



Full Length Article

Mercury stability of byproducts from wet flue gas desulfurization devices



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HIGHLIGHTS

- We investigated mercury release behaviors from gypsum when additives were used.
- The rates of mercury release under different calcination methods were acquired.
- TMT with slow-speed calcination had the best effect on inhibiting mercury emissions.
- Speciation of mercury in gypsum was obtained to explain mercury release behaviors.

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ABSTRACT

Mercury released from wet flue gas desulfurization (WFGD) devices can be inhibited by additives that can transfer mercury to its solid phase. However, the use of additives increases the mercury content in desulfurization gypsum, and the mercury is released again during the calcination process. In this study, NaHS, 2,4,6-trimercaptotiazine, trisodium salt nonahydrate ($\text{Na}_3(\text{C}_3\text{N}_3\text{S}_3) \cdot 9\text{H}_2\text{O}$, or TMT) and sodium dithiocarbamate (DTCR) were used as additives to control mercury emissions in simulated WFGD devices. Then, different calcination methods were adopted to study mercury release behaviors from calcination process. The transformation of mercury compound species on gypsum was also investigated to explain its behavior during calcination. The result showed that the mercury content in the solid phase increased significantly in the presence of additives. Among three additives, simulated desulfurization slurry with TMT had the highest trapping efficiency over mercury. The mercury thermal stability in gypsum increased in the order of using DTCR, TMT and NaHS. Due to the migration of mercury to the solid phase and the stronger thermal stability of resultants, the residual content of mercury in gypsum with additives after calcination were higher than that without additives. In general, using TMT coupled with slow-speed calcination had the best effect on controlling mercury contamination from WFGD slurry and WFGD byproducts. Moreover, it was verified by temperature programmed decomposition experiments that, after using NaHS, TMT and DTCR, the mercury compound in the gypsum was mainly in the form of HgS , $\text{Hg}_3(\text{TMT})_2$, $\text{Hg}(\text{DTCR})_2$, respectively, which explained the mercury release behaviors during calcination.

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1. Introduction

Mercury is one of the most pernicious heavy metal elements in the environment because of its high toxicity, long range transport, persistence and bioaccumulation [1]. In recent years, mercury contamination has increased considerably due to the rapid economic growth with insufficient environmental awareness [2]. Human

activities are responsible for the mercury pollution and worldwide mercury emissions from human activities accounts for 30–55% of global atmospheric mercury emissions [3]. Coal-fired power plants are the primary sources of anthropogenic mercury discharge in China [4]. Currently, some effective strategies such as electrostatic precipitator (ESP), fabric filter (FF) and wet flue gas desulfurization (WFGD) has been adopted to synergistically remove some particulate mercury (Hg^p) and oxidized mercury (Hg^{2+}) from flue gas [5–7]. Compared with Hg^p and Hg^{2+} , element mercury (Hg^0) is less soluble, high volatile and it can hardly be captured by above equipment. Nevertheless, selective catalytic reduction (SCR) devices can enhance the oxidation of Hg^0 to Hg^{2+} which will be typically

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removed by WFGD systems. Withum found that the mercury removal efficiency (on a coal-feed basis) increased to 90% from 50% to 75% when SCR units are applied in coal-fired power plants [8]. In order to reduce the emission of NO_x, most of the coal-fired power plants in China were recently equipped with SCR devices, which would increase the mercury concentration in WFGD slurry [9]. However, Hg²⁺ at high concentration are prone to be reduced by HSO₃⁻ or SO₃²⁻ in slurry, and Hg⁰ is released from the WFGD system, which will cause the excessive emissions of mercury [10,11]. Numerous studies were conducted to resolve this re-emission issue [12–19], and the approach that adding chemical additives such as NaHS, 2,4,6-trimercaptotiazine, trisodium salt nonahydrate (Na₃(C₃N₃S₃)·9H₂O, or TMT) and sodium dithiocarbamate (DTCR) which react with Hg²⁺ to form less soluble precipitation or chelate, were developed to stabilize the Hg²⁺ in gypsum slurry and to inhibit Hg⁰ release successfully because of its convenience and high efficiency [20–22]. Nevertheless, the amount of mercury retained in the solid phase increases with the use of additives, and it poses additional risks for the reuse or disposal of desulfurization gypsum [23].

