Mercury stability of byproducts from wet flue gas desulfurization devices

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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 desulphurization (WFGD) has been adopted to synergistically remove some particulate mercury (Hg\textsuperscript{0}) and oxidized mercury (Hg\textsuperscript{2+}) from flue gas [5–7]. Compared with Hg\textsuperscript{0} and Hg\textsuperscript{2+}, element mercury (Hg\textsuperscript{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\textsuperscript{0} to Hg\textsuperscript{2+} which will be typically
removed by WFGD systems. Withium 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 NOx, 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 SO₃²⁻ or SO₄²⁻ 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-trimercaptotiazole, 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 Hg⁰ 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 flume 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 SO₄²⁻, 200 mmol/L SO₃²⁻, 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 and again the mercury concentration in these samples was diluted to 1 ppm. Reference gypsum samples B4 and B5 containing organic pure mercury compounds Hg₂(TMT)₂ and Hg₂(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

<table>
<thead>
<tr>
<th>No.</th>
<th>Types</th>
<th>Sources</th>
<th>Additives/mercury compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>Reference</td>
<td>Sequential dilution procedure</td>
<td>HgCl₂</td>
</tr>
<tr>
<td>B2</td>
<td>Reference</td>
<td>Sequential dilution procedure</td>
<td>Black HgS</td>
</tr>
<tr>
<td>B3</td>
<td>Reference</td>
<td>Sequential dilution procedure</td>
<td>Red HgS</td>
</tr>
<tr>
<td>B4</td>
<td>Reference</td>
<td>Chelation reaction experiment</td>
<td>Hg₂(TMT)₂</td>
</tr>
<tr>
<td>B5</td>
<td>Reference</td>
<td>Chelation reaction experiment</td>
<td>Hg₂(DTCR)₂</td>
</tr>
<tr>
<td>C1</td>
<td>Gypsum</td>
<td>Simulated WFGD system</td>
<td>–</td>
</tr>
<tr>
<td>C2</td>
<td>Gypsum</td>
<td>Simulated WFGD system</td>
<td>NaHS</td>
</tr>
<tr>
<td>C3</td>
<td>Gypsum</td>
<td>Simulated WFGD system</td>
<td>DTCR</td>
</tr>
<tr>
<td>C4</td>
<td>Gypsum</td>
<td>Simulated WFGD system</td>
<td>TMT</td>
</tr>
<tr>
<td>D1</td>
<td>Filterate</td>
<td>Simulated WFGD system</td>
<td>–</td>
</tr>
<tr>
<td>D2</td>
<td>Filterate</td>
<td>Simulated WFGD system</td>
<td>NaHS</td>
</tr>
<tr>
<td>D3</td>
<td>Filterate</td>
<td>Simulated WFGD system</td>
<td>DTCR</td>
</tr>
<tr>
<td>D4</td>
<td>Filterate</td>
<td>Simulated WFGD system</td>
<td>TMT</td>
</tr>
</tbody>
</table>
slurry after stirring for 30 min and filtrated. The information of samples was listed in Table 1.

2.2. Equipment and method

The laboratory-scale device that simulated mercury retention is shown in Fig. 1. The goal of simulated mercury retention in our research was to acquire the gypsum samples after using different additives, and we also investigated the distribution of mercury among the three phases. The mercury released in the gas phase was carried out by nitrogen flow and passed through the KCl and KMnO₄ + H₂SO₄ solution successively. The oxidized mercury in the airflow was absorbed by the KCl solution. The element mercury was absorbed by the KMnO₄ + H₂SO₄ solution. The absorption liquid and gypsum slurry samples after digestion were measured by cold-vapor atomic fluorescence mercury spectrometer AFS-8220 to obtain the mercury concentration.

