Environmental Pollution 158 (2010) 3347–3353

Contents lists available at ScienceDirect

Environmental Pollution

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

Estimating mercury emissions from a zinc smelter in relation to China's mercury control policies

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Modern scale production equipped with acid plant and Hg reclaiming tower will significantly reduce Hg emissions from zinc smelters in China.

ARTICLE INFO

Article history:
Received 22 April 2010
Received in revised form
17 July 2010
Accepted 24 July 2010

Keywords:
Hydrometallurgical zinc smelting
Hg removal efficiency
Speciation
Emission factor
Control policy

ABSTRACT

Mercury concentrations of flue gas at inlet/outlet of the flue gas cleaning, electrostatic demister, reclaiming tower, acid plant, and mercury contents in zinc concentrate and by-products were measured in a hydrometallurgical zinc smelter. The removal efficiency of flue gas cleaning, electrostatic demister, mercury reclaiming and acid plant was about 17.4%, 30.3%, 87.9% and 97.4% respectively. Flue gas cleaning and electrostatic demister captured 11.7% and 25.3% of the mercury in the zinc concentrate, respectively. The mercury reclaiming tower captured 58.3% of the mercury in the zinc concentrate. About 4.2% of the mercury in the zinc concentrate was captured by the acid plant. Consequently, only 0.8% of the mercury in the zinc concentrate was emitted to the atmosphere. The atmospheric mercury emission factor was 0.5 g t^{-1} of zinc produced for the tested smelter, indicating that this process offers the potential to effectively reduce mercury emissions from zinc smelting.

1. Introduction

Mercury (Hg) is one of the most important environmental contaminants that arouse a global concern due to its toxicity, long-distance transport, persistence and bioaccumulation in the environment. It is estimated that 2320 t of Hg is released annually to the global atmosphere, mainly from fossil-fuel combustion, non-ferrous metal production, artisanal gold mining, cement production, caustic soda production, waste disposal, and pig iron and steel production (Pirrone et al., 2010). Among Asian countries, China is regarded as the largest anthropogenic Hg emission source. Our previous studies indicated that the annual Hg emission from China reached 696 t of Hg in 2003, which contributed about 30% to the global emissions of Hg (Wu et al., 2006; Streets et al., 2005).

Since both Hg and Zn are sulphophilic elements, Hg is an important associated element in Zn ores, especially in zinc sulfide ore. The extraction of Zn from ores requires roasting, sintering, and/or smelting of the ore at high temperatures (900–1000 °C). At these high temperatures, Hg in Zn ore will inevitably be released to the atmosphere during the smelting process. Global emissions to the atmosphere from zinc smelting are about 310 t per year (Pirrone et al., 2010). Driven by strong economic growth in China during the last decade, the demand for ferrous and non-ferrous metals has increased significantly. Increasing trends in zinc production are leading to an increase of Hg releases to the atmosphere. Our previous studies have indicated that zinc smelting has become one of the largest single sectors in total Hg emissions in China, emitting 187.6 t Hg in 2003 (Wu et al., 2006). However, it should be noted that this estimate of emissions from zinc smelting is subject to high uncertainty due to lack of measured emission factors for the various smelting processes. To reliably estimate the Hg emissions from zinc smelters in China, it is imperative to fully understand the behavior and fate of Hg in the different zinc smelting processes and to investigate the atmospheric Hg emission factor of zinc smelters.

Hg emission factors for zinc production are believed to vary widely, depending on the process used and the presence or absence of emission control measures. Previous studies have assumed values of about 7.5–8.0 g t^{-1} for Europe, North America and Australia, and 20 or 25 g t^{-1} for Africa, Asia and South America (Nriagu and Pacyna, 1988; Pirrone et al., 1996; Prasad et al., 2000; Pacyna and Pacyna, 2002; Pacyna et al., 2003, 2006; Streets et al., 2005). Due to the different processes and pollution-control techniques used in China, the Hg emission factors of zinc smelters may differ dramatically from those in developed countries.

Over 95% of the world's zinc is produced from zinc blende (ZnS). Apart from zinc the concentrate contains some 25–30% or more sulfur as well as different amounts of iron, lead and silver and other

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doi:10.1016/j.envpol.2010.07.032

