Full Length Article

Mercury fractions in gypsum and estimation of mercury emission from coal-fired power plants

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ABSTRACT

With continuing improvements in the efficiencies of the flue gas pollution control devices, a greater proportion of mercury emitted from coal fired power plants is in the recovered byproducts, such as fly ash and desulfurization gypsum. The leaching ability and bioavailability of mercury are related with its speciation and finally determine the total emission of mercury from power plants. Therefore, it is important to understand the speciation of mercury in the byproducts. In this study, mercury in the gypsum samples from eleven power plants in Hebei Province, China was determined in five sequential extracts representing fractionation of mercury species, namely water soluble fraction (WS, F1), ion-exchangeable fraction (IE, F2), acid soluble fraction (AS, F3), elemental fraction (EF, F4) and sulfide fraction (SF, F5). The leaching ability and the distribution of mercury in the various fractions from different power plants were examined. The results showed that mercury was dominantly in elemental fraction, and the leaching ability as well as the fraction distribution of mercury varied with samples from different power plants. The rapid release and releasable mercury in gypsum which shouldn't be overlooked were taken into account for the estimation of mercury emission from coal fired power plants. Three models, including Mass Balance model (MB), Emission modification factors model (EMF) and Flue calculation model (FC), were also employed to estimate the possible mercury emission from flue gas in these studied power plants. A comparison of the results from the different models indicated variability among the different models. The mercury re-emission from gypsum to the environment is needed to address the important issue of further improvement of these models for estimation of mercury emission.

1. Introduction

Coal-fired power plant is not only the largest coal consumer but also an primary pollution source of anthropogenic mercury emission [1–4]. Much current research has concerned about atmospheric mercury emission from coal combustion processes [5]. With the improvement of the efficiencies of electrostatic precipitator (ESP), wet flue gas desulfurization (WFGD) and other flue gas pollution control devices, the mercury emission through flue gas can be significantly reduced in coal-fired power plants. As a consequence, relatively more mercury can end up in the byproducts of coal combustion and in pollution control devices. For example, the recovered mercury is usually captured by oxides and minerals in fly ash or gypsum. The mercury remained in these byproducts from coal-fired power plants are normally much higher than that exhausted from flue gas [6]. Mercury in these byproducts could be present in various chemical forms, and some mercury species could be released into the environment [7–10], which could cause secondary pollution. It is more serious that mercury in these byproducts can be directly released out during the beneficial utilization processes of fly ash or gypsum such like brick making, concrete processing or plasterboard processing. The amount of mercury re-emission during these processes was estimated as about 33% of the total amount of mercury emitted from coal-fired power plants through flue gas [1].

Because of the complex process of mercury release from coal combustion, the instantaneous change of mercury emission in flue gas is severe, and it is very difficult to measure the exact contents of mercury in flue gas. In order to save costs, many researchers used theory models to estimate gaseous mercury output from plants. There are three models including Mass Balance model (MB), Emission modification factors model (EMF) and Flue calculation model (FC) normally used [1,6,8–23]. Here, we applied these three models to estimate the possible emission of mercury from the power plants through gas flue and to evaluate the proportion of the leachable mercury in gypsum to the emitted gaseous mercury. Considering the possible variability of the

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results from the different models, the estimation results from these three models were compared and discussed. Much research about estimation of mercury emission didn't take the re-release of mercury from the by-products into account, which may lead to underestimate the mercury emission from power plants. While, the amount of mercury transferred into desulfurization gypsum accounts for about 24.5% of the total input in coal-fired power plants in China, and the mercury in gypsum could be re-released under natural conditions. Gustin [24] pointed out that the exposure conditions of flue gas desulfurization (FGD) materials could affect the mercury emissions from FGD. Shock [25] also found that the release potential of mercury in desulfurization gypsum was significant. The release ability of mercury significantly related with mercury species or fractions in FGD gypsum. Therefore, it is very necessary to quantify and identify the species or fractions of mercury in FGD gypsum and take these fractions into account for the estimation of mercury emission from coal fired power plants.

In this paper, the morphologies of desulfurization gypsum from eleven power plants in Hebei Province were characterized and the fractions of mercury in these desulfurization gypsum samples were examined using a modified five-step sequential chemical extraction method (SCE). The quantity of mercury in the labile fractions, which are ready to be released into the environment, was assessed. Three models were employed to estimate the amounts of possible emission of mercury in these power plants. The results from the different models were compared with each other. This study will provide us an important hint to quantify mercury re-release in FGD gypsum and develop more suitable models to estimate mercury emission from coal fired power plants. Our results will also be beneficial for the safe disposal of gypsum in the future.

