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*NRDC Project- Mercury emissions and release in zinc smelters in China*

## **Final Report**

**Mercury emissions and release in zinc smelters in China**

**Tsinghua University**

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# 1 Overview of zinc smelting sector in China

## 1.1 Status of China's zinc production

### 1.1.1 Primary zinc production in 2015

In 2015, the global zinc production reached 13651 kt. Among them, China's zinc production is about 6115.9 kt, accounting for about 44.8% of the global zinc production. The production in China increased by 1.31% compared with the production of 2014. Other major countries of refined zinc included US, Korea, Canada, Japan, Spain, Australia, Peru, Kazakhstan, and Mexico. Their zinc production in 2015 is shown in Table 1-1.

Table 1-1 Refined zinc production of the world<sup>[1]</sup>

Rank	Country	Production (kt)
	Total	13651
1	China	6115.9
2	Korea	935
3	India	838
4	Canada	553
5	Japan	509
6	Spain	504
7	Australia	472
8	Peru	335
9	Kazakhstan	324
10	Mexico	326

### 1.1.2 Chinese zinc production trends

Since 2005, China's primary zinc production increased from 2759 kt in 2005 to 5880 kt in 2015 <sup>[2]</sup> (Figure 1-1). The refined zinc metal in China was mainly produced in 16 provinces, including Hunan, Yunnan, Shaanxi, Inner Mongolia, Guangxi, Henan, Gansu, Liaoning, Sichuan, Guangdong, Jiangxi, Anhui, Qinghai, Zhejiang, Xinjiang and Guizhou provinces. The zinc production of top ten provinces accounted for 95.1% of national total in 2015. Hunan

province produced 1151 kt, which was about 19.57% of China's total zinc production in 2015.

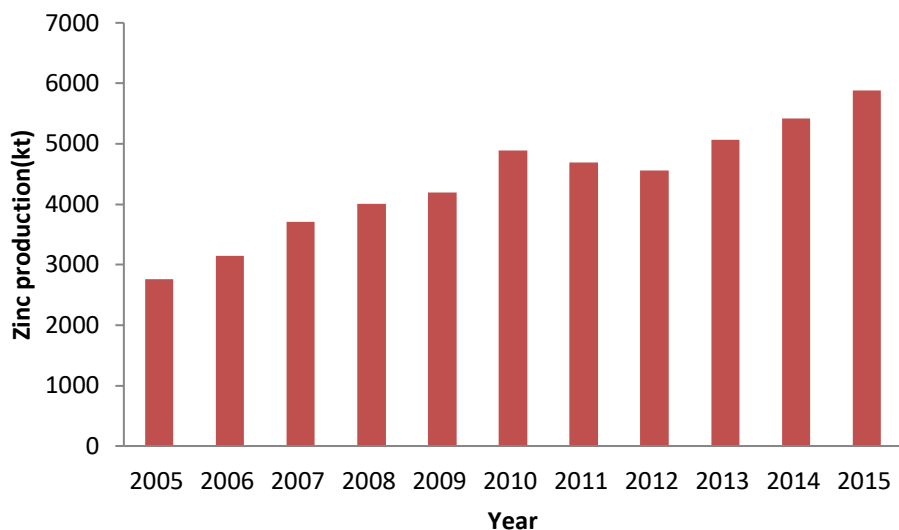


Figure 1-1 Zinc production in China, 2005-2015

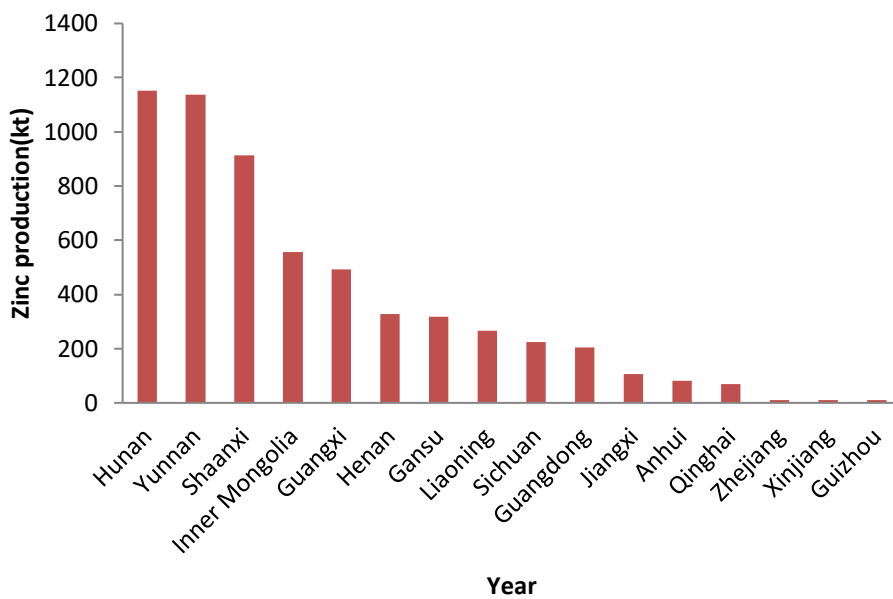


Figure 1-2 Chinese provincial zinc production in 2015

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## 1.2 Zinc smelting process and pollution control devices

### 1.2.1 Zinc smelting processes

Zinc smelting processes in China can be divided into two major types, namely the hydrometallurgical process and the pyrometallurgical process.<sup>[3]</sup> The pyrometallurgical process, where metallic zinc is extracted from zinc oxide materials with carbon as reducing agent at high temperature, can further be divided into the imperial smelting process (ISP), the vertical retort zinc smelting process (VRZSP), the electric zinc furnace (EZF), and various artisanal zinc smelting processes (AZSP). The hydrometallurgical process is the dominant zinc smelting process in China, accounting for 94.6% of national total in 2015. For the pyrometallurgical process, they accounted for 2.1%, 1.8%, 0.9%, and 0.6% of total zinc production, respectively. As to Hg emissions, emission from hydrometallurgical process, AZSP, ISP, RZSP, and EZF accounted for 86.1%, 9.1%, 3.2%, 1.3%, and 0.3%, respectively.

The hydrometallurgical process roasted ZnS concentrates into ZnO at first. Then, metallic zinc is leached from the ZnO in acid solution and finally extracted with electrowinning technology. ZnS concentrates roasting, zinc calcine leaching, leachate purification and zinc electrowinning are the four main parts of this method. In the roasting part, ZnS in the concentrates are oxidized into ZnO at high temperature. This part is similar with pyrometallurgical method. Then the ZnO is leached in the calcine leaching part. This part consists of neutral leaching and acid leaching. Spent electrolyte and sulfuric acid are respectively used in these two kinds of leaching. The acidity using acid leaching method is 30-60 g/L H<sub>2</sub>SO<sub>4</sub> and the temperature is 65-70 °C. The zinc percentage in the leachate is 120 g/L or more. The leachate is then further purified. Traditional purification consists of two sections. First, copper and cadmium are replaced by zinc. Then, cobalt is removed by xanthate. Zinc percentage in leachate is about 16-20%. In order to improve zinc recovery, rotary evaporation reduction technology or hot acid technology is used to deal with zinc leachate. After purification, the zinc sulfate solution flow into electrolysis cell with an additive to produce metallic zinc.

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During the ISP process, carbon is used to reduce zinc and lead from their sintered block in the imperial smelting furnace. Zinc vapor is condensed into liquid zinc in the lead condenser. Lead and slag are released into hearth and further separated in the heating bed. This method is with high raw materials adaptability, which can be used to deal with native ZnS concentrates as well as secondary materials containing lead and zinc. Besides, its energy consumption is lower than the vertical retort zinc smelters. This method consists of three main parts, namely roasting, reducing and volatilizing in imperial smelting furnace and condensation in condenser.

(1) Materials roasting: Lead and zinc concentrates, with 45-60% of Pb and Zn, are desulfurized and sintered into blocks in the sintering machine after mixing with other ingredients containing zinc. Certain strength of the sintering heat block is required so as to ensure its ventilation.

(2) Reducing and volatilizing in imperial smelting furnace: Sintered blocks, lime flux and preheated coke are added into furnace from the roof in sequence. Lead and zinc in the sintered blocks are reduced into metal. Volatile zinc is sent into condenser with CO<sub>2</sub>, CO. Smelting product of crude lead, copper matte and slag flow into the electric bed through the hearth so as to be separated. Flue gas of the slag is emitted after recovering zinc. Copper matte and crude lead are further disposed.

(3) Condensation: Condensation is conducted in the lead rain condenser. The lead rain, raised by the rotor, cool the volatile zinc below 600 °C and is converted into liquid lead at temperature lower than 450 °C. The liquid lead and zinc flow into lead spout and are separated in separation tank. Main technical economic indicators of this method are listed here. Air temperature is 860-1150 °C; condensing efficiency is 90-92%; The percentage of Pb and Zn in the fuming slag is 0.15% and 1.35%; The percentage of Zinc and lead in crude zinc is more than 98% and 1.2-1.5%; The percentage of Zinc and lead in crude lead is 0.1% and more than 98%; the lead and zinc recovery is at least 93% and 94%; the utilization of S in the raw materials is 90-92%.

During the VRZSP process, carbon is used to reduce ZnO at temperature above zinc boiling point in the shaft-type distillation tank. Zinc vapor produced in this process is then condensed into liquid metallic zinc. This process consists of three parts. That is zinc concentrate roasting, calcine briquetting and zinc distillation.

