Atmos. Chem. Phys. Discuss., 15, 32889–32929, 2015
www.atmos-chem-phys-discuss.net/15/32889/2015/
doi:10.5194/acpd-15-32889-2015

Atmospheric Chemistry and Physics Discussions

Mercury transformation and speciation in flue gases from anthropogenic emission sources: a critical review

L. Zhang[1], S. X. Wang[1,2], Q. R. Wu[1], F. Y. Wang[1], C.-J. Lin[3], L. M. Zhang[4], M. L. Hui[1], and J. M. Hao[1,2]

[1]State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China
[2]State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, Beijing 100084, China
[3]Center for Advances in Water and Air Quality, Lamar University, Beaumont, TX, USA
[4]Air Quality Research Division, Science and Technology Branch, Environment Canada, Toronto, Canada

Received: 31 October 2015 – Accepted: 11 November 2015 – Published: 24 November 2015

Correspondence to: S. X. Wang (shxwang@tsinghua.edu.cn)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Mercury transformation mechanisms and speciation profiles are reviewed for mercury formed in and released from flue gases of coal-fired boilers, non-ferrous metal smelters, cement plants, iron and steel plants, municipal solid waste incinerators, and biomass burning. Mercury in coal, ores and other raw materials is released to flue gases in the form of Hg^0 during combustion or smelting in boilers, kilns or furnaces. Decreasing temperature from over 800 °C to below 300 °C in flue gases leaving boilers, kilns or furnaces promotes homogeneous and heterogeneous oxidation of gaseous elemental mercury (Hg^0) to gaseous divalent mercury (Hg^{2+}), with a portion of Hg^{2+} adsorbed onto fly ash to form particulate-bound mercury (Hg_p). Halogen is the primary oxidizer for Hg^0 in flue gases, and active components (e.g., TiO_2, Fe_2O_3, etc.) on fly ash promote heterogeneous oxidation and adsorption processes. In addition to mercury removal, mercury transformation also occurs when passing through air pollution control devices (APCDs), affecting the mercury speciation in flue gases. In coal-fired power plants, selective catalytic reduction (SCR) system promotes mercury oxidation by 34–85 %, electrostatic precipitator (ESP) and fabric filter (FF) remove over 99 % of Hg_p, and wet flue gas desulfurization system (WFGD) captures 60–95 % of Hg^{2+}. In non-ferrous metal smelters, most Hg^0 is converted to Hg^{2+} and removed in acid plants (APs). For cement clinker production, mercury cycling and operational conditions promote heterogeneous mercury oxidation and adsorption. The mercury speciation profiles in flue gases emitted to the atmosphere are determined by transformation mechanisms and mercury removal efficiencies by various APCDs. For all the sectors reviewed in this study, Hg_p accounts for less than 5 % in flue gases. In China, mercury emission has a higher Hg^0 fraction (66–82 % of total mercury) in flue gases from coal combustion, in contrast to a greater Hg^{2+} fraction (29–90 %) from non-ferrous metal smelting, cement and iron/steel production. The higher Hg^{2+} fractions shown here than previous estimates may imply stronger local environmental impacts than previously thought, caused by mercury emissions in East Asia. Future research should focus on determining mer-

ACPD
15, 32889–32929, 2015

cury speciation in flue gases from iron and steel plants, waste incineration and biomass burning, and on elucidating the mechanisms of mercury oxidation and adsorption in flue gases.

1 Introduction

Atmospheric mercury is one of the key focuses in the environmental diplomatic affairs in recent years owing to its toxicity, persistence and long-range transportability. The international treaty on mercury, the Minamata Convention, was adopted worldwide in October 2013 aiming to reduce mercury release into the immediate environments. Coal combustion, cement clinker production, and primary production of ferrous and non-ferrous metals, are predominant sources of global anthropogenic mercury emission (UNEP, 2013). Aside from coal-fired power plants, coal-fired industrial boilers, cement clinker production facilities, and smelting and roasting processes used in the production of non-ferrous metals (lead, zinc, copper and industrial gold), waste incineration facilities, in terms of their rapid growth, are also on the list of key point sources in Annex D for Article 8 of the Minamata Convention.

Mercury has three operationally defined chemical forms: gaseous elemental mercury (Hg^0), gaseous oxidized (or reactive) mercury (Hg^{2+}) and particulate-bound mercury (Hg_p). Hg^0, the most stable form, accounts for over 90 % of the total mercury in the atmosphere. Its residence time is estimated to be several months to over one year (Schroeder and Munthe, 1998; Lindberg et al., 2007; Fu et al., 2012), but could be as short as hours to weeks under specific environmental conditions (Gustin et al., 2008). Hg^{2+} has high water-solubility and thus can be easily scavenged into droplets and adsorbed to surfaces followed by wet and dry deposition. The short residence time (hours to days) of Hg^{2+} leads to more prominent local environmental impacts. Hg_p has a residence time of hours to weeks, and mercury on finer particles can be transported for long distances (Schroeder and Munthe, 1998). Hg^{2+} and Hg_p are also referred to as reactive mercury (RM) due to their high surface reactivity (Rutter and Schauer, 2007).

ACPD
15, 32889–32929, 2015

Mercury speciation profiles in the exhausted flue gases from key sources determine the behavior of atmospheric mercury in the ambient air, while the profiles in the pipeline flue gases are crucial to mercury emission controls.

Different emission sources have different mercury speciation profiles. Even for the same emission category, the profile varies significantly when different combinations of air pollution control devices (APCDs) are applied or different types of fuels or raw materials are used. Different countries or regions have distinguished mercury speciation profiles for similar emission sources because of APCD preferences and fuel (or raw material) properties. The profiles can vary with time as advanced air pollution control technologies are implemented. Inventory experts tend to use more localized and up-to-date profiles from on-site measurements of mercury emission sources. Walcek et al. (2003) employed three sets of profiles respectively for fuel combustion, waste incineration and other manufacturing processes, and found the overall relative emission proportions (REPs) among $Hg^0 : Hg^{2+} : Hg_p$ species for the 1996 inventory of eastern North America to be 47 : 35 : 18. Streets et al. (2005) accomplished a more detailed profile list for different source categories with profiles under different APCDs for coal combustion, and obtained the overall REPs for China in 1999 which were 56 : 32 : 12. Pacyna et al. (2006) developed the 2000 mercury emission inventory for Europe and evaluated the overall REPs to be 61 : 32 : 7. The REPs for anthropogenic mercury emissions from Korea in 2007 were estimated to be 64 : 29 : 7 (Kim et al., 2010a), and those for the 2006 inventory of Australia were 77 : 17 : 6 (Nelson et al., 2012). Our recent study updated the anthropogenic mercury emission inventory of China to the calendar year 2010 based on an abundant database of field measurements, and the REPs of the overall mercury speciation profile were 58 : 39 : 3 (Zhang et al., 2015). Although the ratio of Hg^0 to Hg^{2+} seems to be close to the results from Streets et al. (2005), the sectoral profiles have changed significantly because of the implementation of APCDs in key sources in China. Results from on-site measurements in Chinese power plants, non-ferrous metal smelters and cement plants have substantially improved the speciation profiles.

ACPD
15, 32889–32929, 2015

Mercury speciation profiles of major emission sources in the world have remarkable influences on the assessment of long-range transport of atmospheric mercury. This paper provides a critical review of mercury speciation in flue gases from major anthropogenic emission sources, and elaborates the process of initial mercury release in boilers, kilns or furnaces to its transformation in the flue gases across APCDs. Key factors during the emission process for each source are identified for the enhancement of existing control technologies. Profiles of mercury speciation in different countries and regions are compared by sectors to assess their local and regional environmental impacts.

2 Mercury speciation and transformation in flue gases from coal combustion

2.1 Mercury speciation in flue gas from coal combustion

Nearly all mercury in coal is released into the flue gas in the form of Hg^0 during combustion over 1000 °C. With the decrease of flue gas temperature out of the boiler, a portion of Hg^0 is oxidized to Hg^{2+} mainly by active atomic Cl generated from HCl, Cl_2 or HOCl (Senior et al., 2000). Niksa et al. (2001) discovered that the cycling of atomic Cl is the dominant mechanism of Hg^0 oxidation. This process, including homogeneous and heterogeneous reactions, is driven by thermodynamic equilibrium, but restricted by reaction kinetics (Widmer et al., 2000). Based on the results from bench-scale experiments, L. Zhang et al. (2013a) found that lower total mercury concentration and higher chlorine concentration in flue gas lead to higher Hg^0 oxidation rate. The results from Sterling et al. (2004) showed that SO_2 and NO in flue gas inhibit the oxidation of Hg^0. The homogeneous reaction mechanism usually underestimates the oxidation rate because heterogeneous reactions on fly ash play a more important role under low temperatures (100 to 300 °C). Heterogeneous processes not only accelerate the oxidation of Hg^0 but also contribute to the adsorption of Hg^{2+} onto fly ash to form Hg_p. Bhardwaj et al. (2009) found that specific surface area (SSA), loss on ignition (LOI) and average

ACPD
15, 32889–32929, 2015

particle size positively correlated with both the Hg^0 oxidation and the Hg^{2+} adsorption. Inorganic components such as CuO, TiO_2 and Fe_2O_3 also have significant impacts on the mercury oxidation and adsorption processes (Dunham et al., 2003; Norton et al., 2003; López-Antón et al., 2007).

According to 30 previous on-site measurements in coal-fired power plants and industrial boilers (Kellie et al., 2004; Duan et al., 2005; Lee et al., 2006; Zhou et al., 2006, 2008; Chen et al., 2007, 2008; Yang et al., 2007; Wang et al., 2008, 2010a; Kim et al., 2010b; Zhang et al., 2012a; L. Zhang et al., 2013a), mercury speciation after the boiler and before the APCDs is mainly determined by coal properties, specifically chlorine, mercury and ash contents in coal. Chlorine and mercury contents have the most significant impacts on the percentage of Hg^{2+} in total mercury, while mercury and ash contents highly influence the proportion of Hg_p in total mercury in flue gas. The proportions of Hg^0, Hg^{2+} and Hg_p in the flue gas released from a pulverized-coal (PC) boiler, averaged 56, 34 and 10 %, respectively. However, Hg^{2+} proportion ranged from 5 to 82 % while Hg_p proportion ranged from 1 to 28 %. Besides the coal properties, the boiler type also affects mercury speciation in flue gas. A circulating fluidized bed (CFB) boiler can generate as high as 65 % of Hg_p in flue gas due to more sufficient contact between gaseous phase mercury and fly ash inside the boiler (Zhang, 2012).

