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# Fate of mercury in flue gas desulfurization gypsum determined by Temperature Programmed Decomposition and Sequential Chemical Extraction

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## ABSTRACT

A considerable amount of Hg is retained in flue gas desulfurization (FGD) gypsum from Wet Flue Gas Desulfurization (WFGD) systems. For this reason, it is important to determine the species of Hg in FGD gypsum not only to understand the mechanism of Hg removal by WFGD systems but also to determine the final fate of Hg when FGD gypsum is disposed. In this study, Temperature Programmed Decomposition (TPD) and Sequential Chemical Extraction (SCE) were applied to FGD gypsum to identify the Hg species in it. The FGD gypsum samples were collected from seven coal-fired power plants in China, with Hg concentrations ranging from 0.19 to 3.27  $\mu\text{g/g}$ . A series of pure Hg compounds were used as reference materials in TPD experiments and the results revealed that the decomposition temperatures of different Hg compounds increase in the order of  $\text{Hg}_2\text{Cl}_2 < \text{HgCl}_2 < \text{black HgS} < \text{Hg}_2\text{SO}_4 < \text{red HgS} < \text{HgO} < \text{HgSO}_4$ . The Hg compounds existing in FGD gypsums identified by TPD included  $\text{HgCl}_2$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{Hg}_2\text{SO}_4$ , black HgS and red HgS, of which mercury sulfides were the primary compounds. The results of SCE indicated that Hg was mainly distributed in the strongly complexed phase. The low Hg content in FGD gypsum increases the ambiguity of assigning extraction fractions to certain Hg species by SCE. The fact that the primary compounds in FGD gypsum are HgS phases leads the leaching of Hg in the natural environment to be quite low, but a considerable amount of Hg may be released during the industrial heating process.

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## Introduction

The emission of mercury is becoming a major environmental issue due to its high toxicity and global atmospheric circulation. Recent studies have revealed that coal-fired power plants are one of the largest anthropogenic sources of mercury emission to the atmosphere (Pirrone et al., 1996; Pacyna et al., 2010). In 2007 the total emission of mercury from coal-fired power plants in China was 132 t (Tian et al., 2011). Generally, there are three

forms of mercury in flue gas from coal-fired power plants, vapor-phase elemental mercury ( $\text{Hg}^0$ ), oxidized mercury ( $\text{Hg}^{2+}$ ) and particulate-bound mercury ( $\text{Hg}^p$ ). The compounds of mercury in flue gas from coal combustion may be elemental mercury ( $\text{Hg}^0$ ), mercury chloride ( $\text{HgCl}_2$ ), mercurous chloride ( $\text{Hg}_2\text{Cl}_2$ ), mercury oxide ( $\text{HgO}$ ), mercury sulfate ( $\text{HgSO}_4$ ) and other inorganic species (Kilgroe and Senior, 2003).

Wet Flue Gas Desulfurization (WFGD) systems aimed to control  $\text{SO}_2$  can affect the mobility and emission of mercury in

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flue gas. Soluble oxidized mercury compounds such as  $\text{HgCl}_2$  can be effectively absorbed by a gypsum slurry.  $\text{Hg}^0$  escaping from particle removal devices upstream may also be partially captured by the WFGD system. Recent studies have revealed that the mercury reactions in gypsum slurry are very complicated and the absorbed  $\text{Hg}^{2+}$  in the slurry may be reduced and released as  $\text{Hg}^0$  (Tang et al., 2010; Ochoa-González et al., 2013; Wo et al., 2009). However, the fate of mercury retained in FGD gypsum after the dehydration process of gypsum slurry is not clear and needs more research. The FGD gypsum may be used for wallboard production, soil reclamation and landfill (Heebink and Hassett, 2005; Clark et al., 2001; Álvarez-Ayuso and Querol, 2007). The fate of mercury during the management of FGD gypsum in such scenarios is largely dependent on its own species. Considering that the mercury behavior in flue gas and the mechanisms of mercury removal in WFGD systems could also be highlighted by the identification of mercury species in FGD gypsum, it is imperative to determine the mercury speciation in FGD gypsum.

Sequential Chemical Extraction (SCE) has been widely employed to determine the speciation of mercury in sediments and soils, in which a series of reagents is applied to the same sample to distinguish the solubility of the mercury phases in different extractants (Issaro et al., 2009; Bacon and Davidson, 2008). The five-step SCE procedure for mercury speciation developed by Bloom et al. (2003) has been most widely adopted by researchers. It has been successfully used for the speciation of Hg in samples with Hg content more than 100  $\mu\text{g/g}$  (Bloom et al., 2003; Kim et al., 2003). SCE can provide some useful operational speciation information to assess the stability of mercury in the environment. However, re-adsorption and non-selectivity may make it ambiguous to assign the operational speciation to specific mercury compounds by SCE.

As an alternative method, the Temperature Programmed Decomposition (TPD) method has also been widely used to determine the species of mercury in different solid matrixes, such as contaminated soil, sediment, coal and fly ash (Biester and Scholz, 1996; Biester et al., 2000; Luo et al., 2011; Lopez-Anton et al., 2011). Previous studies have shown that it was possible to distinguish different Hg species in various solid samples by their thermally induced Hg compound decomposition and release characteristics. Rallo et al. (2010) and Liu et al. (2013) employed the TPD method on FGD gypsums and determined the mercury species. However, the precursors of the mercury released and the final fate of mercury in FGD gypsum under different scenarios remained unclear. Since the physicochemical properties of mercury compounds in FGD gypsums may be linked to coal type, flue gas species, WFGD process and many other factors, more research is required to investigate the characteristics of mercury in FGD gypsums so as to determine the final fate of mercury contained in it.