(1) Zinc concentrates roasting: The purpose of this stage is to roast the ZnS concentrates to ZnO and to remove impurities such as S, Pb,

Cd, As, Sb. After roasting at temperature above 1000 °C and with excess air coefficient below 1.1, zinc in the calcine is changed into forms of ZnO or other zinc salts. S in the concentrate is converted into SO<sub>2</sub>, whose concentration can reach 10% or more in the gas. Besides, 98% of Cd in the concentrate is eliminated by volatilizing into gas and the removal efficient for Pb is 70%. The gas is then sent to sulfuric acid production system after purification and the trapped dust is utilized. Four main technical economic indicators are used for this part. Sulfide removal efficient reaches 90%; lead and cadmium recovery are 99.5% and 85% respectively and dust rate is 23%. (2) Calcine briquetting: Satisfactory air permeability, heat transfer performance, heat strength and compressive strength (above 4.9 MPa) of the added material are the main purpose of calcine briquetting and coke. (3) Zinc distillation: In this part, ZnO is reduced into metallic zinc vapor in the atmosphere of CO, about 35% of metallic zinc in the furnace gas. Then the zinc vapor is converted into liquid zinc in the condenser and further casted into zinc ingots after released from the condenser. In this part, the zinc recovery is required to be larger than 94%, spoil zinc percent is smaller than 1.0% and coal consumption is 2.3 t per t Zinc.

### 1.2.2 Air pollution control devices

Generally, APCDs for primary flue gas in most nonferrous metal smelters consist of dust collectors (DC) including cyclone dust collector, waste heat boiler, electrostatic precipitator and fabric filter (or their combination), flue gas scrubber (FGS), electrostatic demister (ESD), mercury reclaiming tower (MRT), conversion and absorption tower (CAT), and flue gas desulfurization (FGD). The CAT may be a double conversion double absorption (DCDA) tower or a single conversion single absorption tower (SCSA). Usually, the above APCDs combined into 6 ypes used in smelters. The proportion of different types of APCDs are provided in Table 1-2<sup>[4]</sup>

Table 1-2 The proportion of metal production from smelters with different types of APCDs in 2014<sup>[4]</sup>

Type	APCDs	Percentage (%)
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Type 1	DC+FGS	0.2
Type 2	DC+FGS+ESD+SCSA	0.2
Type 3	DC+FGS+ESD+DCDA	49.5
Type 4	DC+FGS+ESD+DCDA+DFGD	20.0
Type 5	DC+FGS+ESD+DCDA+WFGD	20.0
Type 6	DC+FGS+ESD+SMR+DCDA	10.1

NOC: no APCDs is applied; DC: Dust collectors; FGS: Flue gas scrubber; ESD: Electrostatic demister; SMR: Specific Hg removal tower; DCDA: Double contact and double absorption tower; SCSA: Single contact and single absorption tower; WFGD: Wet flue gas desulfurization; DFGD: Dry flue gas desulfurization.

### 1.2.3 Water pollution control devices

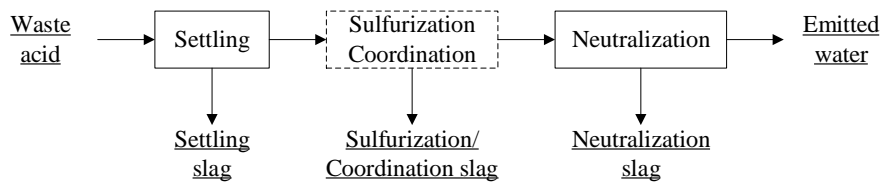


Figure 1-3 Waste acid pollution control process

The main methods used for waste acid disposal included the lime neutralization method, sulfide-neutralization method and biological method. The first method generally consists of two stages, settling (SET) and neutralization (NEU) which we refer to as type 1 in this work. The latter two methods have one additional stage, sulfurization/coordination (SUL), and the latter two methods are classified as type 2.

Table 1-3 Application percentage of different methods for waste acid in 2015<sup>[5]</sup>

Waste acid disposal method	Application percentage (%)
SET+NEU,	33.2

### 1.3 Status of zinc smelting plant

#### 1.3.1 Production and distribution of zinc smelter

To obtain an accurate plant list in China, the data obtained from different sources were evaluated through expert discussion and judgment. Finally, 120 plants were identified as the current zinc plant list in 2015. Most of the smelters are located in southwest of China. The scale of the smelters is mainly medium size or small size. In 2015, there were 15 smelters with production more than 100 kt (including 100 kt), which is shown in Table 1-4.

Table 1-4 The production of China's main zinc smelters in 2015

Rank	Zinc plant	Production (kt)
1	Zhuzhou smelter	500
2	Shaanxi zinc smelter	365
3	South nonferrous metal smelter	300
4	Yuguang zinc smelter	258
5	Bayanchuoer Zijin nonferrous metal smelter	219
6	Chifeng Zhongse zinc smelters	215
7	XiangyunFeilong nonferrous metal smelters	180
8	Dongling zinc smelter	179
9	Hanzhong zinc smelter	169
10	Danxia smelter	118
11	Shaanxi Dongling smelter	118
12	Northwest zinc&lead smelter	117
13	Qujing smelter	115
14	Huize smelter	113
15	Xing'an Copper&zinc Smelter	110





Figure 1-4 Distribution of the main zinc smelters in China

### 1.3.2 The status of smelting technologies adopted in large-scale smelters

Zinc smelters with large-scale in China mainly adopted the hydrometallurgy process. Among these 15 companies, 12 smelters use this technology. Northwest lead & zinc smelter, as well as Dongling zinc smelter, use the imperial smelting process (ISP). Danxia smelter adopted the direct oxygen pressure leaching hydrometallurgy process.

### 1.3.3 The Status of pollution control devices adopts in large-scale smelters

In addition to direct oxygen pressure leaching hydrometallurgy process, other smelting process adopts air pollution control devices for flue gas. Most of the above zinc smelters with pyrometallurgical process adopt the combination of air pollution control devices of dust collector, flue gas scrubber, and acid plants with double contact and double adsorption towers in 2015. In Zhuzhou smelter, the reclaimed tower was installed for mercury recycle. With the requirement of “ultra-low emission” in non-electricity industry, wet flue gas desulfurization system and dry flue gas desulfurization system will be widely installed soon. It is projected that the application proportion of flue gas desulfurization system will be approximately 60% in

2020 <sup>[6]</sup>, which means that the application proportion of type 4 and type 5 in Table 1-2 will reach 60%.

For water pollution control devices, most plants have installed the pollution control devices of type 2, and the mercury concentration in the discharged waste water was generally less than the legal discharge limit.

Due to the overall consideration of production activities and pollution control methods, the zinc smelters with hydrometallurgy process, “ultra-low emission” technology, and water pollution control devices of type 2 will be chosen as tested plants.

## 2 Facility characteristics and waste management/utilization practices in the selected smelters

Based on the overview of the zinc production process in China, we identify the hydrometallurgical process as the targeted zinc smelting process. With the ultra-low emission requirement, the desulfurization flue gas system is gradually required to be installed in zinc smelters and the application proportion is increasing. Thus, we chose two zinc smelters meeting ultra-low emission requirement as our typical smelters. Detailed information of these two smelters is listed as follows.

Table 2-1 Information of the studied zinc smelters

Smelters	Capacity (kt)	Production process	Air pollution control devices for smelting flue gas
Smelter A	250	Electrolytic Process.	DC+FGS+ESD+APD+WFGD
Smelter B	100	Electrolytic Process.	DC+FGS+ESD+APD

NOC: no APCDs is applied; DC: Dust collectors; FGS: Flue gas scrubber; ESD: Electrostatic demister; SMR: Specific Hg removal tower; APD: Double contact and double absorption tower; WFGD: Wet flue gas desulfurization;

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## 2.1 Description of zinc production process

We carried out the field measurements on both Zn production process and the waste disposal process in two Zn smelters. Both of the two smelters produce Zn with an Electrolytic Process. This process has been adopted to produce approximately 95% of refined Zn in China in 2015.<sup>4</sup> This process can be divided into roasting process, and refining process (including leaching, purification, and electrolysis) (Figure 2-1). In the roasting process, the Zn concentrates (mainly ZnS) are roasted into calcine (mainly ZnO) directly in both smelter A and smelter B. The roasting flue gas is cleaned by a combination of APCDs, which include dust collectors (waste heat boiler, cyclone separator and electrostatic precipitator), purification devices, and double conversion and absorption (DCA) towers sequentially. Smelter A has an additional wet flue gas desulfurization tower (WFGD) and electrostatic demister (ESD) to achieve the ultra-low emission requirement. Dust, waste acid and sulfuric acid are produced from the gas cleaning process. In the refining process, calcine, dust and sulfuric acid are inputted into a leaching tank to dissolve the ZnO in the dust and calcine. Metals including silver (Ag), indium (In), cobalt (Co), copper (Cu), cadmium (Cd), and lead (Pb) are dissolved simultaneously, and then separated as slags through leachate purification. The purified leachate is electrolyzed to produce refined Zn while the insoluble materials in the leaching tank are emitted as leaching slag.

## 2.2 Description of waste disposal process

The wastes produced from Zn production process include waste acid, leaching slag and metal slags. The waste acid is stored in a settler and its precipitate (acid slag) is separated by filtration. The supernatant and the filtrate are mixed becoming a weak acid and treated in a waste water station. The drainage is allowed to flow to water. The slags produced from the water station are required to be safely disposed in the newly released *Hazardous waste lists*.<sup>[7]</sup> The leaching slag is roasted in a volatilization kiln in ZnO recovery process. The volatilization kiln gas goes through dust collectors (waste heat boiler and FF) for dust removal. The dust captured by the dust collectors is roasted in a multi-hearth furnace. The flue gas from this

furnace is cleaned by FF before flowing into the same stack with the exhaust volatilization kiln gas. An additional flue gas desulfurization (FGD) tower is installed before the stack to remove SO<sub>2</sub>. Noble metals (including Ag, In, Cd and Co) are retrieved from slags using hydrometallurgical recovery processes. Heavy metals (including Cu and Pb) are recovered by smelting processes, and the flue gases are dedusted by dust collectors.

In addition to the wastes, sulfuric acid also contains mercury. To identify mercury release from the waste disposal process, we also follow the Hg flow and chose one plant which use sulfuric acid to produce fertilizer for testing.