2.2 Mercury transformation across APCDs for coal combustion

2.2.1 Mercury transformation during selective catalytic reduction (SCR)

Figure 1 shows mercury transformation and removal processes across APCDs in coal-fired power plants. The first APCD after the boiler could be the SCR system if applied for NO_x control. The operation temperature in a SCR is typically 300–400 °C. SCR catalysts, usually composed of V_2O_5, WO_3 and TiO_2, significantly promote the Hg^0 oxidation process and increase Hg^{2+} level for downstream removal in PM and SO_2 control devices (Niksa and Fujiwara, 2005). Laboratory-scale studies (Lee et al., 2003;

ACPD
15, 32889–32929, 2015

Bock et al., 2003) showed that Hg^0 oxidant inside SCR is the atomic Cl. The Hg-Cl redox chemistry and the NO-NH_3 redox chemistry occur simultaneously on the active sites of SCR catalyst (L. Zhang et al., 2013b). Therefore, the reaction system in SCR is complicated and influenced by a number of factors. Machalek et al. (2003) pulled subbituminous-derived flue gas into a pilot-scale SCR system and found that the Hg^0 oxidation extent decreased from 40 to 5 % when the space velocity (SV) of SCR was increased from 3000 to 7800 h^{-1}. The influence of NH_3 is more controversial. The study of Machalek et al. (2003) found that NH_3 inhibits the oxidation of Hg^0 inside SCR. Niksa and Fujiwara (2005) theoretically calculated this process and addressed the inhibition mechanism by NH_3 competing with atomic Cl on active sites. However, on-site measurements in three coal-fired power plants showed the opposite results, that is, the increase of NH_3 injection rate promotes Hg^0 oxidation (L. Zhang et al., 2013b). Possible chemical mechanism was proposed for the observed oxidation, but requires further investigation. The concentrations of NO, SO_2 and total mercury and the type and on-duty time of the SCR catalyst also affect the heterogeneous oxidation processes inside SCR (Winberg et al., 2004; Niksa and Fujiwara, 2005; L. Zhang et al., 2013b). Field tests in coal-fired power plants showed an average Hg^0 oxidation rate of 71 % with a range of 34–85 % (Chen et al., 2008; Zhang, 2012; L. Zhang et al., 2013b).

2.2.2 Mercury transformation in electrostatic precipitator (ESP)

Due to its high PM removal efficiency and relatively low cost, ESP is the most widely used PM controller in coal-fired power plants. Over 99 % of Hg_p is removed inside ESP (Wang et al., 2010a). A small portion of Hg^{2+} can also be adsorbed onto fly ash and removed by ESP. The Hg^{2+} capture rate is determined by the unburned carbon (UBC) on fly ash (Senior and Johnson, 2005). The total mercury removal efficiency of ESP is usually in the range of 20–40 % at ~ 5 % UBC content of fly ash. Besides the UBC, the surface property, size, porous structure and mineral composition of fly ash affect the mercury capture rate of ESP as well (Lu et al., 2007). When coal with

ACPD
15, 32889–32929, 2015

high chlorine content is burned, more UBC is generated on fly ash and more Hg^{2+} and Hg_p are formed in flue gas, which in turn increase the mercury capture rate inside ESP. Improvement of ESP for capturing fine particles (e.g., adding electric fields inside ESP) will also increase mercury removal efficiency. Inter-conversion between Hg^0 and Hg^{2+} occurs inside ESP (Zhang, 2012). The charging anode of ESP can neutralize Hg^{2+} and convert it to Hg^0, while Hg^0 in flue gas continues to be oxidized to Hg^{2+} via heterogeneous reactions in ESP under temperatures of 150–200 °C. Therefore, Hg^0 concentration can either increase or decrease inside ESP depending on the processes interplay. On-site measurements showed an average mercury removal efficiency of 29 % for ESP with a large range of 1–74 % (Goodarzi, 2004; Guo et al., 2004; Kellie et al., 2004; Tang, 2004; Duan et al., 2005; Lee et al., 2006; Chen et al., 2007; Yang et al., 2007; Wang et al., 2008, 2010a; Zhou et al., 2008; Kim et al., 2010b; Shah et al., 2010; ICR, 2010; Zhang et al., 2012a). Nevertheless, ESP installed after a CFB boiler can achieve an average of 74 % mercury removal due to the high Hg_p proportion in flue gas (Chen et al., 2007; ICR, 2010; Zhang, 2012).

2.2.3 Mercury transformation in fabric filter (FF)

A higher PM removal efficiency can be achieved by FF than by ESP, especially for fine particles. FF is increasingly applied in coal-fired power plants and industrial boilers in the need of fine particle ($PM_{2.5}$ or PM_1) control. FF has mercury removal efficiencies of 9–92 % with an average of 67 % (Chen et al., 2007; Shah et al., 2008; Wang et al., 2009; ICR, 2010). Besides Hg_p, FF can also remove over 50 % of Hg^{2+}. During the filtration, contact between flue gas and the particles on the cake layer promotes adsorption of Hg^{2+} onto fly ash (Zhang, 2012). The properties of fly ash have the most significant impact on Hg^{2+} adsorption. The dust cake layer also facilitates oxidation of Hg^0.

ACPD
15, 32889–32929, 2015

Some plants apply ESP-FF hybrid precipitator to improve the fine particle removal efficiency. Limited studies suggested an overall mercury removal rate of 39 % in ESP-FF hybrid precipitator (S. X. Wang et al., 2014).

2.2.4 Mercury transformation in wet scrubber (WS)

Coal-fired industrial boilers are usually in a smaller scale compared with the utility boilers. The PM control for industrial boilers are not as advanced as those for power plants in developing countries. For example, WS is most widely adopted in China's industrial boilers. The proportion of Hg_p in flue gas of industrial boilers (1–3 %) is not as high as that of power plants because of the shorter formation times of Hg_p in industrial boilers, especially in small-scale ones. Consequently, the Hg_p removal rate of WS is only about 50 % (Zhang, 2012). SO_2 in flue gas can dissolve in water and form SO_3^{2-}, which could be a reducing agent for Hg^{2+}, leading to low Hg^{2+} capture rates in WS (Chang and Ghorishi, 2003; Omine et al., 2012). The overall mercury removal rate of WS is 23 % on average with a range of 7–59 % (Zhang, 2012).

2.2.5 Mercury transformation during wet flue gas desulfurization (WFGD)

WFGD is the most widely used APCD for SO_2 control in coal-fired power plants. During sulfur (mainly SO_2) scrubbing process, Hg^{2+} is also removed in WFGD. The average mercury removal efficiency of WFGD is 64 %, ranging from 56 to 88 % (Lee et al., 2006; Chen et al., 2007; Kim et al., 2010b; Wang et al., 2010a). Insoluble Hg^0 passes through WFGD without being captured. Similar to that in WS, chemical reduction of the dissolved Hg^{2+} reduces total mercury removal efficiency in WFGD due to re-volatilization of Hg^0 (Wo et al., 2009; Ochoa-Gonzaìlez et al., 2013). Flue gas and slurry composition, operating temperature, limestone injection rate, and slurry pH are the key factors affecting the re-volatilization of Hg^0 (AcunÞa-Caro et al., 2009; Ochoa-Gonzaìlez et al., 2012; Schuetze et al., 2012). WFGD is the crucial step in the co-benefit mercury control technologies in coal-fired power plants. The applications of high-chlorine coal,

ACPD
15, 32889–32929, 2015

SCR and halogen addition can increase the Hg^{2+} proportion in flue gas before WFGD. Therefore, the optimized strategy for WFGD is to stabilize the Hg^{2+} in the WFGD slurry to prevent mercury re-volatilization. The overall mercury removal efficiency of WFGD is on average 45 % with a range of 10–85 % (Yokoyama et al., 2000; Kilgroe et al., 2002; Ito et al., 2006; Lee et al., 2006; Meij and Winkel, 2006; Chen et al., 2007; Kim et al., 2010b; Wang et al., 2010a).

2.3 Mercury speciation profile for coal-fired boilers

Mercury speciation profiles in the flue gas from coal combustion are summarized in Table 1, which considers the transformation of mercury species across different types of APCDs. When no APCD is applied, mercury speciation profile has the largest variability due to the different properties of coal burned. The average proportions of Hg_p are all below 2 % when PM control devices are installed. As commonly used for stoker-fired (SF) industrial boilers, WS removes a large proportion of Hg_p and a small proportion of Hg^{2+}, resulting in a decrease of Hg_p percentage and a slight increase of Hg^0 percentage compared with the case of non-control. The average percentages of Hg^0 and Hg^{2+} in the flue gas exhausted from ESP are 58 and 41 %, respectively. The presence of CFB boiler can increase the proportion of Hg^0. The proportions of Hg^0 and Hg^{2+} are similar in the flue gas after FF, although with large variability. For the combination of ESP + WFGD, the proportion of Hg^0 reaches as high as 84 %. With the existence of SCR, the average proportion of Hg^0 is not as high as that for the combination of ESP + WFGD because of the high oxidation rate of Hg^0 inside SCR. Large uncertainties still exist in flue gas from the combinations of PC + FF, PC + FF + WFGD and CFB + ESP, since scarce speciation data is available.

ACPD
15, 32889–32929, 2015

3 Mercury speciation and transformation in flue gases from non-ferrous metal smelters

3.1 Mercury release and transformation in the roasting/smelting furnaces

Non-ferrous metals (copper, lead and zinc) are mainly produced from sulfide ores. Usually, mercury is released from concentrates to flue gas during the pyrometallurgical process of non-ferrous metals. A typical pyrometallurgical process requires four stages, including dehydration, smelting/roasting, extraction, and refining (Wang et al., 2010b; Zhang et al., 2012b; Wu et al., 2015). Approximately 1 % of mercury in concentrates is released to flue gas in the dehydration kiln, where the temperature varies from 150–700 °C (Song, 2010). Mercury in concentrates is mainly released during smelting/roasting stage. The temperatures in the smelting/roasting, thermal extraction and thermal refining stages are all higher than 800 °C (Li et al., 2010; Wang et al., 2010b). The Hg-S and Hg-O bounds are broken under such high temperatures (Hylander and Herbert, 2008). Almost all mercury compounds are thermally dissociated into Hg^0 considering the thermodynamic stability of Hg^0 at this temperature (Wang, 2011). Mercury release rates during these stages are generally over 98 % (Song, 2010; Li et al., 2010; Wu et al., 2015). The released Hg^0 would be transformed to Hg^{2+} or Hg_p by catalytic oxidation in the flue gas with the existence of gas phase oxidants such as atomic Cl (Galbreath and Zygarlicke, 2000; L. Zhang et al., 2013a).

3.2 Mercury transformation in the roasting/smelting flue gas

Flue gases from the four stages typically go through dust collectors to remove particles. FF or ESP is generally adopted for flue gases from the dehydration, extraction and refining stages, whereas a combination of waste heat boiler, cyclone and ESP is used for the roasting/smelting flue gas (Wu et al., 2012; UNECE, 2013). The flue gas is then cleaned in a purification system including flue gas scrubber (FGS) and electrostatic demister (ESD) before entering the acid plant for SO_2 recovery (see Fig. 2).

