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Full Length Article

Feature changes of mercury during the carbonation of FGD gypsum from different sources

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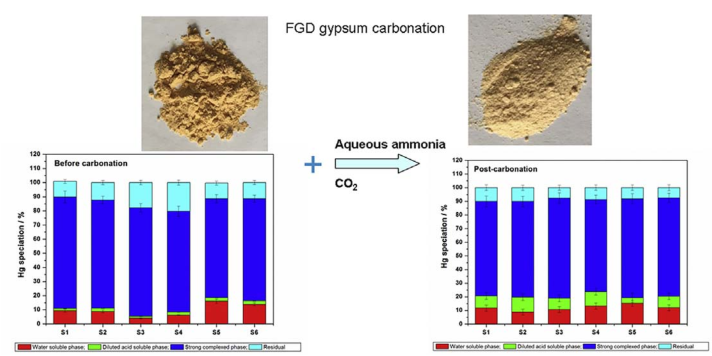
GRAPHICAL ABSTRACT



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ABSTRACT

Flue gas desulfurization gypsum (FGDG), as byproducts in power plants, is produced in large quantities. A novel technology to recycle FGDG in carbonation process has recently been found. However, the potential hazards to human health and to environment originated from heavy metals residual in FGDG have to be considered in the recycled process. In this study, six FGDG samples (denoted as S1-S6) from coal-fired power plants equipped with different FGD configurations were collected. Heavy metal contents in six original FGDG samples and in their corresponding solid products after carbonation were determined by ICP-OES and cold vapor atomic fluorescence spectrometer (CVAFS). As one of toxic heavy metals present in FGDG, Hg speciation variations induced by the carbonation process were focused on and they were confirmed by means of sequential chemical extraction (SCE) method. Original FGDG samples from six sources and their post-carbonation samples have different distribution of heavy metals, due to their FGD processes applied and byproduct compositions as well. Hg contents in all original FGDG samples exceed the 2nd grade of the Chinese National Standard (1 ug g^{-1}), and a decrease in Hg contents for samples from WFGD process can be observed in their post-carbonation. Formation of carbonates and ammonia complex were responsible for the Hg speciation variations.

1. Introduction

Calcium-based flue gas desulfurization (FGD) process has been widely applied as one of commercial processes for SO_2 emission reduction. The byproduct FGD gypsum (FGDG) from calcium-based FGD process is generated in large quantities, but the quality requirements of FGDG heavily hinder its commercialization. In China, the production growth of FGDG has boosted tenfold in the recent decade,

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close to 80 Mt/a [1]. The disposal of the FGDG becomes a critical issue, and otherwise they have to be directed to the landfills for storage [2].

Recently, applications of FGDG recycle have been investigated. For example, FGDG can be used as an agricultural soil amendment, especially in improvement of saline-alkali soil [3,4]. However, some new problems appear since heavy metals originated from the fuel (i.e., coal) usually migrate together with flue gas and finally accumulate in FGD byproduct, including fly ash and gypsum. Unlike fly ash, which has been found to adsorb Hg from the air, FGD materials, typical gypsum, were found to release Hg to the air over time with the addition of water [5]. As a consequence, the potential risk of heavy metals occurs easily once they infiltrate into the soil or underground water, whatever in terms of FGDG recycle or disposal on the landfill [6,7]. The heavy metals distribution in the synthetic gypsum, as well as their removal, has become an attractive issue in very recent years. Vsévolod et. al. found that the leaching and solubility levels of heavy metals were very low when phosphogypsum (PG), which has similar composition and properties to the FGDG, was used to fabricate solid bricks [8]. Wang's impressive results on the saline-alkali soil amelioration with FGDG encouraged us to explore the potential utilization of FGDG in other fields [1].

Some groups including us proposed a method to recycle synthetic gypsum, which is converted into calcium carbonate and ammonium sulfate as valuable products in a simultaneous CO_2 sequestration process [9,10]. The whole reaction can be realized in NH_3(aq) media as formula (1) indicates:

$$CaSO_4{\cdot}2H_2\ O + CO_2 + 2NH_3(aq) \rightarrow (NH_4)_2SO_4 + CaCO_3 \downarrow + 2H_2O \tag{1}$$

As a novel method to recycle FGDG, many researchers report the factors influencing carbonation performances, and good performances for CO_2 sequestration and industrial grade products can be achieved simultaneously [9–11]. To our best knowledge, little attention has been paid on the fate of heavy metals during the FGDG carbonation process so far, while the product (e.g., carbonated materials) can be readily landfilled without the concern of contaminant leaching [11]. Complicated components, pH atmosphere in FGD slurry and management scenarios have significant impacts on the heavy metals (e.g., Hg) release [12] .The purpose of this study is exactly to explore the relationship between heavy metals content and other composition in FGDG from different sources, and to identify the features changes of heavy metals before and after carbonation in ammonia media.

