Combustion Byproducts Recycling Consortium

The Effect of Mercury Controls on Wallboard Manufacture

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submitted by

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DISCLAIMER

Abstract

Pending EPA regulations may mandate 70 to 90% mercury removal efficiency from utility flue gas. A mercury control option is the trapping of oxidized mercury in wet flue gas desulphurization systems (FGD). The potential doubling of mercury in the FGD material and its effect on mercury volatility at temperatures common to wallboard manufacture is a concern that could limit the growing byproduct use of FGD material. Prediction of mercury fate is limited by lack of information on the mercury form in the FGD material. The parts per billion mercury concentrations prevent the identification of mercury compounds by common analytical methods. A sensitive analytical method, cold vapor atomic fluorescence, coupled with leaching and thermodecomposition methods were evaluated for their potential to identify mercury compounds in FGD material. The results of the study suggest that the mercury form is dominated by the calcium sulfate matrix and is probably associated with the sulfate form in the FGD material. Additionally, to determine the effect of high mercury concentration FGD material on wallboard manufacture, a laboratory FGD unit was built to trap the oxidized mercury generated in a simulated flue gas. Although the laboratory prepared FGD material did not contain the mercury concentrations anticipated, further thermal tests determined that mercury begins to evolve from FGD material at 380 to 390°F, consequently dropping the drying temperature should mitigate mercury evolution if necessary. Mercury evolution is also diminished as the weight of the wallboard sample increased. Consequently, mercury evolution may not be a significant problem in wallboard manufacture.

Introduction

Previous analysis of the raw test data from the ICR mercury testing at coal-fired boilers for wet flue gas desulphurization (FGD) systems correlated a high total mercury removal to a high concentration of oxidized mercury. The wet-FGD system acts to control the concentration of SO2 emitted in the flue gas by reacting SO2 in the scrubber with aqueous lime or limestone. The oxidized mercury is absorbed in the FGD material while the less-reactive elemental mercury will pass through the process. Consequently, technology modification to increase proportion of oxidized mercury in the flue gas prior to the wet-FGD unit, or "enhanced wet-FGD control", has become a likely option in mercury control strategies[1]. It's estimated that the mercury concentration in the FGD material could double if wet-FGD is used to control mercury. The prospect of doubling the concentration of mercury in FGD material raises questions about mercury behavior and the possible impacts on beneficial use (i.e., wallboard manufacture) and disposal (RCRA subtitle D or C) .

The intent of this work was to produce in the laboratory high mercury concentrations in FGD material and to determine mercury volatilization on wallboard manufacture and mercury leaching. Additionally, two procedures based on volatilization and leaching profiles for individual mercury compounds were to be evaluated for the potential to indirectly identify the form of mercury in FGD gypsum. Such data would allow the prediction of mercury volatilization and leaching of mercury from FGD gypsum. Unfortunately the ppb concentration of mercury in FGD gypsum prevents compound identification by current analytical methods.

Two recently reported techniques by Milobowski[2] and by Bloom[3] on distinguishing mercury compounds through the use of thermal decomposition profiles and the use of sequential leaching, respectively, provide an interesting application to the present volatilization and leaching study planned. The hypothetical mercury compounds in the FGD material have significantly different vapor pressures at different temperatures and these differences theoretically could be used to distinguish between mercury compounds and identify the mercury form in FGD. Likewise, the differences in solubility of mercury compounds could be used to identify them in a substrate. In this study the very sensitive Tekran Cold Vapor Atomic Fluorescence Spectrometry (CVAFS) provided mercury measurements at ppt concentrations.

Executive Summary

Two methods were investigated to indirectly identify the mercury form in flue gas desulphurization (FGD) gypsum. These methods rely on the widely different vapor pressures and solubility of mercury compounds postulated to be in the FGD gypsum. Solid materials studied included (1) mercury-amended calcium sulfate (2) laboratory-prepared FGD material isolated from a simulated flue gas in a small wet-FGD system (3) and site-collected FGD.

Comparison of the leaching profiles of the mercury-amended calcium sulfate, laboratory-prepared FGD and site-collected FGD samples proves that mercury-amended calcium sulfate cannot be used as a surrogate for FGD material. Nearly all the mercury was leached from the mercury-amended samples; a result dissimilar to the lab-prepared or site-collected FGD samples. Likewise the thermodecomposition profiles of the mercury-amended samples were complex and dissimilar to the lab-prepared and site-collected samples. Of significance, the thermodecomposition profiles after 8 weeks provided clear evidence that the mercury complex in the gypsum had changed in three of the samples. The profiles for mercuric oxide, mercuric sulfate and mercuric chloride amended gypsum were similar to each other and roughly comparable to laboratory-prepared and site-collected FGD gypsum. The mercuric sulfide profile did not change, is not comparable to laboratory-prepared and site-collected FGD gypsum and, consequently, mercuric sulfide is not a primary component of FGD gypsum. Additional tests were conducted to determine if different oxidized forms of mercury in a flue gas would affect the mercury form in the gypsum as determined by thermodecomposition profile. There was no difference in the profiles and both were similar to the site-collected FGD. The conclusion is that the form of mercury in FGD gypsum is probably not a distinct mercury compound but tightly associated with the calcium sulfate matrix. The mercury-gypsum interaction is such that mercury leaching and thermal decomposition is limited compared to a discrete mercury compound in gypsum. The mercury-gypsum interaction can cause other mercury compounds to undergo rearrangement in the gypsum solid phase.

To produce the laboratory-prepared FGD gypsum, parametric tests were designed such that a range of mercury concentrations could be produced, from 0.7 to 4.6 ppm Hg. All mercury in the simulated flue gas was converted to the oxidized form prior to contact with laboratory-scale FGD unit. The mercury concentration of the solids isolated ranged from 0.1 to 0.3 ppm. Any elemental mercury measured as evolving from each experiment did not account for the discrepancy in the solids. The equipment and test design are being scrutinized for appropriate changes. Although the laboratory prepared FGD material did not contain the mercury concentrations anticipated, they were in the range of field FGD gypsum. Further thermal tests on lab and field FGD gypsum demonstrate that mercury begins to evolve from FGD material at 380 to 390°F. The mercury evolution rate increases with an increase in mercury concentration in FGD gypsum and decreases with an increase in weight of a wallboard sample. The conclusion is that if necessary, the wallboard drying temperature could be lowered to mitigate mercury evolution. Considering the large sheets of papered wallboard and that the exposed surface area is the cut edges only, mercury evolution may not be a significant problem. To assess this hypothesis, and possibly establish a predictive method, mercury content and evolution around a large sheet of papered wallboard should be monitored during drying to determine the ratio of evolution to exposed gypsum surface area with mercury initial mercury content.

Ramped temperature thermodecomposition profiles were also used to get a rough idea of the mercury concentration in the solids. For quick determination of mercury concentrations in FGD or other solids, a high temperature thermodecomposition method should be developed with an appropriate QA/QC procedure as an analytical method for mercury.

Experimental

Preparation of Mercury-Amended Calcium Sulfate

Four 50-gram samples of Aldrich ACS reagent calcium sulfate dehydrate were spiked with 0.001 gram of one of the following mercury compounds: mercuric chloride, mercuric oxide, mercuric sulfate and mercuric sulfide. The mixtures were shaken and tumbled for 2 weeks to homogenize, sampled and returned to shaker for an additional 6 weeks and sampled again.