### 3 Onsite investigation of the representative smelters

#### 3.1 Flow chart and sampling sites

The process flow diagram of the studied zinc smelters and the sampling points are shown in Figure 3-1.

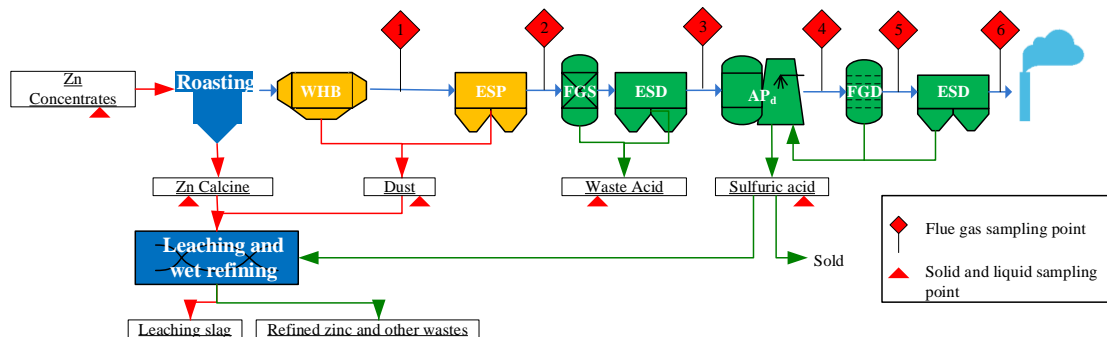


Figure 3-1 Production process and the sampling location in the studied zinc smelter

We collected the waste acid, all corresponding slags, as well as the emitted water during the waste acid disposal process (Figure 1-3)

The sampling points for leaching slag disposal process were listed in the



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Solids such as Zn concentrates; dust captured by WHB, cyclone or ESP were sampled during measurement period. About 1 kg of each sample is collected and conserved in valve bag for further analysis.

### (2) Liquid samples collection

Liquid such as waste gas cleaning water, sulfuric acid were sampled during measurement period. About 50 mL of each sample is collected and conserved in brown glass bottle at normal temperature for further analysis.

### (3) Flue gas samples collection

Figure 3-4 shows the process of the Ontario Hydro Method (OH method) and the revised OH method<sup>[8, 9]</sup>. 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 ( $Hg_p$ ) was collected on the quartz fiber filter. The oxidized Hg ( $Hg^{2+}$ ) was collected in the first three impingers and the elemental Hg ( $Hg^0$ ) was collected in the subsequent impingers. Velocity pressures were measured at each sampling point in the duct using a manometer (XC-572 Source Sampler Console). The gas temperature was directly measured by EPA method 5 probe assemblies.

The Ontario Hydro Method (OH method) was employed for sampling locations with  $SO_2$  concentration less than 1000 ppm, whereas the revised OH method was used for locations with  $SO_2$  concentrations equal to or higher than 1000 ppm.<sup>2</sup> In the OH method, 1 M KCl in the first three impingers was used to absorb  $Hg^{2+}$ , while the  $Hg^0$  was absorbed by the 1% $H_2O_2$ +5% $HNO_3$  in the fourth impinger and 4% $KMnO_4$ +10% $H_2SO_4$  in the following three impingers. The revised OH method aimed to suppress the interference from  $SO_2$ , a large amount of which would deplete  $H_2O_2$  and  $KMnO_4$  and affect the absorption of  $Hg^0$ . The 1 M KCl impingers were replaced with 1 M KOH impingers to sample both  $Hg^{2+}$  and  $SO_2$  and the concentration of  $H_2O_2$  in the fourth impinger was increased from 1% to 3%.

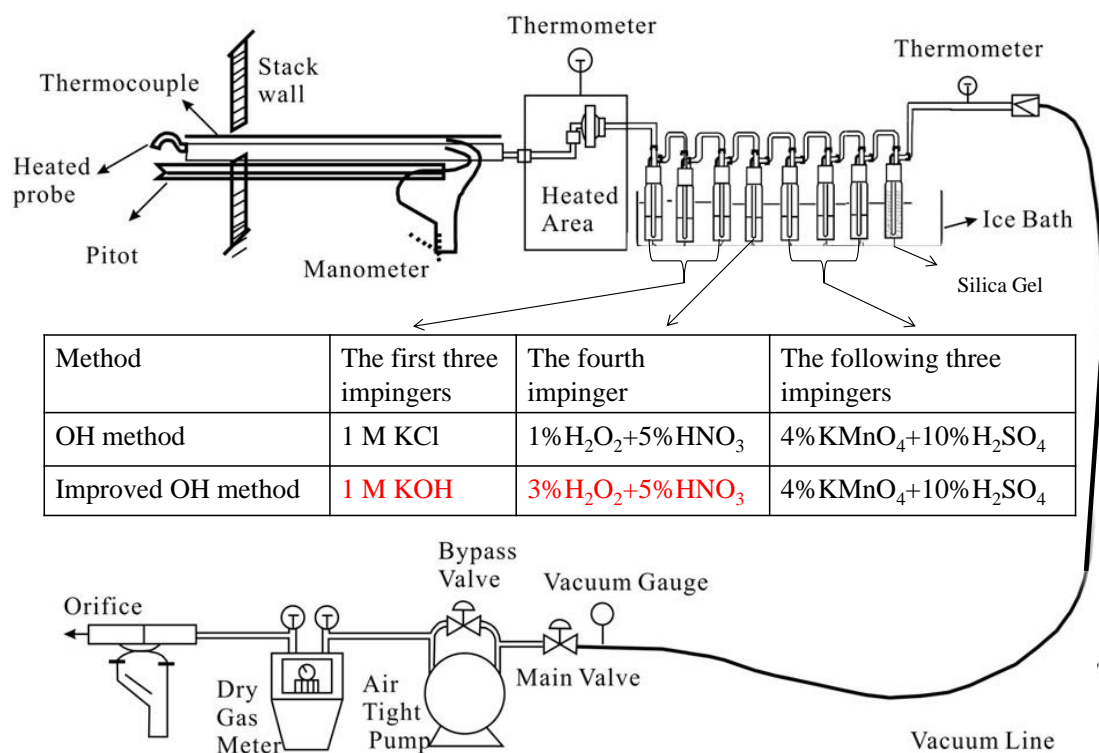


Figure 3-4 Sampling process of OH method and revised OH method

### 3.2.2 Analysis methods

Analysis method for different samples are listed in Table 3-1.

Table 3-1 Analysis method

Sample	Pretreatment	Instruments
Solid samples with high mercury concentration	Air-dried and grounded to 100 mesh, then digested in aqua regia solution	F732-V
Solid samples with low mercury concentration	Air-dried and grounded to 100 mesh	DMA-80
Liquid samples such as waste gas cleaning water, sulfuric acid	Digested in aqua regia solution	F732-V
Absorption solution of gas sampling	Refer to EPA method 29 and Ontario Hydro method	F732-V

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### 3.2.3 Quality assessment and quality control

Before sampling, all bottles were cleaned in the lab by immersion in a 10% HNO<sub>3</sub> (v/v) bath for 24 h, followed by repeated rinses in Milli-Q grade water (18.2 MΩ cm). The flue gaseous Hg sampling system was calibrated after cleaning the sampling line thoroughly, and then, a leak test was performed. More than three parallel samplings under stable operating conditions were conducted to ensure the validity of the results.

Multiple dilutions of a 1000 µg mL<sup>-1</sup> certified Hg standard solution (Hg standard solution, GSB04-1729-2004, supplied by the State Non-ferrous Metals and Electronic Materials Analysis and Testing Center) were used for the calibration of F732-V and the Lumex 915M + pyro attachment. The certified reference material of Zn/Pb ores (Certified reference for the component analysis of rich Zn/Pb ores, GBW07165, supplied by the National Research Center for CRMs of China) was also used as the external standard. Each solid/liquid sample was analyzed three times, at least, to obtain parallel results, with a relative standard deviation of less than 10%.

## 3.3 Analysis results

### 3.3.1 Mercury concentration and speciation in the flue gas

Mercury concentration in the flue gas of smelter A has decreased from more than 10000 µg/m<sup>3</sup> to approximately 2.5 µg/m<sup>3</sup> during the zinc production process. Mercury removal efficiency of current APCD combinations was more than 99% in this smelter. Additional FGD and ESD was installed after DCDA at site 5 and site 6 to achieve ultra-low emission in zinc smelter, which contributed to approximately 4 µg/m<sup>3</sup> of gaseous mercury decrease. However, the reduced mercury was diluted H<sub>2</sub>SO<sub>4</sub>, which was inputted to the system as byproduct. Thus, although gaseous mercury concentration was reduced, mercury release to H<sub>2</sub>SO<sub>4</sub> would increase.

Hg<sup>2+</sup> was the dominant mercury speciation at site 1 and site 2. However, after the wash in FGS, most Hg<sup>2+</sup> was cleaned and Hg<sup>0</sup> was the main species. In DCDA, the high concentration



of  $H_2SO_4$  would oxidize  $Hg^0$  into  $Hg^{2+}$  and  $Hg^{2+}$  proportion at the outlet of DCDA reached as high as 85%. The  $Hg^{2+}$  would be further washed in FGS and ESD.

