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Mercury Speciation of Flue Gas Desulphurization By-Products in Coal-Fired Power Plants in China

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Abstract

The aim of this study was to develop and examine the morphology and distribution of mercury (Hg) in flue gas desulfurization (FGD) by-product. Mercury in the coal of coal-fired power plants is concentrated in the by-products of desulfurization process, and it is widely used as an additive in cement, building materials and other industries. Due to the different stability of various forms of mercury in the environment, subsequent use of products containing desulfurization by-product additives will continue to be released into the environment, endangering human health. Therefore, it is very necessary to study the form and distribution of mercury in the by-products of desulfurization in coal-fired power plants to provide a theoretical basis for subsequent harmless treatment. For content and morphology of mercury analysis, 1 sample of dry FGD ash and 6 samples of wet FGD gypsum were analyzed. The total 7 samples were extracted using a modification of sequential chemical extractions (SCE) method, which was employed for the partitioning Hg into four fractions: water soluble, acid soluble, H_2O_2 soluble, and residual. The Hg analysis was done with United States Environmental Protection Agency (USEPA) method 7471B. Comparing with the wet FGD gypsums of coal-fired boilers, the total Hg content in the dry FGD by-product was as high as 1.22 mg/kg, while the total Hg content in the FGD gypsum is 0.23 - 0.74 mg/kg, which was 2 times over the wet FGD gypsum. The concentration of water soluble Hg in the dry FGD by-product was the highest amount (0.72 mg/kg), accounting for 59.02% of the total mercury. While residual Hg content was 0.16 mg/kg, only about 13.11% of the total mercury. Mercury content in FGD gypsum was expressed in the form of ρ (residual Hg) > ρ (H_2O_2 soluble Hg) > ρ (water soluble Hg) > ρ (acid soluble Hg). The morphology and distribution of mercury in FGD by-products is supposed to be analyzed before utilization, and the impact of mercury on the environment should be considered.

Keywords

Mercury, Mercury Speciation, Flue Gas, Desulphurization, By-Product, Sequential Chemical Extractions, Morphology and Distribution, Gypsum

1. Introduction

Mercury (Hg) is highly toxic, highly volatile, and easy to be enriched in organisms to cause the disease of persistent environmental pollutants [1] [2] [3] [4]. Coal-fired power plants are the main cause of atmospheric mercury emissions in China, which ranks in the top two of the world's most substantial contributors [5]. Hg removal is achieved in the main through dust removal, flue gas desulfurization (FGD), and flue gas denitrification equipments [6]. FGD processes are mainly classified as dry desulfurization and wet desulfurization, and the by-products are FGD ash and FGD gypsum accordingly. Both can be used as cement additives, road construction material and for soil improvement [7]. The mercury in the process of resource utilization may be released into the environment, which will cause environmental pollution [8]. Evaluation of the mercury speciations and predicting its potential impact on the environment is critical in the disposal of FGD by-products.

Desulfurized fly ash includes fly ash, $CaSO_4$, $CaSO_3$ and unreacted desulfurizer [9]. Mercury exists in desulfurized fly ash in four states: 1) chloride, nitrate and sulfate existing in a water soluble state easily enters water body or soil during the stacking process and generates secondary pollution; 2) carbonate and HgO, which cannot dissolve directly in water, but can dissolve in acidic conditions, causing secondary pollution to water or soil during acid rain or under other acidic conditions; 3) elemental mercury absorbed by fly ash or lime is not easily soluble in water, but will be released into the air during long-term stacking; and 4) inert mercury, lattice mercury, etc., mainly mercuric sulfide, are relatively stable in nature and are unlikely to be released or dissolve. They have the least impact on the environment.

Many studies have been carried on coal-fired FGD technology, yet there are fewer examinations of mercury's environmental stability in desulfurization by-products. Mercury in desulfurization by-products may be again released into the environment during stacking, dumping or comprehensive utilization and other disposal processes which are often used in dry process desulfurized fly ash. Secondary pollution is then caused. Therefore, studying the distribution of mercury speciation in desulfurized fly ash offers crucial guidance for assessing the migration and change of mercury in desulfurized fly ash in the natural gaseous and aqueous environment. It also facilitates an appraisal of the mercury pollution effect that may be generated from the method of solid waste disposal and comprehensive utilization, and finally realize harmless treatment of desulfurized fly ash.