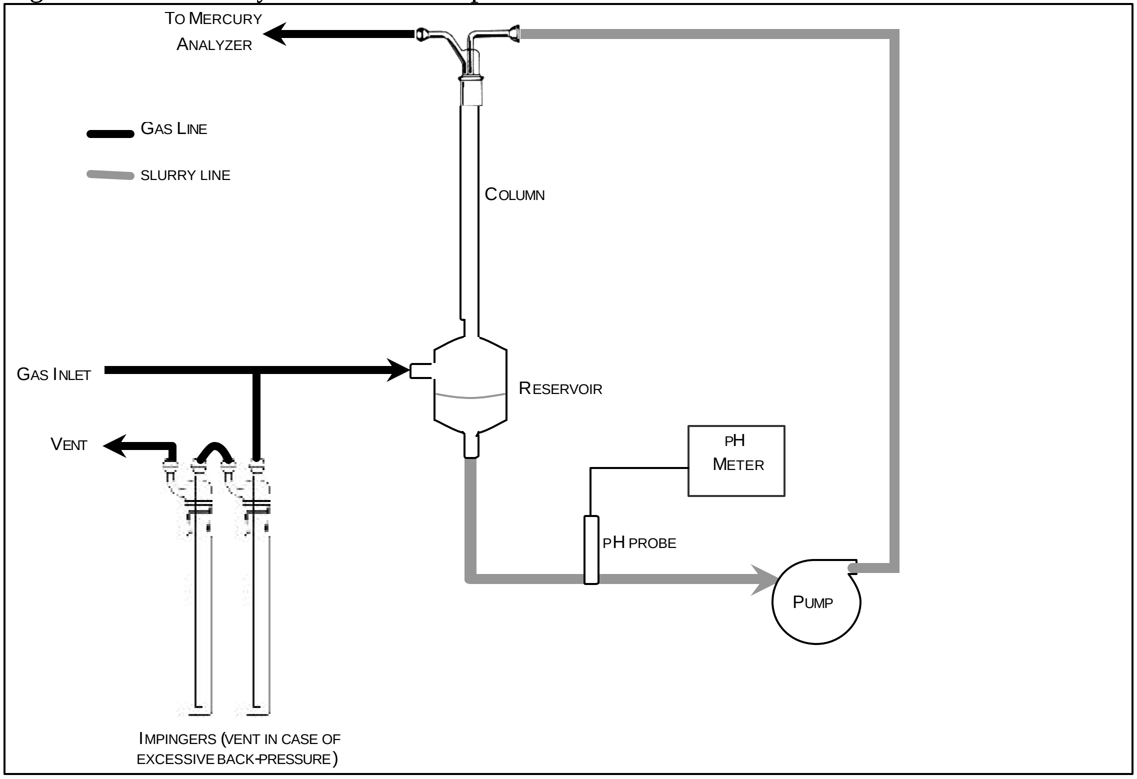
Collection of Coal-Fired FGD Byproduct

Samples of FGD byproduct were obtained at Tennessee Valley Authority's (TVA) Cumberland, Paradise and Widows Creek power plants. These plants trap sulfur dioxide (SO_2) with limestone followed by forced oxidation to calcium sulfate. The Cumberland samples were collected from stacks of filtered FGD byproduct awaiting transfer to the adjoining wallboard Plant. The filtered FGD byproduct stack contained product from the two Cumberland units, both equipped with wet limestone scrubbers capable of > 95% SO_2 removal. The Cumberland selective catalytic reactor (SCR) units were not operable during sample collection. The Paradise sample was collected at the FGD slurry exit that flows into the waste pond. The slurry exiting the pipe is a mixture from the two wet limestone scrubbers at Paradise. Widows Creek samples were collected at a sampling outlet of the Unit 8 wet limestone FGD tank. The Paradise and Widows Creek samples were filtered. All samples were stored on ice for transit to the laboratory, and then frozen till use. The FGD solids were tested for stability by leaching and by mercury volatilization profiles at temperatures consistent with landfill and wallboard environments.

Preparation of a Simulated FGD Byproduct

A diagram of the laboratory FGD is shown in Figure 1. The 119 cm length reactor column was attached to a 200 ml reservoir. A 2 L/min flow of simulated flue gas composed of elemental mercury, sulfur

Figure 1 Laboratory Flue Gas Desulphurization Unit



dioxide, oxygen, water vapor, carbon dioxide, nitrogen dioxide and hydrogen chloride flowed over a mercury oxidation catalyst. The oxidized mercury in the simulated flue gas flowed through the reservoir, up the column and is then contacted with a countercurrent solution containing 5.6 grams of CaCO3 in 145ml water. A centrifugal pump (March Manufacturing model AC-2CP-MD) recycled the slurry until the reaction is complete and sulfur dioxide broke through as signaled by a sharp rise in the pH. Oxygen is circulated through the reactor and the gypsum product was filtered and dried at 50ºC.

The catalyst was gold-coated sand that absorbed elemental mercury from the simulated flue gas. Depending on the flue gas environment, oxidation of elemental mercury is initiated by acid flue gas components and equilibrium is established between elemental mercury absorption, reaction with flue gas components and desorption of oxidized mercury. The concentrations of nitrogen dioxide and hydrogen chloride chosen for this study combine to produce 100% mercury oxidation in the presence of the gold catalyst. (TVA gold catalyst is currently undergoing field tests at the Spruce Plant, City Public Service of San Antonio)

The test design was a 2-factor factorial with variables being mercury and sulfur dioxide concentrations. The constants in the design were 5% oxygen, 10% water vapor, 14% carbon dioxide, 30 ppm nitrogen dioxide and 80 ppm hydrogen chloride gas. The parametric testing included duplicate tests and 3-center points. Mercury analysis of the laboratory-prepared FGD gypsum samples was determined by EPA method 1631.

Wallboard Sample Preparation

Stucco was prepared from all the simulated FGD gypsum samples by heating for 15 min at 285°F. Preliminary tests showed that at 285°F no mercury evolved and water loss was complete within 15 minutes.

A wallboard sample was prepared by adding 4 ml deionized (DI) water to 5.88 gms stucco, letting the mixture set for 30 seconds, stirring for 30 seconds and pouring onto wax paper. The sample was allowed to set for 10 12 minutes. For each wallboard sample produced from the FGD byproducts, 3 chips were selected. The mercury evolution from each chip was followed as it was cured for 10 minutes at 600F as done at the wallboard plant adjacent to the Cumberland Power Plant.

