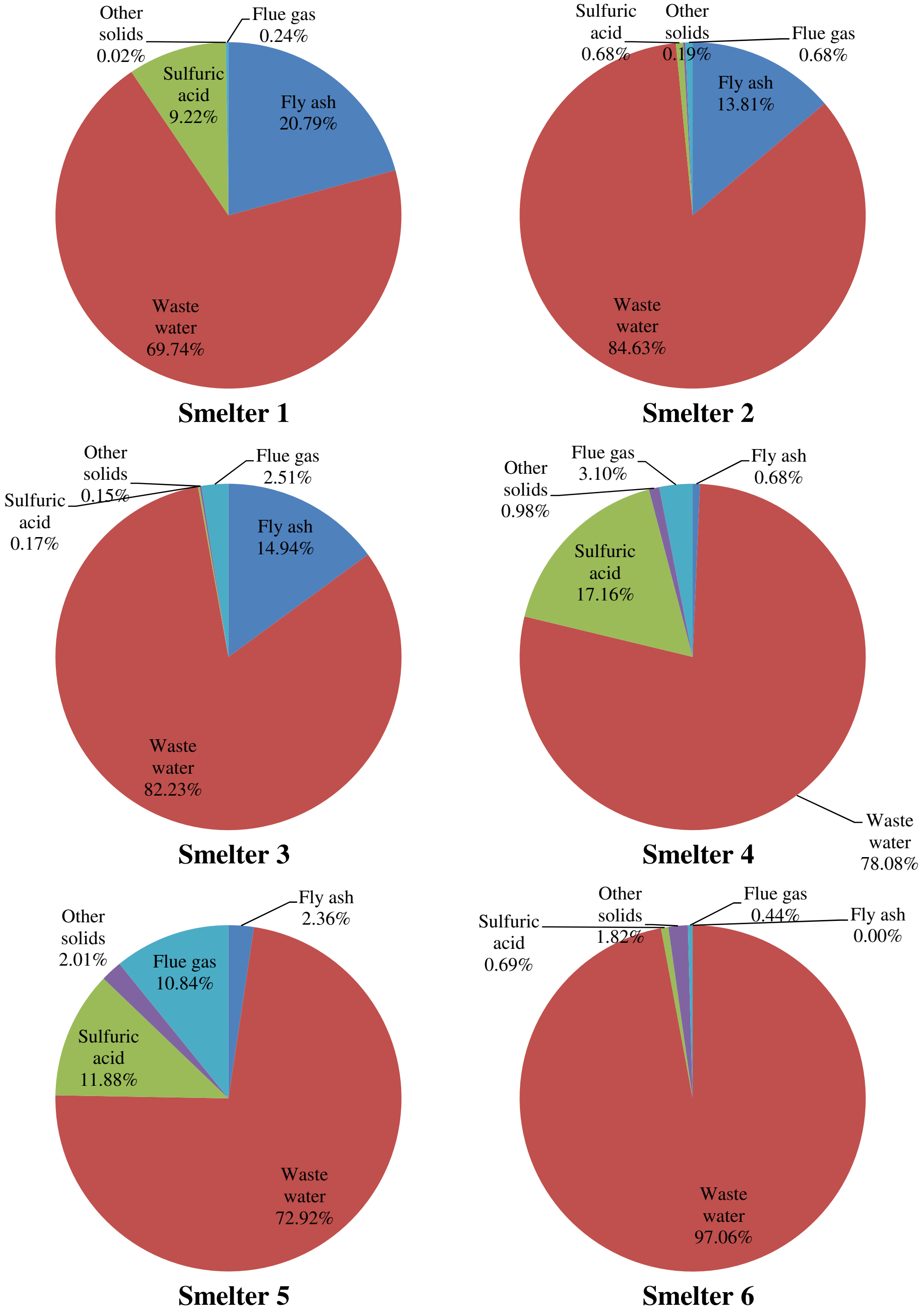

Fig. 4. Fate of mercury in tested smelters.