This study conducted experiments to extract mercury compounds from the seven solid samples, with the efforts to developed methods for specifying mercury in mercury-contaminated FGD residues.

2. Methodology

2.1. FGD By-Products Samples

Samples obtained of dry FGD by-products and wet FGD from 7 coal combustion power plants. The 6 FGD gypsum samples were collected from vacuum belts of the FGD system, and the other 1 sample of dry FGD ash samples was collected from the fabric filters.

2.2. Sequential Chemical Extractions Method

The total Hg was a poor indicator of the toxicological and environmental hazard associated with FGD residues, the sequential chemical extractions (SCE) [10] method was developed to separate mercury compounds of FGD by-products into 4 compound classes. Which were water soluble (mercuric chloride, mercuric nitrate and mercuric sulfate) Hg, acid soluble (mercuric carbonate and mercuric oxide) Hg, H_2O_2 soluble (elemental mercury and organic mercury) Hg, and residual (with mercury sulfide and crystalloid based inert mercury) Hg. And deionized water, 20 mol/L HCl, 30% H_2O_2 solution, and nitrohydrochloric acid were employed as extractants, respectively.

The Hg determination of the SCE extracts was conducted with United States Environmental Protection Agency (USEPA) method 200.7.

The phase state analysis method of mercury in bottom mud and continuous chemical progressive method are referred to for samples of desulfurized gypsum to conduct pretreatment [11] [12], SCE is used to extract leaching solutions for different steps, and US EPA Method 200.7 is also adopted [13] [14], Please refer to Table 1 for the specific analytical steps.

2.3. Analysis Methods and the Detection Limit

Several spectral lines suitable for mercury determination are initially selected via instrument recommendation and with reference to a wavelength table. The spectral line with low background, limited interference and a high signal to noise ratio is taken as analytical spectral line 253.652 nm based on element interference. Hydride generation, inductive coupling and other ion emission spectrum (HG-ICP-AES) are used collectively to test blank solutions a total of 15 times in a way that is both separate and parallel. Mercury detection limit is calculated by using the results as follows:

$$C_L = \frac{KS_b}{S} = \frac{3S_b}{S}$$

where, S—Sensitivity of the method;

S_b—Standard deviation of blank measurement;

K—The parameters were selected according to the requirement of confidence in the minimum value, rational value accepted 3.

The detection limit of element mercury is 0.14 ng/ml. The method sets up the standard curve according to the content range of mercury in samples, and the linearly dependent coefficient of the standard curve of mercury (r) is ≥0.999.

2.4. Accuracy Control Method

The analytical performance of the HG-ICP-AES method established for verification concerning element mercury under different phase states ensures the accuracy of the measurement result. Computerized tests are conducted separately after diluting the standard solutions of mercury (1000 μg/ml). The outcome shows that the measurement result of the method falls within the range of standard value (refer to **Table 2**).

Table 1. The sequential chemical extractions procedure.

Steps		Solid Samples	Liquid Sample
	Take 30 g samples respectively, dry under 105˚C, and seal for analysis.		
A	Extraction method of water-soluble mercury A. Take 10 g sample of desulfurized fly ash and add it to 200 ml deionized water, mix and shock for 30 min under constant temperature, keep static for 2 h, filtrate and separate residue and filter liquor. The Ay of filter liquor is to be measured.	Residue drying	**Ay**
B	Extraction method of acid-soluble mercury B. To add residue of A to 150 ml 20 mol/L HCI, shake drastically, set down for 5 min and add it to 10 ml 1% of $CuSO_4$ solution, mix and shock for 30 min under constant temperature, keep static for 2 h, filtrate and separate residue and filter liquor. The By of filter liquor is to be measured.	Residue drying	**By**
C	Extraction method of hydrogen peroxide mercury C. To add residue of B to 100 ml 30% of H_2O_2, add 10 ml concentrated HCI, keep static for 8 h, filtrate and separate residue and filter liquor. The Cy of filter liquor is to be measured.	Residue drying	**Cy**
D	Extraction method of lattice mercury D. To add residue of C to 40 ml aqua regia, keep it digested for 8 h, filtrate and separate residue and filter liquor. The Dy of filter liquor is to be measured.		**Dy**

Table 2. Analysis of the HG-ICP-AES measurement.