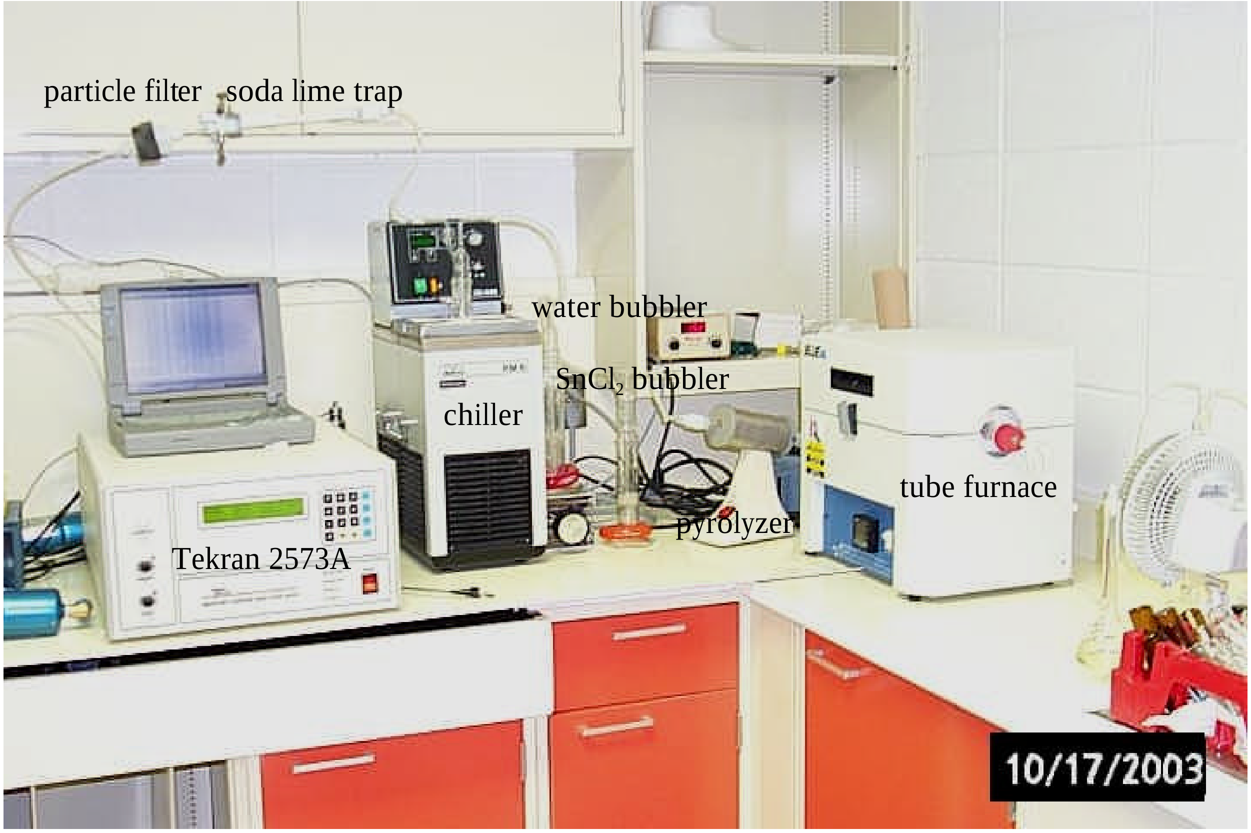
Leaching Procedure

Leaching profiles of mercury-amended calcium sulfate, laboratory-prepared FGD byproduct and site-collected FGD samples were performed in triplicate. Bloom's sequential leaching procedure[3] is described as a 5-step process however the sequence was modified in these tests since most or all the solid was consumed by the second leach. The extraction solutions were DI water (suggests presence of mercuric sulfate and mercuric chloride) and pH 2 HCl (suggest presence of mercuric oxide). The leaching process involved the sequential selective extractions of 0.4 gram aliquots of the homogenized gypsum solids. The extraction was performed using a 100:1 liquid-to-solids ratio in 40 mL vials. Each extraction step is conducted for ~ 18 hrs at room temperature. At the end of each step, the samples were centrifuged, and then the supernatant liquid was filtered through a 0.2 µ filter and rinsed. The combined filtrate and rinse was oxidized by the addition of bromine chloride (BrCl), and diluted to 125 mL prior to analysis for total Hg by EPA Method 1631. After the rinse step, the sample pellet in the centrifuge tube was re-suspended in the next extractant, and the entire process was repeated. The total mercury in each solid is determined by room temperature digestion in aqua regia (4:1 HCl + HNO3) over night using 0.4 gm sample to 10 mL aqua regia. The samples are diluted to 40.0 mL with 0.02 N BrCl in 1N HCl, and aliquots analyzed by US EPA Method 1631.

Thermodecomposition Procedure

The thermodecomposition equipment train is shown in Figure 2. From the far right, the tube furnace is followed by a pyrolyzer, the stannous chloride bubbler, water bubbler, chiller, soda lime trap, particle filter and finally to the Tekran 2537A cold vapor atomic fluorescent detector for mercury measurement. To measure mercury volatilization from a solid sample, about 0.1 gram is placed in the tube furnace and heated. A 1.5 L/min flow of nitrogen carries the mercury evolved by the solid from the tube furnace to the Tekran detector. Thermodecomposition profiles were obtained by using either a ramped temperature (~10 min per °F) vs. time or a constant temperature (140, 400 and 600°F) vs. time. A 1 mL solution of a standard 0.0001 M mercuric chloride solution was periodically introduced into the tube furnace to check analytical accuracy of the train.

Figure 2. Thermodecomposition Train



Tekran Model 2537A Mercury Vapor Analyzer

The Tekran Model 2537A Mercury Vapor Analyzer provides analysis of total mercury in a gas phase in ng/m3. The instrument, as set-up for these tests, traps mercury vapor by a cartridge containing an ultra-pure gold adsorbent from a 1.5 L/min nitrogen gas flow. The amalgamated mercury is thermally desorbed and detected using Cold Vapor Atomic Fluorescence Spectrometry (CVAFS). The Tekran incorporates a dual cartridge design that allows alternate mercury sampling and desorption. While cartridge A is adsorbing mercury during a sampling period, cartridge B is desorbed and analyzed. The roles of the cartridges are then reversed. Desorption operations are performed in an inert, ultra high purity Argon carrier gas. Mercury that was adsorbed onto the gold matrix is released during heating in Argon. The mercury is then carried into the detector. Radiation at 253.7 nm excites any mercury atoms present, which fluoresce and re-radiate at the same wavelength. A detector views the fluorescence produced by the mercury in the cell. The intensity of the fluorescence is directly proportional to the amount of mercury in the cell. A data point is registered every 2 minutes.

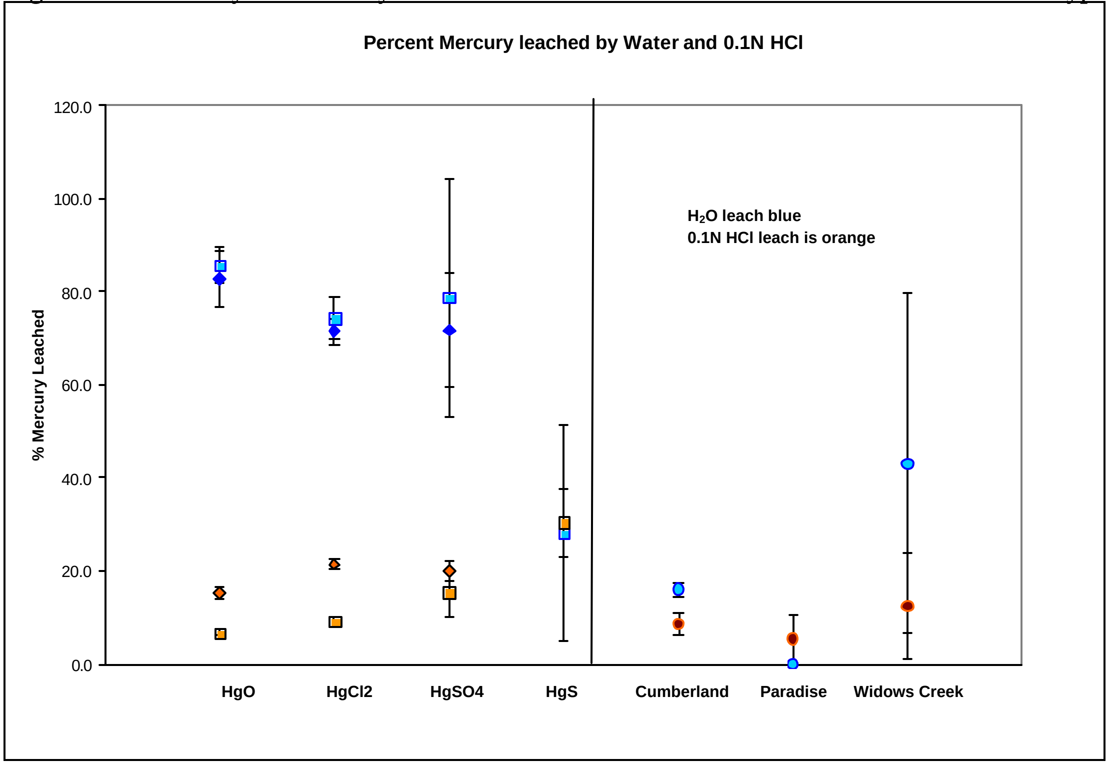
Results and Discussion

Mercury Form in Gypsum.