minerals. Globally, two main zinc smelting processes are in use: (i) a pyrometallurgical process run at high temperatures to produce liquid zinc; (ii) a hydrometallurgical or electrolytic process using aqueous solution in combination with electrolysis to produce a solid zinc deposit. Before metallic zinc can be recovered, by using either hydrometallurgical or pyrometallurgical techniques, sulfur in the concentrate must be removed. This is usually done by roasting or sintering. The concentrate is brought to a temperature of more than 900 °C where zinc sulfide (ZnS) converts into the more active zinc oxide (ZnO). At the same time, sulfur reacts with oxygen giving out sulfur dioxide which subsequently is converted to sulfuric acid. In 1981, a new hydrometallurgical technique called the oxidative pressure leaching process stepped into industrialization. This process does not need either roasting or sintering, it uses zinc sulfide concentrates directly. Currently, there are 6 plants using this process to produce zinc in the world, and one of them is located in China (IZA, 2010; Zhou, 2005). Therefore, the hydrometallurgical process is further divided into Electrolytic Process (EP) and Oxidative Pressure Leaching Process (OPLP). The pyrometallurgical process can further be divided into the Imperial Smelting Process (ISP), the retort zinc smelting process (RZSP), the electric zinc furnace (EZF), and various artisanal zinc smelting processes (AZSP). Total zinc production in China reached 3.16 million t in 2006, of which 71.2% is based on the hydrometallurgical process (99% are EP). Production using pyrometallurgical process, ISP, RZSP, EZF and AZSP, accounted for 7.7%, 5.9%, 13%, and 1.6% of total zinc production, respectively (Jiang, 2006; Zhou, 2005). Using a mass balance method, Feng et al. (2004) calculated Hg emission factors from artisanal zinc smelting, which were 79 g t^{-1} for oxide ores and 155 g t^{-1} for sulfide ores. Li et al. (2008) estimated that the geometric mean Hg emission factor of artisanal zinc smelting in China was 75 g t^{-1}. Li (2007) investigated Hg emission factors from four large-scale zinc smelters and concluded that Hg emission factors varied significantly with different smelting processes, from 5.7 g t^{-1} to 122 g t^{-1}. These studies indicate the high uncertainties of Hg emission factors of zinc smelting in China. Therefore, there is tremendous need to investigate Hg emissions from different zinc smelting processes in China.

This paper presents a comprehensive investigation of Hg emissions from a hydrometallurgical zinc smelter in China. The Hg removal efficiencies of air pollution control devices (APCDs) in the smelting process were evaluated according to the simultaneous measurement of Hg concentrations in the flue gas at the inlet and outlet of the APCDs. The atmospheric Hg emission factor during the Zn smelting process was calculated and the Hg speciation profile in the stack gas emitted to the atmosphere was investigated.

2. Experimental methods

2.1. Smelter studied

The major products of the chosen smelter are Zn, Pb and their alloy. The average consumption of zinc concentrate was 738 t d^{-1} (dry, physical quantity) during our test period. The zinc production was 344 t d^{-1}.

The smelting process is shown in Fig. 1. At the roasting stage, the zinc sulfide (ZnS) concentrate is roasted to zinc oxide (ZnO, or zinc calcine) with the presence of oxygen (i.e. in air). At the same time, the sulfur and Hg in the concentrate are respectively converted into sulfur dioxide (SO_2) and Hg$^\circ$. Then the zinc calcine will be leached with sulfuric acid, which is called the leaching process. Finally the leach liquor from the leaching process will be electrolyzed to obtain zinc ingot metal, which is called the electrolyzing process. The chemical reactions of the roasting, leaching and electrolyzing processes are shown in (R1)–(R3) respectively.

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \tag{R1}$$

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O \tag{R2}$$

$$ZnSO_4 + H_2O \xrightarrow{\text{electrolyze}} Zn + H_2SO_4 + \frac{1}{2}O_2 \tag{R3}$$

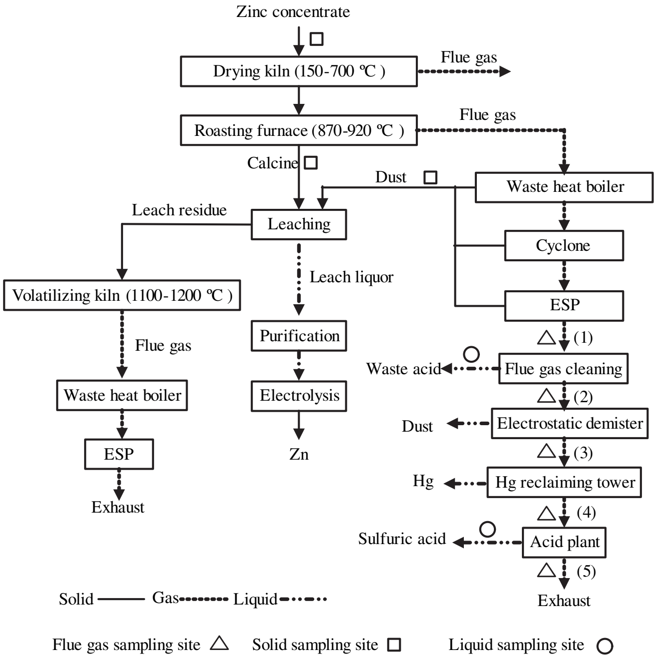

Fig. 1. Production process and the sampling locations in the tested plant.

The flue gas from the roasting furnace goes through a waste heat boiler (WHB), a cyclone, and an electrostatic precipitator (ESP) to remove particulate matter in the gas. The temperatures at the inlet of WHB and outlet of ESP are 850 °C and 310 °C, respectively. A wet scrubber then follows, using recycled dilute sulfuric acid to clean the flue gas, which is called flue gas cleaning. After the flue gas cleaning, the temperature of the flue gas is about 40 °C. After the flue gas cleaning, an electrostatic demister is used to remove water vapor from the gas stream. The Hg in the flue gas is then reclaimed using the Boliden–Norzink technology before it enters an acid plant (Hylander and Herbert, 2008). The Boliden–Norzink process is based on the oxidation of Hg vapor by mercuric chloride to form mercurous chloride. Mercurous chloride is insoluble and precipitates as calomel. The chemical reaction of the Hg reclaiming process is shown in (R4).

$$HgCl_2(\text{liquid}) + Hg(\text{gas}) \rightarrow Hg_2Cl_2(\text{solid}) \tag{R4}$$

In the acid plant, sulfur dioxide is oxidized to sulfur trioxide (SO_3) which is dissolved in strong sulfuric acid. Sulfuric acid is a major by-product of zinc smelting, and up to 2 t of sulfuric acid are produced for each ton of zinc produced at this smelter. The exhaust gas is emitted to the atmosphere after the acid plant.