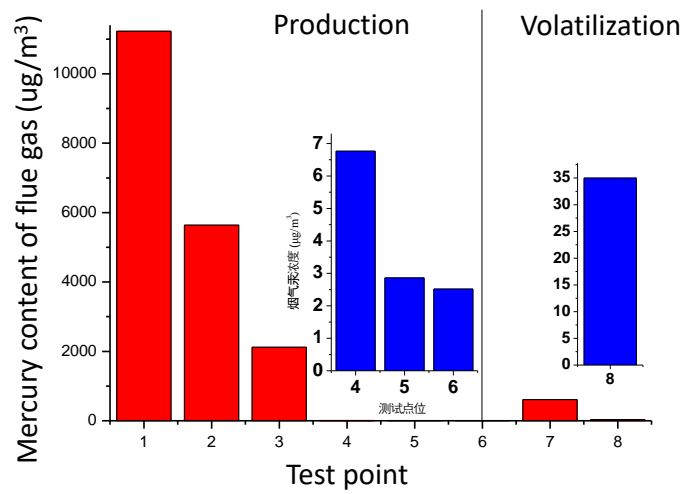


Figure 3-5 Mercury content of flue gas at both production process and volatilization process

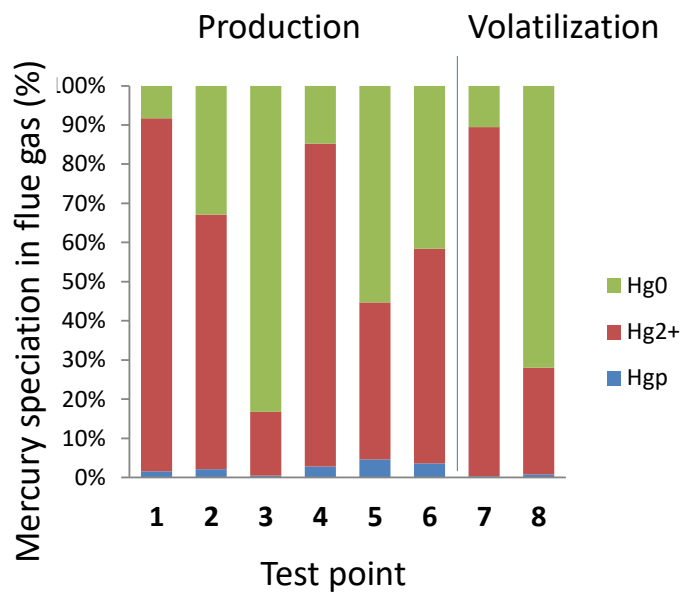


Figure 3-6 Mercury speciation of flue gas at both production process and volatilization process

Similar to what has been observed in smelter A, mercury concentration of different flue gases varied a lot in smelter B. In the gas before acid plant, mercury concentration was  $5564 \mu g m^{-3}$ . The lowest was the flue gas after dehydration, which is  $8 \mu g m^{-3}$ . The proportion of

Hg<sup>2+</sup> in the tested flue gas was low except that after AP. The proportion of Hg<sup>0</sup> was 96% in the gas before AP while Hg<sup>2+</sup> percentage was 4%. After acid plant, the percentage of Hg<sup>2+</sup> rise to 98%. The percentage of Hg<sup>0</sup> and Hg<sup>2+</sup> in the flue gas before desulfuration was 95% and 5%, respectively. In the flue gas after desulfuration were 1% and 99%, respectively. The desulfuration was a process using lime or limestone that absorbed the low concentrate SO<sub>2</sub> in the flue gas, generating the product of material without oxidation, such as calcium sulfite. So, it can't oxidize Hg<sup>0</sup> into Hg<sup>2+</sup>. During the wet desulfuration (FGD), the original Hg<sup>2+</sup> was absorbed, and no new Hg<sup>2+</sup> generated. Thus, the concentration of Hg<sup>2+</sup> declined. Besides, in the process of FGD, the sulfur compound reduced Hg<sup>2+</sup> into Hg<sup>0</sup>.

### 3.3.2 Mercury content in the solid and liquid samples

The mercury content in the solid and liquid samples are listed in the following Table.

Table 3-2 Mercury content in the solid and liquid samples

Process	Samples	Concentration (g t <sup>-1</sup> )	
		Smelter A	Smelter B
Roasting process	Zn concentrates	40.6 ± 11.2	5.7 ± 1.8
	Calcine	0.8 ± 0.1	0.02 ± 0.01
	Dust	23.2 ± 2.1	21.0 ± 3.1
	Waste acid	78.7 ± 12.1	2.4 ± 1.1
	Sulfuric acid	9.1 ± 1.6	0.4 ± 0.1
Refining process	Cu slag	1.4 ± 1.3	8.1 ± 1.5
	Co slag	4.4 ± 0.1	11.6 ± 2.5
	Cd slag	3.9 ± 1.0	0.4 ± 0.1
	Pb slag	1.3 ± 0.2	1.5 ± 0.3
	In slag	5.6 ± 1.5	40.1 ± 1.0
	Leaching slag	0.5 ± 0.1	5.2 ± 2.7
	Ag slag	35.6 ± 1.2	3.3 ± 0.2
	Waste liquid	8.9 ± 2.2	1.0 ± 0.2
ZnO recovery process	Coke powder	0.2 ± 0.1	0.2 ± 0.1
	Na <sub>2</sub> CO <sub>3</sub> /CaCO <sub>3</sub>	0.9 ± 0.1	0.1 ± 0.0
	Na <sub>2</sub> SO <sub>4</sub> /gypsum	-	-
	ZnO	0.3 ± 0.1	0.02 ± 0.01

Waste-water station	SET slag	314.7±10.2	215.5±3.5
	NEU slag	2.5±1.2	1.3±0.5
	SUL slag	404.3±21.2	514.3±31.2
	Drainage	$(1.7 \pm 0.2) \times 10^{-3}$	$(1.1 \pm 0.2) \times 10^{-3}$

### 3.3.3 Mercury balance during production process

Based on the test results, the mercury mass balance in smelter A and smelter B was constructed, as shown in Figure 3.7 and Figure 3.8. In the studied two smelters, the proportion of atmospheric mercury emissions from production process was less than 1%, which indicated high mercury removal efficiency of current APCDs in the production process of zinc smelters in China. The ultra-low emission technologies have led to the reduction of atmospheric mercury emissions, which was transferred to byproduct H<sub>2</sub>SO<sub>4</sub>. Waste acid and sulfuric acid were the two main byproducts from production process. The use of calcine, dust and sulfuric acid transferred mercury into different metal byproducts and leaching slag. Leaching slag and cobalt slag were the metal slags with high mercury amount. But the cobalt slag usually undergoes a hydrometallurgic recovery process while the leaching slag is treated with high temperature methods.

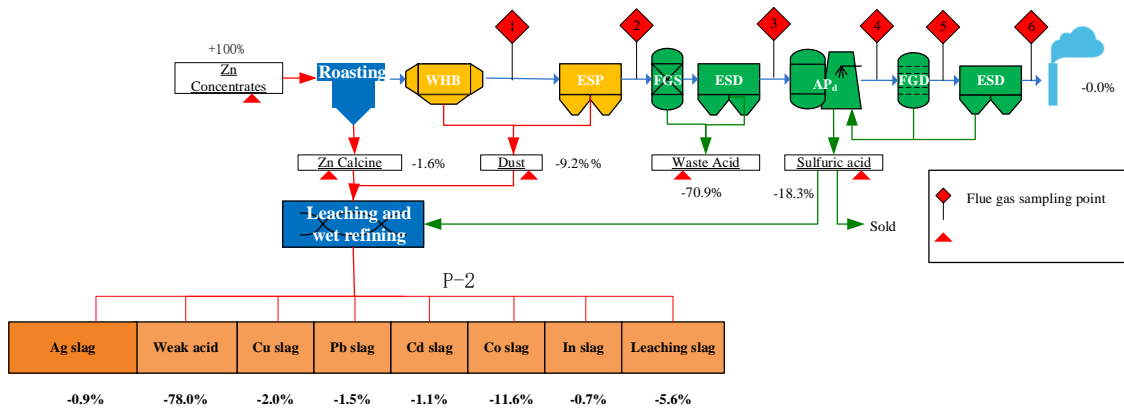


Figure 3-7 Mercury balance in the production process of smelter A

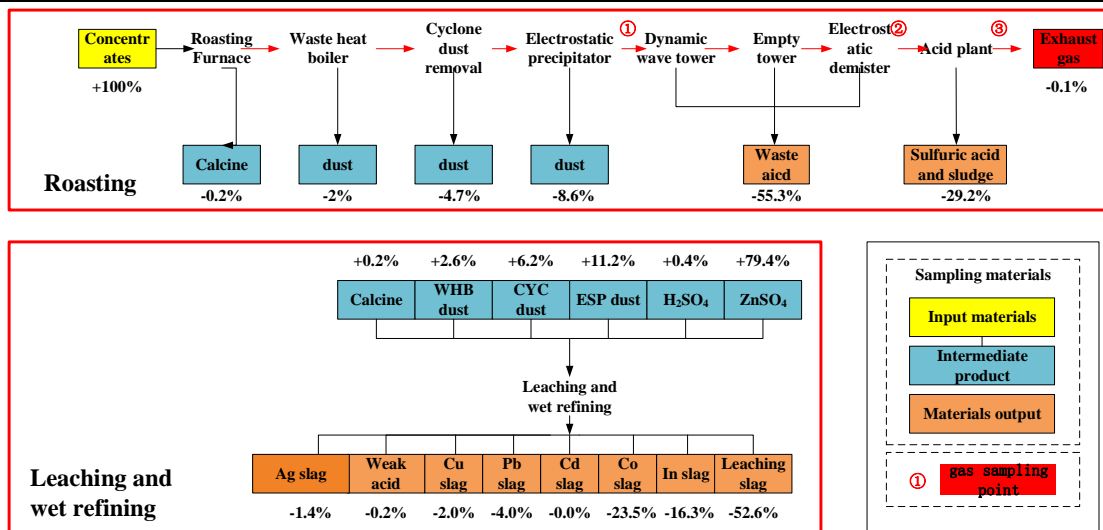


Figure 3-8 Mercury balance in the production process of smelter B

### 3.3.4 Mercury balance during waste disposal process

#### 3.3.4.1 Mercury balance during waste acid disposal process

Waste acid disposal process options mainly include: neutralization and vulcanization method, biological preparation method, lime neutralization method, sulfide-lime ferric salt method and lime ferric salt method. Waste acid disposal process often involves the following all or part of the process. (1) sedimentation process (SET): the waste acid is collected into the collection tank or homogenization tank, and the large particles in the waste acid are freely precipitated in the collection tank to form the waste acid residue; (2) sulfidation or biologics coordination process (SUL): and collection of the supernatant of the tank and the filtrate of waste acid residue into the sulfidation tank. Arsenic and heavy metal ions react with sodium sulfide to form sulfidation residue precipitation; (3) neutralization process (NEU): the supernatant of the vulcanization tank and the filtrate of vulcanization residue enter into the gypsum reaction tank, and the gypsum reacts with waste acid to adjust the pH of the solution. The slag formed by adding gypsum is called gypsum slag. The sulfide reaction is usually carried out before the neutralization of lime and precipitation, which can reduce the amount of gypsum input and the output of gypsum slag in the neutralization reaction. However, due to the overall layout of the plant and the adjustment of disposal process, some smelters will put sulfide

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precipitation after the neutralization reaction of gypsum. Both Smelter A and smelter B have applied the combination of SET+NEU+SUL. For smelter A, they have installed a reclaiming system, but we were not allowed to carry out test. The SET slag and SUL slag were reclaimed in the reclaiming system, while the NEU slag was landfilled. For smelter B, mercury in SET slag and SUL slag was reclaimed in Guiyang province while the NEU slag was landfilled. The mercury concentration in the samples were shown in Table 3-2.