Leaching Profiles

To determine the mercury form in gypsum, a sequential extraction method was applied as describe in the Experimental section. Direct determination of a mercury form in a substrate is not possible by sequential extraction procedures but may suggest the mercury form based on its extraction chemistry. The basis of the evaluation was the results from a series of calcium sulfate mixtures amended with mercuric compounds that were hypothesized to exist in FGD gypsum, mercuric chloride, mercuric oxide, mercuric sulfate and mercuric sulfide.

Figure 3: Solubility of Mercury-Amended Calcium Sulfate and Site-Collected FGD Gypsum



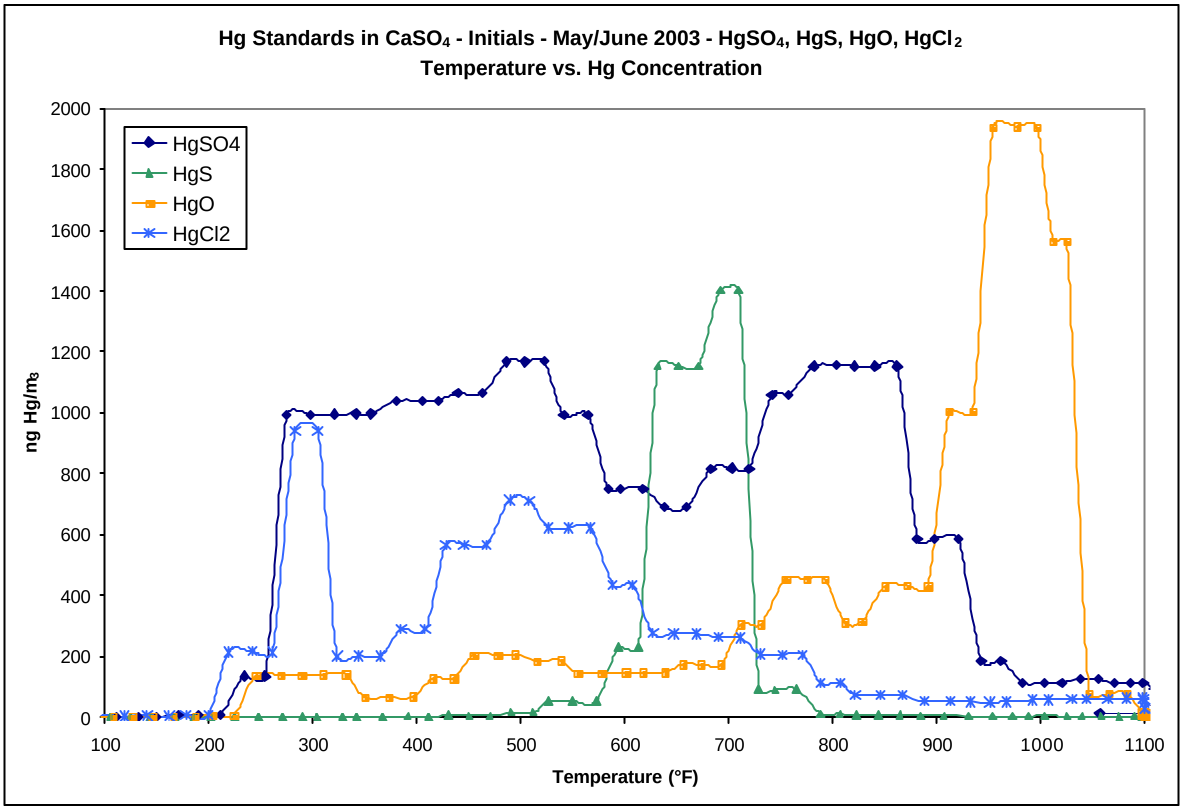
Expectations were that the DI water extraction would preferentially extract mercuric sulfate and mercuric chloride, whereas the HCl extraction would leach mercuric oxide. Neither leaching was expected to affect the mercuric sulfide. Two extraction procedures in triplicate for mercury-spiked gypsum and actual FGD products are shown in Figure 3. The data did not follow expectations. The influence of the calcium sulfate probably overwhelmed the solubility profiles of the mercury compounds. Solubility in water of the respective mercuric salt in gypsum ranged from 30 to 80%. It was concluded that chemical extraction methods are not appropriate for identification of the mercury species in FGD byproduct. The high solubility of mercury in these mixtures compared to the site-collected FGD gypsum suggest that none of these mercury forms may be present in FGD gypsum.

Thermodecomposition Profiles- Ramping Temperatures

Mercury thermodecomposition profiles (ramped temperature vs. mercury evolution) were applied for qualitative determination of mercury evolved based on the decomposition temperature profile of mercury compounds in a substrate. This is a more direct method for determination of mercury species than leaching profiles. A ramping temperature of 10 °F/min was used.

Thermodecomposition profiles of calcium sulfate substrates amended with mercuric chloride, mercuric oxide, mercuric sulfate or mercuric sulfide were collected. As shown in Figure 4 the profiles obtained are distinct for each mercury compound. Two series of the 4 profiles were collected in which samples were run in triplicate. On occasion an inconsistent profile was collected and led to supposition that rearrangement of mercury in calcium sulfate may be occurring.

Figure 4: Thermodecomposition Profiles of Mercury-Amended Calcium Sulfate, 2-week old



To determine if changes in the profiles occur with time, the samples were allowed to tumble and age for another 6 weeks after which time the thermodecomposition profile data was re-collected. As shown in Figure 5, the chloride, oxide and sulfate form of the mercuric complex were affected by the further tumbling in the presence of the calcium sulfate substrate and rearranged into a similar form in the solid as indicated by the similar profiles. The thermodecomposition profiles of the site-collected FGD samples, Figure 6, were somewhat similar to the aged-mercury-amended calcium sulfate samples. The major difference

Figure 5: Thermodecomposition Profiles of Mercury-Amended Calcium Sulfate, 8/9-week old