Gypsum is the primary byproduct from WFGD devices [24], and the major component is calcium sulfate dehydrate (CaSO₄·2H₂O). Desulfurization gypsum is commonly used worldwide as wallboard, or as cement and concrete additive [25]. However, the mercury in flue gas captured by desulfurization gypsum presents risks regarding the potential for mercury exposure when the gypsum is reused. Various studies were conducted to investigate the mercury release from desulfurization gypsum wallboard [26–29]. Scotts Shock measured the mercury volatilization by using small-scale (5 L) glass and Teflon flux chambers with synthetic gypsum wallboard samples [30], and obtained room air mercury concentrations between 0.13 and 2.2 ng/m³, which was well below the U.S. Environmental Protection Agency (EPA) reference concentration. Therefore, the volatilization of mercury from wallboard can be nearly ignored. Conversely, the mercury release from desulfurization gypsum during the manufacturing processes of wallboard is considerably higher. To obtain more valuable gypsum for industrial production, the desulfurization gypsum must be dried and calcined before use to remove the attached water [31]. The mercury trapped on gypsum will be released into atmosphere by thermal treatment during the gypsum production process and causes contamination and adversely affects the health of laborers. The mercury content of gypsum, the thermal stability of mercury compounds in gypsum and their species are the key factors that influence the mercury release behavior [32]. In Sanderson's research, the percentage of mercury loss from the synthetic gypsum feedstocks was 55% and most of the loss occurred across the gypsum calciner [33]. The problem may worsen when mercury content increases after using additives, but current data are not adequate to assess the mercury release from the calcination procedure of desulfurization gypsum with additives. All potential pathways for mercury release should be avoided. It is essential to reduce the mercury release from calcination process of desulfurization gypsum, otherwise, mercury emission control measures in coal-fired power plants will be unavailing [34].

The goal of this study is to investigate the mercury release behaviors from gypsum under different calcination methods with different additives. In this paper, we used three kinds of additives, NaHS, TMT, and DTCR in simulated WFGD system to obtain the desulfurization gypsum, and the mercury migration and sequestration in simulated WFGD slurry are also acquired. Then, different calcination methods were adopted to explore the mercury release behavior from desulfurization gypsum. Moreover, temperature programmed decomposition technique was used to determine the transformation of mercury compound species [35,36], which explained the mercury release performance during the calcination

process. This study provides valuable information to understand the mercury release characteristic when WFGD gypsum is reused or disposed of, and synthetically evaluates the inhibitory effect of additives on mercury release from WFGD slurry and also from byproducts.

2. Materials and methods

2.1. Samples

The gypsum used in the research was pre-calcined at 800 °C for 2 h, and the aim of pretreatment was to overcome the possible error due to some mercury species might have been existed in the gypsum. Four FGD gypsum samples were produced by a laboratory-scale device that simulated mercury retention in a 1 L three-necked flask placed in a magnetic stirring water bath at 55 °C. Group 1 containing no additives was set as a blank, and NaHS, DTCR and TMT were respectively added to simulation gypsum slurry as group 2–4. The simulation gypsum slurry consisted of 5% w/v gypsum, 20 mmol/L Cl⁻, 1 mmol/L SO₃²⁻, 200 mmol/L SO₄²⁻, 100 µg/L Hg²⁺, and the initial pH was set at 5.5. After stirring for two hours, the slurries were filtered to collect four gypsum samples naming C1–C4 and four filtrate samples naming D1–D4, and samples C1–C4 were dried at 45 °C for 1 h to remove the attached water. In the gypsum calcination experiment, gypsum samples C1–C4 were calcined using different methods to obtain calcined-gypsum samples.

Reference gypsum samples B1, B2, B3 contained inorganic pure mercury compounds (HgCl₂, black HgS, red HgS) at the concentration of 1 ppm and were prepared by sequential dilution procedure. 0.1 g of pure mercury compound was evenly mixed with 10 g of treated gypsum to obtain a gypsum sample containing 10,000 ppm of the mercury compound. Then, 0.1 g of the mixture containing 10,000 ppm mercury compound was added to another 10 g treated gypsum to obtain a gypsum sample containing 100 ppm of the mercury compound. This process was repeated again and the mercury concentration in these samples was diluted to 1 ppm. Reference gypsum samples B4 and B5 containing organic pure mercury compounds Hg₃(TMT)₂ and Hg(DTCR)₂ were prepared by a laboratory chelation reaction experiment. Excess additives (TMT or DTCR) and a certain amount of solution containing 100 µg/L Hg²⁺ were added to 5% w/v gypsum slurry. The 5% w/v gypsum slurry was prepared with treated gypsum in a beaker. Then gypsum samples B4 and B5 were obtained from the gypsum

Table 1
Information of the samples.

No.	Types	Sources	Additives/mercury compounds
B1	Reference gypsum	Sequential dilution procedure	HgCl ₂
B2	Reference gypsum	Sequential dilution procedure	Black HgS
B3	Reference gypsum	Sequential dilution procedure	Red HgS
B4	Reference gypsum	Chelation reaction experiment	Hg ₃ (TMT) ₂
B5	Reference gypsum	Chelation reaction experiment	Hg(DTCR) ₂
C1	Gypsum	Simulated WFGD system	–
C2	Gypsum	Simulated WFGD system	NaHS
C3	Gypsum	Simulated WFGD system	DTCR
C4	Gypsum	Simulated WFGD system	TMT
D1	Filtrate	Simulated WFGD system	–
D2	Filtrate	Simulated WFGD system	NaHS
D3	Filtrate	Simulated WFGD system	DTCR
D4	Filtrate	Simulated WFGD system	TMT

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