EF is the mercury emission factor based on the consumption of concentrate; λ is the application rate of a certain combination of smelting technologies and APCDs; i is the combination type of smelting technologies and APCDs; M is the mercury content in metal concentrate; ε is the mercury distribution coefficient; r is the mercury release rate; η is the mercury removal efficiency. DHK stands for dehydration kiln; OF stands for overflow; PS stands for primary smelting; ME stands for metal extraction; RR stands for reclaiming/refining; RC stands for residue cooling; ESP stands for electrostatic precipitator; FF stands for fiber filter; AP stands for acid plant; FGD stands for flue gas desulfurization. If a certain process is not applied, ε equals to zero. If a certain APCD is not applied, η equals to zero. Fly ash from some FFs/ESPs will return to the previous technical processes, under which circumstances η is regarded as zero.

Table 6 shows the parameters for mercury release and removal in the tested smelters. The distribution coefficients for dehydration kiln and overflow are all less than 1%. The average release rate for primary smelting is 99%. ESP can remove 12% of the flue gas mercury averagely. Acid plant with DCDA process has an average

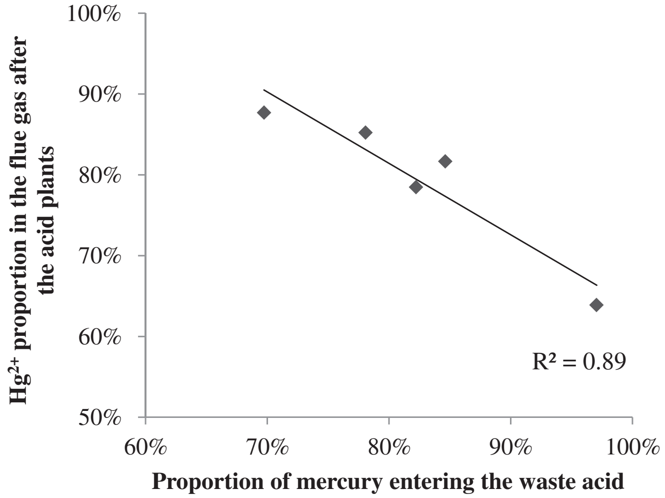

Fig. 5. The correlation between the proportion of mercury entering the waste water and the Hg^{2+} proportion in the flue gas after the acid plants.

Table 7
Mercury emission factors and flue gas mercury emission characteristics.

	Smelter 1 (Zn)	Smelter 2 (Zn)	Smelter 3 (Pb)	Smelter 4 (Cu)	Smelter 5 (Pb)	Smelter 6 (Cu)
Mercury emission factor						
(g Hg/t concentrate consumed)	0.93	0.27	0.60	0.05	0.29	0.02
(g Hg/t metal produced)	2.98	0.57	1.00	0.23	0.49	0.09
Hg emission rate (%)	0.3	0.6	3.2	3.2	13.5	0.5
Fraction of mercury species in flue gas (%)						
Hg^{2+}	61	58	39	32	40	68
Hg^0	39	42	61	68	60	32
Share of each type of flue gas emitted to the air (%)						
Primary smelting	29	24	15	29	88	72
Metal extraction	–	–	26	–	12	–
Reclaiming/refining	–	76	20	–	–	–
Dehydration kiln	54	–	–	29	–	–
Cooling	–	–	38	41	–	–
Overflow	17	–	–	–	–	28