2.2. Sampling procedures

The APCD configuration and the sampling locations are given in Fig. 1. The EPA Method 29 (USEPA, 1996a) was used to quantify total Hg in the flue gas at the inlet/outlet of flue gas cleaning, electrostatic demister, and Hg reclaiming tower. The Ontario Hydro Method (ASTM, 2002) was adopted to measure Hg$^\circ$, Hg^{2+}, and Hg^{p} in the exhaust gas emitted to the atmosphere after the acid plant. The two sampling method chains are shown in Fig. 2. For EPA Method 29, as shown in Fig. 2a, the particulate emissions are isokinetically collected in the heated, glass-lined probe and on an 82.6 mm diameter glass quartz filter heated at 120 °C. Gaseous Hg emissions are collected by a series of impingers. The first three impingers contain H_2O_2–HNO_3 solution (10% H_2O_2–5% HNO_3 for the first two impingers and 1% H_2O_2–5% HNO_3 for the third impinger) to remove SO_2, the next three impingers contain 4% $KMnO_4$–10% H_2SO_4 solution, and the last impinger contains silica gel to remove the moisture in the sample gas.

The Ontario Hydro Method (ASTM, 2002) was adopted for total Hg and speciation profile at the outlet of the acid plant. The samples were withdrawn from the flue gas stream isokinetically through a probe/filter system maintaining the flue gas at 120 °C, which was followed by a series of impingers in an ice bath. The particulate-bound Hg was collected on the quartz fiber filter. The Hg^{2+} was collected in the first three impingers with 1.0 mol/L potassium chloride (KCl) solution. Hg$^\circ$ was collected in the subsequent impingers, of which one impinger contains a 5% nitric acid (HNO_3) and 10% peroxide (H_2O_2) solution and three impingers contain a solution of 10% sulfuric acid (H_2SO_4) and 4% potassium permanganate ($KMnO_4$), as shown in Fig. 2b.

Velocity pressures were measured at each sampling point in the duct by manometer of XC-572 Source Sampler Console. The gas temperature was directly

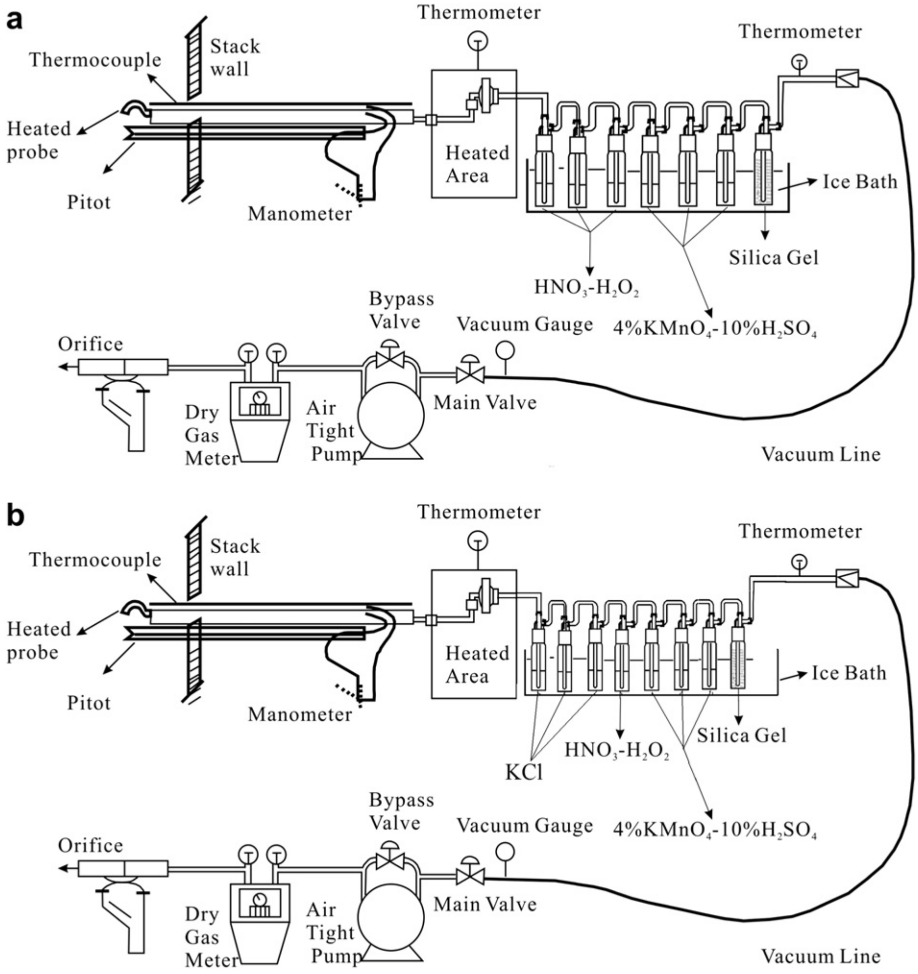

Fig. 2. Flue gas sampling process (a) EPA Method 29 and (b) Ontario Hydro Method.

measured by EPA method 5 (USEPA, 1996b) probe assemblies. Meanwhile, the samples of feed Zinc concentrate, calcine, dust captured by waste heat boilers, cyclone and ESP were collected and stored in polyethylene bags. The waste acid from flue gas cleaning and sulfuric acid were sampled and stored in polyethylene containers.