The emphasis of this study was to determine the speciation of Hg in FGD gypsum from China. Two methods, i.e. TPD and SCE, were used to identify the Hg species in FGD gypsums, and the reliability of the two testing methods was validated. The results were compared and the formation mechanisms of Hg species were discussed with the aim to provide more information towards the full understanding of the behavior and the final fate of mercury in FGD gypsum and make it possible to predict the re-emission of Hg during different disposal methods for FGD gypsum.

## 1. Materials and methods

### 1.1. FGD Gypsum samples

FGD gypsum samples were collected from seven different coal-fired power plants in China. The samples were collected directly from the downstream of the vacuum belt dewatering system when the power plants were under steady load. For each power plant, the sample was collected three times with 1 hr interval between samplings. The samples from the three collections were then homogeneously mixed. Then the FGD gypsums were sealed in clean glass jars and stored at 4°C until testing. The moisture contents of the seven samples were about 10%–20%. The total Hg contents of the samples were determined by Lumex RA-915 M + PYRO-915 (Lumex, Russia) in triplicate and the mean values are presented in Table 1. The contents of Hg in FGD gypsums varied from 0.19 to 3.27  $\mu\text{g/g}$ . Additionally, the samples were selected with respect to the differences in coal types and air pollution control devices, which might influence the species of mercury. As shown in Table 1, the coal types included bituminous, lignite and anthracite, representing all the major coal types burned in the power plants of China. All the power plants tested were equipped with ESP (electrostatic precipitator) and WFGD to control the emission of PM and  $\text{SO}_2$ , while four of them were equipped with Selective Catalytic Reduction (SCR) for  $\text{NO}_x$  removal.

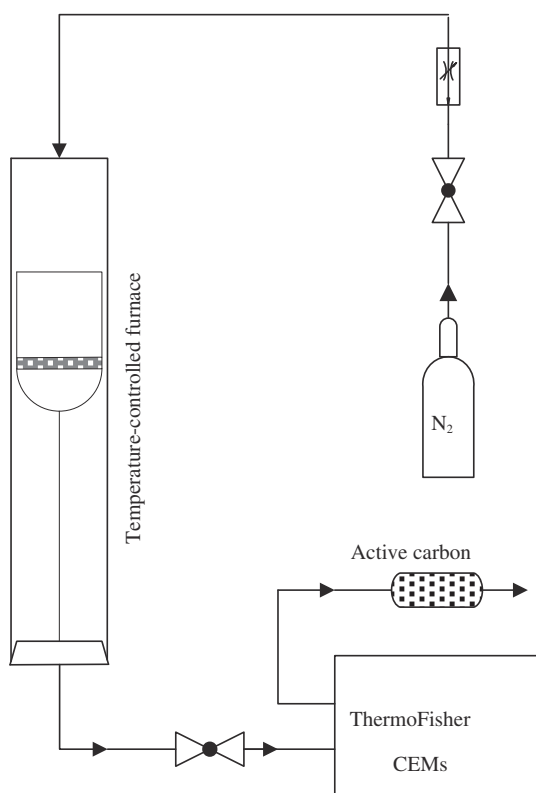
### 1.2. TPD

The TPD technique is based on the different thermal decomposition or desorption temperatures of Hg compounds in FGD gypsums. All the measurements in this study were carried out on a bench-scale fixed-bed reactor combined with an online mercury detector. As shown in Fig. 1, the fixed-bed reactor consists of a temperature-controlled furnace and a quartz reactor. The mercury analyzer is the Mercury Freedom Continuous Emission Monitoring System (Hg-CEMS, Thermofisher, USA) with an atomic fluorescence detector. It can achieve real-time monitoring of total mercury ( $\text{Hg}^0$ ), elemental mercury ( $\text{Hg}^0$ ), and oxidized mercury ( $\text{Hg}^{2+}$ , the difference between  $\text{Hg}^0$  and  $\text{Hg}^0$ ) with the detection limit of  $\text{ng/m}^3$ . The Hg CEMS has two operating modes. For the real-time monitoring of  $\text{Hg}^0$  and  $\text{Hg}^0$ , Hg-CEMS collects a new data point every 1 min, and for the real-time monitoring of  $\text{Hg}^0$  separately, Hg-CEMS collects a new

**Table 1 – Information of tested power plants and samples.**

Sample	Coal type	Air pollution control devices	Hg content of FGD gypsum ( $\mu\text{g/g}$ )
FGD1	Bituminous	ESP + WFGD	0.19 ± 0.01
FGD2	Bituminous	ESP + WFGD	0.28 ± 0.03
FGD3	Bituminous	ESP + WFGD	0.36 ± 0.02
FGD4	Lignite	SCR + ESP + WFGD	0.75 ± 0.03
FGD5	Bituminous	SCR + ESP + WFGD	1.63 ± 0.05
FGD6	Bituminous	SCR + ESP + WFGD	1.87 ± 0.04
FGD7	Anthracite	SCR + ESP + WFGD	3.27 ± 0.09

FGD: flue gas desulfurization, ESP: electrostatic precipitator, WFGD: wet glue gas desulfurization, SCR: selective catalytic reduction.



**Fig. 1 – Schematic diagram of the TPD apparatus. TPD: Temperature Programmed Decomposition.**

data point every 10 sec. In this research, about 1.0 g of the fresh and homogenized samples, without any treatment except crushing, was heated in the furnace from room temperature to 700°C at the rate of 10°C/min. The temperature of 700°C was chosen so as to make sure that all the Hg was released from the samples. The Hg released was carried by a purging nitrogen flow at 2 L/min to the Hg CEMS for detection. All the experiments for each sample were performed three times and the mean values were used to verify the reliability of the data.