Element	Standard value (μg/ml)	Standard uncertainty	HG-ICP-AES (μg/ml)
Mercury	1.20	0.08	1.11
	2.31	0.21	2.07

3. Results and Discussion

3.1. Analysis of the FGD Processes and the By-Products

Figure 1 is the dry FGD process diagram. Flue gas and desulfurizer are mixed in the thionizer by spraying in desulfurizer seriflux or desulfurizer and spray [15] [16], so as to realize FGD in the thionizer. Desulfurized by-products collected by bag filter still contain a certain amount of unreacted desulfurizer which enters the thionizer through circulation, ensuring the full reaction between SO_2 in flue gas and desulfurizer. Adhered to the surface of the bag is desulfurizer which is not fully reacted. SO_2 in flue gas continues to react with desulfurizer on the surface of the bag. This significantly prolongs the reaction duration and improves the utilization factor and desulfurization efficiency of desulfurizer.

Figure 2 shows the typical limestone-gypsum wet FGD process. To achieve higher desulfurization efficiency, wet FGD is used by taking limestone as desulfurizer. Flue gas enters the double circulation absorption tower and is purified after reacting with limestone via two series-wound circulation and washing process. The two circulations of flue gas washing area are Quench circulation (first-level circulation) and Absorber circulation (second-level circulation). Flue gas enters the second-level circulation and washing area and is washed again by high pH seriflux after it is washed by low pH seriflux in the first-level washing area, so that the emission concentration of SO_2 in flue gas is lower than 35 mg/m^3. Spray serifluxes of different pH values are stored in the stock chest of the absorption tower and Absorber Feed Tank (AFT), respectively. The seriflux in the stock chest of the absorption tower is low pH value, and that of AFT is high pH value.

3.2. Total Mercury Contents Analysis for FGD By-Products

Figure 3 is the contents of total Hg in the dry FGD by-products and wet FGD gypsum. Compared with the fly ash, the contents of total Hg in the dry FGD ash is 1.22 mg/kg, while the content of total Hg in the wet FGD gypsum is 0.23 - 0.74 mg/kg, which is about 3 times of the content of total Hg in the FGD gypsum.

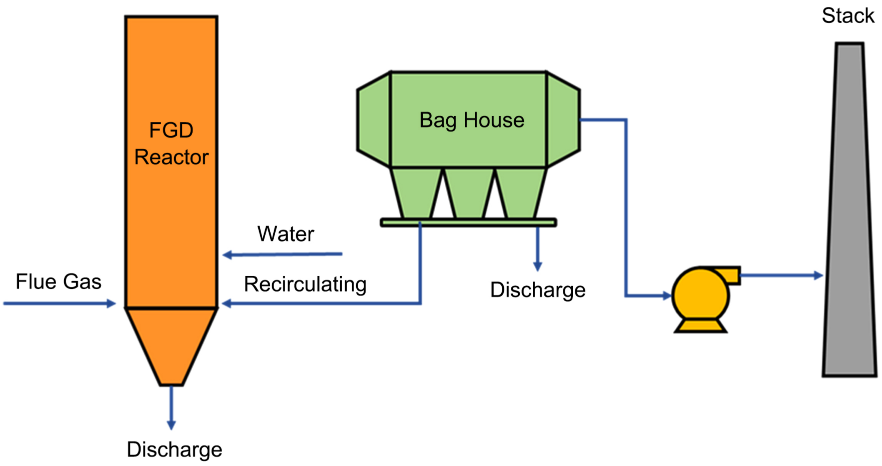

Figure 1. Dry FGD process diagram.

