Mercury Release from FGD

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ABSTRACT

Energy & Environmental Research Center (EERC) researchers and U.S. Environmental Protection Agency (EPA) officials agreed that several gaps exist in the information about mercury release (or retention) related to coal combustion by-products (CCBs). A task focusing on mercury release from the flue gas desulfurization (FGD) gypsum wallboard-manufacturing process from the point of forced oxidation of the FGD material through the kiln-drying process was performed at the EERC. Only 100% FGD gypsum wallboard was investigated.

Calcination appears to be the most likely process in the manufacture of FGD wallboard to release mercury because of product temperatures ranging from 150° to 180°C. Another study indicated that no mercury release was expected at wallboard-curing and drying temperatures of less than 177°C. Laboratory tests are currently being conducted in that study.

Two samples were evaluated in this project. Real-time mercury release using a thermal desorption apparatus showed that mercury release began as early as 176°C. Trials conducted to simulate the calcining of FGD in flash calcining and kettle processes showed that the potential of mercury release exists before that temperature. The amount of mercury released from the FGD could be higher by orders of magnitude when a kettle process is used versus a flash calcining process because of the extreme heating-time differences.

Little mercury release is expected from the FGD material in the board-drying process. Measurements in real production facilities are essential to developing a valid answer to the question of mercury release during FGD gypsum wallboard production.

INTRODUCTION

The release of mercury from coal combustion by-products (CCBs) is a topic of continuing research at the Energy & Environmental Research Center (EERC) and elsewhere. U.S. Environmental Protection Agency (EPA) officials and the EERC researchers agreed that several gaps exist in the information about mercury release (or retention) related to CCBs. One of these gaps is the mercury release from utilized CCBs. EPA and the EERC jointly identified the production of cement, autoclaved aerated concrete, and flue gas desulfurization (FGD) gypsum wallboard as having relatively high potential for mercury release. Each of these products commonly uses a CCB as a raw material and undergoes a heating stage during production.

EERC researchers studied the potential for mercury release from the FGD gypsum wallboard manufacturing process from the point of oxidation of the FGD material to FGD gypsum through the kiln-drying process. The focus of this paper is the calcination step investigating only 100% FGD gypsum wallboard; the impact of additives was not tested.

Calcination changes the form of calcium sulfate from calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) or gypsum to calcium sulfate hemihydrate ($CaSO_4 \cdot ½H_2O$), also known as calcined gypsum, plaster of Paris, or stucco. The β-hemihydrate is primarily present in wallboard gypsum.[1,2] Heating to temperatures ranging from 109° to 130°C will release three-quarters of the chemically combined water in the gypsum.[3] Heating up to 205°C will completely dehydrate the gypsum to form soluble anhydrite ($CaSO_4$).[4–8]

Examples of equipment used to calcine gypsum are a kettle, a rotary calciner, a flash calciner, or a mill calciner. The method used to calcine gypsum is very different using a kettle versus a flash calciner. In a kettle, the FGD gypsum is heated employing gradually increasing temperatures from about 75°C to a final temperature of approximately 170°C in the production of first-settle stucco.[6] This process takes from 1 to 4 hours to drive the moisture off and calcine the FGD.[6–10] Kettles can operate in batch or continuous modes. A portion of an actual kettle thermometer chart, which records the temperature changes during the production of kettle charges, shows that the gypsum (natural gypsum in this example) increased from 77° to 121°C in 15 minutes, held steady at 121°C for 60 minutes, and then increased to a final product temperature of 166°C in 15 minutes.[6] In a flash calciner, hot gas up to 650°C (limited due to steel construction) is introduced to the FGD gypsum, and the dehydration process occurs in only a few seconds.[11,12] The process in one plant occurs in 1½ to 2 seconds. Product temperatures have been reported at 154°C. Some calciners are combinations, such as an impact mill flash calciner. New wallboard manufacturing facilities tend to use the flash calcining process.

Multiton batches of gypsum are calcined per hour for wallboard production. This capacity varies from plant to plant, with a general range of 20 to 70 tons of gypsum calcined per hour.[1,9,13–15] In 2001, the production of wallboard utilized 6,224,872 tons of FGD material in the United States.[16] This accounts for 82% of utilized or 22% of produced FGD material from coal combustion power plants.

EXPERIMENTAL

Samples

Two FGD samples were included in this project. Sample 1 was a wet FGD scrubber calcium sulfite material that was oxidized to calcium sulfate in the laboratory. Sample 2 was dry FGD gypsum that is used in the production of wallboard. The total mercury content of the samples was determined using cold-vapor atomic absorption (CVAA).