ACPD
15, 32889–32929, 2015

To minimize heavy metal emissions, the roasting/smelting flue gas could also require additional mercury removal after the purification system (UNECE, 2013). Since the roasting/smelting stage releases the most mercury, previous studies focus on mercury transformation and removal inside APCDs for the roasting/smelting flue gas (Zhang et al., 2012b; Wu et al., 2015). Figure 3 shows the mercury speciation after APCDs for non-ferrous metal smelters. Overall, the Hg_p proportion is less than 5 % for all non-ferrous metal smelters. Hg^0 is the dominant species in the flue gas after the purification devices in most situation since most Hg^{2+} has been removed. However, when the flue gas goes through the DCA towers, the share of Hg^{2+} increases to 80–98 %.

3.2.1 Mercury transformation in the dust collectors

Dust collectors can remove > 99 % of particles and therefore Hg_p is mostly removed simultaneously. Hg_p proportion after dust collectors is less than 5 % (Zhang et al., 2012b; Wu et al., 2015). Hg^0 can be homogeneously or heterogeneously oxidized in the flue gas, while the charging anode in the ESP can reduce Hg^{2+} to Hg^0. Therefore, the resulting mercury speciation profile after the dust collectors depends on the competition between Hg^{2+} reduction and Hg^0 oxidation. The proportion of Hg^{2+} after dust collectors varies a lot (4–85 %) among different tested smelters (Zhang et al., 2012b; Wu et al., 2015). The total mercury removal efficiency of dust collectors is usually less than 20 %. Test results of three zinc smelters showed mercury removal efficiencies of 9–12 % (Wu et al., 2015). The study of Li et al. (2010) shows lower mercury removal efficiencies of dust collectors (1–5 %). ESP plays the most important role in mercury removal for roasting/smelting flue gas. Zhang et al. (2012b) found an average mercury removal rate of 12 %, which is much lower than the efficiency of ESPs in coal-fired power plants, because of two reasons. Firstly, higher temperature of ESPs in smelters (300–350 °C compared to more or less 150 °C in coal-fired power plants) would restrain the Hg^0 condensation and Hg^{2+} absorption processes (Meij and Winkel, 2006). Secondly, although the dust concentrations in the flue gases of the coal-fired power plants

ACPD
15, 32889–32929, 2015

and the non-ferrous metal smelters are at the same level, mercury concentration in flue gas of non-ferrous metal smelters is two to three orders higher than that in the flue gas of coal-fired power plants (Tang et al., 2007; Wang et al., 2010a, b; Zhang, 2012; Zhang et al., 2012a, b; Wu et al., 2015). Under such conditions, there might not be sufficient active sites on the particles for mercury adsorption in the flue gas of non-ferrous metal smelters.

3.2.2 Mercury transformation in purification systems

The purification system generally includes FGS and ESD. FGS uses diluted sulfuric acid to capture acidic components in the flue gas, while ESD is employed to remove water vapor from the flue gas. Li et al. (2010) and Wang et al. (2010b) found that mercury removal efficiency in FGS was 11–22 %, whereas ESD removed 10–42 % of total mercury in the flue gas. The overall mercury removal efficiency of the purification systems in six tested plants by Zhang et al. (2012b) varies in the range of 72–99 %. Studies of Zhang et al. (2012b) and Kim et al. (2011) show that higher Hg^{2+} in the flue gas entering the purification system leads to higher mercury removal efficiency considering the high solubility of Hg^{2+} in water and sulfuric acid. In addition, Hg^0 would condense to liquid metallic mercury when the temperature of flue gas decreases from 300 to approximately 25 °C at the outlet of the purification system (Song, 2010). Therefore, the dominant mercury species after the purification system is generally Hg^0, with a proportion 43–96 % (Wang et al., 2010b; Zhang et al., 2012b; Wu et al., 2015).

3.2.3 Mercury transformation in other mercury removal systems

Mercury in the flue gas can be removed by other techniques including Boliden–Norzink process, Bolchem process, Outokumpu process, sodium thiocyanate process, selenium scrubber, activated carbon filters, and selenium filter (UNECE, 2013). The removal mechanisms in these processes are either to oxidize Hg^0 into Hg^{2+} or Hg^+ with strong oxidants and then remove oxidized mercury, or to capture Hg^0 with specific ad-

ACPD
15, 32889–32929, 2015

sorbents. The Boliden–Norzink process, the most widely used process in non-ferrous metal smelters, has been installed in more than 40 smelters globally. On-site measurements indicated that its mercury removal efficiency is 83–92 % (Wang et al., 2010b; Li et al., 2010; Wu et al., 2015). In the Boliden–Norzink process, Hg^0 in the flue gas is oxidized to Hg_2Cl_2 by solution containing $HgCl_2$. The yield Hg_2Cl_2 is removed from the circulating solution and then either used for mercury production or stored, whereas the solution is reused after regeneration. Other processes are not as commercialized as the Boliden–Norzink process.

3.2.4 Mercury transformation in the acid plants

An acid plant generally includes dehydration tower, conversion tower and absorption tower. Dehydration tower uses 93–95 % sulfuric acid to remove the water vapor. Conversion tower converts SO_2 into SO_3 with vanadium catalysts. Absorption tower absorbs SO_2 with 98 % sulfuric acid. Tests in one zinc smelter with a mercury reclaiming tower indicates that mercury speciation profile ($Hg^0 : Hg^{2+} : Hg_p$) after the acid plant is 6 : 90 : 4 (Wang et al., 2010b). Wu et al. (2015) found that the proportion of Hg^{2+} increased from 4 to 98 % when passing the acid plant. The total mercury removal efficiency in the acid plant can reach 83 %. On-site measurements in six smelters by Zhang et al. (2012b) showed that the dominant species was Hg^{2+} after the acid plant with the double-conversion-double-absorption process, while Hg^0 became the dominant species after the single-conversion-single-absorption process. The net reaction of mercury in the acid plant is the oxidation of Hg^0, either by the oxidants in flue gas under the vanadium catalysts in the conversion tower or by the concentrated sulfuric acid. However, further studies are required to understand the oxidation mechanisms.

3.3 Mercury speciation profile for non-ferrous metal smelters

Mercury speciation profiles in the flue gases from non-ferrous metal smelters are summarized in Table 2. In early mercury emission inventories, the relative emission pro-

ACPD
15, 32889–32929, 2015

portions (REPs) among $Hg^0 : Hg^{2+} : Hg_p$ species for non-ferrous metal smelters were estimated to be 80 : 15 : 5 (Pacyna and Pacyna, 2002; Streets et al., 2005; Pacyna et al., 2006; Wu et al., 2006). However, recent field tests found that the proportion of Hg^{2+} could reach > 90 % for the smelting/roasting stage with acid plants (Wang et al., 2010b; Zhang et al., 2012b). Besides the smelting/roasting stage, mercury emissions from the slag dehydration and volatilization stages are also significant. According to field experiments in a zinc smelter (Wang et al., 2010b), the mercury emissions from these two stages were 95 and 50 $g\,d^{-1}$, respectively, even higher than that from the roasting process (22 $g\,d^{-1}$). Therefore, the overall mercury speciation profile for non-ferrous metal smelters is not only affected by the roasting/smelting flue gases but also by the dehydration flue gas and the volatilization flue gas. Mass flow analysis in three zinc smelters indicates that mercury emissions from the slag dehydration stage, the slag smelting stage and the volatilization stage accounted for 54–98 % of total emissions, with Hg^0 as the dominant form (Wu et al., 2015). When considering atmospheric mercury emissions from all thermal processes in addition to the roasting process, the emission proportion of Hg^{2+} is reduced to 29–51 % (Wu et al., 2015). In lead smelters, the proportion of Hg^{2+} is about 40 % when considering atmospheric mercury emissions from the extracting and reclaiming processes (Zhang et al., 2012b). The proportion of Hg^{2+} in all exhaust gases is 32–68 % in copper smelters with the double-conversion-double-absorption process installed for the roasting flue gas (Zhang et al., 2012b).

4 Mercury speciation and transformation in flue gas from cement clinker production

4.1 Cement clinker production processes

A mix of raw materials, mainly limestone, are heated up to over 1400 °C and different compositions react to produce clinker. Additives, usually gypsum, are then mixed with clinker and milled to produce cement. The temperature of the final cement production

ACPD
15, 32889–32929, 2015

is usually under 100 °C. Results from temperature programmed decomposition (TPD) experiments indicate that mercury is not released from gypsum at such temperatures (Rallo et al., 2010; López-Antón et al., 2011; Liu et al., 2013). Therefore, we only consider the clinker production process that includes shaft kilns, wet rotary kilns, dry rotary kilns and precalciner processes.

Precalciner process is usually composed of the raw mill system, the coal mill system, the kiln system and the kiln head system. Raw materials are ground and homogenized in the raw mill system, and the high-temperature flue gas generated in the kiln system is used to preheat raw materials. The fuel, usually coal, is prepared in the coal mill system including coal mill and FF. The flue gas from the kiln system is also used to preheat coal. The kiln system for the production of cement clinker includes the preheater, the precalciner and the rotary kiln. The prepared raw materials, namely raw meal, enter the kiln system from one end of rotary kiln (kiln tail), and the coal powder is brought into the kiln system by air from the other kiln end (kiln head). The solid materials flow in opposite direction with the flue gas. The flue gas from kiln head is de-dusted and then emitted into the atmosphere.

4.2 Mercury behavior in cement clinker production process

Mercury behavior in the precalciner clinker production process is more complicated than that in coal-fired power plants. Flue gas generated in the kiln system is usually divided into two parts and used to preheat raw materials and coal, respectively. Mercury in flue gas can be adsorbed onto the surface of raw materials or coal, and then recycled into the kiln system. The dust collectors, usually FF, installed after raw mill or coal mill can capture a large part of mercury in flue gas. However, since the dust collected in precalciner cement production process is often recycled into the kiln system rather than disposed, the mercury removed from FF is recirculated into kiln system with dust. The flue gas generated from kiln head flows through a dust collector, usually ESP, and then emits into the atmosphere. The collected dust at the kiln head is also mixed with raw materials and recycled into the kiln system. Therefore, there are three mercury cycles in

ACPD
15, 32889–32929, 2015

the precalciner clinker production process. Mercury cycling in cement plants has been confirmed in field tests (Mlakar et al., 2010; Paone, 2010; Sikkema et al., 2011; Zheng et al., 2012). A transient model was developed to simulate mercury concentration in flue gas from kiln tail (Senior et al., 2010). This model was based on a series of mass balances from preheater to the whole process.