mercury removal efficiency of 99.6%, while the mercury removal efficiency of acid plant with SCSA process is 83%. The mercury release rates of metal extraction and reclaiming/refining have a large variation range, and so do the mercury removal efficiencies of ESP or FF for these two processes. Mercury emission factor is one of the key parameter to estimate mercury emissions from non-ferrous metal smelting. Table 7 shows the mercury emission factors and the flue gas mercury emission characteristics of tested smelters. The mercury emission factors were first calculated in the forms of mercury emission per ton concentrate consumed. Mercury concentrations in the ore concentrates varied between 0.02 and 0.93 g/t in the investigated smelters. Based on the metal concentration in the concentrate and the metal recovery rate, the product-based mercury emission factors were calculated. The mercury emission factors were 2.98 and 0.57 g Hg/t Zn produced, 1.00 and 0.49 g Hg/t Pb produced, 0.23 and 0.09 g Hg/t Cu produced for zinc, lead and copper smelters, respectively. The mercury emission factor tends to have an order of Zn > Pb > Cu, due to the mercury concentration in the metal concentrate, as given in Table 3.

Table 8 compared the mercury emission factors for non-ferrous metal smelters obtained from this study and those from previous studies. Generally there are two types of mercury emission factors, those measured from a certain type of smelter (i.e., emission factors No. 1–14 in Table 8) and the average of data from literature which is used for emission inventory calculation (i.e., emission factors No. 15–30 in Table 8). Feng et al. (2004) and Li et al. (2008) reported three emission factors for artisanal zinc smelting with no APCDs which are much higher than those for large-scale smelting with APCDs. The factors from this study are close to the one reported by Wang et al. (2010a), but lower than those from measurements by Li et al. (2010). This is because the mercury removal efficiency of acid plants from the study of Li et al. (2010) was in a low range of 29.6–65.3%, while that from this study is as high as 99.6%. Li et al. (2010) did not measure the mercury in flue gas and estimated the mercury removal efficiency of acid plant with a mass balance method. We obtained the efficiency through the method of flue gas mercury measurements, which is much more precise than the method of mass balance. The average mercury emission factors from previous studies (Nriagu and Pacyna, 1988; Pirrone et al., 1996; Pacyna and Pacyna, 2002; Streets et al., 2005; Pacyna et al., 2006; Hylander and Herbert, 2008) vary at a large range, as shown in Table 8. The most important parameters for the overall mercury emission factor are the mercury content in concentrate (M), the mercury removal efficiency (η) and the application rate of a certain combination of smelting technologies and APCDs (λ). The mercury content (M) in the concentrate in China varies largely from less than 1 to 2534 mg/kg (unpublished data), which will highly influence the emission factor. The average mercury removal efficiency of the DCDA acid plants ($\eta_{\text{PS-AP}}$) in the study of Hylander and Herbert (2008) was 99%, slightly lower than that from this study (99.6%). The major difference between our study and these studies is the proportion of artisanal smelting or outdated smelting technologies ($\lambda_{\text{artisanal}}$). Taking zinc smelting for example, the previous study (Hylander and Herbert, 2008) assumed that only about 60% of the Chinese zinc smelters were advanced smelters with ESP + AP in 2007. However, According to the Chinese Statistical Yearbook (CNIA, 2008), 86% of the Chinese zinc smelters has installed APCDs including ESP + AP (DCDA) by 2007, which has high mercury removal efficiency.

The total mercury emission rates for the five smelters with DCDA process varied from 0.3 to 3.2%, while that for Smelter 5 with SCSA process was as high as 13.5%. In the total mercury emitted to the air, the ratio of Hg^{2+}/Hg^0 varied from 0.5 to 2. The considerable fraction of Hg^0 was mainly contributed by the share of dehydration

Table 6
Parameters for mercury release and removal in tested smelters (%).