2.3. Analysis

Liquid and solid samples were collected in the field and analyzed in accordance with US EPA 7470A (USEPA, 1994) for liquid samples and 7473 for solid samples (USEPA, 1998). The impinger solutions were recovered and analyzed using Cold Vapor Atomic Absorption Spectrophotometry (CVAAS), which has a detection limit of 0.05 $\mu g\ L^{-1}$. Solid samples were air dried after homogenization, then milled and ground to <100 mesh for subsequent analysis. Zinc concentrate (200 mg) samples were digested for 30 min using aqua regia at a temperature of 95 °C in a water bath (Li et al., 2005), then a suitable aliquot of the digested sample solution, except for zinc calcine, was measured using CVAAS. Zinc calcine and dust samples were analyzed with a Direct Hg Analyzer (Milestone DMA-80, Italy) having a detection limit of 0.01 ng.

2.4. Quality assurance and quality control

All sampling tests and analysis were repeated to obtain parallel results and reduce uncertainties (see Table 1). The parallel tests were found to be reproducible. Most of the differences came from the fluctuation of flue gas because of the time difference of sampling. The data obtained from tests at the same conditions were averaged to get the final results.

For EPA Method 29 and Ontario Hydro Method, each of the seven impingers in the sampling train was recovered and analyzed separately. Thereby the success of the sample collection could be evaluated. For example, if the Hg captured in the last impinger was less than 5% of the total Hg captured, we could have a reasonable degree of confidence that the majority of the Hg had been successfully collected. Otherwise, we would hypothesize that a considerable breakthrough of Hg had occurred and the sample collection was not successful.

Standard reference material was used to control the analysis quality of Hg concentration in solid samples. The Rich Zinc ore rock (GBW07165 (National Standard Material Management Committee, 2004), certified values is $114 \pm 9\ \mu g\ kg^{-1}$) was $117 \pm 10\ \mu g\ kg^{-1}$ ($n = 20$). The recovery was 102%, the relative percentage difference of sample duplicates was less than 10%.

Table 1
Stack tests at inlet/outlet of APCD.

Sampling site	Dry gas flow ($m^3\ h^{-1}$)	Hg concentration ($\mu g\ m^{-3}$, dry gas)	Hg mass rate ($g\ d^{-1}$)	Number of tests
Outlet of acid plant	80446 ± 634	11 ± 2	22 ± 3	6
Inlet of acid plant	76670 ± 1391	473 ± 86	871 ± 166	6
Outlet of Hg reclaiming tower	73287 ± 636	878 ± 167	1542 ± 287	6
Inlet of Hg reclaiming tower	70495 ± 667	7861 ± 1327	13307 ± 2301	6
Outlet of electrostatic demister	70780 ± 431	6833 ± 827	11602 ± 1339	3
Inlet of electrostatic demister	60291 ± 459	11554 ± 430	16721 ± 740	3
Outlet of flue gas cleaning	59973 ± 415	7876 ± 2337	11324 ± 3285	2
Inlet of flue gas cleaning	57706 ± 260	9879 ± 2769	13691 ± 3897	2

3. Results and discussion

3.1. Hg in feed zinc concentrates

During the test period, three feed zinc concentrate samples were collected daily to analyze for the Hg concentrations. The average Hg concentration in the feed zinc concentrates was 24.7 ± 10.8 g t^{-1} (geometric mean ± standard deviation), varying from 6.9 to 46.3 g t^{-1}. The zinc concentrate used in this plant came from 16 provinces in China and 6 other countries.

3.2. Hg removal efficiencies of APCDs

The Hg removal efficiency of APCDs is defined by equation (1):

$$\eta = \left(1 - \frac{C_{\text{outlet}}Q_{\text{outlet}}}{C_{\text{inlet}}Q_{\text{inlet}}}\right) \times 100\% \tag{1}$$

where η is the Hg removal efficiency. C_{inlet} and C_{outlet} are Hg concentrations in the flue gas at inlet and outlet of APCDs, respectively. Q_{inlet} and Q_{outlet} are the gas flow rates at the inlet and outlet of APCDs, respectively. The results are given in Table 1.

Based on equation (1) and the data in Table 1, we can calculate the Hg removal efficiencies of APCDs. The results are shown in Table 2.