The three mercury cycles cause mercury enrichment in the clinker production process. F. Y. Wang et al. (2014) assessed mercury enrichment process using the ratio of mercury concentration in the exhausted flue gas to the equivalent mercury concentration. The equivalent mercury concentration was defined by dividing the total mercury input from raw materials and coal with the total amount of flue gas emerged in the kiln system. It was found that the mercury concentration was enriched by as high as 4–15 times in two Chinese cement plants. Another study also confirmed this point, with the mercury concentration enriched by over 10 times (Mlakar et al., 2010). Mercury enrichment can affect its emission from cement plants. The cement clinker production process has two modes depending on the operation of raw mill. When the raw mill is on (operation mode), the flue gas flows through raw mill first and then emitted into the atmosphere after dust removal. When the raw mill is off (direct mode), the flue gas directly flows through the FF after the raw mill and emits into the atmosphere. In operation mode, a larger proportion of mercury in flue gas is recirculated and enriched in the system because the combination of raw mill and FF has a higher mercury removal efficiency than FF alone. Therefore, switching between the two modes significantly changes mercury enrichment and concentration in flue gas. It should be noted that mercury concentration in the clinker is low. If no filtered dust is discarded, over 90 % of mercury input from raw materials and coal is eventually emitted into the atmosphere (Paone, 2008; Linero, 2011; Hoenig and Zunzer, 2013).

4.3 Mercury transformation during cement clinker production process

The mercury transformation in cement production process is summarized as Fig. 4. Based on the discussion above, mercury cycling in the clinker production process can

ACPD
15, 32889–32929, 2015

be divided into three stages: vaporization, adsorption and recycling (Sikkema et al., 2011). In mercury vaporization stage, mercury in raw materials and coal is released into the flue gas. Field tests in power plants of previous studies indicated that almost all of the mercury in coal (> 99 %) was vaporized into the flue gas as the elementary form because of the high temperature in coal-fired boilers, which is usually higher than 1000 °C (Tang et al., 2007; Wang et al., 2010a; Zhang et al., 2012a). For the cement clinker production process, mercury in raw materials and coal is mostly released to the flue gas. Mercury concentration in clinker was less than 5 ng g^{-1}, accounting for only 1.9–6.1 % of the total mercury (F. Y. Wang et al., 2014). The compounds of mercury silicates might be the main chemical forms of mercury in clinker (Schreiber et al., 2005). Temperature of raw materials increases continuously from 400 °C at the inlet of the preheater to over 1400 °C in the rotary kiln. Different mercury species have different decomposition and boiling temperatures, as summarized in one previous study (Zheng et al., 2012). Further studies on identification of mercury species in raw meals are needed to understand the mechanism of mercury vaporization in kiln system.

Mercury is oxidized homogeneously and heterogeneously in flue gas. As analyzed by F. Y. Wang et al. (2014), a series of operational conditions in the cement clinker production process can promote mercury oxidation. The oxidation of mercury is usually kinetically limited (Senior et al., 2000; Niksa et al., 2001; Wilcox et al., 2003; Krishnakumar and Helble, 2007; Liu et al., 2010). Residence time over 20 s provides enough reaction time for mercury oxidation. The high concentration of PM in flue gas, usually over 10 g m^{-3}, can catalyze the oxidation; and the addition of Fe-containing material in raw materials can provide more active sites for heterogeneous mercury oxidation (Dunham et al., 2003; Galbreath et al., 2005; Bhardwaj et al., 2009). Vaporized Hg^0 in the kiln system is oxidized during the cooling process of flue gas. Considering that Hg^{2+} can be easily adsorbed onto the surface of PM in flue gas and the PM concentration in flue gas is high, the proportion of Hg_p is therefore high. Mercury speciation in the flue gas entering the raw mill system was measured in three cement plants (F. Y. Wang et al., 2014). The proportion of Hg^{2+} was in the range of 64–76 %, while the proportion

ACPD
15, 32889–32929, 2015

of Hg_p was 21–27 %. Mlakar et al. (2010) found that the proportion of Hg_p in another plant was even higher, ranging in 15–77 %. The high proportion of Hg^{2+} and Hg_p can cause a high mercury removal efficiency in APCDs and other facilities, including dust collectors, raw mill and coal mill. Mercury removal efficiencies of raw mill with FF and coal mill with FF could reach 86–89 and 94–95 %, respectively (F. Y. Wang et al., 2014). The mechanisms of mercury removal in raw mill and FF are different. The removal of Hg_p in FF and adsorption of Hg^{2+} onto the filter cake are considered to be the predominant mechanism in FF (Chen et al., 2007; Wang et al., 2010a). At mercury recycling stage, the removed mercury in raw mill, coal mill and dust collectors is eventually cycled into kiln system with raw mill, coal powder and dust, respectively. Overall, because of the existing mercury cycling and a series of operational conditions promoting mercury oxidation, mercury speciation during clinker production is dominated by Hg^{2+} and Hg_p.

4.4 Mercury speciation profile for cement plants

The mercury emissions from the cement clinker production process were previously considered to be composed of 80 % Hg^0, 15 % Hg^{2+} and 5 % Hg_p (Streets et al., 2005). Recent field results (Mlakar et al., 2010; Won and Lee, 2012; F. Y. Wang et al., 2014) on mercury emission speciation of cement production are shown in Table 3. The proportions of different mercury species fluctuate at a wide range. Won and Lee (2012) found that Hg^{2+} only accounted for 15 % of the total mercury emissions, while other studies (VDZ, 2002; Mlakar et al., 2010; Linero, 2011; F. Y. Wang et al., 2014) showed that Hg^{2+} was the dominant species accounting for 60 to > 90 % of the total mercury.

ACPD
15, 32889–32929, 2015

5 Mercury speciation and transformation in flue gas from iron and steel production

5.1 Iron and steel production process

Iron and steel production is composed of raw material preparation (rotary kilns for limestone and dolomite production and the coking process), sintering machine, blast furnace and convertor. In raw material preparation, limestone and dolomite are roasted in rotary kilns and coking coal is produced in coke oven. Iron ores, coke and limestone (dolomite) are then mixed and sintered in the sintering machine. Products of these two stages are fed to the blast furnace where sinter, coke and limestone are smelted to produce iron, and then the iron is smelted in a convertor to produce steel. There is also another process using steel scrap to produce steel, called electric furnace. To increase the utilization efficiency of energy, coal gas emerged in the coke oven, blast furnace and convertor is collected and burned to generate electricity. The operational conditions in different stages are quite different. The mercury behavior in iron and steel plants is therefore quite complicated.

5.2 Mercury speciation profile for iron and steel plants

There is lack of field test results for iron and steel production process. Mercury is vaporized in high-temperature facilities, including coke oven, sintering machine, blast furnace and convertor. Mercury in the flue gas is oxidized homogeneously and heterogeneously. Part of the mercury is removed in dust collectors and flue gas desulfurization devices, and the remaining mercury in flue gas is emitted into the atmosphere. Field tests indicated that the mercury release rates in coke oven and sintering machine were lower than that in coal-fired boilers (> 99 %) because of the lower temperature in these facilities (Wang et al., 2015). Previous studies indicated that the mercury emissions from sintering machine accounted for about 90 % of total emissions from iron and steel plants (Fukuda et al., 2011). A speciation profile of 80 % Hg^0, 15 % Hg^{2+} and 5 % Hg_p

ACPD
15, 32889–32929, 2015

was applied in Streets et al. (2005). However, oxidized mercury was found to be the predominant species in our recent study (Wang et al., 2015). The proportion of Hg^{2+} in flue gas reached as high as 59–73 % and the proportion of Hg_p was under the detection limit because of the installation of ESPs for the examined iron and steel plants (Wang et al., 2015). The high PM concentration in flue gas and Fe on PM could promote mercury oxidation in flue gas. More field tests need to be conducted on mercury speciation profile of this industry in the future.

6 Mercury speciation and transformation in flue gas from other emission sources

Municipal solid waste (MSW) incineration is a potential predominant source in the global mercury emission inventory. A significant proportion of mercury (80–96 %) in the MSW releases from the incinerator into the flue gas is in the form of Hg^0 at 850–1000 °C (Park et al., 2008). Grate furnace combustor (GFC) and circulation fluidized bed combustor (CFBC) are the two most commonly used incinerators. The flue gas from CFBC has a larger proportion of Hg_p than that from GFC. Typical APCDs are combinations of semi-dry or dry flue gas deacidification (SD-FGD or D-FGD) for SO_2 and HCl removal, activated carbon injection (ACI) for dioxin removal and ESP/FF for PM removal. The overall mercury removal efficiency of the APCDs for MSW incineration ranges from 60 to over 99 % (Zhang et al., 2008; Takahashi et al., 2010). ACI is required in China for the control of persistent organic pollutants (POPs). High Cl content in MSW results in high Hg^{2+} proportion in flue gas. Limestone slurry sprayed in SD-FGD absorbs a large amount of Hg^{2+} and activated carbon adsorbs a large amount of both Hg^0 and Hg^{2+}. Particles from SD-FGD and ACI are captured by the downstream FF. Previous studies in Europe and the USA (Pacyna and Münch, 1991; Carpi, 1997) indicated that the Hg^{2+} proportion in exhausted flue gas ranges from 75 to 85 %. A Korean study found the Hg^{2+} proportion to be in the range of 78–99 % (Park et al., 2008). Based on eight on-site measurements in China, Chen et al. (2013) found that average Hg^{2+} proportion

ACPD
15, 32889–32929, 2015

in the flue gas from the outlet of GFC + SD-FGD + ACI + FF is 96 %, while that from the outlet of CFBC + SD-FGD + ACI + FF is 64 %.

Biomass burning has attracted increasing global attention. Biomass can be divided into fuel wood, crop residues and biomass pellets. Usually, there is no APCD for biomass burning. Wei (2012) found that Hg^0 in flue gas from biomass burning is 70–90 % of total mercury while that of Hg^{2+} ranges from 5 to 9 %. Hg_p proportion differs a lot between different biomass fuel types: 12, 25 and 1 % for fuel wood, crop residues and biomass pellets, respectively. Hu et al. (2012) differentiated the emission factors for biomass burning and cooking/heating in rural areas to be 0.035 and 0.515 g Hg t^{-1} biomass burned, respectively. W. Zhang et al. (2013) tested 25 types of fuel wood, 8 types of crop residues and 2 types of biomass pellets, and found that the mercury release rate during biomass burning is 78–99 %. The mercury speciation profile (ratio of Hg^0, Hg^{2+} and Hg_p to total Hg) for fuel wood was 76, 6 and 18 %, and that for crop residue was similar (73, 4 and 23 %). However, the speciation profile for biomass pellets is quite different. Due to the more complete combustion, Hg^0 accounts for as high as 97 % in the flue gas from of biomass pellets combustion. W. Zhang et al. (2013) calculated mercury emission from biomass burning in China and gave the shares of Hg^0, Hg^{2+} and Hg_p at 74, 5 and 21 %, respectively.