2. Materials and methods

Six FGDG samples were collected from six coal-fired power plants equipped with various FGD configurations as Table 1 shows. The chemical composition determined by X-Rays Fluorescence (XRF) spectrometers are listed in Table 2. X-ray diffraction (XRD) was applied for structure determination of FGDG samples. According to the descriptions in previous literatures [13], microwave technique was adopted to digest all of FGDG samples on a 1000 W microwave digestion system (Milestone), and afterwards an inductively coupled plasma spectrometry (ICP-OES, Varian 720-ES) device was used to determine the contents of heavy metals, including Pb, Cu, Fe, Mn and Zn, in the original samples

Table 1
Chemical compositions of 6 FGDG samples (wt%).

	CaO	SO_3	Al_2O_3	Fe_2O_3	CuO	PbO	Cr_2O_3	CdO	Others
S1	72.71	25.96	–	0.88	0.028	–	0.082	0.056	0.28
S2	74.79	22.87	0.39	0.26	0.0004	0.029	0.075	0.025	1.56
S3	43.09	31.78	24.48	0.51	0.0086	0.012	0.067	–	0.052
S4	31.84	23.42	43.96	0.46	0.015	–	0.029	–	0.28
S5	63.81	34.97	–	0.61	0.014	–	0.0095	0.089	0.50
S6	62.70	35.36	–	1.62	0.044	–	0.11	–	0.17

and post-carbonation samples respectively. Determination of Hg and As were conducted on an online cold vapor atomic fluorescence spectrometer (CVAFS) mercury / arsenic analyzer (QM201C, Jingsheng Instrument Co., China). Before determining the heavy metals contents in the post-carbonation samples, the corresponding post-carbonation samples should be dried to achieve constant weight.

The heavy metals speciation present in the FGDG samples or their post-carbonation samples were quantitatively extracted by a modified sequential chemical extraction (SCE) procedure and then determined by CVAFS mercury / arsenic analyzer [14]. The Fig. 1 gives the SCE schematic diagram.

The small-scale carbonation experiment of FGDG was conducted in a three-necked flask, in which 500 ml ammonia solution and 50 g FGD samples were mixed into suspended slurry and then 99.99% CO_2 from gas cylinder was bubbled at a certain flow rate. The detail carbonation process can be found in Ref. [15].

3. Results and discussion

3.1. Calcium components in FGDG samples

Due to the inhibition effects of sulfite on the speciation of some heavy metals (e.g., Hg) [16], and adsorption effect of carbonate on heavy metals(e.g., Pd, Cd) [17], it is necessary to determine the calcium components in FGDG samples. Table 3 presents the calcium components in six FGDG samples, denoted respectively as calcium sulfate, calcium sulfite and calcium carbonate. For the sake of recycle, high quality FGDG byproducts with lower calcium sulfite and calcium carbonate content are desired [18].However, the difference in the ways the FGD products are oxidized causes to the content variations of calcium sulfite. Generally, a wet FGD scrubber without forced air oxidation will create the FGD product containing as much as 30–87% of S as sulfite [19]. In cases of S1, S3 and S4, the lower sulfite content and higher sulfate contents can be attributed to the wet FGD process with forced air oxidation applied. In contrast, the sulfate contents are lower than 85% in case of S2 and S5 (84.86% and 84.45%, respectively), which originate from the dry or semi-dry FGD process with poor oxidation effects [20]. On the other hand, higher carbonate contents, accounting for 6.92% and 12.42% in S2 and S5, are found. Excess carbonate present in FGDG indicates lower utilization efficiency for limestone. In dry or semi-dry FGD process, (e. g., NID or CFB), it is more difficult for calcium carbonate to be consumed sufficiently without non-aqueous phase.

3.2. Heavy metal contents in original FGDG and post-carbonation products

In this study, some major and trace elements, including Fe, Mn, Zn, Cu, Pb, As and Hg, were determined (Fig. 2a-g). The content ranges of Zn, Cu, Pb, As and Hg in all samples are respectively 2.42–15.83 ug g^{-1}, 1.73–21.31 ug g^{-1}, 0.36–1.20 ug g^{-1}, 3.32–11.28 ug g^{-1}, 2.78–5.79 ug g^{-1}. Zn, Cu and Pb in the FGDG samples are far below the 2nd grade of the Chinese National Standard (GB15618-1995), which is listed in Table 4. However, the As contents in six samples are close to the Standard limits and notably Hg contents in all samples even exceed the Standard limits. The contents of Hg and As in FGD products are strongly dependent on the flue gas purification process adopted. The Hg content in S4 is 5.79 ug g^{-1}, five times more than the second grade of Standard. The highest Hg content in S4 is associated with the WFGD process, in which only oxidized mercury can be removed but Hg^0 can't be. Even in some cases, complicated reactions of Hg reduction in slurry containing various ions (e.g., sulfite), still contribute to the high Hg contents in the residues [21]. Dry FGD process (e.g., NID or CFB) seems to be favorable for Hg hold, because its solid products have high capacity to adsorb Hg^0 and Hg^{2+} [22]. Therefore, in spite of positive effects of FGD on removal of heavy metals in flue gas, a portion of heavy metals are still incorporated into the FGD residues or solid