The mercury release curves of pure mercury compounds (e.g.  $\text{HgCl}_2$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{HgS}$ ,  $\text{HgO}$ ,  $\text{HgSO}_4$ , and  $\text{Hg}_2\text{SO}_4$  etc.) were obtained first as references that could be used as fingerprints to identify the release curves of FGD gypsum samples. The reference samples were prepared by diluting pure mercury compounds with FGD gypsum that had already been calcined at 700°C for 3 hr to remove all the existing mercury. The concentration of mercury in the reference samples was approximately 1 to 2  $\mu\text{g/g}$ .

### 1.3. SCE

Sequential Chemical Extraction (SCE) was carried out according to the five-step procedure developed by Bloom et al. (2003). Since Bloom's procedure was developed for the speciation of Hg in contaminated soils and sediments with mercury concentration more than 100  $\mu\text{g/g}$ , our method adopted the liquid–solid ratio of 10 instead of 100 to address the fact of low mercury content in FGD gypsums. At the end of each step, the extracted solution was centrifuged and filtered through a 0.45  $\mu\text{m}$  glass fiber membrane filter. The filtrate was then

analyzed for Hg concentration by a Hydra II AA. All the extractions were carried out in triplicate and the mean values are presented. Briefly, the details of the five extraction steps are described below:

**Fraction 1.** water soluble phase. 4 g of fresh FGD gypsum sample without any treatment except crushing was shaken (end to end) with 40 mL de-ionized water for 18 hr.

**Fraction 2.** stomach acid soluble phase. The residue from Fraction 1 was shaken with 40 mL 0.1 mol/L  $\text{CH}_3\text{COOH}$  and 0.01 mol/L  $\text{HCl}$  for 18 hr.

**Fraction 3.** organocomplexed phase. The residue from Fraction 2 was leached in 40 mL 1 mol/L  $\text{KOH}$  for 18 hr.

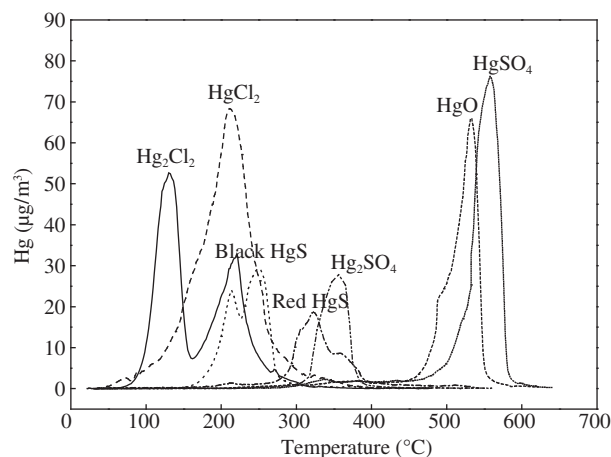
**Fraction 4.** strongly complexed phase. The residue from Fraction 3 was extracted by 40 mL 12 mol/L  $\text{HNO}_3$  for 18 hr.

**Fraction 5.** residual. The residue from Fraction 4 was digested with aqua regia.

## 2. Results and discussion

### 2.1. TPD Studies on reference samples

The Hg release ( $\text{Hg}^0$ ) curves obtained by thermal decomposition of various reference samples are shown in Fig. 2. The reference samples studied included  $\text{HgCl}_2$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{HgS}$ ,  $\text{HgO}$ ,  $\text{Hg}_2\text{SO}_4$  and  $\text{HgSO}_4$ , as they were the most likely compounds that might exist in FGD gypsum (Kilgroe and Senior, 2003). Given the different crystalline structures of black  $\text{HgS}$  (metacinnabar) and red  $\text{HgS}$  (cinnabar), both of them were included in the research. The characteristics of Hg release temperature are summarized in Table 2. It can be seen that the Hg compounds can be distinguished by their specific peak temperatures and peak ranges, and a previous study has revealed that multiple Hg species in a mixture can be determined without interference (Lopez-Anton et al., 2010). The order of Hg release temperature was  $\text{Hg}_2\text{Cl}_2 < \text{HgCl}_2 < \text{black HgS} < \text{Hg}_2\text{SO}_4 < \text{red HgS} < \text{HgO} < \text{HgSO}_4$ . The release order agreed well with the studies from Lopez-Anton et al. (2010) and Liu et al. (2013). However,



**Fig. 2 – Thermal decomposition curves of reference samples.  $\text{Hg}^0$ : elemental mercury;  $\text{Hg}^t$ : total mercury.**

**Table 2 – Hg release temperatures of reference samples.**

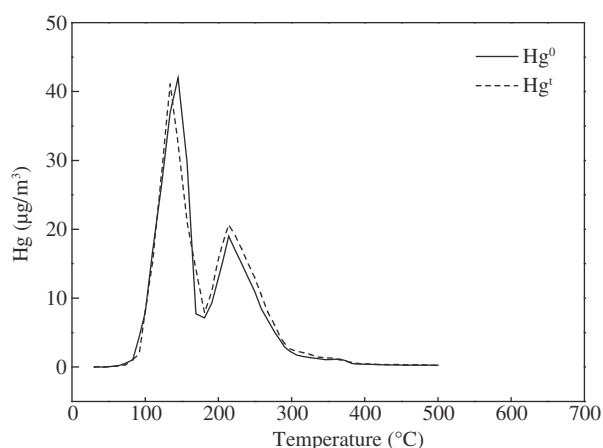
Mercury compounds	High peak temperature (°C)	Peak range temperature (°C)
HgCl <sub>2</sub>	210 ± 5	90–305
Hg <sub>2</sub> Cl <sub>2</sub>	131 ± 9, 227 ± 5	85–308
Black HgS	216 ± 2, 256 ± 8	170–310
Hg <sub>2</sub> SO <sub>4</sub>	323 ± 7	200–425
Red HgS	351 ± 5	300–380
HgO	527 ± 10	460–550
HgSO <sub>4</sub>	567 ± 15	500–600

differences in the peak temperatures and decomposition temperature ranges did exist when compared with other studies. This might due to the difference in heating rate, pressure, and composition and flow rate of carrier gas. Furthermore, differences in the binding matrix for Hg might also affect the Hg release temperature (Raposo et al., 2003; Feng et al., 2004). The reference samples used in this study were generated by diluting pure mercury compounds in FGD gypsum without mercury. The matrix effect had been minimized so as to represent the Hg compounds in real FGD gypsum.