Based on the mass flow and mercury concentration in the samples, mercury mass balance in the wastewater stations were established. We noticed that the mercury concentrations in the discharged water of both smelters were lower than the special emission limit of 0.01 mg/L, which indicated that mercury release to water from zinc smelters have achieved great improvement in the past years. More than 99.9% of mercury was release to waste acid slag. These acid slags were treated as hazardous wastes in the newly revised *Hazardous waste lists*. Thus, these products should be safely disposed.

#### **3.3.4.2 Mercury balance during leaching slag disposal process**

The most common disposal method of zinc leaching slag in China is rotary kiln volatilization. This method used raw coal as fuel and the materials were roasted in the rotary kiln under 1100-1300 °C to produce zinc oxide products. The rotary kiln flue gas entered the dust collector. After the dust removal by the dust collector, the flue gas entered into the multi-chamber furnace to remove chlorine and fluorine. The product zinc oxide was returned to the leaching system or sold out. The flue gas from multi-chamber furnace was desulfurized together. The dust removal by the fabric filter re-entered to the multi - chamber furnace. Smelter A applied Na<sub>2</sub>CO<sub>3</sub> desulfurization technology while smelter B adopted gypsum wet desulfurization technology.

According to the mass balance in smelter A, mercury was inputted to rotary kiln as coal coke, leaching slag, and Na<sub>2</sub>CO<sub>3</sub> accounting for 21.7%, 63.3%, and 14.9%, respectively. Leaching slag was the dominant inputted raw materials into smelter A. As to mercury output, most mercury was released into Na<sub>2</sub>SO<sub>4</sub>, accounting for 86.7% of total output. The proportion of mercury emission to air decreased to about 5.3%. In smelter B, mercury was mainly inputted

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with leaching slag, accounting for 99.5% of total mercury input. 99% of this mercury was emitted to air before the installation of WFGD. However, with the ultra-low emission requirement, the WFGD reduced almost 80% of the mercury into gypsum.

### 3.3.4.3 Mercury balance during sulfuric acid utilization process

The utilization of  $H_2SO_4$  was more complicated. The  $H_2SO_4$  was used in fertilizer production plant, mining plant, smelting plant, etc. The fertilizer production plant was one of the most important utilizers. Thus, we further studied mercury flows in one fertilizer production plant. The results showed that the concentration of mercury in phosphorus concentrate was 0.11 g/g and that in sulfuric acid was 0.26 g/g. Since the consumption of phosphorus concentrate was about 1.7 times that of sulfuric acid, the mercury input of phosphorus concentrate and sulfuric acid accounted for 41.8% and 58.2% of the total mercury input respectively. From the perspective of mercury output, the mercury concentration of phosphogypsum was 0.09 g/g, while that of phosphate fertilizer was 0.19 g/g. Since about 3 t of phosphogypsum was produced for every 1t of phosphate fertilizer produced, the proportion of mercury in the phosphogypsum output system exceeds the proportion of mercury in phosphate fertilizer products. As can be seen from Figure 3-9 the proportion of mercury entering phosphogypsum and phosphate fertilizer was 58.1% and 40.6% of the total output respectively. The proportion of mercury discharged from the reaction tank exhaust gas was about 1.0%, and the proportion of mercury into the washing waste liquid and the tail gas from the drying kiln was 0.3%.

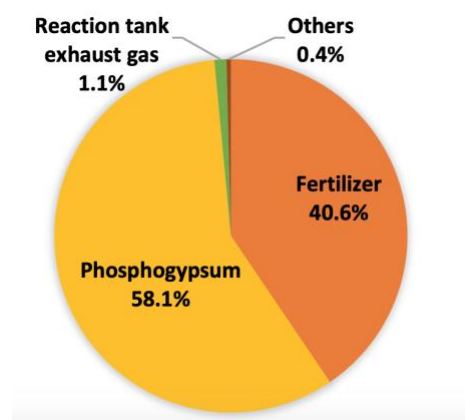


Figure 3-9 Mercury balance in the sulfuric acid utilization process

## 4 Extrapolation of investigated results to zinc production as a whole

### 4.1 Extrapolation method

Based on the mercury flow in the studied smelters, we extrapolated the investigated results to the whole zinc production industry by building the mercury emission and release model based on flow analysis method. This model consisted of three sub-models, including an Hg input sub-model, an Hg distribution sub-model for the metals production processes, and an Hg distribution sub-model for the wastes disposal processes. The targeted year is 2015. However, due to the limitation of available data, especially data for waste disposal processes, we used the data during 2010-2015 as needed.

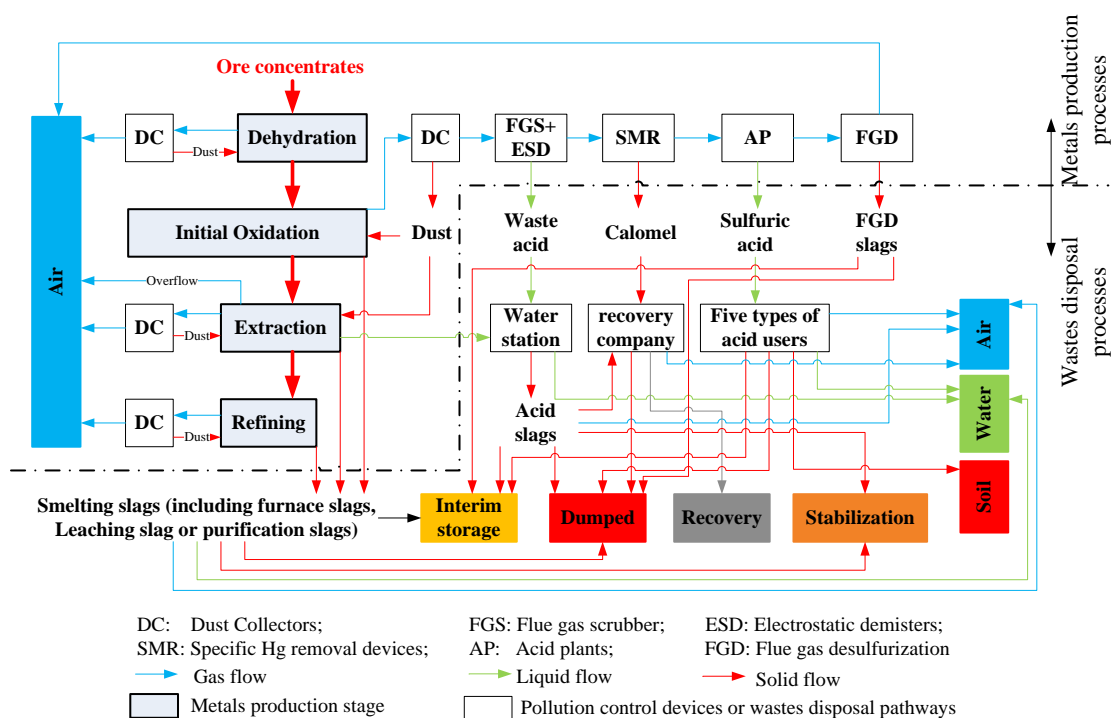


Figure 4-1 Mercury emission and release model based on flow analysis method

#### 4.1.1 Hg input sub-model

Hg input was calculated as the product of the Hg concentration in the consumed

concentrates and the concentrates consumption. The mercury (Hg) input ( $Q_{com,ij}$ ) is the product of Hg concentration in the consumed concentrates ( $C_{com,i}$ ) and the concentrates consumption ( $M_{com,ij}$ ).

$$Q_{com,ij} = C_{com,i} M_{com,ij} \quad (E1)$$

where  $i$  and  $j$  refers to province and metal production processes.  $Q_{com}$  is Hg input, t.  $M_{com}$  is the concentrates consumed, t (Table 4-1). The concentrates consumption was derived from metal production, zinc content of ores, and the recovery of metal during production (Table 4-2).  $C_{com}$  is the Hg concentration in the consumed concentrated,  $\mu\text{g g}^{-1}$ .  $C_{com,i}$  is calculated based on the Hg content in the concentrates supplied by  $k$  province or imported country.

$$C_{com,i} = \frac{\sum_j \sum_{k \geq i} C_{su,k \rightarrow ij} M_{su,k \rightarrow ij}}{\sum_j M_{com,ij}} \quad (E2)$$

where  $C_{su,k \rightarrow ij}$  is the Hg concentration in the produced/imported concentrates transported to  $j$  technology in  $i$  province for metal extraction, the detailed data was provided in the study of Wu et al. (2012)<sup>[10]</sup>.  $M_{su,k \rightarrow ij}$  is the concentrates transportation matrix, which is derived from the study by Wu et al., (2012) and Wu (2015).<sup>[5, 11]</sup>

Table 4-1 Zinc concentrates consumption in different provinces in 2015

Province	Concentrates consumption (kt)	Province	Concentrates consumption (kt)
Anhui	47	Jiangxiix	187
Fujian	30	Liaoning	535
Gansu	637	Inner Mogolia	1522
Guangdong	461	Qinghai	45
Guangxi	1027	Shaanxi	1885
Guizhou	12	Sichuan	709
Henan	516	Yunnan	2129
Hunan	1806	National total	<b>11547</b>



#### 4.1.2 Hg distribution sub-model for the metals production processes

Generally speaking, the metals production processes were generally divided into four stages, including dehydration, initial oxidation, extraction, and refining.