The flue gas cleaning, which includes a retention tower and a packed tower, is designed to decrease the temperature of the flue gas and remove the particulates and other harmful elements including fluoride, arsenic, etc. The flue gas adiabatically expands in the retention tower and then is washed with dilute sulfuric acid in the packed tower. The temperature of the flue gas is about 300 °C at the inlet of the retention tower and about 40 °C at the outlet of the packed tower. When going through the packed tower the Hg^{2+} in the flue gas is absorbed by the recycled dilute sulfuric acid. According to our measurements, the average Hg removal efficiency of flue gas cleaning is about 17%.

An electrostatic demister is used to remove the water vapor in the flue gas. The electrostatic demister removes about 30% of the Hg in the flue gas. The relative high removal efficiency may be due to some of the Hg being trapped by the water vapor and removed by the demister.

The average Hg removal efficiency of the Hg reclaiming process was 88%, ranging from 82.8% to 92.1%.

The flue gas, which is rich in SO_2 after the Hg reclaiming stage, goes to the acid plant to produce sulfuric acid. Double-converter and double-absorption technology is adopted in the tested plant. The flue gas is dried by 93% sulfuric acid first, then passes through the catalytic converter tower where SO_2 is converted to SO_3. The SO_3 in flue gas is absorbed by 98% sulfuric acid. The lean SO_3 gas leaving the absorption tower flows into the catalytic converter tower for oxidation, followed by a second absorption tower. Our measurements indicated that the Hg removal efficiency of the acid plant averaged 97.4%, ranging from 96.5% to 98.2%, which was in line with the estimation by Hylander and Herbert (2008).

Table 2
Mercury removal efficiencies of APCDs.

APCD	Hg removal efficiency (%)			Number of tests
	Minimum	Maximum	Average ± Standard deviation	
Flue gas cleaning	17.0	17.7	17.4 ± 0.5	2
Electrostatic demister	21.0	42.2	30.3 ± 10.9	3
Hg reclaiming tower	82.8	92.1	88.0 ± 3.5	6
Acid plant	96.5	98.2	97.4 ± 0.6	6

Two factors may lead to the high Hg removal efficiency of the acid plant. The first reason is that Hg° can be catalytically oxidized by V_2O_5, which is the catalyst for SO_2 conversion to SO_3 in the acid plant. Recent studies have shown that specific metal oxides such as V_2O_5 can catalyze the oxidation of elemental Hg (Kamata et al., 2008; Lee and Bae, 2009). When the V_2O_5 loading rate is 15%, the conversion rate of Hg° is over 60% (Kamata et al., 2008). The other reason is that concentrated sulfuric acid can oxidize Hg° into Hg^{2+} directly. There are some Hg removal technologies based on this chemical transformation. The Bolchem Process is one such technology, which uses sulfuric acid (99% at ambient temperature) to oxidize the gaseous Hg and dissolve the oxidized Hg; the acid is then diluted to 80 percent and Hg is precipitated as sulfide with thiosulfate (IPPC, 2001). The chemical reaction in the Bolchem Process is shown as (R5).

$$Hg + H_2SO_4 + \frac{1}{2}O_2 \rightarrow HgSO_4 + H_2O \tag{R5}$$

3.3. Hg speciation in exhaust air

Hg speciation in the exhaust gas from the acid plant is given in Fig. 3. The average concentrations of Hg^{2+}, Hg° and Hg^p were 10.24, 0.71 and 0.37 μg m^{-3}, respectively. The corresponding percentages of Hg^{2+}, Hg° and Hg^p were 90%, 6% and 4%, respectively. Pacyna and Pacyna (2002) provided a very different speciation profile for non-ferrous metal smelting, which was 80% Hg°, 15% Hg^{2+} and 5% Hg^p. The difference in our results may be explained by the flue gas from the acid plant, which oxidized the elemental Hg in the presence of V_2O_5 catalyst and concentrated sulfuric acid.

3.4. Atmospheric Hg emission factor

The Hg emission factor (F_{emission}) is defined as the amount of Hg emitted to the atmosphere per ton of zinc produced during the smelting process. F_{emission} was estimated by the following equation:

$$F_{\text{emission}} = \frac{M_{\text{Hg,emission}}}{M_{\text{Zn,production}}} \tag{2}$$

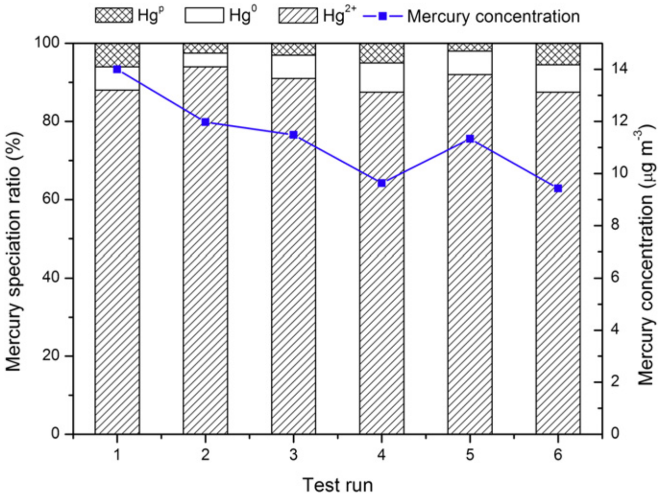

Fig. 3. Mercury concentrations and speciation distribution in exhaust of acid plant.

where $M_{\mathrm{Hg,emission}}$ represents the total amount of Hg emission to the atmosphere from the zinc smelting process, $M_{\mathrm{Zn,production}}$ represents the zinc production that was calculated from

$$\mathrm{M}_{\mathrm{Zn,production}} = M_{\mathrm{feed}} C_{\mathrm{feed}} \phi \tag{3}$$

where M_{feed} represents the total amount of the feed zinc concentrate in the smelter; C_{feed} means zinc concentration in the feed zinc concentrate ($C_{\mathrm{feed}} = 49\%$, data from the plant's report); ϕ represents the overall recovery of zinc from the final smelting process ($\phi = 95\%$, data provided by the smelter). The zinc production was 344 t d^{-1}.

