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Characterization and leaching toxicities of mercury in flue gas desulfurization gypsum from coal-fired power plants in China

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HIGHLIGHTS

- Hg pollutant characters in FGD gypsums around China were evaluated.
- Total content and chemical species of Hg displayed regional characters.
- Hg in FGD gypsums mainly distributed in strong complex F4 phase.
- TCLP and SPLP tests indicated low mobility of Hg in FGD gypsum.

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ABSTRACT

Flue gas desulphurization (FGD) gypsum samples were collected from 70 power plants in 20 provinces in China. The total Hg concentration, chemical speciation and leaching toxicity of Hg in the samples were determined. The total Hg concentrations ranged from not detectable (ND) to 4330 μg/kg with an average of 891 μg/kg and a median of 629 μg/kg. The Hg concentrations in the FGD samples had obvious regional characteristics. Provinces in the central part of China had higher average Hg concentrations in the FGD gypsum than other provinces. Selective sequential extraction (SSE) used for chemical speciation analysis showed that water soluble and human stomach acid soluble (F1 + F2) percentages ranged from ND to 25.2% of the total Hg, and strong complex Hg (F4) was the dominant chemical species, which accounted for more than 60% of the total Hg in most samples. Moreover, the leaching Hg concentrations from Toxicity Characteristic Leaching Procedure (TCLP) and Synthetic Precipitation Leaching Procedure (SPLP) tests were all below the regulation level of leaching toxicity. The average percentage of leaching Hg from TCLP and SPLP was approximately 3% of the total Hg, indicating limited Hg mobility in FGD gypsum. The Hg potential leaching from FGD gypsum was approximately 0.65 tons per year.

1. Introduction

In China, coal-fired power plants produced large amounts of combustion residuals, including fly ash and flue gas desulfurization (FGD) gypsum [1]. Due to the increasingly strict air control policy, the amount of combustion by-products has increased rapidly. Specifically, FGD gypsum output reached 52 million tons per year in 2012, and the total reutilization rate was only approximately 56% [2]. A large amount of FGD gypsum ended up in landfills or outdoor storage. It is well known that Hg can be co-removed from flue gas during air pollution control and retains its combustion residuals [3,4], causing potential Hg release. Mercury in fly ash and its effects on the environment during management and application have been widely investigated [5–8]. Comparatively, there were fewer reports on Hg in FGD gypsum. However, its safe treatment and disposal have raised concerns [9,10]. Al-abed et al. [11] reported that Hg concentrations in FGD gypsum in Pennsylvania, USA, ranged from 1000 to 2300 μg/kg and had a higher leaching at acidic pH levels. Wang et al. [12] found Hg concentrations in plant stems increased when FGD gypsum is present in soil.

It has been reported that Hg in flue gas released from coal during combustion exists primarily as Hg^0, oxidized Hg (Hg^{2+}) and particulate Hg (Hg_p). Hg_p and partial Hg^{2+} can be removed by particle control devices and enter fly ash, whereas FGD gypsum can retain up to 95% of Hg^{2+} [13]. Therefore, Hg in fly ash and FGD gypsum varies with the ratio of different Hg speciation in flue gas. Hg levels in flue gas depend on the Hg concentration and the chemical composition of coal as well as the method of air pollution control processes [14,15]. Thus, it is expected that there are different total Hg levels in FGD gypsum from different regions. However, the Hg concentrations in FGD gypsum and Hg concentration distributions

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throughout different regions of China haven't received enough attention. There were only limited data regarding the Hg concentration of FGD gypsum from several power plants; the total Hg concentration was reported between 150 and 2470 μg/g [16–18]. Furthermore, there are a number of power plants, and a few samples may not reflect the actual levels of Hg in FGD gypsum in China.

As previously mentioned, most Hg^{2+} is removed from flue gas during the FGD process. However, when Hg^{2+} enters FGD gypsum, it interacts with FGD gypsum through different mechanisms, forming a different chemical speciation. Sun et al. [17] used a modified sequential selective extraction method to determine the chemical speciation of Hg in FGD gypsum collected from four coal-fired power plants in Zhejiang Province, China. The method differentiated Hg into four groups. The results showed that Hg in FGD gypsum from the different power plants had different distribution characteristics. Al-abed et al. [11] reported that 99% of Hg in FGD gypsum stayed in a strong complex and residue phase. These results suggested that the Hg chemical speciation in FGD gypsum varied from place to place, thus causing different environmental behaviors during disposal and reutilization. Furthermore, chemical speciation of heavy metals in soil is closely correlated with its bioavailability [19,20]. Thus, determination of chemical speciation aside from the total concentration of Hg will be helpful to understand the biogeochemical cycle of Hg and predict its environmental fate in FGD gypsum from different regions.

In this study, we collected FGD gypsum samples from 70 power plants in 20 provinces, and determined their Hg characteristics. The total Hg and the chemical speciation of Hg were analyzed with a sequential selective extraction (SSE) method. A toxicity characteristic leaching procedure (TCLP) and a synthetic precipitation leaching procedure (SPLP) were performed to evaluate the leaching toxicity of Hg.