7 Comparison of mercury speciation profiles in different countries and regions

Table 4 summarizes the sectoral mercury speciation profiles in different countries and regions (Pacyna et al., 2006; AMAP/UNEP, 2008; Chrystall and Rumsby, 2009; Kim et al., 2010a; Lin et al., 2012; Nelson et al., 2012; Zhang et al., 2015). China and South Korea have compiled extensive speciation profiles based on observational data collected at anthropogenic mercury emission sources. The inventories for Europe and New Zealand used same speciation data as the global inventory for coal combustion, which is close to the results of South Korea. China has different speciation data for coal combustion, where the proportion of Hg^0 is higher than that reported in other

ACPD
15, 32889–32929, 2015

countries. This is probably because the high WFGD installation rate in China results in higher Hg^{2+} removal efficiency. Mercury speciation for coal-fired power plants, industrial and residential coal combustion are also different. Residential coal combustion has the lowest Hg^{2+} proportion while industrial coal combustion has the highest. This is mainly influenced by the boiler type and the APCDs applied. Residential stove has a short temperature-decrease time, which reduces formation of Hg^{2+}. The APCDs applied for industrial coal combustion have a lower Hg^{2+} removal efficiency than those applied for coal-fired power plants.

Global inventory applied similar speciation profiles for most other industrial sectors, i.e., 80 % Hg^0, 15 % Hg^{2+} and 5 % Hg_p. The inventories estimated in China and South Korea provide speciation profiles for different sectors. The sectors of non-ferrous metal smelting (including zinc, lead and copper), cement production and iron and steel production in China have higher Hg^{2+} proportions than most of the other countries, which is caused by catalytic mercury oxidation in acid plants in non-ferrous metal smelters and the intensive heterogeneous mercury oxidation in cement plants and steel plants. The higher Hg^{2+} proportions imply that mercury emission from East Asia could have more local environmental impacts than previously expected. Our recent study (L. Wang et al., 2014) indicated that anthropogenic sources in China contribute 35–50 % of the total mercury concentration and 50–70 % of the total deposition in polluted regions in China.

8 Conclusions

Hg^0 is the predominant mercury species in exiting flue gases from coal-fired power plants due to the high Hg_p removal efficiency of ESP or FF and the high Hg^{2+} removal efficiency of WS or WFGD. The enhancement of Hg^0 oxidation in SCR and by halogen injection is effective for mercury emission control in coal-fired power plants. On the contrary, Hg^{2+} tends to be the principal form in the flue gases emitted from non-ferrous metal smelters, cement plants and iron and steel plants. Catalytic metallic

ACPD
15, 32889–32929, 2015

components and high PM concentrations in flue gases are the two primary causes. Flue gas purification systems and processes in acid plants for non-ferrous metal smelting contribute to the largest amount of mercury removal in non-ferrous metal smelters. Specific mercury reclaiming tower in non-ferrous metal smelters preferentially releases Hg^0 to downstream flue gases. The key to mercury emission controls in cement plants is to break the mercury cycling processes during the dust recirculation for the kiln, raw mill and coal mill. Since Hg^{2+} dominates the mercury speciation of emissions from cement plants and iron and steel plants, WS or WFGD could be implemented for mercury abatement.

Mercury speciation profiles for key sources reported in recent studies are significantly different from those obtained in early studies. This is partially because the APCDs used in these sources have advanced in the past two decades. Another reason lies in the lack of on-site measurements in early emission estimates where certain speciation profiles were assumed. Adoption of different APCDs and use of different fuels or raw materials cause distinct differences found in mercury speciation profiles applied in different countries or regions. Large proportion of Hg^{2+} from non-ferrous metal smelters, cement plants and iron and steel plants calls for local attention. There are still large uncertainties in the speciation profiles at key sources, such as iron and steel plants, waste incineration and biomass burning. More on-site measurements for these sources should be carried out to complete the database of mercury emission speciation. Research is also needed in understanding the mechanism of mercury oxidation and adsorption in flue gases with different compositions, which benefits mercury emission controls. Accurate speciation profiles improve the performance of regional transport and dispersion models to better assess the environmental impacts of mercury emissions into the atmosphere.

Acknowledgements. This work was funded by Major State Basic Research Development Program of China (973 Program) (No. 2013CB430001 and No. 2013CB430003) and National Natural Science Foundation of China (No. 21307070).

ACPD
15, 32889–32929, 2015

References

Acunña-Caro, C., Brechtel, K., Scheffknecht, G., and Braß, M.: The effect of chlorine and oxygen concentrations on the removal of mercury at an FGD-batch reactor, Fuel, 88, 2489–2494, 2009.

Arctic Monitoring and Assessment Programme (AMAP) and United Nations Environment Programme (UNEP): Technical Background Report to the Global Atmospheric Mercury Assessment, Geneva, Switzerland, 2008.

Bhardwaj, R., Chen, X. H., and Vidic, R. D.: Impact of fly ash composition on mercury speciation in simulated flue gas, J. Air Waste Manage., 59, 1331–1338, 2009.

Bock, J., Hocquel, M. J. T., Unterberger, S., and Hein, K. R. G.: Mercury oxidation across SCR catalysts of flue gas with varying HCl concentrations, US Environmental Protection Agency-Department of Energy-EPRI Combined Power Plant Air Pollutant Control Symposium, 19–20 May 2003, Washington, DC, USA, 2003.

Carpi, A.: Mercury from combustion sources: a review of the chemical species emitted and their transport in the atmosphere, Water Air Soil Poll., 98, 241–254, 1997.

Chang, J. S. and Ghorishi, S. B.: Simulation and evaluation of elemental mercury concentration increase in flue gas across a wet scrubber, Environ. Sci. Technol., 37, 5763–5766, 2003.

Chen, J., Yuan, D., Li, Q., Zheng, J., Zhu, Y., Hua, X., He, S., and Zhou, J.: Effect of flue-gas cleaning devices on mercury emission from coal-fired boiler, P. CSEE, 28, 72–76, 2008.

Chen, L., Duan, Y., Zhuo, Y., Yang, L., Zhang, L., Yang, X., Yao, Q., Jiang, Y., and Xu, X.: Mercury transformation across particulate control devices in six power plants of China: the co-effect of chlorine and ash composition, Fuel, 86, 603–610, 2007.

Chen, L. G., Liu, M., Fan, R. F., Ma, S. X., Xu, Z. C., Ren, M. Z., and He, Q. S.: Mercury speciation and emission from municipal solid waste incinerators in the Pearl River Delta, South China, Sci. Total Environ., 447, 396–402, 2013.

Chrystall, L. and Rumsby, A.: Mercury Inventory for New Zealand 2008, available at: http://www.mfe.govt.nz/sites/default/files/mercury-inventory-new-zealand-2008.pdf (last access: 23 November 2015), 2009.

Duan, Y., Cao, Y., Kellie, S., Liu, K., Riley, J. T., and Pan, W.: In-situ measurement and distribution of flue gas mercury for a utility PC boiler system, J. Southeast Univ., 21, 53–57, 2005.

ACPD
15, 32889–32929, 2015

Dunham, G. E., Dewall, R. A., and Senior, C. L.: Fixed-bed studies of the interactions between mercury and coal combustion fly ash, Fuel Process. Technol., 82, 197–213, 2003.
Eriksen, D. Ø., Tokheim, L. A., Eriksen, T. A., Meyer, J., and Qvenild, C.: Assessment of mercury emission at Norcem's cement kiln by the use of ^{203}Hg-tracer, J. Radioanal. Nucl. Ch., 273, 739–745, 2007.
Fu, X. W., Feng, X. B., Sommar, J., and Wang, S. F.: A review of studies on atmospheric mercury in China, Sci. Total Environ., 421–422, 73–81, 2012.
Fukuda, N., Takaoka, M., Doumoto, S., Oshita, K., Morisawa, S., and Mizuno, T.: Mercury emission and behavior in primary ferrous metal production, Atmos. Environ., 45, 3685–3691, 2011.
Galbreath, K. C. and Zygarlicke, C. J.: Mercury transformations in coal combustion flue gas, Fuel Process. Technol., 65–66, 289–310, 2000.
Galbreath, K. C., Zygarlicke, C. J., Tibbetts, J. E., Schulz, R. L., and Dunham, G. E.: Effects of NO_x, α-Fe_2O_3, γ-Fe_2O_3, and HCl on mercury transformations in a 7-kW coal combustion system, Fuel Process. Technol., 86, 429–448, 2005.
Goodarzi, F.: Speciation and mass-balance of mercury from pulverized coal fired power plants burning western Canadian subbituminous coals, J. Environ. Monitor., 6, 792–798, 2004.
Guo, X., Zheng, C., Jia, X., Lin, Z., and Liu, Y.: Study on mercury speciation in pulverized coal-fired flue gas, P. CSEE, 24, 185–188, 2004.
Gustin, M. S., Lindberg, S. E., and Weisberg, P. J.: An update on the natural sources and sinks of atmospheric mercury, Appl. Geochem., 23, 482–493, 2008.
Hoenig, V. H. R. and Zunzer, U.: Guidance document on BAT-BEP for mercury in the cement industry, Technical report of the European Cement Research Academy (ECRA) on behalf of WBCSD Cement Sustainability Initiative, TR-ECRA 0049a/2013/M, available at: http://www.unep.org/chemicalsandwaste/Portals/9/CSI_Hg-Report_final_10_06_13.pdf (last access: 23 November 2015), 2013.
Hu, D., Zhang, W., Chen, L., Chen, C., Ou, L. B., Tong, Y. D., Wei, W., Long, W. J., and Wang, X. J.: Mercury emissions from waste combustion in China from 2004 to 2010, Atmos. Environ., 62, 359–366, 2012.
Hylander, L. D. and Herbert, R. B.: Global emission and production of mercury during the pyrometallurgical extraction of nonferrous sulfide ores, Environ. Sci. Technol., 42, 5971–5977, 2008.