As shown in Fig. 1, Hg emissions to the atmosphere are mainly in the flue gas from the drying kiln, volatilizing kiln, and acid plant. According to Table 1, there was 22 g Hg emitted from the flue gas out of the acid plant each day. The Hg emissions from drying kiln and volatilizing kiln were calculated based on the mass balance of Hg. The Hg contents in zinc concentrate, calcine, dust from waste heat boiler, and dust captured by cyclone and ESP were analyzed and are given in Table 3.

The inlet and outlet temperatures of the drying kiln were 700 °C and 150 °C respectively. Part of the Hg in the zinc concentrate is emitted to the flue gas at such temperatures. The Hg contents of zinc concentrate at the outlet of the drying kiln were 0.5% lower than those in the inlet zinc concentrate, which indicated that 148 g d^{-1} Hg was emitted to the flue gas from the drying kiln. The flue gas then passed through a cyclone and a scrubber, which respectively captured about 1.7 and 0.2 t dust each day. The Hg contents in dust collected by cyclone and scrubber were 33.1 ± 4.4 and 18.5 ± 7.8 g d^{-1}, respectively. There was about 95.4 g d^{-1} Hg emitted to the atmosphere from the drying kiln.

Hg emitted from the volatilizing kiln came from the calcine and the dust captured from the waste heat boiler, cyclone and ESP. During the test period, about 436 t d^{-1} calcine and 270 t d^{-1} dust were produced, which contained 211 g d^{-1} of Hg, as shown in Table 3. These calcine and dusts were leached first and then the leaching residues were fed to the volatilizing kiln. There was almost no Hg emitted during leaching because of the low temperature, and most Hg in the calcine and dust transported to the leaching residue (207 g d^{-1}) then entered into the volatilizing kiln. The temperature in the volatilizing kiln was 1100–1200 °C. At such high temperature, most of the zinc as well as Hg in the leaching residue were released into the flue gas. Then when the flue gas went through the WHB and ESP, ZnO and some of the Hg in the flue gas were captured. To estimate the removal efficiency of the WHB and ESP, we collected 14 leaching residue samples and 8 ZnO dust samples. The Hg concentrations of the leaching residue and the ZnO dust were 0.9 ± 0.4 g t^{-1} and 2.2 ± 4.3 g t^{-1}. The atmospheric Hg emission from the volatilizing kiln was 50 g d^{-1}.

The total atmospheric Hg emissions from the drying kiln, the volatilizing kiln, and the acid plant were 168 g d^{-1}. Therefore, the atmospheric Hg emission factor was estimated to be 0.5 g t^{-1} zinc produced, which is much lower than previous data used in the Hg emission inventory studies for China (Wu et al., 2006; Streets et al., 2005). This is because this smelter used very good technology and installed advanced air pollution control devices. However, the atmospheric Hg emission factor here may not be representative of all zinc smelters in China.

There are several factors affecting the atmospheric Hg emission factors of zinc smelters. The first factor is the Hg content of the zinc concentrates. During our testing period, the mean Hg concentration of the zinc concentrate used in the tested smelter was 24.7 g t^{-1}. However, with our sampling of zinc concentrate for the whole year of 2008 at this smelter, we found that the mean Hg content of zinc concentrate was 41.3 g t^{-1}, much higher than that during our test. Secondly, air pollution control devices significantly affect the atmospheric emissions. The tested plant in this study installed advanced air pollution control devices including ESP, flue gas cleaning tower, demister, Hg reclaiming tower and the acid plant, which removed most of the Hg in the flue gas. It should be noted that the results here only represent this particular plant. The large deviation in some data also indicates there are uncertainties in our results. Comprehensive field measurements are needed to fully understand the Hg emissions from various types of Chinese zinc smelters and to improve the accuracy of emission inventories.

3.5. *Hg fate in the zinc smelting process*

We conducted a Hg mass balance analysis to evaluate the fate of Hg in the zinc concentrate. During the testing period, there was 18229 g d^{-1} Hg entering the plant as part of the zinc concentrate. The outputs of Hg include waste acid from flue gas cleaning, dust from electrostatic demister, recycled Hg from reclaiming tower, sulfuric acid, and atmospheric emissions. According to Table 1 and atmospheric emissions, the total Hg output for the whole smelter was 20267 g d^{-1}. The Hg recovery rate for the whole smelter is 111%. The difference between the input and output of Hg is mainly because of the fluctuations of Hg in zinc concentrates during the test.

Table 3
Mercury contents in zinc concentrate and by-products.