In the dehydration stage, a small amount of Hg in the concentrates was released into the flue gas. Generally, the flue gas was de-dusted via dust collectors, and the dust and dehydrated concentrates were generally sent to the initial oxidation stage. Thus, only atmospheric Hg was emitted in this stage. The Hg distribution in this stage was calculated as follows.

The Hg emitted to atmosphere is

$$GE_{d,ij} = Q_{d,ij}\gamma_{d,j}(1-\eta_{d,j}) \quad (E3)$$

where  $Q_d$  is Hg input into the dehydration stage, which equals to the Hg amount in the ore concentrates consumed, t;  $GE_d$  is the Hg emitted to the atmosphere in the dehydration stage, t;  $i, j$  and  $d$  refer to the province, metals production processes and dehydration stage, respectively;  $\gamma_d$  is the Hg release rate in the dehydration stage, %;  $\eta_d$  is the Hg removal efficiency of the dust collectors in the dehydration stage, %.

Table 4-2 Dominant parameters applied in the model

Metal	Process	Release rate (%)				Distribution factor (%)			Hg removal efficiency (%)			M C (%)	RR (%)
		$\gamma_d$	$\gamma_s$	$\gamma_e$	$\gamma_r$	$\xi_{of}$	$\xi_{ss}$	$\xi_{se}$	$\eta_d$	$\eta_e$	$\eta_r$	$\alpha$	$\varphi$
	EP	0.8	99.4	0.0	0.0	0.9	0.0	0.0	11.5	0.0	0.0	49.9	94.9
	EZF	0.5	99.4	59.1	57.2	0.6	0.0	0.6	11.5	11.5	11.5	49.9	96.9
Zn	RZSP	0.5	99.4	59.1	57.2	0.6	0.0	0.6	11.5	11.5	11.5	49.9	94.6
	ISP	0.1	99.1	65.7	57.2	1.0	0.0	0.9	40.1	40.1	40.1	49.9	96.9
	AZSP	0.0	99.4	59.1	57.2	0.6	0.0	0.6	0.0	0.0	0.0	49.9	94.6

MC: Metal content; RR: Recovery rate; EP: Electrolytic process; ISP: Imperial smelting process; RZSP: Retort zinc smelting process; EZF: Electric zinc furnace; AZSP: Artisanal zinc smelting process; RPSP:

In the initial oxidation stage, the Hg input ( $Q_s$ ) is the Hg amount in the dehydrated concentrates and dust.

$$Q_{s,ij} = Q_{d,ij}(1 - \gamma_{d,j} + \gamma_{d,j}\eta_{d,j}) \quad (E4)$$

Most Hg in the dehydrated concentrates and the dust was released to the flue gas in the smelting or roasting furnace, leaving a small amount of Hg in the furnace slag or intermediate products.<sup>[8, 12]</sup> The furnace slag and intermediate products from the Zn processes were further used in their corresponding production processes.<sup>[13, 14]</sup> The initial oxidation stage was generally considered as the largest release point for air pollutants. Thus, flue gas typically must undergo a thorough de-dusting and required additional Hg removal being desulfurization in certain cases.<sup>[11, 15]</sup> The air pollution control devices were combined into 6 types in 2015, and reproduced as Table 4-3.<sup>[5]</sup> We applied the data in 2014 for the estimation in this study.<sup>[4]</sup> The Hg in the emitted gas ( $GE_s$ ) from the initial oxidation stage is:

$$GE_{s,ij} = Q_{s,ij}\gamma_{s,j} \sum_m \theta_{m,ij}(1 - \eta_m) \quad (E5)$$

Table 4-3 Application percentage of different types of APCD combinations in 2014 (%)

APCD combinations	Type	Application proportion (%)
DC+FGS	Type 1	0.2
DC+FGS+ESD+SCSA	Type 2	0.2
DC+FGS+ESD+DCDA	Type 3	49.5
DC+FGS+ESD+SMR+DCDA	Type 4	20.0
DC+FGS+ESD+DCDA+DFGD	Type 5	20.0
DC+FGS+ESD+DCDA+WFGD	Type 6	10.1

APCDs: Air pollution control devices; None: no APCDs is applied; DC: Dust collectors; FGS: Flue gas scrubber; ESD: Electrostatic demister; SMR: Specific Hg removal tower; DCDA: Double contact and double absorption tower; SCSA: Single contact and single absorption tower; WFGD: Wet flue gas desulfurization; DFGD: Dry flue gas desulfurization.

***The Hg in the flue gas was removed into wastes and byproducts, including dust, waste acid, calomel, sulfuric acid and FGD slag.*** Only one smelter produced calomel in China, which was reported in previous study of Wang et al., (2010). The dust was reused in the initial oxidation stage, or in the extraction stage, or was sent to another metal production system to recover valuable metals.<sup>[13, 16, 17]</sup> Only a subset of smelters used the dust to recover valuable metals in 2015.<sup>[18]</sup> Thus, we assumed that dust was reused in the onsite metals production processes. Waste acid was generally sent out of the metals production systems and disposed at the waste water stations. Thus, the Hg amount in the waste acid output of the metal production system ( $I_{wa}$ ) is as follows.

$$I_{wa,ij} = Q_{s,ij} \gamma_{s,j} \sum_m \theta_{m,ij} (1 - \eta_{dc}) \eta_{fgs+esd} \quad (E6)$$

where  $\gamma_s$  is the percentage of Hg released from the concentrates and dust into the flue gas, %;  $\theta$  is the application percentage of a certain type of air pollution control device, %;  $m$  refers to the type of air pollution control device;  $\eta_{dc}$  and  $\eta_{fgs+esd}$  are the Hg removal efficiency of the dust collectors, and the flue gas scrubber+electrostatic demister, %.

The calomel released out of the metal production process was sent to the qualified Hg recovery company. The Hg in the calomel ( $I_{smr}$ ) is as follows.

$$RM_{smr,ij} = Q_{s,ij} \gamma_{s,j} \sum_m \theta_{m,ij} (1 - \eta_{dc}) (1 - \eta_{fgs+esd}) \eta_{smr} \quad (E7)$$

where  $\eta_{smr}$  is the Hg removal efficiency of the specific Hg removal tower, %.

The sulfuric acid was released out the metals production systems as byproduct. Hg in the sulfuric acid ( $I_{sa}$ ) is as follows.

$$I_{sa,ij} = Q_{s,ij} \gamma_{s,j} \sum_m \theta_{m,ij} (1 - \eta_{dc}) (1 - \eta_{fgs+esd}) (1 - \eta_{smr}) \eta_{sa} \quad (E8)$$

where  $\eta_{sa}$  is the Hg removal efficiency of the sulfuric acid plants, %.

***The FGD slags from the initial oxidation stage were divided into sodium sulfate, activated coke, ammonia sulfate and FGD gypsum*** according to the desulfurization technology applied. The Hg in the first three types was primarily input into chemical plants, ***and the Hg in FGD gypsum was mostly used as raw materials for cement.*** We

assumed that 50% of the Hg in desulfurization wastes ( $I_{fgd}$ ) from the initial oxidation stage was passed to the chemical plants and the remainder was fixed in the cement.

$$I_{fgd,ij} = Q_{s,ij} \gamma_{s,j} \sum_m \theta_{m,ij} (1 - \eta_{dc}) (1 - \eta_{fgs+esd}) (1 - \eta_{smr}) (1 - \eta_{sa}) \eta_{fgd} \quad (E9)$$

where  $\eta_{fgd}$  is the Hg removal efficiency of the FGD tower, %.

In the pyrometallurgical extraction and refining stage, the Hg distribution was quite similar as that in the dehydration stage. In the extraction stage, exhaust overflow gas was present in addition to the extraction gas. Dust collectors were used for gas cleaning. We assumed that all dust was returned to the extraction furnace.

The Hg input into the extraction stage ( $Q_e$ ) is

$$Q_{e,ij} = Q_{d,ij} (1 - \gamma_{d,j} + \gamma_{d,j} \eta_{d,j}) (1 - \gamma_{s,j} - \xi_{ss,j}) \quad (E10)$$

The Hg output of the metals production processes with the extraction furnace slags ( $I_{es}$ ) is

$$I_{es,ij} = Q_{e,ij} \xi_{es,j} \quad (E11)$$

where  $\xi_{es}$  is the percentage of Hg in the furnace slag in total Hg input into extraction stage, %.

The Hg emitted to the atmosphere from the extraction stage is

$$GE_{e,ij} = Q_{e,ij} \gamma_{e,j} (1 - \eta_{e,j} + \xi_{of} \eta_{e,j}) \quad (E12)$$

where  $\gamma_e$  is the percentage of Hg released into the flue gas from the material for the extraction stage, %;  $\eta_e$  is the Hg removal efficiency of the dust collectors for the extraction stage, %;  $\xi_{of}$  is the percentage of Hg into the overflow gas in the total Hg of the flue gas, %.