	Smelter 1	Smelter 2	Smelter 3	Smelter 4	Smelter 5	Smelter 6
Dehydration kiln (DHK)						
ε_{DHK}	0.1	–	–	0.9	–	–
$\eta_{\text{DHK-FF}}$	0.0	–	–	0.0	–	–
Overflow (OF)						
ε_{OF}	1.0	–	–	–	–	0.1
$\eta_{\text{OF-FF}}$	94.3	–	–	–	–	–
$\eta_{\text{OF-FGD}}$	31.0	–	–	–	–	–
Primary smelting (PS)						
r_{PS}	–	99.2	96.0	97.8	98.0	99.6
$\eta_{\text{PS-ESP}}$	20.0	13.9	13.8	0.0	2.4	0.0
$\eta_{\text{PS-AP}}$	99.9	99.8	99.6	99.1	83.1	99.7
Metal extraction (ME)						
r_{ME}	–	–	58.0	–	–	–
$\eta_{\text{ME-FF}}$	–	–	54.0	–	2.5	–
Reclaiming/refining (RR)						
r_{RR}	–	74.5	93.7	–	–	–
$\eta_{\text{RR-ESP/FF}}$	–	8.1	51.7	–	–	–
Residue cooling (RC)						
ε_{RC}	–	–	1.3	2.0	–	–
$\eta_{\text{RC-FF}}$	–	–	25.4	34.2	–	–

Table 8
Comparison of mercury emission factors for non-ferrous metal smelting in different studies.

No.	Smelting technology	APCDs	Emission factors	Metal	References
1	Artisanal smelting	None	79	Zn	Feng et al. (2004)
2	Artisanal smelting	None	155	Zn	Feng et al. (2004)
3	Artisanal smelting	None	75	Zn	Li et al. (2008)
4	Hydrometallurgy	AP (DCDA) + MR	0.5	Zn	Wang et al. (2010a)
5	Hydrometallurgy	AP (DCDA) + MR	5.7	Zn	Li et al. (2010)
6	Hydrometallurgy	AP (DCDA)	31	Zn	Li et al. (2010)
7	VR smelting	AP (DCDA)	34	Zn	Li et al. (2010)
8	ISP smelting	AP (DCDA)	122	Zn	Li et al. (2010)
9	ISP smelting	AP (DCDA)	2.98	Zn	This study
10	Hydrometallurgy	AP (DCDA)	0.57	Zn	This study
11	Bath smelting	AP (DCDA)	1.00	Pb	This study
12	Flash smelting	AP (DCDA)	0.23	Cu	This study
13	Sintering	AP (SCSA)	0.49	Pb	This study
14	Bath smelting	AP (DCDA)	0.09	Cu	This study
15	Average of all technologies and APCDs		8–45	Zn	Nriagu and Pacyna (1988)
16	Average of all technologies and APCDs		2–4	Pb	Nriagu and Pacyna (1988)
17	Average of all technologies and APCDs		25	Zn	Pirrone et al. (1996)
18	Average of all technologies and APCDs		3	Pb	Pirrone et al. (1996)
19	Average of all technologies and APCDs		20	Zn	Pacyna and Pacyna (2002)
20	Average of all technologies and APCDs		3	Pb	Pacyna and Pacyna (2002)
21	Average of all technologies and APCDs		10	Cu	Pacyna and Pacyna (2002)
22	Average of all technologies and APCDs		86.6	Zn	Streets et al. (2005)
23	Average of all technologies and APCDs		43.6	Pb	Streets et al. (2005)
24	Average of all technologies and APCDs		9.6	Cu	Streets et al. (2005)
25	Average of all technologies and APCDs		7.5–8	Zn	Pacyna et al. (2006)
26	Average of all technologies and APCDs		3	Pb	Pacyna et al. (2006)
27	Average of all technologies and APCDs		5–6	Cu	Pacyna et al. (2006)
28	Average of all technologies and APCDs		12.09	Zn	Hylander and Herbert (2008)
29	Average of all technologies and APCDs		15.71	Pb	Hylander and Herbert (2008)
30	Average of all technologies and APCDs		5.81	Cu	Hylander and Herbert (2008)

Note: the unit of the mercury emission factor is g Hg/t metal produced. VR – vertical retort; ISP – Imperial Smelting Process; AP – acid plant; MR – mercury reclaimer; SCSA – single-conversion single-absorption process; DCDA – double-conversion double-absorption process.