Real-Time Mercury Release

The samples were analyzed for real-time mercury release using atomic absorbance. A 150-mg aliquot of each sample was heated from ambient temperature to 650°C at rates of 25°C per minute and 50°C per minute. This procedure was used to determine the temperature(s) at which the release of mercury compounds occurred. This was performed using the apparatus shown in Figure 1, which was connected to an atomic absorption spectrophotometer (AAS). The Teflon compression fitting is heated to ensure that any water vapor released from the FGD material does not condense and interfere with the mercury signal in the AAS.

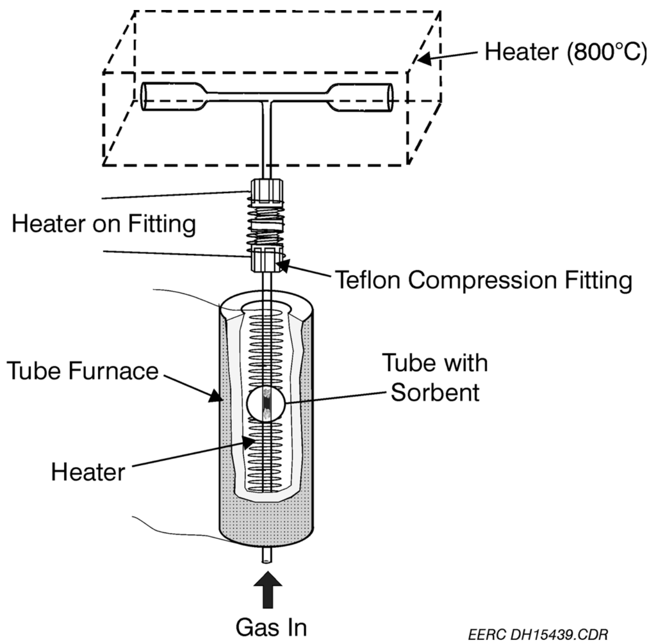

Figure 1. Thermal desorption apparatus.

Oil Bath

An oil bath setup was also used to measure mercury release from the samples (see Figure 2). It was used to raise the temperature of the samples more quickly than the thermal desorption apparatus in an effort to more closely represent flash calcination.

The oil was heated to 195°–197°C, providing for the collection of mercury vapor in the temperature ranges found in the FGD during calcination for wallboard manufacture. For each trial, an aliquot of FGD material was placed into a U-tube. Gold-coated quartz traps were placed on each end of the U-tube. The U-tube was placed in the heated oil bath. Nitrogen was passed through the system at a flow rate of 20 mL/min. Any mercury present in the nitrogen was scrubbed in the gold-coated quartz pretrap. The nitrogen then moved any mercury vapor released from the FGD gypsum samples to a gold-coated quartz collection trap. This collection trap was heated to approximately 120°C to

Figure 2. Oil bath setup.

evaporate the moisture released from the gypsum during the calcining process. Mercury was captured on the collection traps in 1-, 3-, or 10-minute increments. Up to four sequential measurements were taken for each sample trial run. Each gold-coated quartz collection trap was analyzed for mercury content by atomic absorption.

Temperature profiles were determined for the two samples. The oil temperature was 195°C for Sample 1, and temperature profiles for Sample 2 were determined in 154°C and 193°C oil baths. The temperature profiles were performed to determine how quickly the samples heated and also to determine when the samples lost water, changing from calcium sulfate dihydrate to calcium sulfate hemihydrate.

RESULTS AND DISCUSSION

Total Mercury Content

The total mercury content of the CCBs as determined by CVAA was 163 ng/g for Sample 1 and 126 ng/g for Sample 2.

Real-Time Mercury Release

Real-time mercury release was determined using the thermal desorption apparatus. Measurable mercury release began at an average of 188°C for the samples, with a range of 176°–208°C when heated at a rate of 25°C/min. The quantity of mercury released increased until the samples reached temperatures of approximately 263° and

269°C for Samples 1 and 2, respectively. Examples of thermal curves obtained for the samples are shown in Figure 3. It is clear from these thermal desorption curves that Sample 1 released more mercury than Sample 2 and that the rate of mercury release is higher for Sample 1.