ACPD
15, 32889–32929, 2015

Information Collection Request (ICR): Results from onsite measurements in USA, Washington, DC, USA, 2010.
Ito, S., Yokoyama, T., and Asakura, K.: Emissions of mercury and other trace elements from coal-fired power plants in Japan, Sci. Total Environ., 368, 397–402, 2006.
Kellie, S., Duan, Y., Cao, Y., Chu, P., Mehta, A., Carty, R., Liu, K., Pan, W., and Riley, J. T.: Mercury emissions from a 100-MW wall-fired boiler as measured by semicontinuous mercury monitor and Ontario Hydro Method, Fuel Process. Technol., 85, 487–499, 2004.
Kilgroe, J., Sedman, C., Srivastava, R., Ryan, J., Lee, C., and Thorneloe, S.: Control of mercury emissions from coal-fired electric utility boilers: interim report including errata dated 3-21-02, EPA-600/R-01-109, EPA Office of Research and Development, National Risk Management and Research Laboratory: Research Triangle Park, NC, USA, 2002.
Kim, J. H., Park, J. M., Lee, S. B., Pudasainee, D., and Seo, Y. C.: Anthropogenic mercury emission inventory with emission factors and total emission in Korea, Atmos. Environ., 44, 2714–2721, 2010a.
Kim, J. H., Pudasainee, D., Yoon, Y. S., Son, S. U., and Seo, Y. C.: Studies on speciation changes and mass distribution of mercury in a bituminous coal-fired power plant by combining field data and chemical equilibrium calculation, Ind. Eng. Chem. Res., 49, 5197–5203, 2010b.
Kim, J. H., Pudasainee, D., Jung, S. J., and Seo, Y. C.: Speciation and mass balance of mercury in non-ferrous metals manufacturing facilities, The 10th International Conference on Mercury as a Global Pollutant, 24–29 July 2011, Halifax, Nova Scotia, Canada, 2011.
Krishnakumar, B. and Helble, J. J.: Understanding mercury transformations in coal-fired power plants: evaluation of homogeneous Hg oxidation mechanisms, Environ. Sci. Technol., 41, 7870–7875, 2007.
Lee, C. W., Srivastava, R. K., Ghorishi, S. B., Hastings, T. W., and Stevens, F. M.: Study of speciation of mercury under simulated SCR NO_x emission control conditions, US Environmental Protection Agency-Department of Energy-EPRI Combined Power Plant Air Pollutant Control Symposium, 19–20 May 2003, Washington, DC, USA, 2003.
Lee, S. J., Seo, Y. C., Jang, H. N., Park, K. S., Baek, J. I., An, H. S., and Song, K. C.: Speciation and mass distribution of mercury in a bituminous coal-fired power plant, Atmos. Environ., 40, 2215–2224, 2006.

ACPD
15, 32889–32929, 2015

Li, G. H., Feng, X. B., Li, Z. G., Qiu, G. L., Shang, L. H., Liang, P., Wang, D. Y., and Yang, Y. K.: Mercury emission to atmosphere from primary Zn production in China, Sci. Total Environ., 408, 4607–4612, 2010.
Lin, C. J., Shetty, S. K., Pan, L., Pongprueksa, P., Jang, C., and Chu, H. W.: Source attribution for mercury deposition in the contiguous United States: regional difference and seasonal variation, J. Air Waste Manage., 62, 52–63, 2012.
Lindberg, S. E., Bullock, R., Ebinghaus, R., Engstrom, D., Feng, X. B., Fitzgerald, W., Pirrone, N., Prestbo, E., and Seigneur, C.: A synthesis of progress and uncertainties in attributing the sources of mercury in deposition, Ambio, 36, 19–32, 2007.
Linero, A. A.: Synopsis of mercury controls at Florida cement plants, The 104th Annual Conference and Exhibition of the Air and Waste Management Association, 21–24 June 2011, Orlando, Florida, USA, 2011.
Liu, J., Qu, W., Yuan, J., Wang, S., Qiu, J., and Zheng, C.: Theoretical studies of properties and reactions involving mercury species present in combustion flue gases, Energ. Fuel., 24, 117–122, 2010.
Liu, X. L., Wang, S. X., Zhang, L., Wu, Y., Duan, L., and Hao, J. M.: Speciation of mercury in FGD gypsum and mercury emission during the wallboard production in China, Fuel, 111, 621–627, 2013.
López-Antón, M. A., Perry, R., Abad-Valle, P., Díaz-Somoano, M., Martínez-Tarazona, M. R., and Maroto-Valer, M. M.: Speciation of mercury in fly ashes by temperature programmed decomposition, Fuel Process. Technol., 92, 707–711, 2011.
Lu, Y., Rostam-Abadi, M., Chang, R., Richardson, C., and Paradis, J.: Characteristics of fly ashes from full-scale coal-fired power plants and their relationship to mercury adsorption, Energ. Fuel., 21, 2112–2120, 2007.
Machalek, T., Ramavajjala, M., Richardson, M., and Richardson, C.: Pilot evaluation of flue gas mercury reactions across an SCR unit, US Environmental Protection Agency-Department of Energy-EPRI Combined Power Plant Air Pollutant Control Symposium, 19–20 May 2003, Washington, DC, USA, 2003.
Meij, R. and Winkel, H. T.: Mercury emissions from coal-fired power stations: the current state of the art in the Netherlands, Sci. Total Environ., 368, 393–396, 2006.
Mlakar, T. L., Horvat, M., Vuk, T., Stergaršek, A., Kotnik, J., Tratnik, J., and Fajon, V.: Mercury species, mass flows and processes in a cement plant, Fuel, 89, 1936–1945, 2010.

ACPD
15, 32889–32929, 2015

Nelson, P. F., Morrison, A. L., Malfroy, H. J., Cope, M., Lee, S., Hibberd, M. L., Meyer, C. P., and McGregor, J.: Atmospheric mercury emissions in Australia from anthropogenic, natural and recycled sources, Atmos. Environ., 62, 291–302, 2012.

Niksa, S. and Fujiwara, N.: A predictive mechanism for mercury oxidation on selective catalytic reduction catalysts under coal-derived flue gas, J. Air Waste Manage., 55, 1866–1875, 2005.

Niksa, S., Helble, J. J., and Fujiwara, N.: Kinetic modeling of homogeneous mercury oxidation: the importance of NO and H_2O in predicting oxidation in coal-derived systems, Environ. Sci. Technol., 35, 3701–3706, 2001.

Norton, G. A., Yang, H., Brown, R. C., Laudal, D. L., Dunham, D. E., and Erjavec, J.: Heterogeneous oxidation of mercury in simulated post combustion conditions, Fuel, 82, 107–116, 2003.

Ochoa-Gonzaìlez, R., Díaz-Somoano, M., Loìpez-Antoìn, M. A., and Martínez-Tarazona, M. R.: Effect of adding aluminum salts to wet FGD systems upon the stabilization of mercury, Fuel, 96, 568–571, 2012.

Ochoa-Gonzaìlez, R., Díaz-Somoano, M., and Martínez-Tarazona, M. R.: Influence of limestone characteristics on mercury re-emission in WFGD systems, Environ. Sci. Technol., 47, 2974–2981, 2013.

Omine, N., Romero, C. E., Kikkawa, H., Wu, S., and Eswaran, S.: Study of elemental mercury re-emission in a simulated wet scrubber, Fuel, 91, 93–101, 2012.

Pacyna, E. G. and Pacyna, J. M.: Global emission of mercury from anthropogenic sources in 1995, Water Air Soil Poll., 137, 149–165, 2002.

Pacyna, E. G., Pacyna, J. M., Steenhuisen, F., and Wilson, S.: Global anthropogenic mercury emission inventory for 2000, Atmos. Environ., 22, 4048–4063, 2006.

Pacyna, J. M. and Münch, J.: Anthropogenic mercury emission in Europe, Water Air Soil Poll., 56, 51–61, 1991.

Paone, P.: Mercury controls for the cement industry, Cement Industry Technical Conference, 28 March–1 April 2010, Colorado Springs, Colorado, USA, 2010.

Park, K. S., Seo, Y. C., Lee, S. J., and Lee, J. H.: Emission and speciation of mercury from various combustion sources, Powder Technol., 180, 151–156, 2008.

Rallo, M., López-Antón, M. A., Perry, R., and Maroto-Valer, M. M.: Mercury speciation in gypsums produced from flue gas desulfurization by temperature programmed decomposition, Fuel, 89, 2157–2159, 2010.

ACPD
15, 32889–32929, 2015

Rutter, A. P. and Schauer, J. J.: The effect of temperature on the gas – particle partitioning of reactive mercury in atmospheric aerosols, Atmos. Environ., 41, 8647–8657, 2007.
Schreiber, R. J., Kellet, C. D., Joshi, N., and Skokie, I. L.: Inherent mercury controls within the Portland cement kiln system, Portland Cement Association, Skokie, IL, USA, 2005.
Schroeder, W. H. and Munthe, J.: Atmospheric mercury – an overview, Atmos. Environ., 32, 809–822, 1998.
Schuetze, J., Kunth, D., Weissbach, S., and Koeser, H.: Mercury vapor pressure of flue gas desulfurization scrubber suspensions: effects of the pH level, gypsum and iron, Environ. Sci. Technol., 46, 3008–3013, 2012.
Senior, C. and Johnson, S.: Impact of carbon-in-ash on mercury removal across particulate control devices in coal-fired power plants, Energ. Fuel., 19, 859–863, 2005.
Senior, C., Montgomery, C. J., and Sarofim, A.: Transient model for behavior of mercury in Portland cement kilns, Ind. Eng. Chem. Res., 49, 1436–1443, 2010.
Senior, C. L., Sarofim, A. F., Zeng, T., Helble, J. J., and Mamani-Paco, R.: Gas-phase transformations of mercury in coal-fired power plants, Fuel Process. Technol., 63, 197–213, 2000.
Shah, P., Strezov, V., Prince, K., and Nelson, P. F.: Speciation of As, Cr, Se and Hg under coal fired power station conditions, Fuel, 87, 1859–1869, 2008.
Shah, P., Strezov, V., and Nelson, P.: Speciation of mercury in coal-fired power station flue gas, Energ. Fuel., 24, 205–212, 2010.
Sikkema, J. K., Alleman, J. E., Ong, S. K., and Wheelock, T. D.: Mercury regulation, fate, transport, transformation, and abatement within cement manufacturing facilities: review, Sci. Total Environ., 409, 4167–4178, 2011.
Song, J. X.: Study on atmospheric mercury emissions from typical zinc smelting process, M.S. thesis, Tsinghua University, Beijing, 2010.
Sterling, R. O., Qiu, J. R., and Helble, J. J.: Experimental study of mercury homogeneous reaction chemistry under post-flame conditions, The 227th Spring ACS National Meeting, 28 March–1 April 2004, Anaheim, CA, USA, 2004.
Streets, D. G., Hao, J. M., Wu, Y., Jiang, J. K., Chan, M., Tian, H. Z., and Feng, X. B.: Anthropogenic mercury emissions in China, Atmos. Environ., 39, 7789–7806, 2005.
Takahashi, F., Shimaoka, T., and Kida, A.: Atmospheric mercury emissions from waste combustions measured by continuous monitoring devices, J. Air Waste Manage., 62, 686–695, 2012.