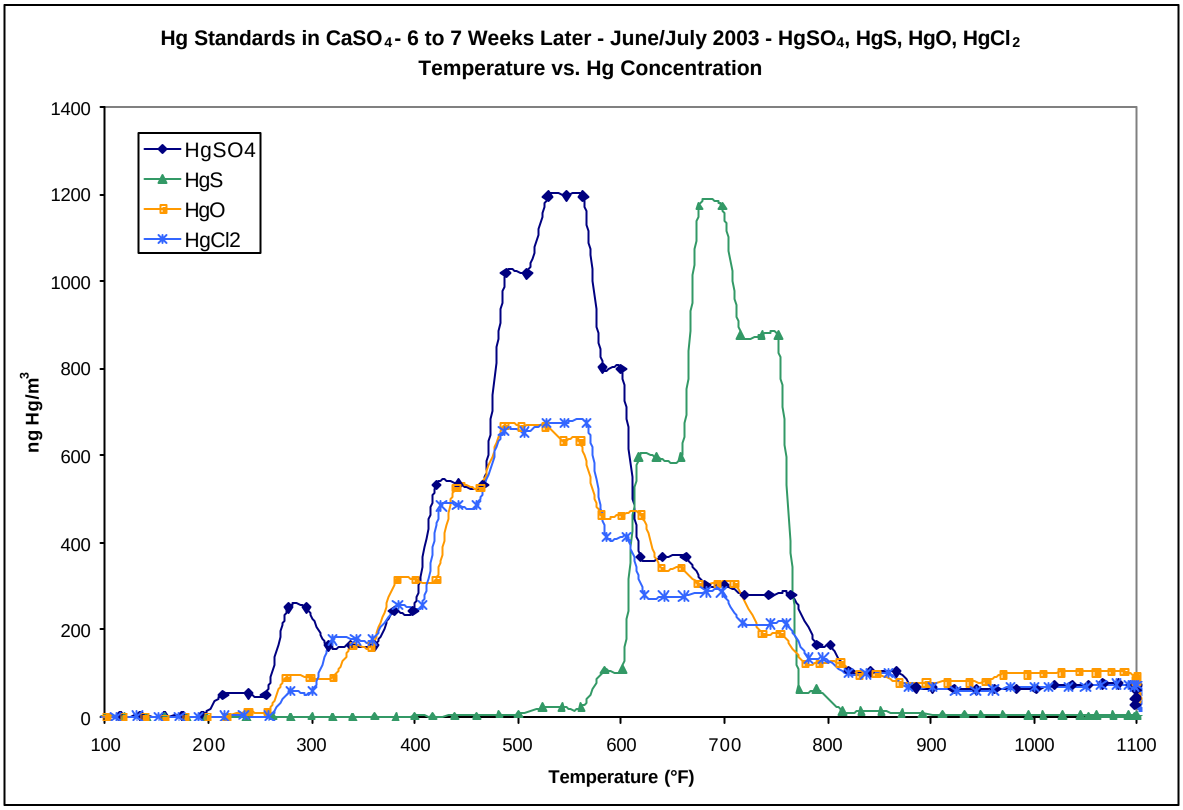
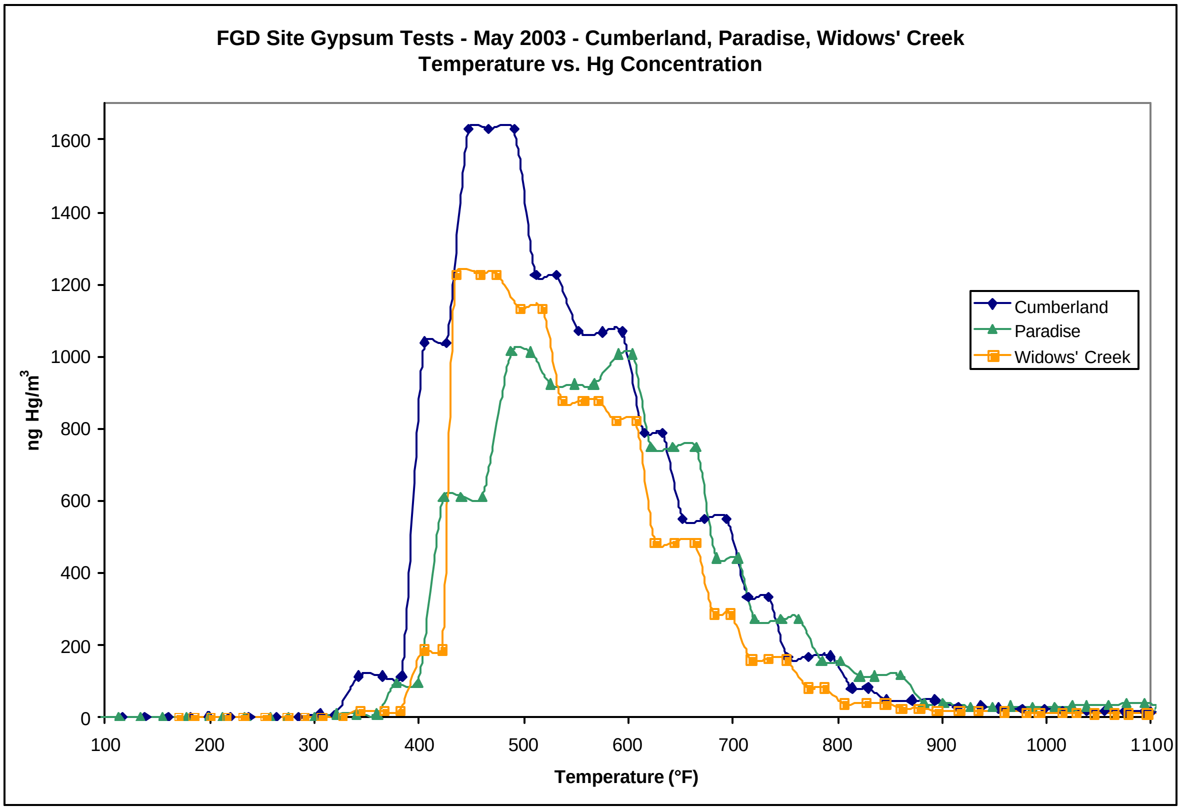


Figure 6: Thermodecomposition Profiles of Site-Collected FGD gypsum



concerned the temperature at which mercury began to evolve, 200°F for the mercury-amended samples compared to 390°F for the site-collected FGD samples. The Cumberland sample evolved mercury at 340°F however the sharp rise began at 390°F

It was concluded in comparing the site-collected FGD and the aged-mercury-amended calcium sulfate thermodecomposition profiles that the mercuric compounds used to amend the calcium sulfate samples were being transformed in the calcium sulfate matrix. The transformation is probably related to the sulfate in the matrix, a mercury and multiple-sulfate coordination perhaps. Consequently, the mercury form in the FGD byproduct is probably not a distinct mercuric chloride, -sulfate or –oxide but rather forms a complex structure with its sulfate environment. The mercuric sulfide amended calcium sulfate profile was unique among the profiles in that the calcium sulfate environment did not change its initial profile and as it was dissimilar to site-collected FGD; the mercuric sulfide is not a component in the FGD byproduct.