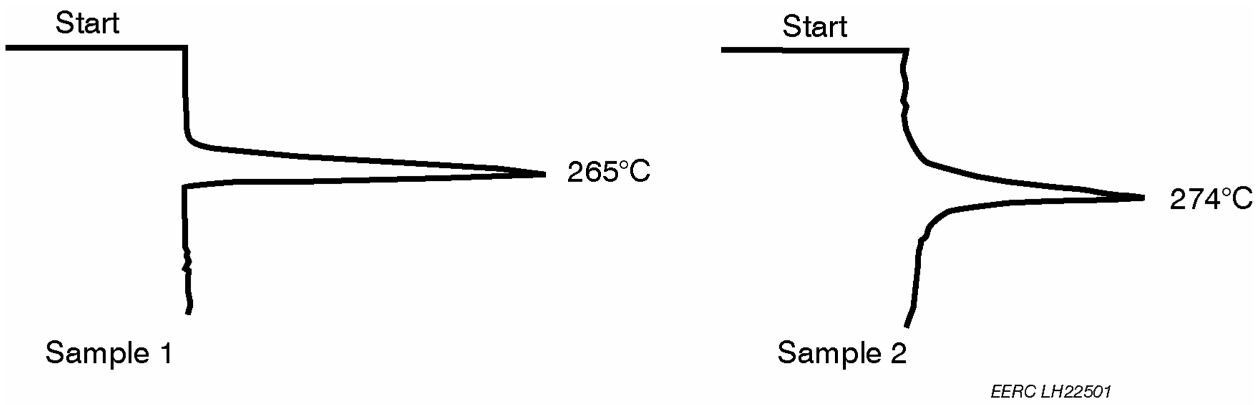

Figure 3. Thermal curves from ambient temperature to 650°C at 25°C/min for Samples 1 and 2, respectively.

One wallboard manufacturer reports product temperatures of 71°C in the first step and 154°C in the second step of calcination. The second step is flash calcination. This laboratory method indicates that no measurable mercury would be released from the tested samples at the temperatures utilized in the mentioned calcining process.

The product temperature in a kettle is approximately 170°C at the end of heating; therefore, the potential for mercury release from the calcined FGD gypsum appears minimal. The peak of mercury occurred sooner when the samples were heated at 25°C/min rather than at 50°C/min. Therefore, heating the gypsum at 3°C/min in a production plant[6] could result in mercury releasing before 176°C. Also, the FGD gypsum could be at mercury-releasing temperatures for a couple of minutes, depending on the individual FGD sample and the kettle parameters. The slower heating rate in wallboard manufacturing facilities could potentially release more mercury than was observed in this laboratory method.

Oil Bath

Each sample was heated in the oil bath setup in an attempt to simulate the calcining process. The samples were heated in the oil bath for a total of 3–30 minutes per trial. During a trial, mercury vapor was collected for 1, 3, or 10 minutes on a gold-coated quartz trap, the trap was removed, and another gold-coated quartz trap was attached to the system to collect mercury for another time increment. This was repeated up to four collections. Figure 4 shows the cumulative concentration of mercury released from the FGD gypsum in each trial run as well as the percentage of total mercury that was released for that sample. The concentration of mercury release in the first heating