The characteristics of the Hg species released from the reference samples were also monitored by Hg-CEMS, which could distinguish Hg<sup>0</sup>, Hg<sup>2+</sup> and Hg<sup>t</sup> in real time. By comparing the recorded data of all the reference samples, it was noticed that there was no obvious difference between Hg<sup>0</sup> and Hg<sup>t</sup>. Fig. 3 shows the Hg species release curves of Hg<sub>2</sub>Cl<sub>2</sub> as an example. The release curves of Hg<sup>0</sup> and Hg<sup>t</sup> were consistent with each other. This indicated that the Hg released from all samples was actually in elemental form. The Hg compounds were broken down during the thermal process and the sublimation of Hg compounds did not occur. This may be due to the low mercury concentration in the sample.

## 2.2. TPD studies on FGD gypsum samples

The Hg release curves (Hg<sup>t</sup>) generated by thermal decomposition of the seven FGD gypsum samples are shown in Fig. 4. By integrating the peak area of each Hg release curve, the recoveries of Hg were calculated, which represented the ratio of mercury released to the total mercury content in the tested

**Fig. 3 – Hg species release curves of Hg<sub>2</sub>Cl<sub>2</sub>.**

FGD gypsum (as shown in Table 3). The recoveries of the seven FGD gypsum samples were 95.3%–119.2%. This meant that all of the Hg in the FGD gypsum samples was released during the thermal decomposition. The close-to-100% recovery also indicated that the method used in this research was valid and reliable. Furthermore, by comparing the Hg<sup>0</sup> and Hg<sup>t</sup> released during the thermal decomposition of each FGD gypsum sample, no obvious difference was found between these two parameters. Fig. 5 shows the Hg species release curves of FGD5 as an example. This observation suggested that the Hg released from FGD gypsum samples was also all in the form of Hg<sup>0</sup>.

To identify which compound contributed to Hg release, peaks of FGD gypsum samples were separated by Peakfit 4.0 software based on the ‘fingerprints’ of the decomposition of reference samples. The species of Hg compounds were identified and their mass distribution is summarized in Table 3. It can be seen that mercury sulfides (both black HgS and red HgS) were the main species present in all of the seven FGD gypsum samples, with their mass contents ranging from 69% to 100%. Between them, black HgS was the dominant compound. HgCl<sub>2</sub> also appeared in FGD1, FGD4 and FGD5 with contents of 11.8%, 18% and 13.8%, respectively. Hg<sub>2</sub>Cl<sub>2</sub> could be found in FGD7 with the content of 6.2%. Hg<sub>2</sub>SO<sub>4</sub> could be found in FGD1 and FGD5 with contents of 18.1% and 17.2%.

Mercury reactions in gypsum slurry before the dehydration process are controlled by pH, temperature, concentrations of sulfite, chloride and other initial reactants (Blythe et al., 2008). This makes the reactions in gypsum slurry quite complicated. Although HgCl<sub>2</sub>, Hg<sub>2</sub>Cl<sub>2</sub>, and Hg<sub>2</sub>SO<sub>4</sub> could be found in the FGD gypsum samples, mercury sulfides were undoubtedly the dominant compounds in all the samples. This indicated that the Hg species in FGD gypsum seemed to have no direct connection with the coal types and APCDs. The Hg retained in gypsum slurry was mainly captured as soluble oxidized mercury (HgCl<sub>2</sub>) from flue gas. Some Hg<sup>p</sup> escaping from ESP might also be scrubbed by the WFGD system, such as Hg<sub>2</sub>Cl<sub>2</sub>, which should be in the solid state at the boiler’s outlet temperature. HgCl<sub>2</sub>, Hg<sub>2</sub>Cl<sub>2</sub> and Hg<sub>2</sub>SO<sub>4</sub> might be present on the surface of FGD gypsum by adsorption or as Hg<sup>p</sup> retained by gypsum particles. As for mercury sulfide, it was common in FGD gypsum, although sulfide is not normally present in FGD gypsum slurry. However, some research did suggest that sulfide ion might form in the FGD liquors by disproportionation of sulfite (Eq. (1)), which was catalyzed by mercury (Blythe et al., 2008). The sulfide ion would then react with mercury ion to form mercury sulfide (Eq. (2)). Mercury sulfide is almost completely insoluble and can be easily separated from the liquid phase, which could then promote the disproportionation and precipitation reaction. This reaction mechanism might eventually lead mercury sulfide to be the primary species in FGD gypsum samples.