The gypsum calcination experiment was conducted on a fixed-bed reactor device. In typical facilities that produce wallboard, the temperature in the calcining unit is between 128 °C and 163 °C to obtain the eligible gypsum [33], and the process usually lasts 1–4 h to remove the moisture while it provides potential risk for mercury release [37]. In our research, we aimed at investigating the mercury release through different calcining methods. According to the heating mode for this experiment was set as follows: (1) the calcination temperature was set at 100 °C, lasted for 2 h as the slow-speed calcination; (2) the calcination temperature was set at 150 °C, lasted for 15 min as the medium-speed calcination; (3) the calcination temperature was set at 300 °C, lasted for 10 s as the fast-speed calcination. To simulate the gypsum calcining process, gypsum samples C1–C4 were placed in a quartz reactor, and the calcination temperature was controlled by tube furnace to increase to the preselected temperature and maintained for the particular duration. The gypsum samples were weighed before and after calcination, to obtain the mass loss of gypsum during calcination process. All gypsum samples were measured by Hydra C (Teledyne Technologies Company, USA) to assess the release of mercury. Hydra C is a solid mercury analyzer and its detection limit is 0.01 ng/g.

The apparatus of temperature programmed decomposition procedure consisted of a tube furnace, a fixed-bed reactor, a mercury speciation transformation device, and the continuous mercury analyzer VM3000, as is shown in Fig. 2. Gypsum samples C1–C4 and B1–B5 were placed in a quartz reactor, and the temperature was controlled by a tube furnace that increased from 20 °C to 600 °C at the rate of 10 °C/min, with a carrier nitrogen flow of 1.5 L/min. The carrier gas that flow past the reactor brought mercury compounds into quartz tube. The quartz tube was kept at 1.5 L/min. The carrier gas was delivered to continuous mercury analyzer VM3000, in which the detection limit of real-time gas mercury content was 1 ng/m³. All connecting lines used in experiment were made from Teflon or quartz tube, and were covered by an electric heater strip to maintain a constant 120 °C to avoid any error caused by mercury adsorption or deposition of the Hg species on the inner surface of tubes.

The rate of mercury release in calcination experiments was calculated by the following formula.

\[
\text{Rate of mercury release} = \frac{Hg_{\text{after}} - Hg_{\text{before}}}{Hg_{\text{before}}} \quad (1)
\]

\(Hg_{\text{before}}\) is the mercury concentration of gypsum before calcination, \(Hg_{\text{after}}\) is the mercury concentration of gypsum after calcination. The \(Hg_{\text{after}}\) were corrected according to the mass loss of gypsum during calcination process.

3. Results and discussion

3.1. Effects of additives on mercury migration

 Certain additives have been investigated for their behaviors on removing mercury. Ochoa-Gonzalez found that NaHS and TMT reacted with \(Hg^{2+}\) to form insoluble \(HgS\) and \(Hg_3(TMT)_2\) precipitants [38]. Numerous electronegative polar groups containing sulfur in DTCR combined with \(Hg^{2+}\) to form cross-linked and insoluble chelates. Thus, NaHS, DTCR and TMT can commendably stabilize \(Hg^{2+}\) in slurry and inhibit \(Hg^0\) release. The relevant equations are shown as (2)–(4).

\[
Hg^{2+} + NaHS \rightarrow HgS + Na^+ + H^+ \quad (2)
\]

\[
Hg^{2+} + 2DTCR \rightarrow Hg(DTCR)_2 \quad (3)
\]

\[
3Hg^{2+} + 2TMT \rightarrow Hg_3(TMT)_2 \quad (4)
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\]

\[
3Hg^{2+} + 2TMT \rightarrow Hg_3(TMT)_2 \quad (4)
\]

Fig. 3 depicts the characteristics of mercury migration among three phases before and after using additives. A sharp decline of the rate of \(Hg^0\) release was observed from the initial 12.1% to 0.9%, 0.4% and 0.4% by adding NaHS, DTCR, and TMT, respectively. This result suggested that NaHS, DTCR and TMT had an obvious effect to inhibit \(Hg^0\) release from slurry, and corresponded with prior research by Sun [39]. Moreover, the \(Hg^{2+}\) concentration in the gas phase decreased in the presence of additives, with the highest decrease from the original 3.4% to 0.4% after the addition of TMT. These results indicated that additives remarkably weakened the mercury migration to gas phase in the WFGD system.