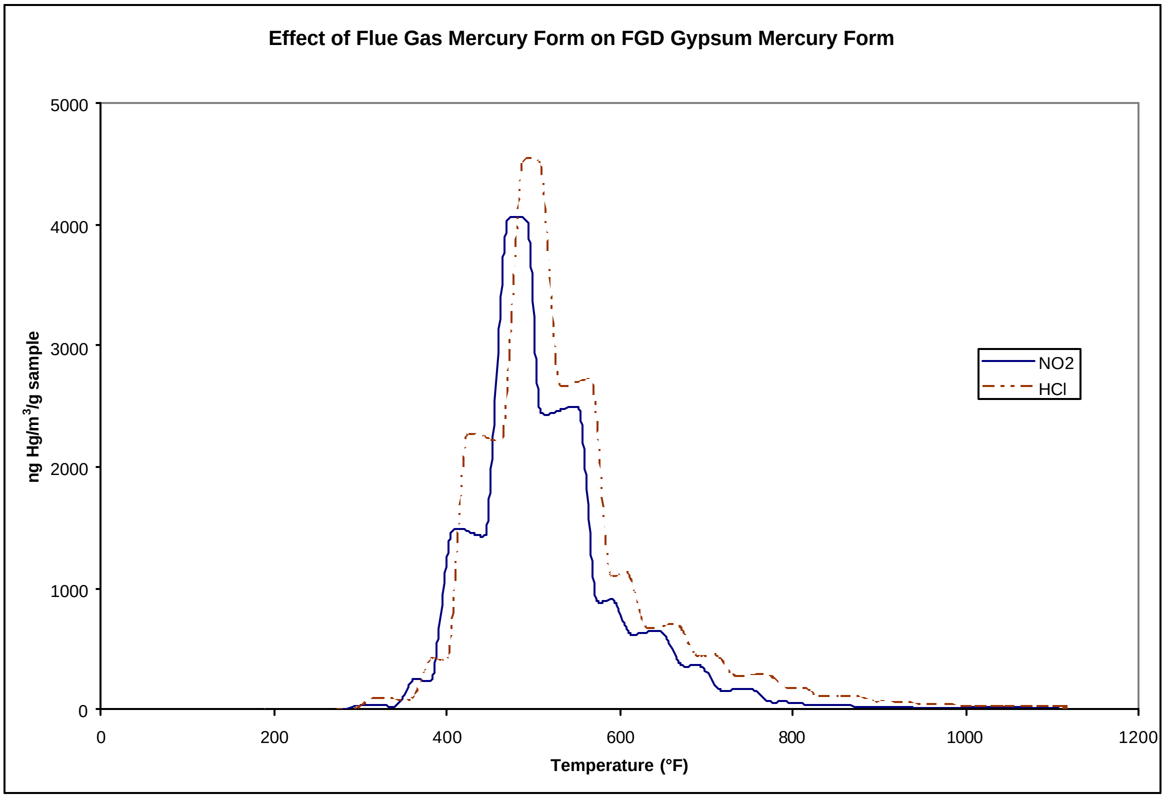
Laboratory-Prepared FGD Gypsum

Preliminary Tests

Preliminary tests were conducted on the laboratory FGD unit with no mercury in the simulated flue gas and with elemental mercury in the simulated flue gas. The thermodecomposition profiles of the two simulated FGD materials formed indicate that, as expected, no mercury was captured in these products.

Tests were performed to determine if the mercury form in flue gas could affect the mercury form in the laboratory-prepared FGD gypsum as determined by thermodecomposition profiles. To accomplish

Figure 7: Thermodecomposition Profile of Laboratory FGD Gypsum Prepared from a Simulated Flue Gas with Different Oxidized Forms of Mercury



this, use was made of the fact that the oxidation catalyst in our tests will oxidize mercury in the presence of either hydrogen chloride (HCl) or nitrogen dioxide (NO2). The most likely oxidized mercury formed with HCl is mercuric chloride ($HgCl_2$) and with NO2 is mercuric oxide (HgO). If the form of oxidized mercury in the simulated flue gas also exists in the laboratory-prepared FGD gypsum then different thermodecomposition profiles should occur. Two tests were conducted such that either HCl or NO_2 was present to oxidized mercury over the catalyst in a simulated flue gas. The thermodecomposition profiles of Figure 7 show that both mercury evolution profiles are similar; consequently the mercury form in the solid is similar which suggests that the mercury form in the flue gas does not govern the ultimate form of mercury in the FGD product. Significantly, the thermodecomposition profiles of these simulated FGD products were comparable to site-collected FGD material as shown in Figure 6.

Parametric Design and Mass Balance Results

Following the experimental design protocol, a series of eleven laboratory-prepared FGD products were produced that were analyzed along with the filtrates for mass balance information. Comparison of mercury concentrations in simulated FGD products vs. site-collected FGD indicated that the mercury concentration in a majority of the simulated FGD products was from 0.1 to 0.3 ppm, typical of many actual FGD byproducts.

Analysis of the collated data from the simulated FGD tests established that a mercury mass balance was not obtained. Less than 30% of the input mercury was recovered from each test. Comparisons of theoretical results to test results are listed in Tables 1 and 2. It is evident that the mercury concentration in the gypsum is well below the theoretical of 0.72 to 4.55 ppm based on the concentration of mercury added to the system. The percent mercury recovered in the gypsum product compared to the theoretical was less than 20%. The percent calcium sulfate recovered was, on average, 70% of the theoretical 9.4 grams calculated to be produced.

Table 1. Parametric Test Design

Design	Concentration, ppm		Reaction	gypsum	
Test	Hg	SO2	min	gms	ppm Hg
1	1.0	525	1628	9.40	2.90
2	1.0	525	1628	9.40	2.90
3	1.6	525	1628	9.40	4.55
4	1.6	525	1628	9.40	4.55
5	1.0	2100	407	9.40	0.72
6	1.0	2100	407	9.40	0.72
7	1.6	2100	407	9.40	1.14
8	1.6	2100	407	9.40	1.14
9	1.3	1313	651	9.40	1.48
10	1.3	1313	651	9.40	1.48
11	1.3	1313	651	9.40	1.48

Table 2. Test Conditions and Results

Design	Concentration		Reaction	gypsum		filtrate		% Total Hg
Test	Hg, ng/min	SO2, ppm	min	gms	ppm Hg	Vol., ml	ng Hg/L	Recovered
1	16.7	543	1424	6.42	0.23	89.8	1458	7
2	16.7	532	1470	6.07	0.10	69.9	4562	4
3	26.2	515	1285	6.85	0.18	87.9	5209	5
4	26.2	544	1423	7.22	0.22	87.6	5676	6
5	16.7	2135	305	6.39	0.13	82.4	2261	20
6	16.7	2124	360	7.17	0.14	99.2	563	18
7	26.2	2135	325	5.57	0.21	91.6	266	14
8	26.2	2089	350	6.69	0.20	74.0	360	16
9	21.4	1318	555	7.53	0.22	105.8	469	14
10	21.4	1358	499	6.49	0.25	100.7	3432	18
11	21.4	1341	550	5.98	0.44	132.8	91	22

As the tests progressed a TVA mercury monitor[4] was set up to measure the elemental mercury evolved as analytical data indicated that most of the mercury was not being trapped in the gypsum. The monitoring results indicated that some elemental mercury was evolved, but not enough to explain the low mercury concentrations in the FGD gypsum. The mass balance data suggest that either oxidized mercury was evolved during the simulated FGD tests or more likely deposited elsewhere in the system. One likely candidate for mercury deposition and release is the centrifugal pump. Another consideration is the mercury capture/release was negatively affected by the lengthy time required for complete reaction. Modifications to the laboratory FGD unit are planned.

Leaching Profiles

Leaching of the FGD product samples with water and 0.1N HCl was completed as described in Experimental section. In Figure 8, the result of each leaching test is listed by test number (test parameters as shown in Table 1). The water leach typically removed less than 15% of the mercury in the products from laboratory FGD system. Subsequent leaching of the filtered solid by 0.1N HCl removed an additional 10 to 30% of the mercury. Mercury recovery from the laboratory-prepared FGD solid is drastically reduced from that observed in the mercury-amended calcium sulfate mixtures (40-80%). The leaching results of the site-collected FGD byproduct are shown in Figure 8 as test numbers 12, 13 and 14. Cumberland gypsum showed a profile most comparable to the laboratory-prepared FGD data.