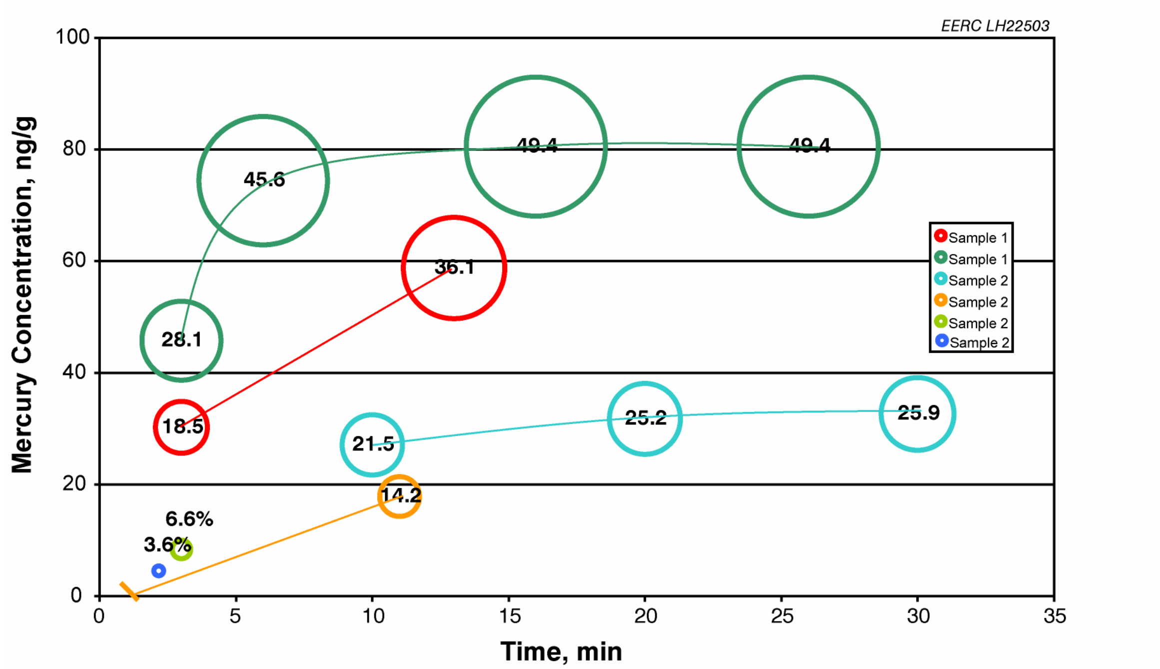

Figure 4. Cumulative mercury release from each trial run in 195°–197°C oil baths. Bubble size equals percentage of total mercury.

increment was used to calculate the rate of release shown in Table 1. Table 1 also lists the temperature of the FGD gypsum at the end of the first heating period.

Within 30–45 seconds, a significant portion of the moisture appeared to be released from the samples. The temperature profiles indicated that in this time frame the samples were at 130°–150°C, indicating that the calcination of $CaSO_4 \cdot 2H_2O$ to $CaSO_4 \cdot ½H_2O$ was occurring. The samples then appeared fairly dry and decreased slightly in temperature before slowly increasing to the temperature of the oil, which occurred at approximately 5 minutes. Limited moisture was noted after the initial 30–45 seconds.

Calcination of FGD gypsum using flash calcination occurs in a few seconds; one wallboard manufacturer reports that the process takes 1½ to 2 seconds. In that production facility, the inlet gas temperature is 537°–593°C, and the outlet gas temperature is 153°–156°C. The product temperature is not seen above 154°C. Table 2 was developed in an attempt to relate the information from Table 1 to the mercury release that may occur in the calcination of ton amounts of FGD gypsum in a wallboard manufacturing facility. The amount of mercury released per hour, per day, and per year in grams was calculated based on a 50-ton/hour calcination. An average of 487 g and 97 g for Samples 1 and 2, respectively, was estimated as the yearly release of mercury from one wallboard manufacturing facility. However, these values are most likely too high because the samples were at temperatures higher than 154°C by the end of each collection period during the trial runs. The actual mercury release during flash calcining may be relatively low, as seen in Sample 2b, because the heating time is very short and

Table 1. First Heating Increment of Each Trial Run in 195° –197°C Oil Baths

Sample	Heating Time, min	FGD Temperature at End of Heating, °C	Calculated Rate of Release, ng/g/min
1a	3	180°C	10.07
1b	3	180°C	15.25
2a	10	192°C	2.71
2b	1	160°C	NA*
2c	3	175°C	2.79
2d	2.2	163°C	2.09

* Not applicable.

Table 2. Estimated Mercury Release in the Flash Calcining Process from One Wallboard Manufacturing Facility

Sample	Calculated Mercury Release, ng/g	Calculated Mercury Release, g/ton	Calculated Mercury Release in 1 hour, g	Calculated Mercury Release in 1 day, g	Calculated Mercury Release in 1 year, g
1a	0.974	0.000883	0.0442	1.060	387
1b	1.474	0.001337	0.0669	1.605	586
2a	0.262	0.000238	0.0119	0.285	104
2b	NA*	NA	NA	NA	NA
2c	0.169	0.000244	0.0122	0.293	107
2d	0.202	0.000183	0.0092	0.220	80

* Not applicable.

the product temperature remains low. The use of a kettle to calcine the FGD gypsum, however, presents a different situation in regard to mercury release.

Although heating the samples with the thermal desorption apparatus did not show measurable mercury release until 165° and 172°C for Samples 1 and 2, respectively, release was evident when the samples were heated in a 154°C oil bath. Each sample was heated for 16 minutes in the 154°C oil bath, and the cumulative amount of mercury released was 29% and 11% of the total mercury available in Samples 1 and 2, respectively. Table 3 shows the mercury release from the three time increments of collection for each sample. A temperature profile was not determined for Sample 1 because of sample size.