By measuring the mercury concentration in liquid phase, we found that there were 23.4% of the total mercury content in the filtrate without additives, while it turned to 8.4%, 1.1%, 0.4% after adding NaHS, DTCR, TMT, respectively. Therefore, the additives drastically decreased the \(Hg^{2+}\) concentration in the desulfurization filtrate and desulfurization wastewater. In addition, \(Hg^{2+}\) in liquid...
can be transferred to insoluble Hg\(^0\) by aqueous ionic chemistry [40], and the re-emission levels were highly related to the Hg\(^{2+}\) concentration. As a result, the addition of NaHS, DTCR and TMT can also significantly diminish the Hg\(^0\) re-emissions from the WFGD gypsum slurry and desulfurization wastewater.

The effect of additives on mercury migration to the solid phase was acquired by measuring the mercury content of gypsum samples. The mercury remaining in gypsum sample without additives was 833.1 ng/g, and it increased to 1412.3 ng/g, 1806.8 ng/g, and 1941.4 ng/g by adding NaHS, DTCR and TMT. The result indicated that these additives will markedly enhance the capacity of gypsum to trap mercury. TMT had the most outstanding effect on trapping mercury as 98.8% of total mercury was fixed on gypsum when it was added. Therefore, the use of NaHS, DTCR and TMT altered the characteristics of mercury migration in WFGD. Specifically, the proportion of Hg released and Hg\(^{2+}\) in filtrate both decreased because of the formation of insoluble Hg precipitant and chelates attached on the gypsum. The capturing of mercury as a stable solid species is better than having mercury flowing out with flue gas or into wastewater [41]. Further research regarding the release of mercury from gypsum is needed to evaluate the influence of additives on industrial gypsum production.

### 3.2. Thermal stability of mercury in gypsum

#### 3.2.1. Release of mercury during calcination

The effects of additives on the thermal stability of mercury in gypsum can be obtained by comparing mercury content of samples before and after calcination. The amount of mercury release and the rate of mercury release under different calcination methods are shown in Table 2. In most cases, the gypsum samples with additives presented lower mercury release rate than the original samples, which proved that mercury compounds generated on the function of additives had excellent thermal stability.

Mercury contamination from gypsum calcination procedures was closely related to the processing modes and the kinds of additive. Thus, studying the mercury release behaviors on different treatment schemes is important for controlling mercury re-emissions in the gypsum industry. The data in Table 2 shows that the mercury release worsened dramatically when temperatures increased from 100 °C to 300 °C. Besides, the gypsum produced by slow-speed calcination has a better phase composition. Therefore, low-temperature, namely low-speed calcination, is a both environment-friendly and high-quality method to dispose desulfurization gypsum.

Additives are another critical factor on mercury release since the mercury compounds in gypsum were influenced by types of additives. Under identical calcination condition, the rates of mercury release successively decreased after using DTCR, TMT and NaHS, and this suggested that the inhibitory effect on mercury release was strengthened in the order of DTCR, TMT, NaHS. Furthermore, the rates of mercury release in samples C2 and C4 were less than C1 under all types of methods, while the performance of gypsum sample C3 was supernormal with C2 and C4 on the procedure of high-speed calcination and it released more mercury than C1. Therefore, the use of NaHS and TMT enhanced the thermal stability of mercury in gypsum, while DTCR weakened the thermal stability under high temperature.

According to the analysis, using NaHS as additive and treating gypsum by low-speed calcination had the best effect on reducing mercury release in gypsum. The experimental results confirmed the inference that the amount of mercury release was 80.5 ng/g in this method, and the rate of mercury release was 5.7%, which were both lowest among all experiment conditions.

#### 3.2.2. Residual content of mercury in gypsum

Gypsum after calcination is processed into different gypsum products such as wallboard and concrete retarder, and the residual mercury content after calcination had profound effects on the quality of gypsum products. Fig. 4 describes the residual content of mercury in experimental gypsum samples after calcination. It can be concluded that additives will increase the mercury concentration remained in gypsum samples. Specifically, the residual mercury content in gypsum samples with DTCR under high-speed calcination was the lowest, and under slow-speed calcination, the residual content of mercury in gypsum samples with NaHS was the lowest. Three gypsum samples had similar residual mercury content under medium-speed calcination. Fig. 4 also indicates that the residual mercury content decreased with increased temperature because mercury compounds prefer to decompose in high temperature, and the residual mercury content in gypsum sample with NaHS did not significantly change under different calcination methods.

