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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 μg/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 Hg_2Cl_2 < $HgCl_2$ < black HgS < Hg_2SO_4 < red HgS < HgO < $HgSO_4$. The Hg compounds existing in FGD gypsums identified by TPD included $HgCl_2$, Hg_2Cl_2, Hg_2SO_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.

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 (Hg^0), oxidized mercury (Hg^{2+}) and particulate-bound mercury (Hg^P). The compounds of mercury in flue gas from coal combustion may be elemental mercury (Hg^0), mercury chloride ($HgCl_2$), mercurous chloride (Hg_2Cl_2), mercury oxide (HgO), mercury sulfate ($HgSO_4$) and other inorganic species (Kilgroe and Senior, 2003).

Wet Flue Gas Desulfurization (WFGD) systems aimed to control SO_2 can affect the mobility and emission of mercury in

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flue gas. Soluble oxidized mercury compounds such as $HgCl_2$ can be effectively absorbed by a gypsum slurry. Hg^p 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 Hg^{2+} in the slurry may be reduced and released as 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 be 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 μg/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 μg/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 SO_2, while four of them were equipped with Selective Catalytic Reduction (SCR) for 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 (Hg^t), elemental mercury (Hg^0), and oxidized mercury (Hg^{2+}, the difference between Hg^t and Hg^0) with the detection limit of ng/m^3. The Hg CEMS has two operating modes. For the real-time monitoring of Hg^t and Hg^0, Hg-CEMS collects a new data point every 1 min, and for the real-time monitoring of Hg^t 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 (μg/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.