Sample and its locations	Production (t d^{-1}, dry weight)	Hg contents (g t^{-1})	Number of samples	Hg amount (g d^{-1})
Zn concentrate at inlet of drying kiln	738	24.7 ± 10.8	15	18229
Zn concentrate at outlet of drying kiln	738	24.5 ± 10.1	15	18081
Dust captured by cyclone after drying kiln	1.7	33.1 ± 4.5	8	56
Dust captured by scrubber after drying kiln	0.2	18.5 ± 7.8	8	4
Zn calcine at inlet of leaching	436	0.05 ± 0.1	14	22
Dust from WHB (fed into leaching)	135	1.0 ± 1.1	13	135
Dust captured by cyclone (fed into leaching)	108	0.2 ± 0.2	14	22
Dust captured by ESP (fed into leaching)	27	1.2 ± 1.5	14	32
Leaching residue	230	0.9 ± 0.4	14	207
ZnO dust captured	71	2.2 ± 4.3	8	156

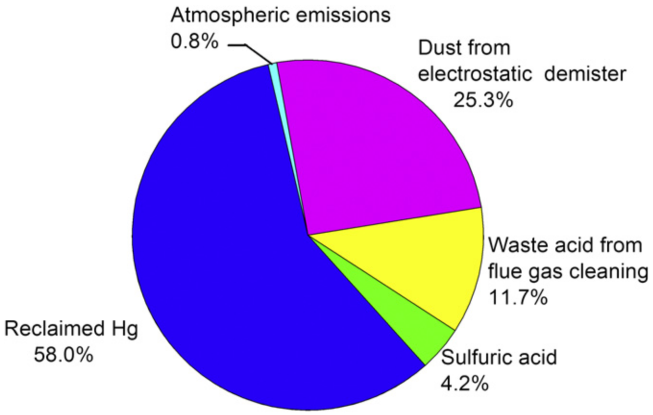

Fig. 4. Mercury fate in zinc smelting process.

According to our tests, flue gas cleaning and electrostatic demister respectively captured 11.7% and 25.3% of the Hg output. The Hg reclaiming tower recycled 58.0% of the Hg output. Another 4.2% of the Hg output was captured by the acid plant. Only 0.8% of total Hg was emitted to the atmosphere. The fate of Hg is given in Fig. 4.

3.6. *Hg control policy implication*

According to Table 1, the Hg emission from the outlet of electrostatic demister was 11602 g d^{-1}, so in the absence of the Hg reclaiming tower and the acid plant, the total Hg emissions from drying kiln, volatilizing kiln and outlet of the electrostatic demister to atmosphere would be 11748 g d^{-1}. In this case, the Hg emission factor would be 34 g t^{-1}, which would be 68 times the Hg emission factor with Hg reclaiming tower and acid plant. According to our investigation, 474 kt zinc, 15% of the total zinc production in China in 2006, was produced in small-scale zinc smelters, where neither Hg reclaiming tower nor acid plant was equipped. Using an emission factor of 34 g t^{-1}, Hg emission from these small-scale zinc smelters would be 16 t. If we close these small-scale smelters and build a new large-scale zinc smelter with Hg reclaiming tower and acid plant, the Hg emission would be reduced to as low as 0.2 t (adopting the Hg emission factor of 0.5 g t^{-1}). This analysis suggests that integration of small-scale zinc smelters and installation of Hg reclaiming tower and acid plants may effectively reduce 15.8 t of atmospheric Hg emission from zinc smelters in China. To further decrease the Hg emissions, measures have to be taken to remove the Hg emitted from the drying kiln and the volatilizing kiln.

4. Conclusions

Our study revealed that a combination of Hg reclaiming, sulfuric acid plant, electrostatic demister and flue gas cleaning could remove Hg from the flue gas effectively. With operation of all these air pollution control devices, only 0.8% of Hg in the zinc concentrate was emitted to the atmosphere. The atmospheric Hg emission factor was 0.5 g t^{-1}, much lower than previous estimates. The Hg removal efficiency of flue gas cleaning, electrostatic demister, Hg reclaiming and acid plant was about 17.4%, 30.3%, 87.9% and 97.4% respectively. About 58.3% of Hg in the zinc concentrate was captured by the Hg reclaiming tower. More than 40% of Hg in the zinc concentrate went to dust, waste acid and sulfuric acid. More attention should be paid to the treatment and fate of these by-products to avoid re-emission of Hg later. Our test results indicated a high percentage of Hg^{2+} in the flue gas after the acid plant, which has a shorter lifetime in the atmosphere. This implies that atmospheric Hg emissions from this kind of zinc smelter may cause significant local and regional environmental problem. In future, more tests should be conducted to investigate the chemical transformation of Hg species in the flue gas.

Acknowledgment

This work was sponsored by U.S. EPA, MEP's Special Funds for Research on Public Welfares (200909024), and the Natural Science Foundation of China (No. 20937002). We would like to express our thanks to the management group and workers of the smelter for their support.

References

ASTM D6784-02, 2002. Standard Test Method for Elemental, Oxidized, Particle-bound, and Total Hg in Flue Gas Generated from Coal-fired Stationary Sources (Ontario-Hydro Method). ASTM International, Pennsylvania, USA.