<table>
<thead>
<tr>
<th>Samples (additives)</th>
<th>Amount of mercury release (ng/g)</th>
<th>Rate of mercury release (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 °C + 2 h</td>
<td>150 °C + 15 min</td>
</tr>
<tr>
<td>C1 (None)</td>
<td>193.3</td>
<td>348.3</td>
</tr>
<tr>
<td>C2 (NaHS)</td>
<td>80.5</td>
<td>156.8</td>
</tr>
<tr>
<td>C3 (DTCR)</td>
<td>186.1</td>
<td>578.2</td>
</tr>
<tr>
<td>C4 (TMT)</td>
<td>157.3</td>
<td>592.1</td>
</tr>
</tbody>
</table>
3.2.3. Total trapping efficiency

Synthetically considering the gypsum calcination experiment results, it was remarkable that using NaHS had the great inhibition effect and also the lowest residual mercury content under slow-speed calcination. However, the less mercury was released, the more it remained in the gypsum. This phenomenon could be attributed to the difference in initial mercury content of desulfurization gypsum. The initial mercury content of gypsum with NaHS was much lower than gypsums with DTCR or TMT, owing to its poor trapping ability. In order to comprehensively assess the effect of treating methods, we summarized the total trapping efficiency by calculating the percentage of mercury trapped in final gypsum product based on the amount of mercury entering WFGD system. The calculation formula is as follows:

\[ \eta_{\text{total}} = \eta_{\text{solid}} \times (1 - \eta_{\text{release}}) \]  

\( \eta_{\text{total}} \) is the total trapping efficiency, \( \eta_{\text{solid}} \) is the proportion of mercury in the solid phase in simulated WFGD systems, \( \eta_{\text{release}} \) is the rate of mercury release in calcination procedure.

As is shown in Fig. 5, using TMT coupled with slow-speed calcination had the highest total trapping efficiency which reached 90.76%, while the efficiency of using NaHS with slow-speed was 84.54%, although it had the lowest mercury release rate in calcination process. Therefore, taken as a whole, adding TMT and calcinating desulfurization gypsum at slow-speed had the best effect on controlling mercury emissions from the WFGD system.

The mercury release behaviors during calcination and the residual content largely depend on the species of mercury compounds and their characteristics. Therefore, we conducted temperature programmed decomposition experiments to study the effects of additives on transformation of mercury compounds and their thermal stabilities.

3.3. Release characteristics of reference samples

Fig. 6 describes the thermal decomposition curves of gypsum samples containing pure mercury compounds in temperature programmed decomposition procedures, including HgCl_2, black HgS, red HgS, \( \text{Hg}_3(\text{TMT})_2 \) and \( \text{Hg(DTCR)}_2 \). The peak of decomposition temperature and the range of decomposition temperature were significantly disparate in gypsum samples containing different pure mercury compounds. HgCl_2 had the lowest decomposition temperature among pure mercury compounds, with a decomposition temperature range of HgCl_2 from 110°C to 220°C, and the peak of decomposition temperature was 168°C. The decomposition temperature range of \( \text{Hg}_3(\text{TMT})_2 \) was 170–290°C, and the peak of decomposition temperature was 235°C. The decomposition temperature range of \( \text{Hg(DTCR)}_2 \) was 110–270°C, and the curve showed two peaks with temperature of 198°C and 235°C. Therefore, \( \text{Hg}_3(\text{TMT})_2 \) had better thermal stability than \( \text{Hg(DTCR)}_2 \). According to the research by Biester, the crystalline structure of black HgS was cubic while the crystalline structure of red HgS was diamond, and the inconsistencies in crystalline structures resulted in black HgS having lower decomposition temperature than red HgS [42]. In this study, the decomposition temperature range of red HgS was 110–270°C, and the peak of decomposition temperature was 198°C. Therefore, \( \text{Hg}_3(\text{TMT})_2 \) had better thermal stability than \( \text{Hg(DTCR)}_2 \). According to the research by Biester, the crystalline structure of black HgS was cubic while the crystalline structure of red HgS was diamond, and the inconsistencies in crystalline structures resulted in black HgS having lower decomposition temperature than red HgS [42]. In this study, the decomposition temperature range of red HgS was 270–370°C, and the peak of decomposition temperature was 235°C. The decomposition temperature range of black HgS was 175–350°C, and the curve showed two peaks with temperature of 215°C and 320°C. The temperature programmed decomposition experiments results proved that the thermal stability of mercury compounds in gypsum can be arranged in increasing order as HgCl_2 < \( \text{Hg(DTCR)}_2 \) < \( \text{Hg}_3(\text{TMT})_2 \) < black HgS < red HgS. Decomposition characteristics of reference gypsum samples during temperature programmed decomposition procedures are summarized in Table 3.