Although red HgS is more common and stable in the natural environment, black HgS has been found to be the dominant compound in FGD gypsum samples. The precipitation reaction at



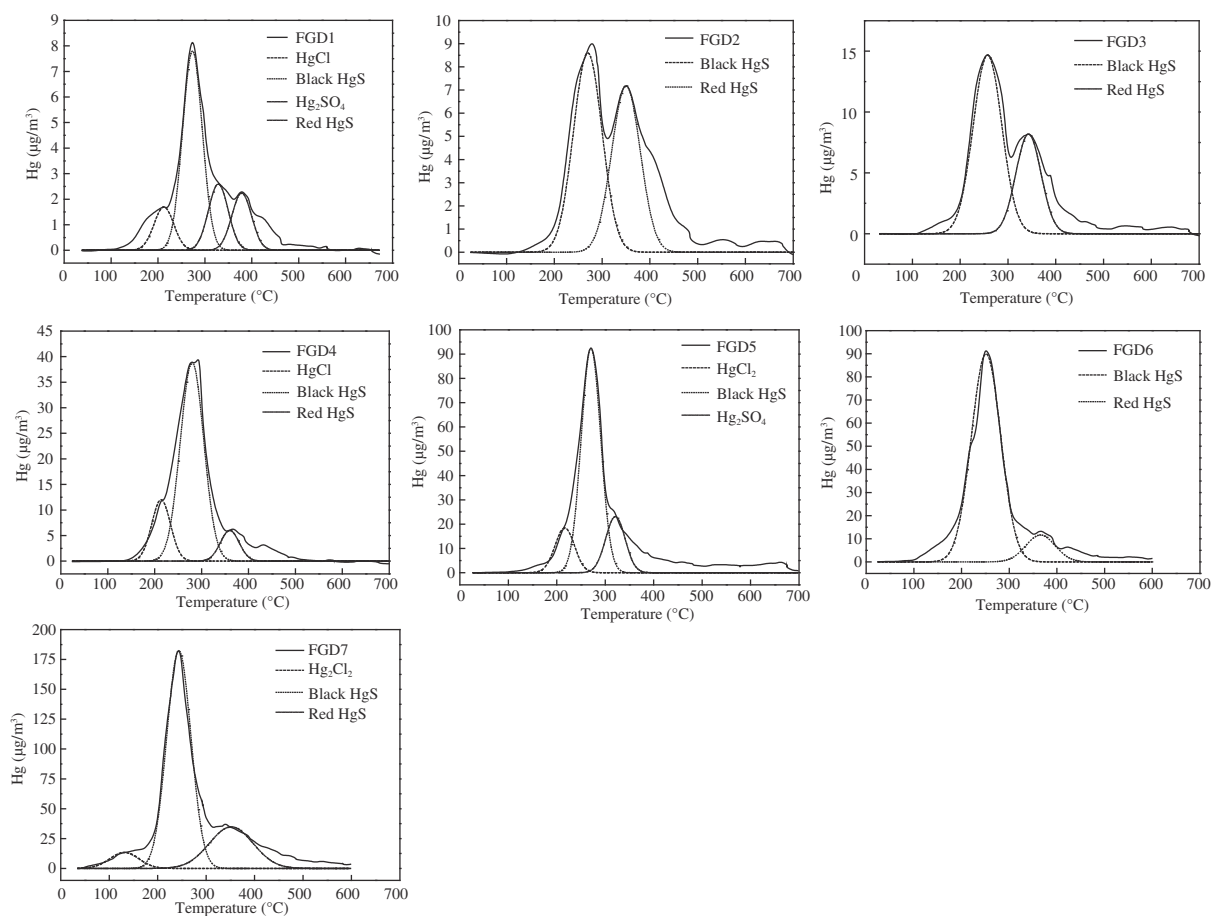


Fig. 4 – Thermal decomposition curves of FGD (flue gas desulfurization) gypsum samples.

low temperature could yield black HgS (Rumayor et al., 2015). Furthermore, the red HgS might be photosensitive and could be transformed to black HgS during exposure to sunlight. This was especially remarkable when halogens were present (McCormack, 2000). There were considerable amounts of halogens such as chloride and fluorine present in the FGD gypsum slurry.

### 2.3. SEC studies of FGD gypsum samples

The results of the SCE tests are summarized in Table 4. The recoveries of Hg in FGD gypsum samples were about 100% except for FGD1, which was probably caused by its very low Hg content (0.19 μg/g) and the associated difficulties in Hg recovery. The recovery indicated that almost all of the Hg

had been extracted by the five-step extraction, most of which was extracted in Fraction 4. For all the samples, the sum of the mass percentage distributions of Fraction 4 and Fraction 5 accounted for more than 90% of the total mercury in the gypsum; and the percentage distribution of Fraction 1, Fraction 2 and Fraction 3 was quite low, except that 10.27% of Hg was extracted in Fraction 1 of FGD1.

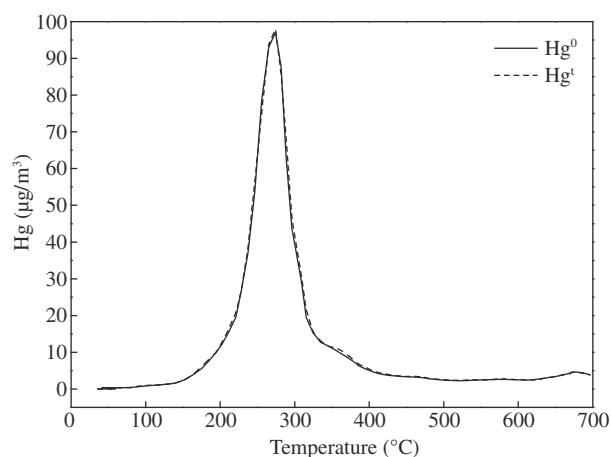
### 2.4. Comparisons of TPD and SCE results

In all the FGD gypsum samples examined, the Hg species identified by TPD were mainly mercury sulfides dominated by black HgS. In the SCE, most of the Hg was extracted in Fraction 4. A considerable amount of Hg was also extracted in Fraction 5.

