



Full Length Article

Mercury release and fraction transformation during desulfurization gypsum aging process (UV irradiation)

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ABSTRACT

The transformation of mercury fractions under both natural environmental conditions and ultraviolet irradiation (UV) conditions was studied in this work. Mercury in desulfurization gypsum was divided into five fractions by sequential extraction procedure depending on its bioavailability. The five fractions were named as water soluble fraction (F1), ion-exchangeable fraction (F2), acid soluble fraction (F3), elemental fraction (F4), and sulfide fraction (F5). The results from our study demonstrated that the proportion of different fraction was in the following order: elemental fraction > water soluble fraction > acid soluble fraction > ion-exchangeable fraction > sulfide fraction. The results indicated that mercury could be released from desulfurization gypsum during aging process and the release process could be promoted via ultraviolet irradiation. The release amount increased with the irradiation time and intensity (up to 25.1% of the total initial amount). The percentage of mercury in F1 decreased gradually with aging time, while the percentage of mercury in elemental and residual fractions increased gradually. Our research will be helpful for the survey and understand of mercury emission from desulfurization gypsum.

1. Introduction

Mercury (Hg) has received growing attentions from legislative organizations, policy makers and researchers because of its high toxicity, volatility and bio-accumulation properties. Large amount of Hg can be released during coal combustion, and then redistributed among the components of flue gas or the residues of coal combustion. With wide applications of air pollution control equipments, more and more mercury will be removed from flue gas and enriched into solid waste (fly ash, slag, desulfurization gypsum) during the pollution control process in power plants. Most of oxide and particle forms of mercury in flue gas can be captured during the desulfurization process and transferred into gypsum. Oxidation and reduction can occur to mercury in our environment in the presence of sunlight [1–4]. Meanwhile, substantial decrease of Hg in sediments during the period of higher UV radiation was also observed. Zhang [5] took the lead in proving that there was a certain relationship between fluctuation of air ions concentration (AIC) and intensity of ultraviolet (UV) irradiations in a small chamber. Liu [6] demonstrated that more effective UV photons, [•]OH, [•]O and O₃ could be produced with UV radiation increasing in a ultraviolet (UV)/H₂O₂ system. Thereby, the removal of Hg⁰ could be enhanced when the

mercury containing matrix was exposed to UV irradiation. When the soil was exposed to UV-C radiation, atmospheric Hg deposition and O₃ destruction were simultaneously observed [7]. Furthermore, several reports showed that mercury emissions from natural substrates were positively correlated with light exposure [7–18].

Pekney [1] demonstrated that the full spectrum light exposure have no observable effect on mercury flux in fly ash, flue gas desulfurization gypsum (FGD), and wallboard (FGD product). Zhu [19] pointed out that the individual and combined effects of the most important parameters (temperature, UV exposure, and FGD water content) controlled the emission of Hg from FGD. The results indicated that the competition between reduction of bivalent mercury and oxidation of the elemental mercury might determine promotion or inhibition on mercury emission from FGD by UV irradiation.

More and more evidences indicated that the distribution, mobility, toxicity and biological availability of mercury were dependent on not only their total concentrations but also their fractions [20–23]. More reliable information about the behavior and risk of mercury in FGD gypsum can be obtained by speciation analysis. Therefore, it is important to identify the fractions of mercury in gypsum and to evaluate their possible transformation under various conditions. There were

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many reports about mercury release during thermal treatment of FGD gypsums [24–29]. However, few attempts were made to evaluate the role of UV radiation in mercury emission, especially the change of mercury fractions in gypsum. To the best of our knowledge, this may be the first report about the transformation of Hg fractions in FGD gypsum from coal fired power plant undergoing UV irradiation. Our research will be beneficial for the researches about mercury survey and re-emission of mercury in gypsum in the future.

2. Materials and methods

2.1. Sample collection and processing

FGD gypsum samples were collected from two coal fired power plants in Hebei province, China. The combustion units were pulverized coal furnaces. When the sampling was conducted, four sub-samples were collected in the same FGD gypsum storage at a time interval of 30 min and the sub-samples were merged together as one sample. 1.0 kg of gypsum was collected for each plant and the sample was immediately put into a polyethylene bag. The residue air in the bag was punched out and sealed after sampling. The collected samples were shipped to the lab as soon as possible. The received samples were frozen dried on receiving, and then milled to obtain the homogenized subsamples with a 80-mesh sieve. The pretreated samples were subjected to our following experimental procedures.