2. Materials and methods

2.1. Sample collection

FGD gypsum samples were collected from 70 coal-fired power plants in 20 provinces, China. The sample sites are shown in Fig. 1a. The collected samples were preserved in sealed plastic bags and sent to the laboratory as soon as possible. Upon arrival at the lab, the samples were stored at −4 °C in the refrigerator.

Because of the possible fluctuations of Hg concentrations in FGD gypsum, samples from four power plants in Shanghai and Anhui Provinces were collected each day during monitoring periods of four to eight weeks.

2.2. Total Hg content and Fe, Al analysis

The moisture of the samples was measured by drying the samples at 105 °C overnight. The moisture was calculated as the weight difference of the sample before and after drying. The moisture ranged from 1.3% to 51%. The FGD gypsum samples were oven-dried at 40 °C before analysis. The total Hg concentrations were determined by mixing FGD gypsum with 5 mL distilled water and 5 mL aqua regia, then oscillating the samples on an end-over-end shaker for 24 h at room temperature [21]. The mixture was finally centrifuged at 3000 rpm for 15 min. The supernatant was filtered through a 0.45 μm membrane, before the Hg concentration was determined by cold vapor atomic absorption spectrometry (CVAAS) (HUAGUANG F732-VJ, Shanghai) with Hg^{2+} being reduced to Hg^0 by the addition of $SnCl_2$.

For Fe and Al concentrations in FGD gypsum, the samples were placed in a 60 mL PTFE tube and digested with a mixture of 10 ml HNO_3, 5 ml $HClO_4$ and 10 ml HF on a graphite digestion block at 135 °C. The addition of the mixed acid was repeated several times until the solution was clear. The residual solution was filtered with a 0.45 μm cellulose acetate membrane and diluted to 50 mL in volumetric flasks with deionized water. Quantification of Fe and Al concentrations in the solution were determined by an inductively coupled plasma atomic emission spectrometry (ICP-AES) (LEEMAN Prodigy, USA).

2.3. Hg chemical speciation by SSE method

A five-step sequential selective extraction method developed by Bloom et al. [21] was performed to determine the Hg speciation in FGD gypsum. This method differentiated Hg compounds into different behavioral classes instead of species-specific information. The five extraction solutions adopted included deionized water, 0.1 M CH_3COOH + 0.01 M HCl, 1 M KOH, 12 M HNO_3 and aqua regia. The extracted Hg was defined as water soluble Hg (F1), human stomach acid soluble Hg (F2), organo-chelated Hg (F3), strong complex Hg (F4) and residue Hg (F5).

2.4. Leaching tests

The US EPA's TCLP [22] and SPLP [23] were used to estimate the Hg leaching potential from FGD gypsum. TCLP simulates the leachability of solids in an acidic environment of municipal landfills. The TCLP extraction fluid used in this work included 17.25 mL of glacial acetic acid (CH_3COOH) that was added to a glass volumetric flask, and then diluted with deionized water to 1000 mL (pH of 4.93 ± 0.05). One gram of gypsum was mixed with 20.0 mL of solution, maintaining the same solution-to-solids ratio of 20:1, according to the standard procedure. Samples were extracted for 18 ± 2 h in a 50-mL centrifuge tube at room temperature by end-over-end tumbling at 30 rpm. After extraction, the samples were centrifuged for 20 min at 3000 rpm, and the supernatant was filtered through a 0.45 μm filter. The filtrates were then oxidized and preserved by adding 2% (v/v%) of 0.2 M BrCl. The Hg concentration in filtrates was determined by CVAAS. For the SPLP, sulfuric acid and nitric acid (mass ratio 2:1; pH = 3.20 ± 0.05) were used as extraction fluids to conduct the solid waste-extraction procedure for leaching toxicity and estimate the effect of acid rain on FGD gypsum. Two grams of sample and 20 mL of extraction fluid were combined into a glass volumetric flask. The extraction and determination procedures were similar to those of the TCLP.

2.5. Quality control

The Hg concentration was expressed as dry weight basis. To ensure accurate determination of the Hg concentration, the standard addition method was applied to the total Hg determination and the standard recovery rate was calculated. The recovery rates ranged from 80% to 106%. A blank sample was analyzed in each batch test to eliminate the effect of impurities in the reagent. All analyses were performed in triplicates and the results were expressed as the mean ± standard deviation.

3. Results and discussion

3.1. Spatial distributions of total Hg in FGD gypsum

Fig. 1 displays the total Hg concentrations in the FGD gypsum samples from the different provinces and the frequency distribution of Hg in all of the FGD gypsum samples. The Hg concentration in each FGD gypsum sample is displayed in SI Table 1. The Hg concentrations ranged from not detectable to 4330 ± 620 μg/kg, and showed obvious regional differences. FGD gypsum from Shanxi,