Table 3 – Mass distribution of different Hg compounds in FGD gypsum samples (%).

	FGD1	FGD2	FGD3	FGD4	FGD5	FGD6	FGD7
HgCl <sub>2</sub>	11.8 ± 1.7			18.0 ± 2.5	13.8 ± 0.6		
Hg <sub>2</sub> Cl <sub>2</sub>							6.2 ± 0.8
Black HgS	54.4 ± 0.3	54.5 ± 3.0	66.3 ± 1.8	73.0 ± 0.5	69.0 ± 2.8	88.5 ± 2.3	69.8 ± 3.3
Hg <sub>2</sub> SO <sub>4</sub>	18.1 ± 1.6				17.2 ± 2.2		
Red HgS	15.7 ± 0.2	45.5 ± 3.0	33.7 ± 1.8	9.0 ± 2.1		11.5 ± 2.3	24.0 ± 2.5
Recovery	104.7 ± 7.1	110.6 ± 8.9	119.2 ± 5.1	112.6 ± 4.8	107.2 ± 1.6	99.8 ± 3.3	95.3 ± 3.7

FGD: flue gas desulfurization.



**Fig. 5 – Hg species release curves of sample FGD5.  $\text{Hg}^0$ : elemental mercury;  $\text{Hg}^{\text{T}}$ : total mercury. FGD: flue gas desulfurization.**

Based on the model extraction profiles given by Bloom et al. (2003), the strongly complexed phase was extracted in Fraction 4 and the main relevant compound removed was  $\text{Hg}^0$ . As for Fraction 5, the typical compounds removed were mercury sulfides. There seemed to be some disagreement between the two methods. However, it should be pointed out that the model extraction profiles for the pure compounds of SCE were generated by conducting the extraction procedure on the pure Hg-containing compounds, which were diluted in an inert kaolinite matrix with the total Hg concentrations ranging from 1000 to 44,000  $\mu\text{g/g}$ . The reported Hg concentrations were obviously higher than those in the FGD gypsum samples tested in this research. As the concentration of total Hg in a sample decreased, it would become more and more difficult to assign an extraction fraction to a particular Hg species class through SCE, especially for the low-Hg-level samples in which the total Hg concentrations were below 100  $\mu\text{g/g}$  (Bloom et al., 2003).

Since Hg captured in a WFGD system is mainly in the form of oxidized mercury,  $\text{Hg}^0$  is not likely to be the main species in FGD gypsum. From the speciation information of TPD,  $\text{HgS}$  rather than  $\text{Hg}^0$  might be extracted in Fraction 4. In general,  $\text{HgS}$  should not be soluble in any concentration of  $\text{HNO}_3$  and will only be dissolved in aqua regia. However, it could be found that almost all of the  $\text{HgS}$  was extracted by 12 M  $\text{HNO}_3$  by comparing the results of the two methods. There might be some chloride present in FGD gypsum samples and 0.01 mol/L HCl was used in the extraction of Fraction 2. Even after the

washing-up of the step 1, 2 and 3 extraction procedures, there might be a trace chloride remnant existing in the extraction of Fraction 4. The chloride would be oxidized to form  $\text{Cl}_2$  by concentrated  $\text{HNO}_3$  (Eq. (3)) and  $\text{HgS}$  would then be oxidized to soluble form by  $\text{Cl}_2$  (Eq. (4)) (Mikac et al., 2003). Although the oxidization and dissolution amount of  $\text{HgS}$  might be small in absolute value, the proportion would become larger and larger as the total Hg concentration decreased. The end result would be that most of the  $\text{HgS}$  was extracted in Fraction 4 in SCE. Moreover, most of the FGD gypsum solids were dissolved in Fraction 4 during the extraction, which could be contributed by the enhancement of  $\text{CaSO}_4$  dissolution by nitric acid. This would be beneficial for the release of Hg absorbed on the gypsum surface or enclosed inside gypsum particles. As a result, the Hg extraction in Fraction 4 was further improved.



Meanwhile, for other more soluble compounds besides mercury sulfide, there were also some differences between the two methods. Based on the model extraction profiles from Bloom et al. (2003), the typical compound removed in Fraction 1 was  $\text{HgCl}_2$ , whilst the target compounds in Fraction 2 were  $\text{HgO}$  and  $\text{HgSO}_4$ . Since there was no organic Hg existing in FGD gypsum, the typical compound removed in Fraction 3 was thought to be  $\text{Hg}_2\text{Cl}_2$ . The results of the two methods did not agree with each other except for the  $\text{HgCl}_2$  species in FGD1, of which the contents identified by TPD and SCE were 11.8% and 10.27%. The inconsistencies of the two methods might be caused by the soluble Hg species being reabsorbed and released again in the subsequent more aggressive extraction fractions. This shifted proportion might become larger and larger as the total Hg concentration decreased. There were also other reasons that might lead to the observed inconsistencies, (1) the Hg species might be enclosed within large and insoluble particles; (2) the reagents adopted may not be selective enough for the target Hg species; (3) the precipitation of new mineral phases may occur during the extraction (Bacon et al., 2008; Kim et al., 2003).