Total Hg contents were determined by digesting the gypsum samples in aqua regia (3:1 HCl:HNO₃). 0.1 g of sample and 12 mL of aqua regia were put into a PTFE container. After pre-digestion for 12 h at room temperature, the samples were heated at 60 °C in a water bath for 12 h. The digested sample was diluted to 50 mL with DI water after cooling down to room temperature. The solution was transferred into a centrifuge tube and centrifuged at 4000 rpm for 15 min. Total Hg in the supernatant was then determined. The contents of Hg in solvents or matrix were also determined before sample analysis and deducted from the contents of samples. Certified reference materials (CRM) (GBW-07405) were used to calculate the accuracy and precision of the method. The CRM was digested with the same digestion method for gypsum samples, and the total mercury was determined. The recovery was calculated from the ratio of the measured value to the reference value ($0.29 \pm 0.04 \mu\text{g g}^{-1}$) in CRM. In this study, the recoveries and precision were evaluated by measuring the same sample CRM for nine times on different days. The recoveries and RSD were calculated, respectively. The recoveries and precision (RSD) were listed in Table 1. The obtained recoveries ranged from 79.3% to 120.7% (n = 9). The detection limit (DL) of the instrument for Hg was 0.05 ng mL^{-1} . These results indicated that the analytical method was reliable and precise enough for our study.

2.2. UV irradiation procedure

UV lights were set inside separate chambers which were put in a well ventilated room. Four UV lamps with the frequency of 14 W, 24 W,

Table 1
Precision of the methodology (GBW-07,405).

	Value ($\mu\text{g g}^{-1}$)	Recovery (%)	Average (%)	SD	RSD (%)
The first day	0.28	96.6	103.4	12.1	11.7
	0.28	96.6			
	0.27	93.1			
	0.28	96.6			
	0.34	117.2			
	0.35	120.7			
The second day	0.25	86.2	82.8	3.4	4.1
	0.23	79.3			
	0.24	82.8			

36 W, 55 W were used in our study. 13.0 g gypsum sample was put in a glass petri dish, then put the dish under the UV lamp. To avoid the enhance of temperature caused by UV irradiation, the distance between UV lamp and sample was kept about 50 cm. In order to ensure the accuracy, 3 parallel samples were applied. Five conditions including UV14 W, 24 W, 36 W, 55 W irradiation and dark were applied in our experiment. 1.1 g sample was taken from each dish after 24 h. 0.1 g of the taken sample was digested for the determination of total mercury. Another 1.0 g of sample was used for the speciation analysis of mercury with sequential extraction procedure. The residual sample was then put into the petri dish again to continue the exposure experiment under the supposed conditions. Hg concentration was measured every day, while the Hg speciation analysis was recorded in every 5 days during 10 days exposure (Fig. 1).

2.3. Sequential extraction of various fractions of mercury in FGD gypsum

A modified five-step sequential extraction procedure was employed to identify Hg fractions in FGD gypsum samples (Table 2). The procedure classified the fractions of Hg in gypsum as water soluble fraction (F1), ion-exchangeable fraction (F2), acid soluble fraction (F3), elemental fraction (F4), and sulfide fraction (F5).

1.0 g of gypsum sample was taken for the extraction procedure. 20.0 mL of deionized water was added into the centrifuge tube and shaken on an end to end shaker at 300 rpm at room temperature. The extraction was then centrifuged at 4000 rpm for 15 min and the supernatant was removed with a pipette. 5.0 mL of DI water was refilled into the residue pellet and vortexed vigorously for 3 min to resuspend the solid residue. The extraction vials were re-centrifuged and rinsed. The rinse solution was combined with the extract from the same sample and diluted to 25 mL with deionized water. After each extraction step, the extract was centrifuged, filtered through a $0.45 \mu\text{m}$ nylon filters and stored at 4 °C before determination. The solid residue from each step was subjected to the next extraction step by adding the corresponding solvent.

The extraction was carried out in triplicates for each step per sample. To minimize the contamination from the matrix, the background content of Hg in each extraction solvent was also determined and deducted. Quality control of the method was assessed by comparing the sum of Hg extracted in steps 1–5 with total Hg from a single extraction with aqua regia. The flow chart of the whole process was shown in Fig. 2.

2.4. Instruments and reagents

The gypsum samples were characterized using X-ray diffraction (XRD, D/Max-2550 pc, Rigaku Inc., Japan) with a CuK α radiation at a scanning rate of 8° min^{-1} in the 2θ range from 10° to 80° . Hg contents in solution were detected by a cold-vapour atomic fluorescence mercury analyzer (Suzhou Qing An Instrument Co., China). Four UV lamps ($\lambda = 254 \text{ nm}$, UV-C) with the frequency of 14 W, 24 W, 36 W, 55 W were used in our study. Deionized (DI) water was supplied by EASY pure LF System ($18.2 \text{ M}\Omega$) (Barnstead Thermolyne, USA). Hg standard solutions were prepared by dilution in deionized water from the Hg stock solution (National Standard Material Research Center, P.R. China). Glasses and plastic containers were soaked in 50% HNO₃ (V/V) and 10% HNO₃ (V/V) for at least 24 h, respectively, and the containers were rinsed with deionized water three times before use to avoid Hg contamination. The extracts were stored in plastic tubes in dark and cool conditions (4 °C) before analysis. In order to minimize Hg contamination from solvent matrix, all of the reagents used in our experiment were analytical grade or better and the background contents of mercury were checked before use.

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