kiln, cooling and reclaiming/refining flue gas emitted to the air. As mentioned previously, in the primary smelting flue gas emitted to the air, most of the mercury was in the form of oxidized mercury except Smelter 5. However, in Smelter 1, the dehydration kiln flue gas accounted for more than half of the mercury emission, while the reclaiming flue gas took the lead in Smelter 2. For Smelter 3 and Smelter 4, the cooling flue gas took up the largest share. The dominance of primary smelting flue gas was only found in Smelter 5 and Smelter 6. Therefore, it is very important to control the mercury emission of dehydration kiln, reclaiming and cooling flue gases.

Based on the above discussion, there are a few measures that China can take to control mercury emissions from non-ferrous metal smelters. Switching the concentrate with high mercury content into those with low mercury content is an easy way to reduce mercury emissions. The retrofit of SCSA with DSDA and installation of mercury recovery devices will significantly reduce the mercury emissions. More importantly, the mercury emission of dehydration kiln, reclaiming and cooling flue gases should be paid enough attention. Further studies shall be conducted to identify the fate of mercury in sulfuric acid as it may be used as a raw material for the production of other materials including fertilizers, which could then re-introduce mercury into the crop food chain.

4. Conclusions

Field measurements in six non-ferrous metal smelters were carried out in this study. Although different smelters have different techniques, a typical non-ferrous metal smelting technique consists of three procedures: primary smelting, metal extraction and reclaiming/refining. Primary smelting, the highest-temperature procedure, is the key procedure in non-ferrous metal smelters. Over 96% of the mercury in metal concentrates enters into the primary smelting flue gas. The acid plants have a total mercury removal efficiency of over 99%, except for that in Smelter 5. The mercury removal efficiency in these acid plants is positively related to the total mercury concentration in the primary smelting flue gas entering into the acid plant. The acid plant in Smelter 5 with SCSA process removed 83% of the total mercury in the primary smelting flue gas. Inside acid plants, 70–97% of the mercury goes into the waste water, and 1–17% ends up in the sulfuric acid products.

The proportions of Hg^{2+} in the primary smelting flue gas are high except for Smelter 5, due to the mercury oxidation in the conversion and absorption process. The mercury speciation in the flue gas after the acid plant is influenced by the SO_2 concentration in the flue gas. Higher mercury retention in the waste water will lead to a significant decrease in Hg^{2+} proportion in flue gas, and thus the percentage of Hg^{2+} in the flue gas after the acid plant will be lower. However, the Hg^0 share is much higher in the flue gas from dehydration kiln, reclaiming, and cooling, which results the higher fraction of Hg^0 in mercury emissions. The mercury emission factors were 2.98 and 0.57 g Hg/t Zn produced, 1.00 and 0.49 g Hg/t Pb produced, 0.23 and 0.09 g Hg/t Cu produced for zinc, lead and copper smelters, respectively. The emission factors obtained from this study are much lower than those from most previous studies, implying that previous studies might overestimate the mercury emissions from non-ferrous metal smelting in China. Smelter 5 with a total mercury emission rate of 13.5% indicated that the SCSA process in the acid plant has much lower mercury removal efficiency than that of the DCDA process and thus should be phased out from the smelting industry in China.

The mercury emission factor in this study was calculated according to the mercury content in the metal concentrate, mercury release rates, mercury distribution coefficients, and mercury removal efficiencies by APCDs. The values of these parameters can be used to establish a technology-based mercury emission factor model. With the emission factor model and the detail activity information such as application rate, metal production amount by smelting process and APCD configuration, an accurate technology-based inventory of mercury emissions from non-ferrous metal smelters in China can be developed.

Acknowledgment

This work was funded by National Science Foundation of China (No. 20937002), MEP's Special Funds for Research on Public Welfares (No. 200909024), and Norwegian government.

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