The most abundant Hg species in FGD gypsum determined by TPD was mercury sulfides; this was consistent with previous studies (Rumayor et al., 2015; Sui et al., 2015). As for SCE, the Hg in FGD gypsum was mainly extracted in Fraction 4, and this was consistent with studies from Al-abad et al. (2008) and Sun et al. (2014). The low content of Hg in FGD gypsum led to the shifted extraction being non-negligible, which was insignificant when

**Table 4 – Mass distribution of the extracted phases in FGD gypsum samples (%).**

Extraction step	FGD1	FGD2	FGD3	FGD4	FGD5	FGD6	FGD7
Fraction 1	10.27 ± 6.97	1.71 ± 0.37	1.93 ± 0.55	0.69 ± 0.09	3.21 ± 0.14	0.22 ± 0.08	1.97 ± 0.22
Fraction 2	0.42 ± 0.14	0.33 ± 0.27	1.44 ± 0.45	0.09 ± 0.01	0.47 ± 0.09	0.15 ± 0.01	0.20 ± 0.02
Fraction 3	0.77 ± 0.15	0.55 ± 0.23	0.49 ± 0.09	0.13 ± 0.03	0.01 ± 0.00	0.95 ± 0.10	0.23 ± 0.03
Fraction 4	77.19 ± 8.34	87.43 ± 0.78	88.18 ± 1.01	96.45 ± 0.23	94.59 ± 1.13	96.5 ± 0.31	95.19 ± 0.27
Fraction 5	11.36 ± 1.68	9.98 ± 0.98	7.97 ± 1.36	2.64 ± 0.25	1.73 ± 0.96	2.17 ± 0.20	2.40 ± 0.26
Recovery	74.99 ± 4.44	102.68 ± 4.18	96.71 ± 8.49	101.19 ± 3.17	96.20 ± 5.61	90.79 ± 3.20	99.02 ± 3.85

FGD: flue gas desulfurization.

Hg content was high. Based on the Hg speciation information from TPD, it was thought that HgS rather than Hg<sup>0</sup> was extracted in Fraction 4. Therefore, TPD was thought to be a useful way for the determination of Hg species in FGD gypsum, while the low content of Hg in FGD gypsum makes it ambiguous to assign the extraction fraction to a particular Hg species in SCE by just comparing with the model extraction profiles given by Bloom et al. (2003). More research is needed to improve the scheme of SCE for the speciation of Hg in FGD gypsum, such as the extractants used in each step, liquid to solid ratio, and extraction time.

### 2.5. Fate of Hg in FGD gypsum

Although it might become difficult for SCE to assign an extraction fraction to a particular Hg species when the Hg concentration in sample is below 100 µg/g, SCE did provide some operational speciation information for Hg which could be helpful in assessing the behavior of Hg in FGD gypsum in the natural environment. The percentage distribution of Fraction 1 (water soluble phase) and Fraction 2 (mild acid soluble phase) of the FGD gypsum samples was quite low, and this was consistent with the fact that HgS phases were the primary compounds in FGD gypsum determined by the TPD method. This indicated that the Hg in FGD gypsum should be fairly stable and that leaching of Hg should be very low during waste management in different scenarios in the natural environment. The Hg extraction in Fraction 3 was also very low, and the content of organic mercury was negligible. This was beneficial for the landfilling of gypsum, since the toxicity of organic mercury is much higher than that of inorganic mercury. Besides, it could be reasonably expected that mercury in FGD gypsum might be released in the gas phase during the calcination process of wallboard production, based on the release curves of FGD gypsum samples from TPD, even though the temperature in the industrial process (about 160°C) is lower than the peak temperature of the decomposition of mercury sulfides. In a typical process, calcination may last 1–2 hr and Hg release in wallboard production should not be neglected; and the Hg release may mainly occur in the form of Hg<sup>0</sup>. In general, the combination of TPD and SCE can give a comprehensive judgment on the fate of Hg in FGD gypsum both in industrial processes and the natural environment.

### 3. Conclusions

Two methods, TPD and SCE, were employed to identify the Hg species in FGD gypsums. The existing Hg compounds in FGD gypsums determined by TPD included HgCl<sub>2</sub>, Hg<sub>2</sub>Cl<sub>2</sub>, Hg<sub>2</sub>SO<sub>4</sub>, black HgS and red HgS, of which mercury sulfides were the primary compounds. The Hg species seemed to have no direct connection with coal types and APCDs, and the Hg in FGD gypsum would release as Hg<sup>0</sup> in industrial heating processes. As for SCE, Hg was mainly extracted in Fraction 4 and Fraction 5, while Fraction 4 was dominant. The results of SCE suggested that the Hg in FGD gypsums was relatively stable and the leaching of Hg should be very low in the natural environment. The Hg species could be identified by the TPD method, while the low Hg content in FGD gypsum made it ambiguous to assign an extraction fraction to a particular Hg species by SCE.