Thermodecomposition Profiles

The laboratory-prepared FGD samples were evaluated for mercury evolution using a ramped-temperature thermodecomposition. The profiles are similar to each other, Figure 9, and are analogous to the site-collected FGD material, Figure 6. It is concluded that the mercury form in both materials is the same or similar. The ramped-thermodecomposition data show that mercury evolution begins to rise sharply at ~380°F with the maximum mercury evolution occurring around 450 to 550°F. To reduce mercury evolution, if necessary, during drying of wallboard sheets, a simple reduction of dry temperature to around 380 to 390°F could be made.

Figure8. Comparison of Mercury Leached by Water and 0.1N HCl from Laboratory-Prepared and Site-Collected FGD gypsum

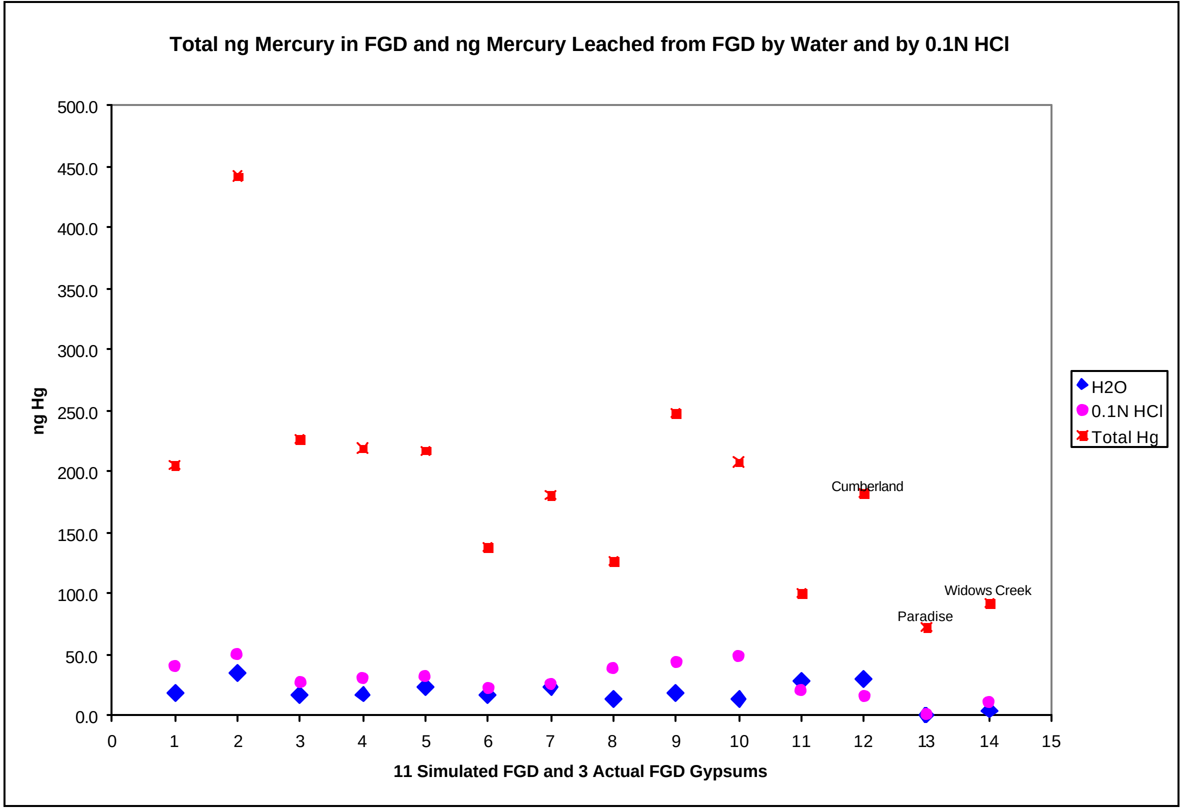
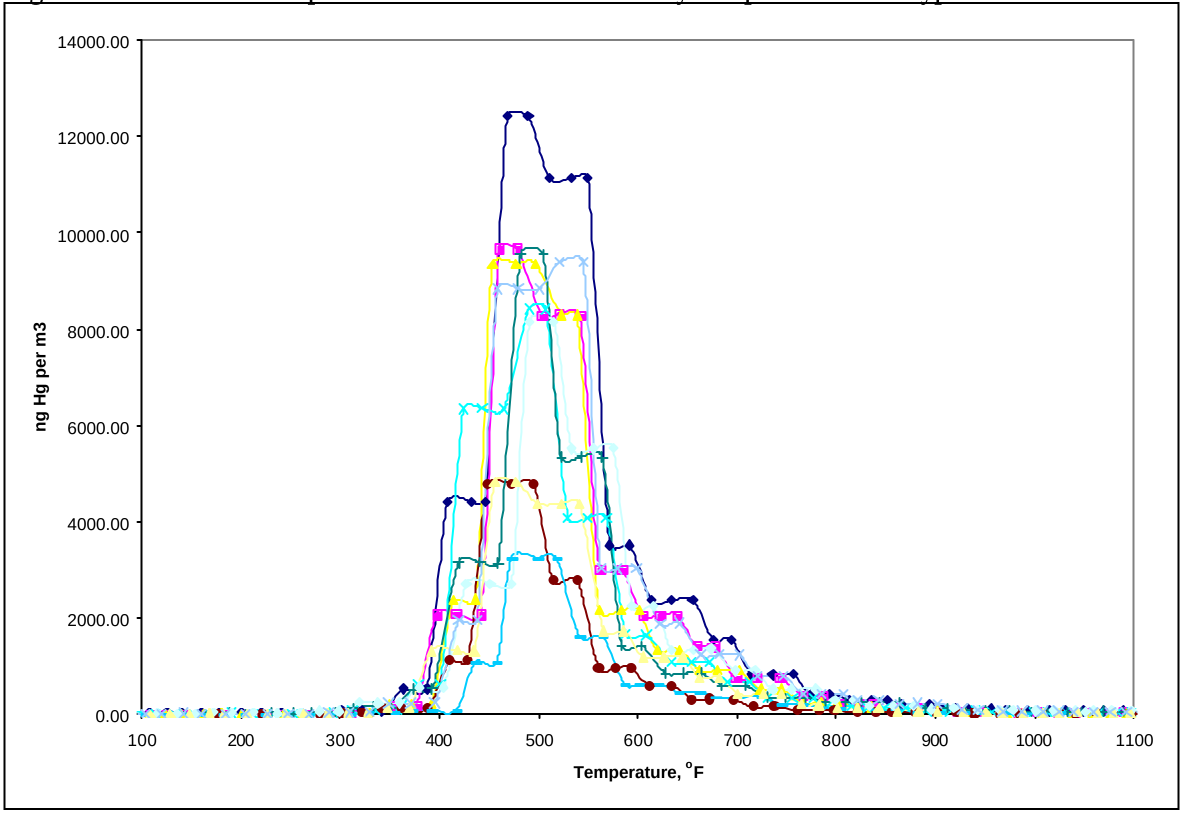


Figure 9: Thermodecomposition Profiles of Laboratory-Prepared FGD Gypsum



Constant Temperature Profiles of Site-Collected FGD Byproduct

Constant temperature mercury evolution profiles were collected at 120, 400 and 600°F for the 3 site-collected samples, Cumberland, Paradise and Widows Creek. No mercury was detected for the 120°F test over a 4-hour test period. The profiles for the 400 and 600°F temperatures are shown in Figures 10 and 11. From the figures, each series of tests require around 15 minutes for the tube furnace to reach the set temperature. The FGD materials begin to evolve mercury prior to the set temperature in each case. Mercury evolution for the 400°F test begins at 380-390°F as shown in Figure 10, whereas for the 600°F test, the first observed mercury evolution for the same materials is from 480 to 550°F. It can be concluded that for processes that involve short quick heating that very little if any mercury may be evolved, for example, the 3-second heating at 900°F of FGD gypsum to produce stucco.