European commission. Integrated Pollution Prevention and Control (IPPC), 2001. Reference Document on Best Available Techniques in the Non-ferrous Metals Industries. European Commission, Brussels, Belgium.

Feng, X., Li, G., Qiu, G., 2004. A preliminary study on Hg contaminations to the environment from artisanal zinc smelting using indigenous method in Hezhang county, Guizhou, China. Part I: Hg emissions from zinc smelting and its influences on the surface water. Atmospheric Environment 38, 6223–6230.

Hylander, L.D., Herbert, R.B., 2008. Global emission and production of Hg during the pyrometallurgical extraction of nonferrous sulfide ores. Environmental Science & Technology 42 (16), 5971–5977.

IZA (International Zinc Association), 2010. The production of zinc. http://www.iza.com/production.html (available online Jul. 13th 2010).

Jiang, J., 2006. Current status and recent technical progress of zinc smelting in China. China Nonferrous Metallurgy 10 (5), 19–23 (in Chinese).

Kamata, H., Ueno, S., Naito, T., Yamaguchi, A., Ito, S., 2008. Hg oxidation by hydrochloric acid over a VOx/TiO_2 catalyst. Catalysis Communications 9 (14), 2441–2444.

Lee, W., Bae, G., 2009. Removal of elemental Hg (Hg(O)) by nanosized V2O5/TiO2 Catalysts. Environmental Science & Technology 43 (5), 1522–1527.

Li G., 2007. Preliminary studies on zinc smelting emission Hg to atmosphere and its effect to the environment in China, PhD thesis, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, PR China, 1–110 (in Chinese with English abstract).

Li, G., Feng, X., Qiu, G., Bi, X., Li, Z., Zhang, C., Wang, D., Shang, L., Guo, Y., 2008. Environmental Hg contamination of an artisanal zinc smelting area in Weining County, Guizhou, China. Environmental Pollution 154, 21–31.

Li, Z., Feng, X., He, T., Yan, H., Liang, L., 2005. Determination of total Hg in soil and sediment by aquaregia digestion in the water bath coupled with cold vapor atom fluorescence spectrometry. Bulletin of Mineralogy, Petrology and Geochemistry 24 (2), 140–143 (in Chinese).

National Standard Material Management Committee, 2004. Standard Material Directory of P.R.China. China Metrology Press, Beijing.

Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333, 134–139.

Pacyna, E.G., Pacyna, J.M., Steenhuisen, F., Wilson, S., 2006. Global anthropogenic Hg emission inventory for 2000. Atmospheric Environment 40 (22), 4048–4063.

Pacyna, E.G., Pacyna, J.M., 2002. Global emissions of Hg from anthropogenic sources in 1995. Water Air Soil Pollution 137, 149–165.

Pacyna, J.M., Pacyna, E.G., Steenhuisen, F., Wilson, S., 2003. Mapping 1995 global anthropogenic emissions of Hg. Atmospheric Environment 37 (S1), 109–117.

Pirrone, N., Cinnirella, S., Feng, X., Finkelman, R.B., Friedli, H.R., Leaner, J., Mason, R., Mukherjee, A.B., Stracher, G.B., Streets, D.G., Telmer, K., 2010. Global Hg emissions to the atmosphere from anthropogenic and nature sources. Atmospheric Chemistry and Physics 10, 5951–5964. 2010.

Pirrone, N., Keeler, G.J., Nriagu, J.O., 1996. Regional differences in worldwide emissions of Hg to the atmosphere. Atmospheric Environment 30 (17), 2981–2987.

Prasad, P., Niemi, D., Powers, B., 2000. A North American inventory of anthropogenic Hg emissions. Fuel Processing Technology, 65–66. 101–105.

Streets, D.G., Hao, J., Wu, Y., Jiang, J., Chan, M., Tian, H., Feng, X., 2005. Anthropogenic Hg emissions in China. Atmospheric Environment 39 (40), 7789–7806.

USEPA, 1994. Method 7470a: Hg in liquid waste (Manual cold-vapor technique). http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/7470a.pdf (available online Mar. 18th 2010).

USEPA, 1996a. Method 29. Determination of metals emissions from stationary sources. http://www.epa.gov/ttn/emc/promgate/m-29.pdf (available online Mar. 18th 2010).

USEPA, 1996b. Method 5. Determination of particulate matter emissions from stationary sources. http://www.epa.gov/ttn/emc/promgate/m-05.pdf (available online Mar. 18th 2010).

USEPA, 1998. Method 7473. Hg in solids and solutions by thermal decomposition amalgamation and atomic absorption spectrophotometry. http://www.epa.gov/epawaste/hazard/testmethods/sw846/pdfs/7473.pdf (available online Mar. 18th 2010).

Wu, Y., Wang, S., Streets, D.G., Hao, J., Chan, M., Jiang, J., 2006. Trends in anthropogenic Hg emissions in China from 1995 to 2003. Environmental Science & Technology 40 (17), 5312–5318.

Zhou T., 2005. Industrial study on pressure leaching of high-ferrous zinc sulphide concentrate. Master thesis, Kunming University of Science and Technology, Kunming 650093, PR China, 1–48 (in Chinese with English abstract).