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### REFERENCES

- Al-Abed, S.R., Jegadeesan, G., Scheckel, K.G., Tolaymat, T., 2008. Speciation, characterization, and mobility of As, Se, and Hg in flue gas desulfurization residues. *Environ. Sci. Technol.* 42 (5), 1693–1698.
- Álvarez-Ayuso, E., Querol, X., 2007. Stabilization of FGD gypsum for its disposal in landfills using amorphous aluminium oxide as a fluoride retention additive. *Chemosphere* 69 (2), 295–302.
- Bacon, J.R., Davidson, C.M., 2008. Is there a future for sequential chemical extraction? *Analyst* 133 (1), 25–46.
- Biester, H., Scholz, C., 1996. Determination of mercury binding forms in contaminated soils: mercury pyrolysis versus sequential extractions. *Environ. Sci. Technol.* 31 (1), 233–239.
- Biester, H., Gosar, M., Covelli, S., 2000. Mercury speciation in sediments affected by dumped mining residues in the drainage area of the Idrija mercury mine, Slovenia. *Environ. Sci. Technol.* 34 (16), 3330–3336.
- Bloom, N.S., Preus, E., Katon, J., Hiltner, M., 2003. Selective extractions to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils. *Anal. Chim. Acta* 479 (2), 233–248.
- Blythe, G.M., DeBerry, D.W., Pletcher, S., 2008. Bench-scale kinetics study of mercury reactions in FGD liquors. Final Report: DE-FC26-04NT42314 for the National Energy Technology Laboratory, Austin.
- Clark, R.B., Ritchey, K.D., Baligar, V.C., 2001. Benefits and constraints for use of FGD products on agricultural land. *Fuel* 80 (6), 821–828.
- Feng, X.B., Lu, J.Y., Grégoire, D.C., Hao, Y.J., Banic, C.M., Schroeder, W.H., 2004. Analysis of inorganic mercury species associated with airborne particulate matter/aerosols: method development. *Anal. Bioanal. Chem.* 380 (4), 683–689.
- Heebink, L.V., Hassett, D.J., 2005. Mercury release from FGD. *Fuel* 84 (11), 1372–1377.
- Issaro, N., Abi-Ghanem, C., Bermond, A., 2009. Fractionation studies of mercury in soils and sediments: a review of the chemical reagents used for mercury extraction. *Anal. Chim. Acta* 631 (1), 1–12.
- Kilgroe, J., Senior, C., 2003. Fundamental science and engineering of mercury control in coal-fired power plants. The Air Quality IV Conference, Arlington, VA.
- Kim, C.S., Bloom, N.S., Rytuba, J.J., Brown, G.E., 2003. Mercury speciation by X-ray absorption fine structure spectroscopy and sequential chemical extractions: a comparison of speciation methods. *Environ. Sci. Technol.* 37 (22), 5102–5108.
- Liu, X.L., Wang, S.X., Zhang, L., Wu, Y., Duan, L., Hao, J.M., 2013. Speciation of mercury in FGD gypsum and mercury emission during the wallboard production in China. *Fuel* 111, 621–627.
- Lopez-Anton, M.A., Yuan, Y., Perry, R., Maroto-Valer, M.M., 2010. Analysis of mercury species present during coal combustion by thermal desorption. *Fuel* 89 (3), 629–634.
- Lopez-Anton, M.A., Perry, R., Abad-Valle, P., Diaz-Somoano, M., Martinez-Tarazona, M.R., Maroto-Valer, M.M., 2011. Speciation of mercury in fly ashes by temperature programmed decomposition. *Fuel Process. Technol.* 92 (3), 707–711.
- Luo, G.Q., Yao, H., Xu, M.H., Gupta, R., Xu, Z.H., 2011. Identifying modes of occurrence of mercury in coal by temperature programmed pyrolysis. *Proc. Combust. Inst.* 33 (2), 2763–2769.
- McCormack, J.K., 2000. The darkening of cinnabar in sunlight. *Mineral. Deposita* 35 (8), 796–798.

- Mikac, N., Foucher, D., Niessen, S., 2003. Influence of chloride and sediment matrix on the extractability of HgS (cinnabar and metacinnabar) by nitric acid. *Anal. Bioanal. Chem.* 377 (7–8), 1196–1201.
- Ochoa-González, R., Díaz-Somoano, M., Martínez-Tarazona, M.R., 2013. Effect of anion concentrations on Hg 2+ reduction from simulated desulphurization aqueous solutions. *Chem. Eng. J.* 214 (4), 165–171.
- Pacyna, E.G., Pacyna, J.M., Sundseth, K., Munthe, J., Kindbom, K., Wilson, S., Steenhuisen, F., Maxson, P., 2010. Global emission of mercury to the atmosphere from anthropogenic sources in 2005 and projections to 2020. *Atmos. Environ.* 44 (20), 2487–2499.
- Pirrone, N., Keeler, G.J., Nriagu, J.O., 1996. Regional differences in worldwide emissions of mercury to the atmosphere. *Atmos. Environ.* 30 (17), 2981–2987.
- Rallo, M., Lopez-Anton, M.A., Perry, R., Maroto-Valer, M.M., 2010. Mercury speciation in gypsums produced from flue gas desulfurization by temperature programmed decomposition. *Fuel* 89 (8), 2157–2159.
- Raposo, C., Windmüller, C.C., Junior, W.A.D., 2003. Mercury speciation in fluorescent lamps by thermal release analysis. *Waste Manag.* 23 (10), 879–886.
- Rumayor, M., Díaz-Somoano, M., López-Antón, M.A., Ochoa González, R., Martínez Tarazona, M.R., 2015. Temperature programmed desorption as a tool for the identification of mercury fate in wet-desulphurization systems. *Fuel* 148, 98–103.
- Sui, Z., Zhang, Y., Li, W., Orndorff, W., Cao, Y., Pan, W.P., 2015. Partitioning effect of mercury content and speciation in gypsum slurry as a function of time. *J. Therm. Anal. Calorim.* 119 (3), 1611–1618.
- Sun, M., Hou, J., Cheng, G., Baig, S.A., Tan, L., Xu, X., 2014. The relationship between speciation and release ability of mercury in flue gas desulfurization (FGD) gypsum. *Fuel* 125, 66–72.
- Tang, T.M., Xu, J., Lu, R.J., Wo, J.J., Xu, X.H., 2010. Enhanced Hg2+ removal and Hg0 re-emission control from wet fuel gas desulfurization liquors with additives. *Fuel* 89 (12), 3613–3617.
- Tian, H.Z., Wang, Y., Xue, Z.G., Qu, Y.P., Chai, F.H., Hao, J.M., 2011. Atmospheric emissions estimation of Hg, As, and Se from coal-fired power plants in China, 2007. *Sci. Total Environ.* 409 (16), 3078–3081.
- Wo, J., Zhang, M., Cheng, X., Zhong, X., XU, J., Xu, X., 2009. Hg 2+ reduction and re-emission from simulated wet flue gas desulfurization liquors. *J. Hazard. Mater.* 172 (2–3), 1106–1110.