In the refining stage, the Hg input ( $Q_r$ ) is

$$Q_{r,ij} = Q_{d,ij} (1 - \gamma_{d,j} + \gamma_{d,j} \eta_{d,j}) (1 - \gamma_{s,j} - \xi_{ss,j}) (1 - \gamma_{e,j} - \xi_{es,j}) \quad (E13)$$

The Hg concentration of the materials input to the refining stage was generally less than 30 ng g<sup>-1.5</sup> Thus, the mobile Hg in this stage was notably lower than that in

other stages. Solid wastes ( $OD_r$ ) including furnace slag and dust produced in this stage were assumed to be discarded.

$$OD_{rs,ij} = Q_{r,ij} (\xi_{rs,j} + \gamma_{r,j} \eta_{r,j}) \quad (E14)$$

where  $\gamma_r$  is the percentage of Hg released into the flue gas from the material for the refining stage, %;  $\xi_{rs}$  is the percentage of Hg in the furnace slag in total Hg input into refining stage, %.  $\eta_r$  is the Hg removal efficiency of the dust collectors for the refining stage. The limited Hg in the refined metal is negligible. The atmospheric Hg emissions from the refining stage ( $GE_r$ ) are

$$GE_{r,ij} = Q_{r,ij} \gamma_{r,j} (1 - \eta_{r,j}) \quad (E15)$$

For the electrolytic Zn process, the wet methods were used in both the extraction and refining stages. Thus, the Hg was distributed into several slags and waste acid.

$$I_{ex,i} = \theta_x Q_{e,ep} \quad (E16)$$

$$\sum_x \theta_x = 1 \quad (E17)$$

where  $Q_{e,ep}$  is the Hg input into the extraction stage of the electrolytic Zn process, t;  $I_{ex}$  is the Hg amount in  $x$  slag, t;  $\theta_x$  is the Hg distribution factor during the Zn extraction and refining stages %;  $x$  refers to the leaching slags, Ag slag, Cu slag, Cd slag, Co slag, In slag, Pb slag and waste acid.

Table 4-4. Hg distribution in the slags and waste acid from Zn extraction/refining stages<sup>[5, 8]</sup>

Zn smelting slag and waste acid	Leaching slag	Ag concentrates	In slag	Co slag
$\theta_x$ (%)	28.4	4.2	10.5	10.0
Zn smelting slag and waste acids	Cu slag	Cd slag	Pb slag	Waste acid
$\theta_x$ (%)	3.5	7.1	6.1	30.2

### 4.1.3 Hg distribution sub-model for the waste disposal processes

The wastes disposal processes considered in this study primarily included sulfuric acid utilization processes, waste acid disposal processes, and smelting slags disposal processes. The recoveries of Hg from acid slags and calomel were calculated in the sector of Hg distribution as a component of the waste acid disposal processes. The Hg distribution in the flue gas desulfurization (FGD) slags disposal processes was based on the assumption that Hg was either dumped or placed in interim storage at the chemical plants. The detailed disposal methods and assumptions applied for the main intermediated wastes and byproducts are shown in Table 4-5.

Table 4-5 Disposal methods and assumptions made for the wastes/byproduct produced from the metals production processes

Stage	Wastes/ Byproduct	Disposal method
Dehydration	Dust	Used as raw materials in the oxidation stage
Initial oxidation	Dust	1) Used as raw materials in the extraction stage; 2) Returned to the oxidation process;
	Waste acid	Disposed in the waste acid station. The settling slag was sent to qualified Hg recovery companies, returned to the smelting furnace, or temporarily stored in the smelters. The temporarily stored settling slag acid slag which was produced in 2015 was assumed to be equal to the disposal amount in 2014. Thus, the settling slag was either recycled or returned to the smelter. The sulfurization slag was assumed to be sent to a qualified Hg recovery company. The

		neutralization slag was primarily reused in the cement plant.
	Sulfuric acid	Used in the fertilizer plants, chemical plants, dealers, smelters and concentrating mill.
	Calomel	Sold to Hg recovery company
	FGD slags	Including FGD gypsum, ammonia sulfate, sodium sulfate, zinc sulfate. 1) the FGD gypsum was mainly sent to cement plant; 2) the ammonia sulfate and sodium sulfate were sent to chemical plants; 3) the zinc sulfate was used in the extraction process.
	Furnace slags	Only a small amount produced in several smelters. We assumed no furnace slag was produced in the Zn smelters.
Extraction	Dust	Assumed no dust produced since more than 80% of Zn was extracted with hydrometallurgical processes.
	Furnace slags/Leaching slag/Purification slags	Most leaching slags were roasted in the volatilization kiln at the temperature larger than 800 °C. The purification slags generally included Ag slag, In slag, Co slag, Cu slag, Cd slag, and Pb slag. The Ag, Co and In slag were used to recover metals with hydrometallurgical process. The smelters generally recovered Cd and Pb slags with pyrometallurgical process. Both the pyrometallurgical process and hydrometallurgical process were used to recover Cu.
Refining	Furnace slags	Assumed discarded.

#### 4.1.3.1 Hg distribution in the sulfuric acid utilization process

Hg distribution in the sulfuric acid utilization process is

$$Q_{sa,k} = \sum_i \sum_j I_{sa,ij} \theta_{k,i} \quad (E18)$$

$$OP_{t,k} = \sum_k Q_{sa,k} \delta_{t,k} \quad (E19)$$

where  $Q_{sa,k}$  is the Hg input with sulfuric acid into  $k$  department, t;  $\theta_x$  is the percentage of Hg deliver to  $k$  department in the total Hg input with the sulfuric acid, %; The  $k$  department refers to the fertilizer plant, chemical plant, concentrating mill, smelters and dealers;  $\delta_{t,k}$  is the percentage of Hg in the  $k$  department that passed to  $t$  fate, %. The parameter  $t$  refers to the fate of Hg during utilization of sulfuric acid. The fates include interim storage, dumped, and emissions to air, water or soil.

Table 4-6 Hg distribution in different sulfuric acid users (%)<sup>[5, 19]</sup>

Sulfuric acid users	Sulfuric acid produced in Zn smelters
Dealers	20.1
Zn smelters	16.1
Other smelters	24.2
Fertilizer	26.1
Chemical plants	6.2
Concentrating mills	7.3

Table 4-7 Hg distribution factors in different fates in the sulfuric acid users <sup>[5, 8, 19, 20]</sup>

Sulfuric acid users	Air	Water	Soil	Dumped	Interim storage
Dealers	0.0	0.0	0.0	0.0	100.0
Zn smelters	23.6	0.8	2.0	71.3	2.2
Other smelters	0.0	2.0	2.0	96.0	0.0
Fertilizer	1.4	0.1	40.6	57.9	0.0
Chemical plants	2.5	0.1	5.0	58.4	34.0



Concentrating mill	0.0	24.5	2.0	73.5	0.0
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#### 4.1.3.2 Hg distribution in the waste acid disposal process

The main methods used for waste acid disposal included the lime neutralization method, lime-ferric salt neutralization method, sulfide-neutralization method and biological method.<sup>[21, 22]</sup> The first two methods generally consisted of two stages, including settling (set) and neutralization (neu), which refer to as type 1 in this work. The latter two methods have one additional stage, sulfurization/coordination (sul), and the latter two methods are classified as type 2. The Hg emitted into water ( $LE_{wa}$ ) is

$$LE_{wa} = \sum_i \sum_j (I_{wa,ij} + 30.2\% Q_{e,iep}) (1 - \eta_{set}) [\theta_1 + \theta_2 (1 - \eta_{sul})] (1 - \eta_{neu}) (1 - \eta_{asr}) \quad (E20)$$

where  $\eta_{set}$ ,  $\eta_{sul}$ ,  $\eta_{neu}$  and  $\eta_{asr}$  is the Hg removal efficiency of the setting, sulfurization/coordination, neutralization and arsenic removal stage, respectively, %.  $\theta_1$  and  $\theta_2$  is the application percentage of type 1 and type 2, %; the 30.2% here is the percentage of Hg into the waste acid in the leaching and refining stages of the Zn electrolytic process.

In the waste acid disposal process, the Hg was distributed into settling slag, sulfurization/coordination slag, and neutralization slag. The settling slag was sent to qualified Hg recovery companies, returned to the smelting furnace, or temporarily stored in the smelters in 2012. The percentages of Hg in the settling slag sent to each disposal method were  $\theta_{set1}$ ,  $\theta_{set2}$ , and  $\theta_{set3}$ , respectively. However, the acid slag was classified as hazardous wastes in the revised *Hazardous Waste List*. Thus, we assumed that the temporarily stored acid was distributed into other disposal ways (qualified Hg recovery companies or smelting furnace) according to existing proportion. The sulfurization slag was assumed to be sent to a qualified Hg recovery company. The neutralization slag was primarily sent to cement plants or landfilled. We assumed that neutralization slag from zinc smelters using SET+SUL+NEU was sent to cement plants.

Thus, the Hg amount into the qualified Hg recovery company ( $RM_{wa}$ ) is

$$RM_{wa} = \sum_i \sum_j (I_{wa,ij} + 30.2\% Q_{e,iep}) \eta_{set} \theta_{set1} + I_{wa,ij} \theta_2 (1 - \eta_{set}) \eta_{sul} \theta_{sul1} \quad (E21)$$

The Hg amount in the slags ( $OD_{wa}$ ) sent to cement plant is

$$OD_{wa} = \sum_i \sum_j (I_{wa,ij} + 30.2\% Q_{e,iep}) (1 - \eta_{set}) [\theta_1 + \theta_2 (1 - \eta_{sul})] \eta_{neu} \theta_1 \quad (E22)$$

The Hg amount in the slags ( $OD_{fit}$ ) landfilled is

$$OD_{fit} = \sum_i \sum_j (I_{wa,ij} + 30.2\% Q_{e,iep}) (1 - \eta_{set}) [\theta_1 + \theta_2 (1 - \eta_{sul})] \eta_{neu} \theta_2 \quad (E23)$$

The Hg in the settling slags returned to the metals production process ( $IR_{wa}$ ) is

$$IR_{wa} = \sum_i \sum_j (I_{wa,ij} + 30.2\% Q_{e,iep}) \eta_{set} \theta_{set3} \quad (E24)$$

The reutilization of settling slag led to the atmospheric Hg emission ( $GE_{wa}$ ) is

$$GE_{wa} = (I_{wa,ij} + 30.2\% Q_{e,iep}) \gamma_s (1 - \eta_{s,min}) \quad (E25)$$

where  $\eta_{s,min}$  is the minimal Hg removal efficiency of the APCDs for the initial oxidation stage, %. The removed Hg was assumed to be temporarily stored in the smelters. The Hg recovered from the calomel and waste acid slag is

$$RE_{wa} = (RM_{wa} + RM_{smr,ij}) \times \lambda_{RE} \quad (E26)$$

where  $\lambda_{RE}$  is the recovery rate of the Hg from the calomel and waste acid slag, %. In this work, we used the 95% as the recovery rate.<sup>[23]</sup> We assumed that about 1% of the Hg emitted to atmosphere and the rest was discarded with the dumped slags.