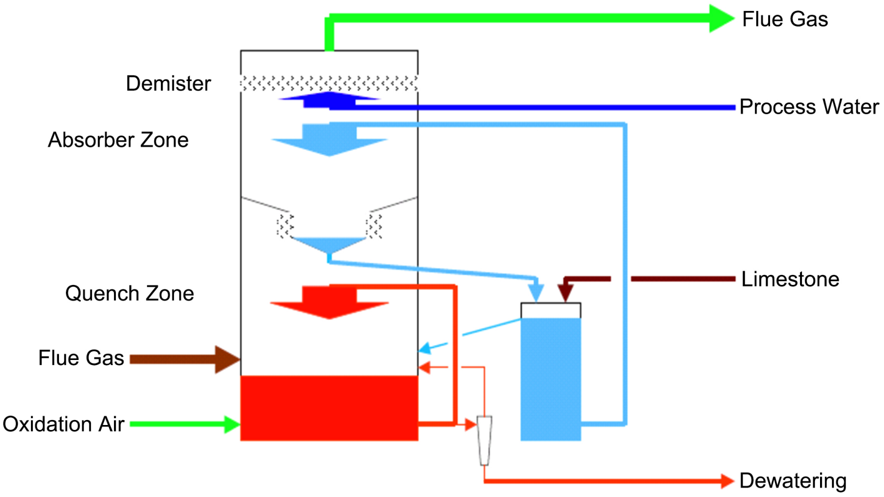

Figure 2. Wet FGD process diagram.

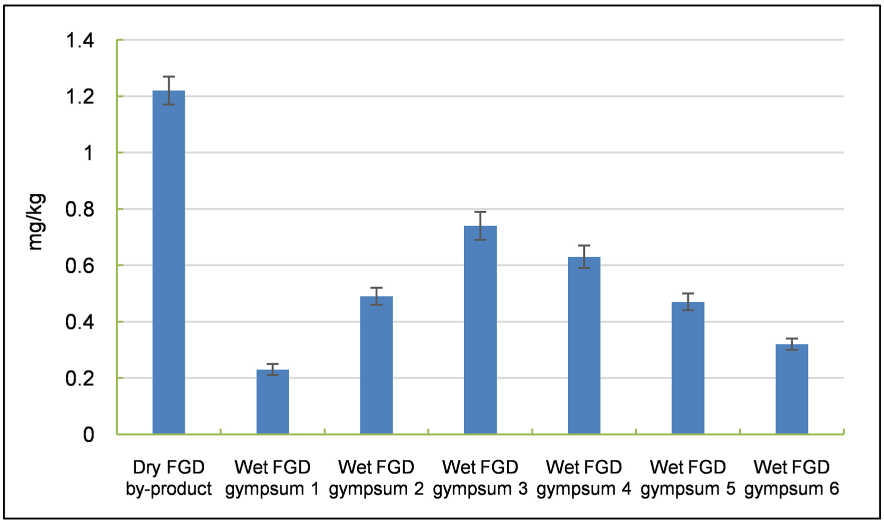

Figure 3. The contents of total Hg in the dry FGD by-products and wet FGD gypsum.

Due to the low temperature of flue gas in the bag filter, the desulfurization ash adheres to the surface of the bag, which prolongs the contact adsorption time of fly ash and lime desulfurizer with mercury vapor, which is conducive to the physical and chemical adsorption of mercury vapor by desulfurization ash, as more Hg can be adsorbed by the dust collector than that of the wet FGD process.

Figure 4 and Figure 5 are the Scanning Electron Microscope (SEM) images of dry and wet FGD by-products. After comparison, it's found that dry FGD by-product has more micropores on the surface, which is conducive to improving the mercury absorption action. Circulated desulfurized fly ash and desulfurizer have larger specific surface area and stronger absorption capacity of mercury vapor. Meanwhile, desulfurized fly ash particles bind to the surface of the bag, extending the absorption time of desulfurizer of mercury vapor. Mercury vapor changes to granular mercury collected by the bag filter, which helps collect most of the granular mercury [17].