![Fig. 4. Residual content of mercury after calcination.](image)

![Fig. 5. Total trapping efficiency under different methods.](image)

![Fig. 6. Release characteristics of reference samples in temperature programmed decomposition procedure.](image)

![Table 3](image)
3.4. Transformation of mercury compounds in gypsum

The mercury release curves acquired from gypsum samples C1–C4 during temperature programmed decomposition procedures are presented in Fig. 7. The results showed that the decomposition temperature range of gypsum sample C1 was 122–240 °C, which showed good agreement with decomposition temperature of HgCl₂. The peak of decomposition temperature was 166 °C, which was also in accordance with that of HgCl₂. Therefore, the mercury compound existing in gypsum C1 was mainly in the form of HgCl₂. Sample C2 had the highest peak of decomposition temperature of 245 °C, and the decomposition temperature of sample C2 ranged from 181 °C to 350 °C which was in consistent with that of black HgS. However, the filtrate of slurry with NaHS contained 8.4% of total mercury, implying that there was still a part of Hg²⁺ that could not be captured by NaHS to form HgS. Consequently, black HgS was the main species of mercury compounds in gypsum C2, with a small amount of HgCl₂. When DTCR was added to the slurry, the decomposition temperature range of gypsum sample C3 was 129–269 °C and the peak of decomposition temperature was 194 °C, which corresponded to that of Hg(DTCR)₂. This suggested that the Hg²⁺ in slurry nearly combined with DTCR to form Hg(DTCR)₂, and Hg(DTCR)₂ was precipitated on gypsum C3. Analogously, the mercury release curve of sample C4 was similar to that of Hg₃(TMT)₂, which demonstrated that almost all Hg²⁺ were converted into Hg₃(TMT)₂ by TMT when TMT was added to the slurry. In conclusion, black HgS, Hg₃(TMT)₂, and Hg(DTCR)₂ were the primary mercury compounds existing in gypsum after adding NaHS, TMT, and DTCR, respectively. Considering the thermal stability of these reference samples, the results well explained the mercury release behaviors during calcination when using various additives.

4. Conclusions

This paper first investigated the effects of three additives on the mercury migration among three phases in WFGD. Then, gypsum calcination experiments were conducted to explore the impacts on the thermal stability of mercury. TMT, DTCR and NaHS significantly reduced the mercury transferred to gas and liquid phases, and enhanced the ability to trap mercury to solid gypsum. The capacity of trapping mercury to gypsum decreased in the order of TMT, DTCR and NaHS. The thermal stability of mercury in gypsum increased with the use of DTCR, TMT and NaHS gradually. The residual content of mercury in gypsum with additives after calcination was higher than those without additives, due to the migration of mercury to its solid phase. Adopting NaHS as additive with slow-speed calcination was the most effective method to reduce mercury re-emissions in the gypsum calcination process. In general, the method of using TMT coupled with slow-speed calcination had the best effect on controlling mercury contamination from the WFGD slurry and WFGD byproducts. Temperature programmed decomposition procedures confirmed that the peak of decomposition temperature and the range of decomposition temperature gradually decreased in the order of HgS, Hg₃(TMT)₂, Hg(DTCR)₂ and HgCl₂. Finally, when using NaHS, TMT and DTCR as additives, the mercury compounds in the gypsum were mainly in the form of HgS, Hg₃(TMT)₂ and Hg(DTCR)₂, which well explained the mercury release behaviors during calcination.

Acknowledgments

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