Calcination of FGD gypsum using a kettle takes from 1 to 4 hours. Mercury release will not occur during this whole time period. As stated earlier, the FGD gypsum in a kettle increases in temperature from 121° to 166°C in the last 15 minutes of heating. Mercury release should only occur in this part of the cycle. Table 4 uses the cumulative mercury release from the 16 minutes of heating in the oil bath in an attempt to correlate laboratory values with the mercury release that may occur in the calcination of FGD gypsum in a wallboard manufacturing facility. The amount of potential mercury release per batch, per day, and per year in grams was calculated based on a 50-ton/batch calcination. Samples 1 and 2 are estimated to have yearly releases of mercury from one wallboard manufacturing facility of approximately 10 and 3 kg, respectively.

Table 3. Mercury Release in a 154°C Oil Bath

Sample	Heating Time, min	FGD Temperature at End of Heating, °C	Mercury Concentration, ng/g	% of Total Mercury
1	1–3	ND*	12.18	7.5%
1	3–6	ND	6.22	3.8%
1	6–16	ND	28.00	17.2%
2	1–3	140°C	1.42	1.1%
2	3–6	140°C	5.00	4.0%
2	6–16	152°C	7.12	5.7%

* Not determined.

Table 4. Estimated Mercury Release in the Kettle Calcining Process from One Wallboard Manufacturing Facility

Sample	Laboratory Mercury Release, ng/g	Calculated Mercury Release, g/ton	Calculated Mercury Release in 1 batch, g	Calculated Mercury Release in 1 day, g	Calculated Mercury Release in 1 year, g
1	46.40	0.0421	2.105	28.87	10,536
2	13.54	0.0123	0.614	8.42	3075

CONCLUSIONS

Predicting and measuring mercury release from manufactured products during and after processing is not a simple matter. Several mercury compounds as well as elemental mercury itself can volatilize. Mercury even at room temperature has a significant vapor pressure and can volatilize in the absence of additional heat. The same is not true of other mercury compounds except methylated mercury species, which are not expected to be present initially in gypsum or manufactured wallboard. It is known that oxidized mercury species are the forms of mercury that are predominantly trapped in wet scrubbers of the kind used to produce calcium sulfite and calcium sulfate FGD materials. Because of this, three oxidized mercury species, mercuric chloride ($HgCl_2$), mercuric oxide (HgO) and, possibly, mercuric nitrate ($Hg[NO_3]_2$) are the primary mercury compounds likely to be incorporated into FGD. It is most likely that the bulk of the oxidized mercury present is mercuric chloride. Lower concentrations of elemental mercury can also be present. Mercuric chloride volatilizes unchanged at 300°C; mercuric oxide decomposes into oxygen and mercury at 400°–500°C; mercuric nitrate, however, slowly decomposes over time forming some mercury metal. It is easy to see that the most likely mercury compounds are somehow being reduced to elemental mercury, which can be released during the heating steps in wallboard manufacturing. Even elemental mercury incorporated into FGD material is likely complexed or bound in some manner. This is evident because of the extremely low concentrations of free mercury vapor given off by unheated FGD material.[17] Residual sulfite in the FGD material could reduce mercury compounds, but there are likely other unknown mechanisms of reduction responsible for the bulk of the mercury release, at least from oxidized mercury species. Determining the mechanisms of reduction was, however, beyond the scope of this project.

It should be kept in mind that although it was attempted to reproduce heating conditions in the lab as they might occur in production, this was still a laboratory simulation. Measurements in real production facilities are essential to developing a valid answer to the question of mercury release during wallboard production. Despite this, there are correlations that can be made from the laboratory data.

The potential for mercury release during the calcining process of FGD gypsum wallboard production exists. Another study indicated that no mercury release was expected at wallboard-curing and drying temperatures of less than 177°C. However, the data presented here indicate that mercury may be released by the time the FGD gypsum reaches a temperature of 140°C.

The amount of mercury released from FGD material could be higher by orders of magnitude when a kettle process is used versus a flash calcining process because of the extreme time differences utilized. In these laboratory experiments, Sample 1 released more mercury than Sample 2, resulting in significant differences on the calculated release in 1 year at a plant within each calcination process. Therefore, it should be noted that the total mercury content and subsequent release of mercury from FGD gypsum is sample-specific.

Many new wallboard manufacturing facilities are being built near sources of FGD gypsum and are also leaning away from the use of kettles for calcining the gypsum. Flash calciners and kettles were investigated in this study; however, other equipment such as rotary calciners is also used in wallboard manufacturing plants. The effect of additives used in the wallboard manufacturing process on the release of mercury was not investigated.

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