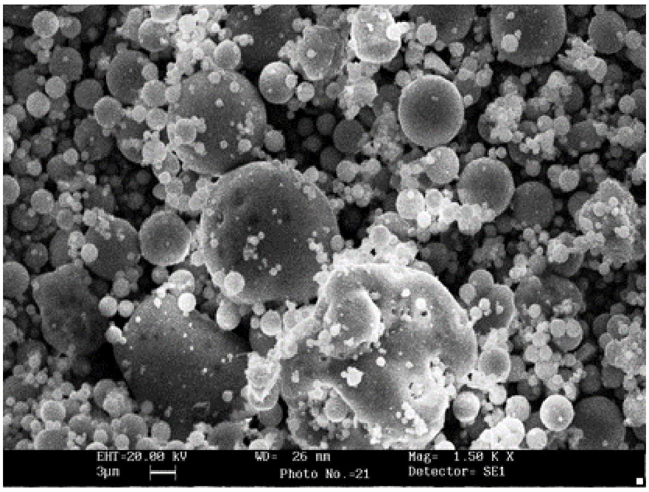

Figure 4. SEM image of dry FGD by-product.

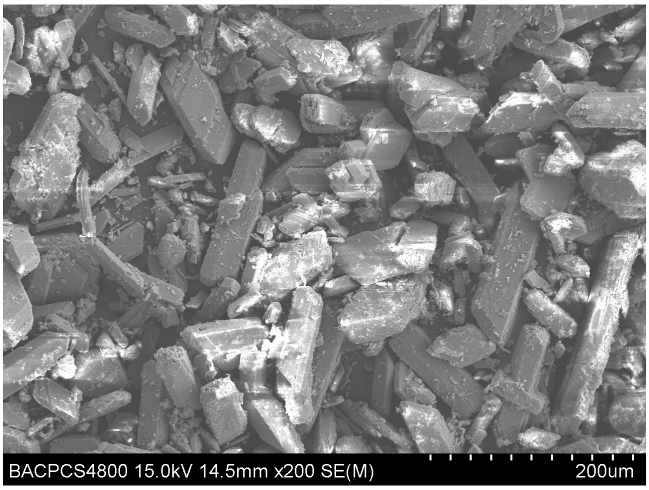

Figure 5. SEM image of wet FGD gypsum.

3.3. The Mercury Speciation Content in FGD By-Products

Table 3 and Table 4 show the distribution and percentage contents of different forms of mercury in the FGD by-products, respectively.

The concentration of water soluble Hg in the dry FGD by-product was the highest amount of 0.72 mg/kg, accounting for 59.02% of the total mercury. while residual Hg content was 0.16 mg/kg, only about 13.11% of the total mercury.

The contents of water-soluble mercury and H_2O_2 mercury in dry FGD by-products are clearly higher than other samples. This is in the main determined by the element of mercury vapor in flue gas. Mercury vapor in flue gas primarily exists in the forms of Hg_g^0 and Hg_g^{2+}, including around 20% - 50% of Hg_g^0 and 50% - 80% of Hg_g^{2+} [18]. As the temperature of flue gas in the bag filter is low, desulfurized fly ash adheres to the surface of bag, extending the contact and absorption time of fly ash and lime desulfurizer with mercury vapor. This aids the physical and chemical absorption of desulfurized fly ash of mercury vapor and enables the bag filter to absorb more Hg_g^0 and Hg_g^{2+}.

Table 3. Mercury speciation of the FGD by-product samples.

Samples	Water soluble Hg (mg/kg)	Acid soluble Hg (mg/kg)	H_2O_2 soluble Hg (mg/kg)	Residual Hg (mg/kg)	Total Hg (mg/kg)
Dry FGD by-product	0.72	0.14	0.20	0.16	1.22
Wet FGD gypsum 1	0.03	0.01	0.08	0.11	0.23
Wet FGD gypsum 1	0.09	0.06	0.21	0.16	0.52
Wet FGD gypsum 2	0.15	0.10	0.22	0.27	0.74
Wet FGD gypsum 3	0.17	0.12	0.19	0.20	0.68
Wet FGD gypsum 4	0.09	0.06	0.18	0.16	0.49
Wet FGD gypsum 5	0.04	0.02	0.08	0.12	0.26

Table 4. Percentage of the mercury speciation.