ACPD
15, 32889–32929, 2015

Tang, S.: The mercury species and emissions from coal combustion flue gas and landfill gas in Guiyang, PhD thesis, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, China, 2004.
Tang, S. L., Feng, X. B., Qiu, J. R., Yin, G. X., and Yang, Z. C.: Mercury speciation and emissions from coal combustion in Guiyang, southwest China, Environ. Res., 105, 175–182, 2007.
United Nations Economic Commission for Europe (UNECE): Guidance document on best available techniques for controlling emissions of heavy metals and their compounds from the source categories listed in annex II to the Protocol on Heavy Metals, Geneva, Switzerland, 2013.
United Nations Environment Programme (UNEP): Global Mercury Assessment 2013: Sources, Emissions, Releases and Environmental Transport, Geneva, Switzerland, 2013.
Verein deutscher Zementwerke e.V. (VDZ): Activity Report 1999–2001, Düsseldorf, Germany, 2002.
Walcek, C., de Santis, S., and Gentile, T.: Preparation of mercury emissions inventory for eastern North America, Environ. Pollut., 123, 375–381, 2003.
Wang, F. Y., Wang, S. X., Zhang, L., Yang, H., Wu, Q. R., and Hao, J. M.: Mercury enrichment and its effects on atmospheric emissions in cement plants of China, Atmos. Environ., 92, 421–428, 2014.
Wang, F. Y., Wang, S. X., Zhang, L., Yang, H., Gao, W., Wu, Q. R., and Hao, J. M.: Mercury mass flow in iron and steel production process and its implications for mercury emission control, J. Environ. Sci., in press, 2015.
Wang, L., Wang, S. X., Zhang, L., Wang, Y. X., Zhang, Y. X., Nielsen, C., McElroy, M. B., and Hao, J. M.: Source apportionment of atmospheric mercury pollution in China using the GEOS-Chem model, Environ. Pollut., 190, 166–175, 2014.
Wang, Q. W.: New technology for treatment of mercury-containing acidic wastewater from gas washing process in lead and zinc smelting by biologics, PhD thesis, Central South University, Changsha, 2011.
Wang, S. X., Zhang, L., Li, G. H., Wu, Y., Hao, J. M., Pirrone, N., Sprovieri, F., and Ancora, M. P.: Mercury emission and speciation of coal-fired power plants in China, Atmos. Chem. Phys., 10, 1183–1192, doi:10.5194/acp-10-1183-2010, 2010a.
Wang, S. X., Zhang, L., Hao, J. M., Chen, J. B., Li, Z. G., Yan, N. Q., and Qu, Z.: Interim Report for Emission Inventory and Isotopic Characteristics of Mercury from Anthropogenic Sources in China, Interim Workshop for 973 Project "The Pollution Characteristics, Environmental

ACPD
15, 32889–32929, 2015

Processes and Emission Control Principle of Mercury in China", 10 August 2014, Guiyang, China, 2014.
Wang, S. X., Song, J. X., Li, G. H., Wu, Y., Zhang, L., Wan, Q., Streets, D. G., and Chin, C. K.: Estimating mercury emissions from a zinc smelter in relation to China's mercury control policies, Environ. Pollut., 158, 3347–3353, 2010b.
Wang, Y., Duan, Y., Yang, L., and Jiang, Y.: An analysis of the factors exercising an influence on the morphological transformation of mercury in the flue gas of a 600 MW coal-fired power plant, J. Eng. Therm. Energ. Power, 23, 399–403, 2008.
Wang, Y., Duan, Y., Yang, L., Zhao, C., Shen, X., Zhang, M., Zhuo, Y., and Chen, C.: Experimental study on mercury transformation and removal in coal-fired boiler flue gases, Fuel Process. Technol., 90, 643–651, 2009.
Wei, W.: Emission of mercury from biomass fuels burning in rural China, M.S. thesis, Peking University, Beijing, China, 2012.
Widmer, N. C., West, J., and Cole, J. A.: Thermochemical study of mercury oxidation in utility boiler flue gases, The 93rd Air and Waste Management Association Annual Meeting, 18–22 June 2000, Salt Lake City, UT, USA, 2000.
Wilcox, J., Robles, J., Marsden, D. C. J., and Blowers, P.: Theoretically predicted rate constants for mercury oxidation by hydrogen chloride in coal combustion flue gases, Environ. Sci. Technol., 37, 4199–4204, 2003.
Winberg, S., Winthum, J., Tseng, S., and Locke, J.: Evaluation of mercury emissions from coal-fired facilities with SCR-FGD systems, DOE/NETL Mercury Control Technology R&D Program Review, Pittsburgh, PA, USA, 2004.
Wo, J., Zhang, M., Cheng, X., Zhong, X., Xu, J., and Xu, X.: Hg^{2+} reduction and re-emission from simulated wet flue gas desulfurization liquors, J. Hazard. Mater., 172, 1106–1110, 2009.
Won, J. H. and Lee, T. G.: Estimation of total annual mercury emissions from cement manufacturing facilities in Korea, Atmos. Environ., 62, 265–271, 2012.
Wu, Q. R., Wang, S. X., Zhang, L., Song, J. X., Yang, H., and Meng, Y.: Update of mercury emissions from China's primary zinc, lead and copper smelters, 2000–2010, Atmos. Chem. Phys., 12, 11153–11163, doi:10.5194/acp-12-11153-2012, 2012.
Wu, Q. R., Wang, S. X., Hui, M. L., Wang, F. Y., Zhang, L., Duan, L., and Luo, Y.: New insight into atmospheric mercury emissions from zinc smelters using mass flow analysis, Environ. Sci. Technol., 49, 3532–3539, 2015.

ACPD
15, 32889–32929, 2015

Yang, X., Duan, Y., Jiang, Y., and Yang, L.: Research on mercury form distribution in flue gas and fly ash of coal-fired boiler, Coal Sci. Technol., 35, 55–58, 2007.
Yokoyama, T., Asakura, K., Matsuda, H., Ito, S., and Noda, N.: Mercury emissions from a coal-fired power plant in Japan, Sci. Total Environ., 259, 97–103, 2000.
Zhang, H., He, P. J., and Shao, L. M.: Fate of heavy metals during municipal solid waste incineration in Shanghai, J. Hazard. Mater., 156, 365–373, 2008.
Zhang, L.: Emission characteristics and synergistic control strategies of atmospheric mercury from coal combustion in China, PhD thesis, Tsinghua University, Beijing, China, 2012.
Zhang, L., Wang, S. X., Meng, Y., and Hao, J. M.: Influence of mercury and chlorine content of coal on mercury emissions from coal-fired power plants in China, Environ. Sci. Technol., 46, 6385–6392, 2012a.
Zhang, L., Wang, S. X., Wu, Q. R., Meng, Y., Yang, H., Wang, F. Y., and Hao, J. M.: Were mercury emission factors for Chinese non-ferrous metal smelters overestimated? Evidence from onsite measurements in six smelters, Environ. Pollut., 171, 109–117, 2012b.
Zhang, L., Daukoru, M., Torkamani, S., Wang, S. X., Hao, J. M., and Biswas, P.: Measurements of mercury speciation and fine particle size distribution on combustion of China coal seams, Fuel, 104, 732–738, 2013a.
Zhang, L., Wang, S. X., Wang, F. Y., Yang, H., Wu, Q. R., and Hao, J. M.: Mercury transformation and removal in three coal-fired power plants with selective catalytic reduction systems, The 11th International Conference on Mercury as a Global Pollutant, 28 July–2 August 2013, Edinburgh, Scotland, UK, 2013b.
Zhang, L., Wang, S. X., Wang, L., Wu, Y., Duan, L., Wu, Q. R., Wang, F. Y., Yang, M., Yang, H., Hao, J. M., and Liu, X.: Updated emission inventories for speciated atmospheric mercury from anthropogenic sources in China, Environ. Sci. Technol., 49, 3185–3194, 2015.
Zhang, W., Wei, W., Hu, D., Zhu, Y., and Wang, X. J.: Emission of speciated mercury from residential biomass fuel combustion in China, Energ. Fuel., 27, 6792–6800, 2013.
Zheng, Y., Jensen, A. D., Windelin, C., and Jensen, F.: Review of technologies for mercury removal from flue gas from cement production processes, Prog. Energ. Combust., 38, 599–629, 2012.
Zhou, J., Wang, G., Luo, Z., and Cen, K.: An experimental study of mercury emissions from a 600 MW pulverized coal-fired boiler, J. Eng. Therm. Energ. Power, 21, 569–572, 2006.
Zhou, J., Zhang, L., Luo, Z., and Hu, C.: Study on mercury emission and its control for boiler of 300 MW unit, Therm. Power Gener., 37, 22–27, 2008.

ACPD
15, 32889–32929, 2015

Table 1. Speciation profile of mercury emissions from coal combustion (%).

No.	Boiler type	APCD combination	Hg^0	Hg^{2+}	Hg_p	No. of tests
1	PC/SF	None	56 (8–94)	34 (5–82)	10 (1–28)	13
2	SF	WS	65 (39–87)	33 (10–60)	2.0 (0.2–4.5)	6
3	PC	ESP	58 (16–95)	41 (5–84)	1.3 (0.1–10)	31
4	PC	ESP + WFGD	84 (74–96)	16 (4–25)	0.6 (0.1–1.9)	7
5	PC	SCR + ESP + WFGD	74 (16–96)	26 (4–84)	0.2 (0.1–0.4)	6
6	PC	FF	50 (25–63)	49 (36–75)	0.5 (0.1–1.0)	3
7	PC	FF + WFGD	78	21	0.9	1
8	CFB	ESP	72	27	0.6	1

Notes: PC boiler – pulverized-coal boiler; SF boiler – stoker-fired boiler; CFB boiler – circulating fluidized bed boiler; WS – wet scrubber; ESP – electrostatic precipitator; FF – fabric filter; WFGD – wet flue gas desulfurization; SCR – selective catalytic reduction.

ACPD
15, 32889–32929, 2015

Table 2. Speciation profiles of mercury emissions from non-ferrous metal smelters (%).

Metal type	APCD combinations	Hg^0	Hg^{2+}	Hg_p	Reference
Non-ferrous metal	N.S.	80	15	5	Streets et al. (2005) Pacyna et al. (2006) Wu et al. (2006)
Zinc	DC + PS + MRT + AP_d	71	28	1	Wu et al. (2015)
Zinc	DC + PS + AP_d	55	44	1	Zhang et al. (2012b) Wu et al. (2015)
Lead	DC + PS + AP_s	40	60	0	Zhang et al. (2012b)
	DC + PS + AP_d	39	61	0	Zhang et al. (2012b)
Copper	DC + PS + AP_d	50	50	0	Zhang et al. (2012b)

Notes: N.S. – not specific; DC –dust collector; PS – purification system; MRT – mercury reclaiming tower; AP_d – acid plant with double-conversion-double-absorption processes; AP_s – acid plant with single-conversion-single-absorption processes.

ACPD
15, 32889–32929, 2015

Table 3. Proportions of emitted mercury species from cement clinker production (%).

Production processes	Hg^0	Hg^{2+}	Hg_p	References
N.S.	80	15	5	Streets et al. (2005)
N.S.	85	15	0	Won and Lee (2012)
Precalciner process (raw mill off)	16.0	75.7	8.3	Mlakar et al. (2010)
Precalciner process (raw mill on)	43.1	45.5	11.4	Mlakar et al. (2010)
Precalciner process	9.2	90.8	0.0	F. Y. Wang et al. (2014)
Precalciner process	38.7	61.3	0.0	F. Y. Wang et al. (2014)
Precalciner process	23.4	75.1	1.6	F. Y. Wang et al. (2014)

Note: N.S. – not specific.