Table 4-8 Application percentage of different methods for waste acid disposal (%)

Waste acid disposal method	Zn smelter
SET+NEU, $\theta_1$	63.2
SET+SUL+NEU, $\theta_2$	36.8

SET: Settling; NEU: Neutralization; ASR: Arsenic; SUL: Sulfurization/Coordination

Table 4-9 Percentage of Hg distributed among different disposal ways (%)

Acid slags disposal ways	Disposal proportion (%)
Reclaimed in the Hg recovery company <sup>[24]</sup>	13.8
Landfill	51.9
Roasted in the smelter	34.3

The detailed disposal procedure for leaching slags was described in our previous studies<sup>[8, 25]</sup>. The method used to calculate the Hg distribution in the Zn leaching slags disposal processes was similar to that for the metals production processes. The Hg in the leaching slags was calculated in (E16). Both dust collectors and flue gas desulfurization towers were assumed to be used for air pollution control in the large smelters, whereas only dust collectors were used in other smelters. The dust (mainly zinc oxide product) and FGD slags were temporarily stored in the smelters. The furnace slag consisted of ferrous slag, which was used in building materials. The Hg in this material was assumed to be stabilized.

$$GE_{ls} = \sum_i \sum_j I_{ls,ij} \gamma_{ls} (1 - \eta_{dc}) (1 - \theta_{ds} \eta_{ds}) \quad (E27)$$

$$IS_{ls} = \sum_i \sum_j I_{ls,ij} \gamma_{ls} (\eta_{dc} + \theta_{ds} \eta_{ds} - \eta_{dc} \theta_{ds} \eta_{ds}) \quad (E28)$$

$$ST_{ls} = \sum_i \sum_j I_{ls,ij} (1 - \gamma_{ls}) \quad (E29)$$

where  $GE_{ls}$ ,  $IS_{ls}$  and  $ST_{ls}$  respectively refers to the amount of Hg emitted to air, temporarily stored and stabilized during leaching slags disposal process.  $\gamma_{ls}$  is the Hg released rate in the furnace and is approximately 93.2%.  $\eta_{dc}$  and  $\eta_{ds}$  are the Hg removal efficiencies of dust collectors and FGD towers and are  $4.3 \pm 3.1\%$  and  $38.5 \pm 27.6\%$ . The values for the Hg release rate and Hg removal efficiency were assigned based on field experiments conducted at three Zn smelters.<sup>[8]</sup> We assumed that the Hg removal efficiencies fit the normal distributions. The standard deviation of the Hg removal efficiency was used to generate the uncertainty, and  $\theta_{ds}$  was the application percentage of FGD towers in the Zn smelters with a value 36.8%.

The Hg distribution in the Zn purification slags is calculated as follows.

$$OP_{t,x} = \sum_t \sum_i I_{ex,i} \delta_t \quad (E30)$$

where  $x$  refers to the Zn smelting slags, including leaching slag, Ag slag, Cu slag, Cd slag, Co slag, In slag and Pb slag (The fate of Hg in the waste acid and leaching slags were calculated);  $t$  refers to the Hg fates, including interim storage, discarded with slags, or emitted to air or water.  $\delta_t$  is the percentage of Hg into each fate, % (Table 4-9). Table 4-10 The percentage of Hg into different fates in the utilization process of Zn purification slags (%).<sup>[5]</sup>

Slags	Pyrometallurgical process			Hydrometallurgical process		
	Air	Dumped	Interim storage	Dumped	Water	Interim storage
Ag slag	–	–	–	5.0	90.0	5.0
Cu slag	55.0	31.3	13.7	5.0	90.0	5.0
Cd slag	48.5	37.8	13.7	–	–	–
Co slag	–	–	–	5.0	90.0	5.0
Pb slag	77.1	9.2	13.7	–	–	–
In slag	–	–	–	5.0	90.0	5.0

## 4.2 Calculated results

### 4.2.1 Hg input to zinc smelters in 2015

Mercury input to zinc smelters in 2015 was approximately 878 t. Most of mercury was inputted in Shaanxi and Gansu province due to their consumption of high mercury concentrates. Other provinces such as Sichuan, Guangdong, Yunnan were with high mercury input due to high consumption of ore concentrates.



Figure 4-2 Mercury input in 2015

#### 4.2.2 Atmospheric mercury emissions from zinc production process in 2015

Atmospheric mercury emissions from zinc production process in 2015 was approximately 27 t, accounting for approximately 3% of total mercury output. The rest of mercury was released to waste acid, leaching slag, metal slags and desulfurization gypsum. Mercury in the waste acid accounted for 47.2% of total mercury input and approximately 22.7% of mercury was released to sulfuric acid.

#### 4.2.3 Atmospheric mercury emissions from waste disposal process in 2015

Total atmospheric mercury emissions from waste disposal process reached 49 t in 2015. The dominant atmospheric mercury emission points in the waste disposal process included waste acid disposal process, metal disposal process, leaching slag disposal process, and sulfuric acid disposal process. Atmospheric mercury emissions from waste disposal process was approximately 7 t due to the recycling of acid slag to the roasting process. Leaching slag treatment contributed to approximately 25 t of atmospheric mercury emissions according to this study, which was lower than our previous estimation in 2012. That is because many desulfurization towers were installed during 2012-2015, which contributed to large amount of mercury reduction. Atmospheric mercury emissions from metal disposal process were about 12 t in 2015. That was due

to the secondary smelting of metals from the leaching process. Mercury was an impurity in these metal wastes, which was still lacking notice currently.

Table 4-10 Mercury emissions from different processes.

Process	Emission point	Emissions (t)	Note
Production process	Smelting furnace	27	Mainly from hydrometallurgical process
Waste disposal process	Waste acid disposal process	7	Recovering Hg from SUL slag and calomel; Smelting slag in the furnace
	Leaching slag treatment	25	Recovering ZnO from leaching slag
	Metal slag disposal	12	Metal slag from the leaching step of production process was treated to recover metal. The pyrometallurgical process led to mercury emissions.
	Sulfuric acid disposal	5	Smelter using sulfuric acid to produce metals

## 5 Policy implication and recommendation

The test result in the production process of these two smelters indicated that most mercury inputted into zinc production process has been removed by APCD combinations. After the application of ultra-low emission technologies (additional FGD+ESD after DCDA), the emitted mercury concentrations reached as low as 10  $\mu\text{g}/\text{m}^3$ , which was almost similar to the emission level in the coal-fired power plants. In addition, the mercury removal efficiency of the APCD combinations reached as high as 99%. Thus, atmospheric mercury emissions from zinc smelters have been better controlled in current zinc smelters.

However, attention should be paid on the wastes and byproducts, since atmospheric

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mercury emissions from these sources may exceed emissions from the production process itself. The primary zinc production process only contributed about 27 t of atmospheric mercury emissions due to highly synergic mercury removal efficiency of current air pollution control devices. However, the waste disposal process would further contribute about 49 t of atmospheric mercury emissions. Currently, atmospheric mercury emission from waste disposal process has not been controlled in the Minamata Convention on Mercury under Article 8. However, to effectively control mercury pollution in China, mercury emission from waste disposal process should receive more attention, and be addressed as part of China's sector Convention implementation plan and/or as part of environmentally sound waste management under Article 11 of the Convention.

Specifically, we recommend three improvements to waste management methods. First, we recommend the recovery and landfill of waste acid slags instead of returning to the roaster to avoid the re-emission of mercury.

Second, the leaching slag disposal process was one significant emission point. However, the application of desulfurization gypsum systems could effectively capture atmospheric mercury and improve the total mercury emission efficiency to 86.7%. Thus, we advise the further expansion of desulfurization gypsum system to middle and small scale smelters.

Third, recycling metal from metal wastes is an important sources-saving measure. However, the air pollution control devices for secondary recycling facilities are not comparable to the primary metal production process. Thus, to reduce mercury emissions from secondary metal production process, one possible way is to use the metal wastes with ore concentrates in the primary metal smelters.

Emission estimates from several waste or byproduct management scenarios were outside the scope of this report. For example, we did not estimate emissions resulting from wastes sent to cement plants. However, according to our investigation, some of the wastes (mainly gypsum) have been disposed in some cement plants as raw materials with coordinated co-treatment of hazardous wastes. During this procedure, the mercury

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in the raw materials was emitted to air again. Thus, attention should be paid on the raw materials which was inputted into cement plants.

We also did not estimate emissions resulting from fertilizer application. Sulfuric acid was one important mercury output from zinc smelters. However, the utilization of sulfuric acid in the fertilizer plants would input mercury into their production system. Fertilizer is highly-related with human's health. The utilization of fertilizer not only led to the direct release of mercury to soil but also impacted the human's food. Thus, special technology should be applied to reduce the mercury in sulfuric acid. In addition, we noticed that phosphorus concentrate was one potential mercury source of anthropogenic system. Thus, the contribution from the use of phosphorus concentrate to mercury flow in China should be evaluated.

It should be noticed that due to the limit of available data, the wastes flow for a national map was based on the situation in 2012 with slight revision according to the policy and technology development during 2012-2015 and based on certain assumption. Thus, emission data from waste disposal process were subjected to higher uncertainty than emissions from production process. Future national investigation was still required to update the data to cover 2015 and beyond.

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