Samples	Water soluble Hg (%)	Acid soluble Hg (%)	H_2O_2 soluble Hg (%)	Residual Hg (%)
Dry FGD by-product	59.02	11.48	16.39	13.11
Wet FGD gypsum 1	13.04	4.35	34.78	47.83
Wet FGD gypsum 1	17.31	11.54	40.38	30.77
Wet FGD gypsum 2	20.27	13.51	29.73	36.49
Wet FGD gypsum 3	25.00	17.65	27.94	29.41
Wet FGD gypsum 4	18.37	12.24	36.73	32.65
Wet FGD gypsum 5	15.38	7.69	30.77	46.15

The Hg content in the wet FGD gypsum is expressed in the form of water soluble Hg (0.03 - 0.17 mg/kg), acid soluble Hg (0.01 - 0.12 mg/kg), hydrogen peroxide soluble Hg (0.08 - 0.22 mg/kg), and the residual Hg (0.11 - 0.27 mg/kg), which cover the percentages of 13.04% - 25.00%, 4.35% - 17.65%, 27.94% - 40.38%, and 29.41% - 47.83 %, respectively. Mercury content in wet FGD gypsum was expressed in the form of ρ (residual Hg) > ρ (H_2O_2 soluble Hg) > ρ (water soluble Hg) > ρ (acid soluble Hg).

Mercury in wet desulfurization gypsum mostly exists in the forms of H_2O_2 soluble and Residual, accounting for 70.61% of total mercury on average. Compared with dry FGD by-products, mercury in the two forms only accounts for 29.50% of total mercury. This is mainly because spraying desulfurized seriflux in the wet desulfurization process can absorb divalent mercury compounds in flue gas. Relatively smaller amounts of water-soluble mercury and acid-soluble mercury enter desulfurized gypsum through crystallization as the content of mercury compounds in flue gas is also relatively lower.

In the meantime, the fly ash in flue gas enters desulfurized seriflux and enriches through repeated desulfurized seriflux circulation under wet FGD process [19], as shown in **Figure 4**. Fly ash mercury may be attached to the surface of microsphere or micelle in the form of zero-valent simple substance, and some mercury may replace other metallic elements with divalent combined state and combine in lattice, such as HgS. Therefore, most mercury is mainly contained in particles in wet desulfurized gypsum and, at the same time, particles have more lattice mercury.

4. Conclusions

The stability and potential impact on environment of Hg should be taken into account regarding the utilization of the solid by-products from the coal-fired power plants, especially for the FGD by-products.

It was assumed that the wet FGD gypsum was safer in utilization, since the total Hg concentration was about 0.23 - 0.74 mg/kg, composing mainly the inert mercury, including the H_2O_2 soluble mercury and the residual mercury. While the total Hg concentration of dry FGD by-product was much higher than that of wet FGD gypsum, which is as high as 1.22 mg/kg.

Because the retention time of dry FGD is much longer in FGD reactor and the baghouse, the content of water soluble Hg is over 0.72 mg/kg, which is mainly accumulated with mercuric chloride, mercuric nitrate and mercuric sulfate from the flue gas, covering the percentage of 59.02% correspondently. The dry FGD residual is mainly composed of large particles of FGD agent settled down by the FGD equipment or the fabric filters, and the residual Hg concentration is 0.16 mg/kg, which accounts only 13.11% of the total mercury.

The Hg content in the FGD gypsum is expressed in the form of water soluble Hg (0.03 - 0.17 mg/kg) > acid soluble Hg (0.01 - 0.12 mg/kg) > hydrogen peroxide soluble Hg (0.08 - 0.22 mg/kg) > residual Hg (0.11 - 0.27 mg/kg), which cover the percentages of 13.04% - 25.00%, 4.35% - 17.65%, 27.94% - 40.38%, and 29.41% - 47.83%, respectively.

In wet desulfurization gypsums, mercury mostly exists in the states of H_2O_2 soluble and Residual, accounting for 70.61% of total mercury on average. Compared to dry FGD by-products, mercury in the two forms only accounts for 29.50% of total mercury.

This study proposes a detection method for the form and distribution of mercury in the desulfurization by-products of coal-fired power plants, which provides strong support for the subsequent research on the harmlessness of desulfurization by-products.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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