2. Materials and methods

2.1. Sample collection and processing

The FGD gypsum samples used in this study were collected from eleven coal fired power plants in Hebei province, China (Fig. 1). There are eleven cities in Hebei Province and we collected the samples from the power plant in each city. The power plants were equipped with the different air pollution control devices (APCD) including electrostatic precipitator (ESP), wet desulfurization device (WFGD) and selective catalytic reduction (SCR). As for convenience, the studied power plants were numbered as A-K. The samples (coal, slag, fly ash and the desulfurization gypsum) were collected under full load operation conditions. The coal samples were collected from the coal conveying belt which deliver the well mixed coal into the burning furnace. The slag samples were collected from slag pit. The fly ash samples were collected from ESP sampling position. The FGD gypsum samples were collected from the gypsum storage. In order to ensure the continuity, the coal ash, slag and gypsum samples were successively collected at a time interval of 30 min. 5.0 kg of the material were collected for each sample. All of the samples were collected in June 2015. Power plant K didn't have desulfurization equipment at that time. Therefore, we didn't collect gypsum sample at Plant K.

The collected sample was put into a polyethylene bag immediately. Then the residue air in the bag was punched out and sealed before shipping to the lab. The samples were frozen dried when they were received. The dried samples were then milled and split until the homogenized samples were obtained with a particle diameter of 80-mesh.

2.2. Instruments and reagents

The structures of the gypsum samples were characterized using X-ray diffraction (XRD, D/Max-2550 pc, Rigaku Inc., Japan) with a CuKa radiation at a scanning rate of 8°/min in a 2θ range from 10° to 80°. The Hg content in solution was detected by a cold vapor atomic
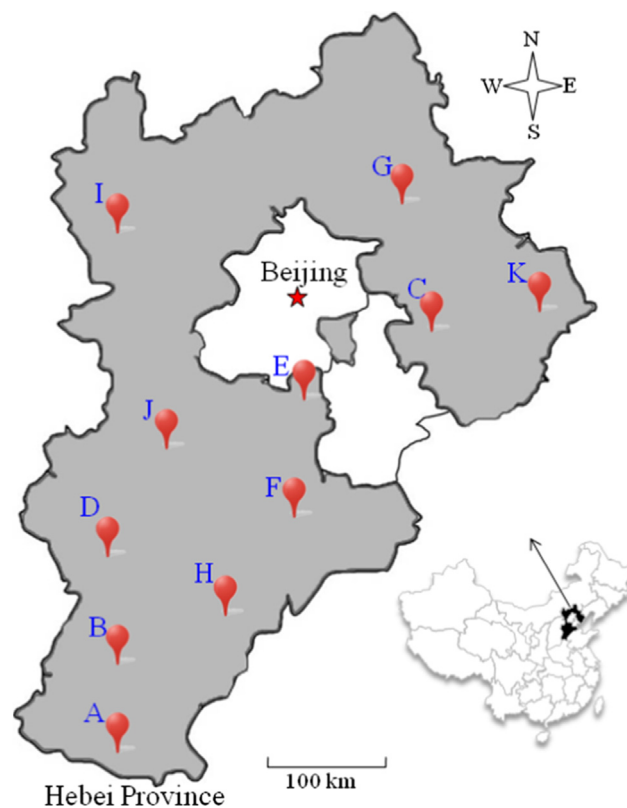

Fig. 1. Gypsum sampling sites.

fluorescence mercury analyzer (Suzhou QingAn Instrument Co., China).

Deionized (DI) water was supplied by EASY pure LF System (18.2 MΩ) (Barnstead Thermolyne, USA). Hg standard solutions were prepared in deionized water from a Hg stock solution (National Standard Material Research Center, P. R. China). Glass and plastic containers were soaked in 50% HNO_3 (V/V) and 10% HNO_3 (V/V), respectively, for at least 24 h and 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 case of Hg contamination from the solvent matrix, all of the reagents used in our experiment were analytical grade or better and the background values of mercury were checked.

2.3. Total mercury

The total contents of mercury in the gypsum samples (or other samples) were determined after digestion with aqua regia (3:1 HCl: HNO_3). 0.1 g of sample and 12.0 mL of aqua regia were put into a PTFE container. In order to make the samples to be totally digested, the gypsum samples were pre-digested with aqua regia for 12 h at room temperature. After pre-digestion, the samples were then heated at 60 °C in a water bath for another 12 h. The digested sample was diluted to 50 mL with DI water after cooling down to the 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 content of Hg in solvent or matrix was also determined before sample analysis and deducted from the content of sample. A standard reference material (SRM) (GBW-07405) was used to control the accuracy and precision of the analytical procedure. The obtained recoveries of mercury (the ratio of the measured total mercury contents to the certified value, $0.29 \pm 0.04 \, \mu g \cdot g^{-1}$) ranged from 80% to 120% (n = 3). The detection limit (DL) of the instrument for Hg was 0.05 ng/mL. These results indicated that the analytical method was reliable and precise enough for our study.