ACPD
15, 32889–32929, 2015

Table 4. Comparison of sectoral mercury speciation profiles for different countries and regions (%).

Countries or regions	Global			China			South Korea			Europe			USA			Australia			New Zealand		
Inventory year	2005			2010			2007			2000			2005			2006			2008		
Mercury emission source	Hg^0	Hg^{2+}	Hg_p	Hg^0	Hg^{2+}	Hg_p	Hg^0	Hg^{2+}	Hg_p	Hg^0	Hg^{2+}	Hg_p	Hg^0	Hg^{2+}	Hg_p	Hg^0	Hg^{2+}	Hg_p	Hg^0	Hg^{2+}	Hg_p
Coal-fired power plants	50	40	10	79	21	0	47	46	7	50	40	10	57	40	4	77	17	6	50	40	10
Industrial coal combustion	50	40	10	66	32	2				50	40	10							50	40	10
Residential coal combustion	50	40	10	82	17	1				50	40	10							50	40	10
Stationary oil combustion	50	50	0	50	40	10	23	10	68	50	50	0	61	28	12	77	17	6			
Mobile oil combustion	50	50	0	50	40	10	87	13	0	50	50	0	61	28	12	77	17	6			
Biomass fuel combustion	80	15	5	74	5	21															
Municipal solid waste incineration	20	60	20	96	0	4	36	61	3	25	58	17	61	28	12	77	17	6			
Cremation	80	15	5	96	0	4	65	12	23							80	10	10			
Zinc smelting	80	15	5	30	65	5	73	11	16	75	13	13	61	26	13	77	17	6	80	15	5
Lead smelting	80	15	5	57	38	5	38	8	54	75	13	13	61	26	13	77	17	6	80	15	5
Copper smelting	80	15	5	47	48	5	28	38	34	75	13	13	61	26	13	77	17	6	80	15	5
Large-scale gold production	80	15	5	80	15	5										77	17	6			
Artisanal and small-scale gold mining	100	0	0	80	15	5															
Mercury production	80	20	0	80	15	5															
Cement production	80	15	5	34	65	1	83	16	1	80	17	3				77	17	6	80	15	5
Iron and steel production	80	15	5	34	66	0	15	80	5	83	17	0	80	10	9	77	17	6	80	15	5
Chlor-alkali production	70	30	0	100	0	0				70	30	0				77	17	6			
References	AMAP/UNEP (2008) Pacyna et al. (2006)			Zhang et al. (2015)			Kim et al. (2010b)			Pacyna et al. (2006)			Lin et al. (2012)			Nelson et al. (2012)			Chrystall and Rumsby (2009)		

ACPD
15, 32889–32929, 2015

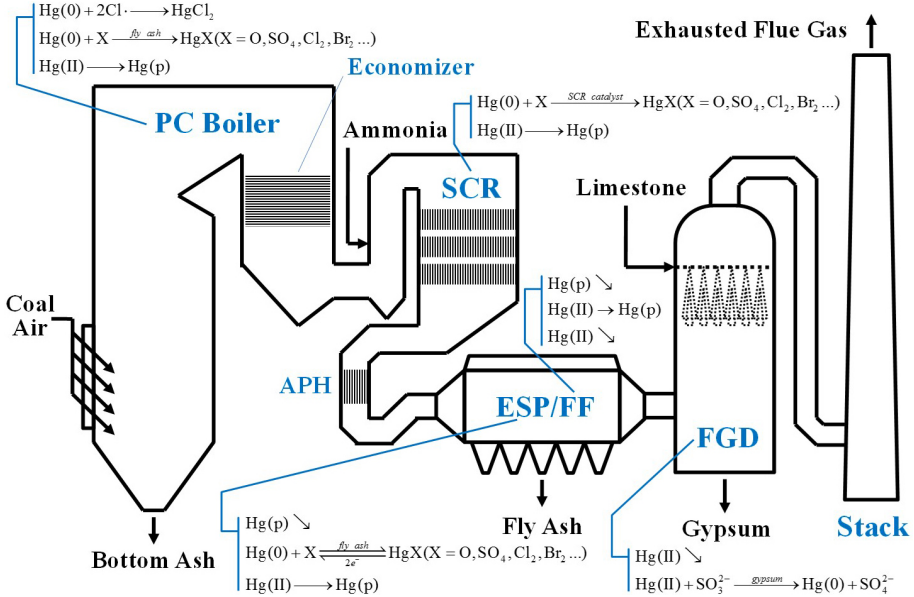

Figure 1. Mercury transformation and removal across APCDs in coal-fired power plants.

ACPD
15, 32889–32929, 2015

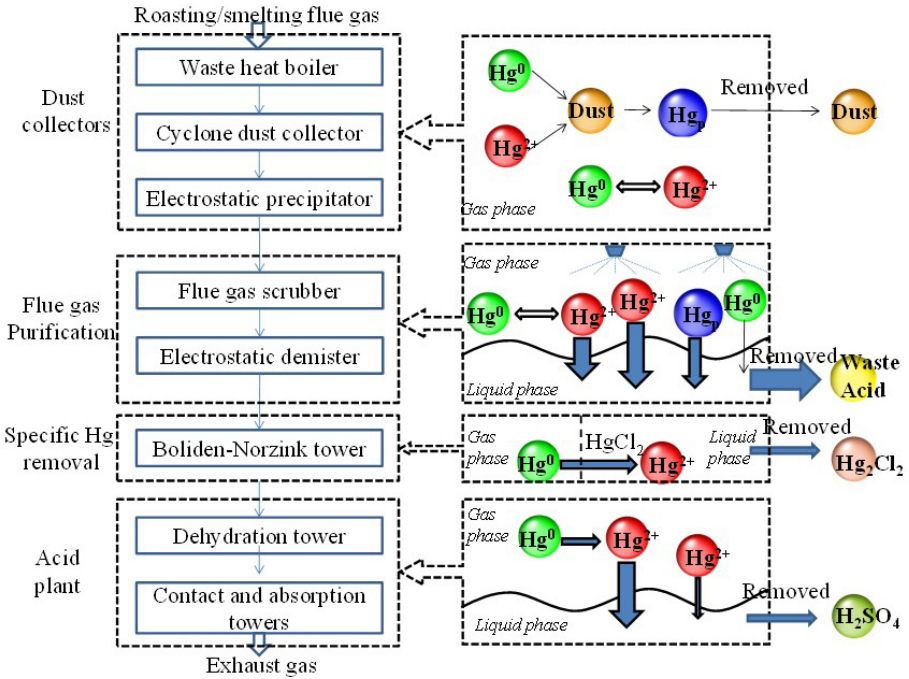

Figure 2. Mercury transformation and removal in roasting/smelting flue gas.

ACPD
15, 32889–32929, 2015

Mercury transformation and speciation in flue gases

L. Zhang et al.

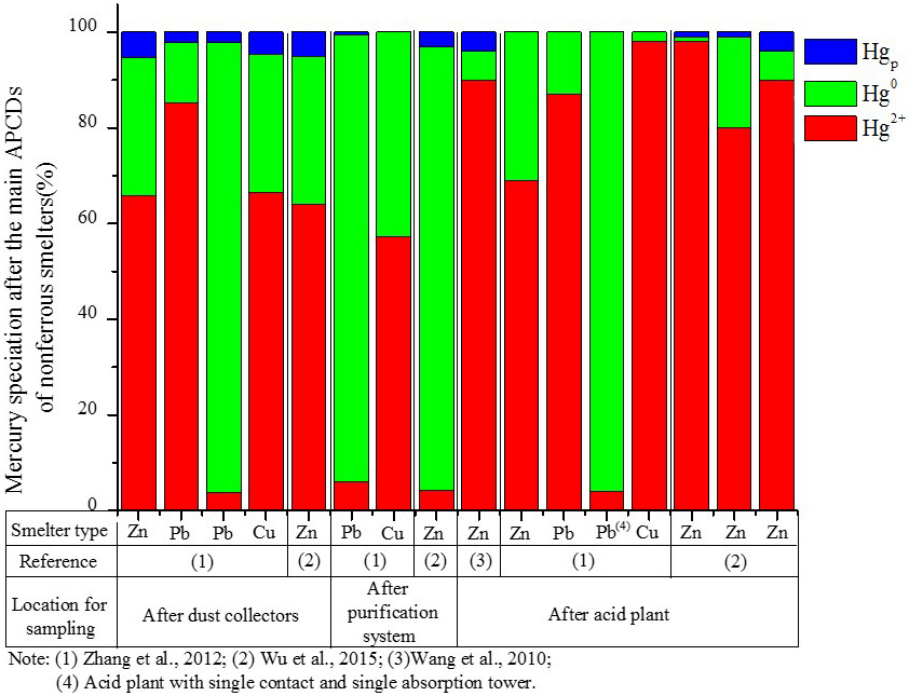

Figure 3. Mercury speciation after APCDs for non-ferrous metal smelters.

ACPD
15, 32889–32929, 2015

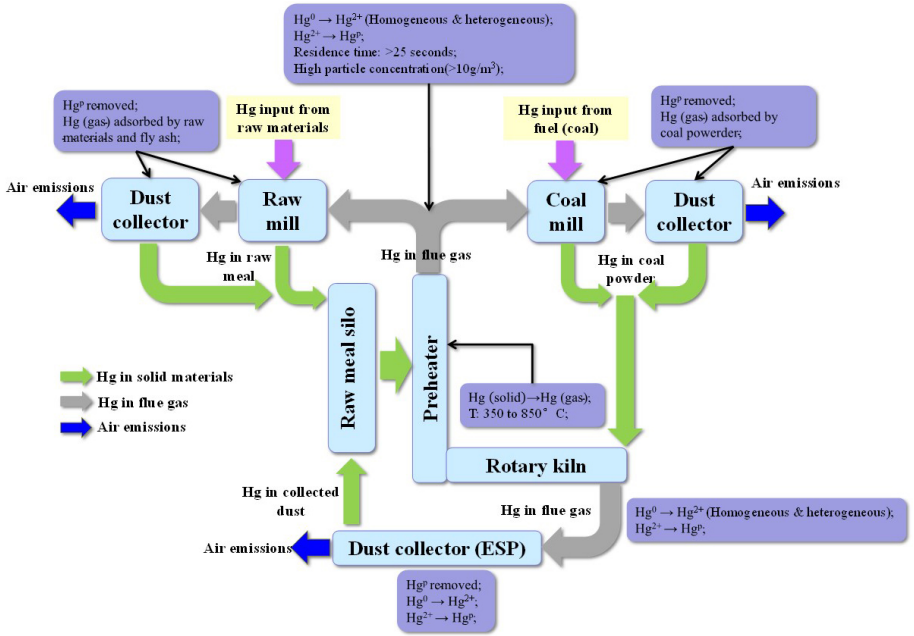

Figure 4. Mercury transformation in the precalciner cement production process.

ACPD
15, 32889–32929, 2015