Wallboard Product and Mercury Evolution at 600°F for 10 minutes

A wallboard product was prepared as described in the Experimental section. The evolution of mercury at the drying temperature (600°F) used at Gypsum plant adjacent to Cumberland Power Plant was chosen as test temperature for evaluating the mercury evolution from the wallboard samples prepared from the simulated FGD materials. Mercury evolution from several different weights of wallboard was followed as it was cured for 10 minutes at 600°F. Three chips of wallboard sample at different weights were selected from each FGD test. Figure 12 shows that as the weight of the chip increased, the ng of mercury evolved per gram of wallboard decreased. This implies that a large wallboard panel, papered on both sides, may be expected to evolve very little mercury in the 10-minute drying process.

Figure 10. Thermodecomposition Profile of Site-Collected FGD Gypsum at 400°F

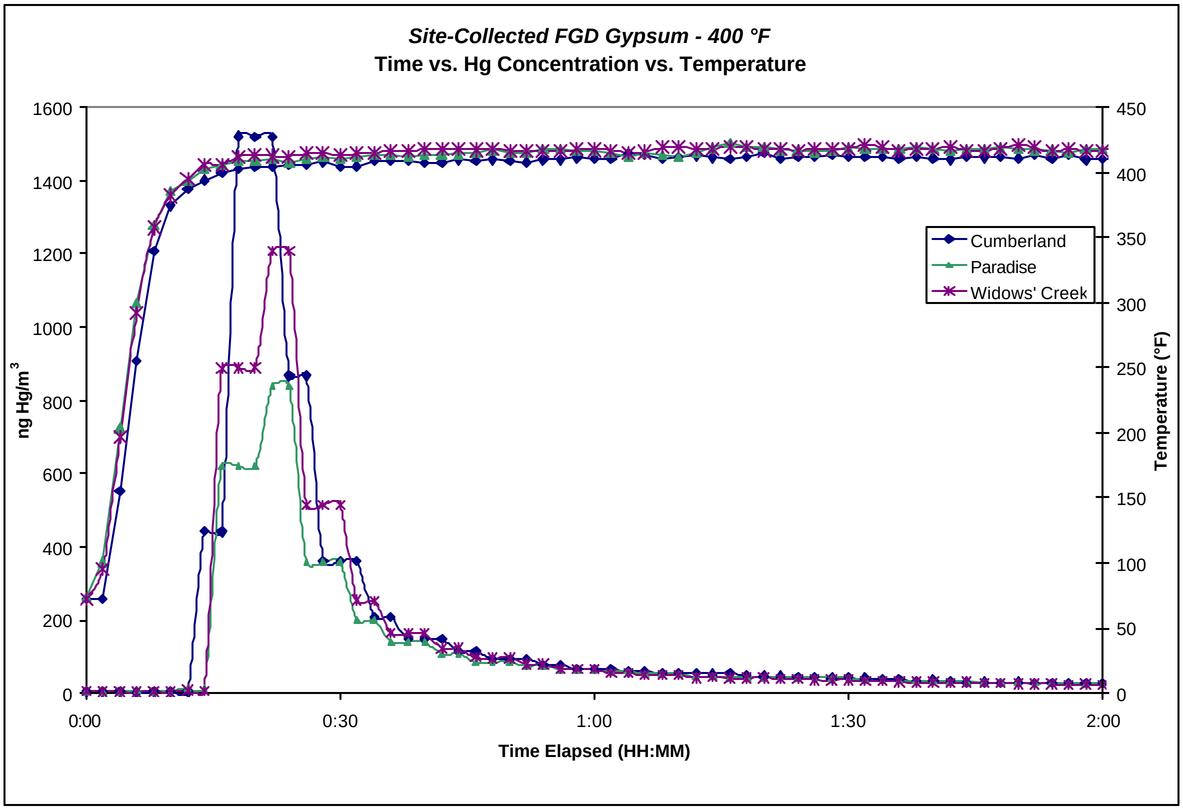


Figure 11. Thermodecomposition Profile of Site-Collected FGD Gypsum at 600°F

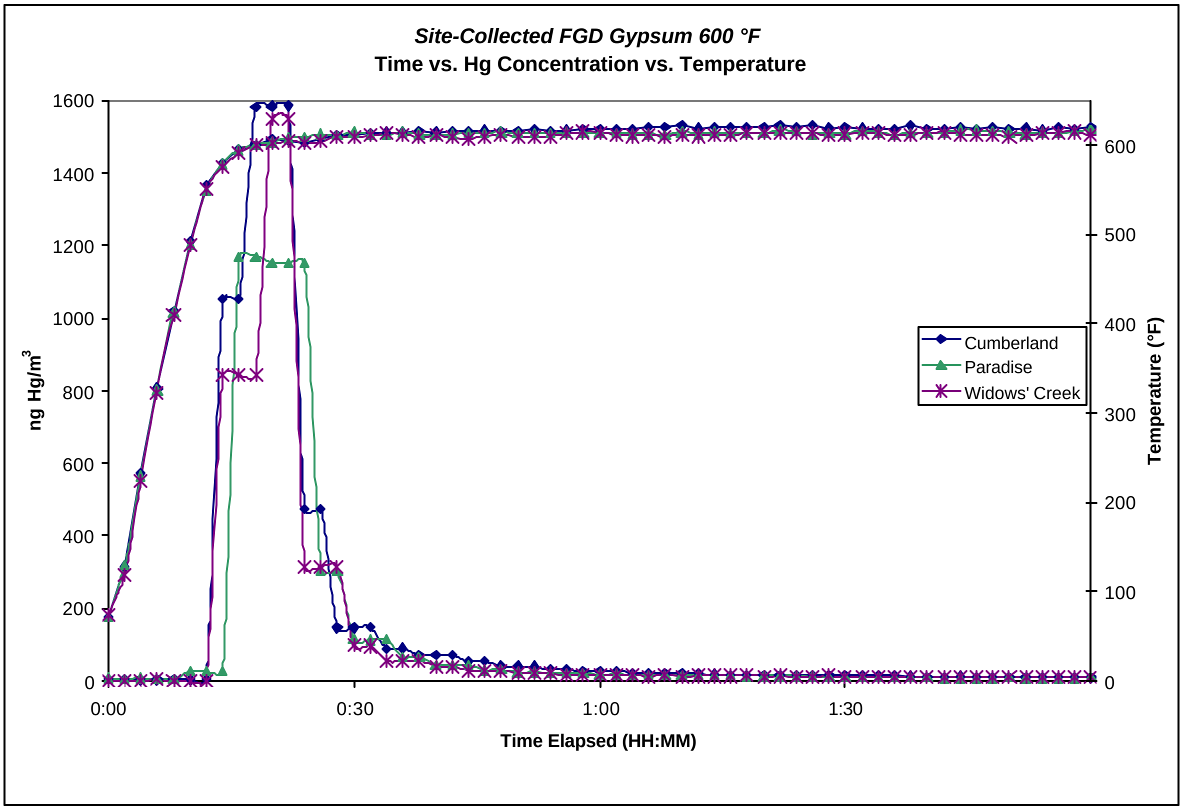
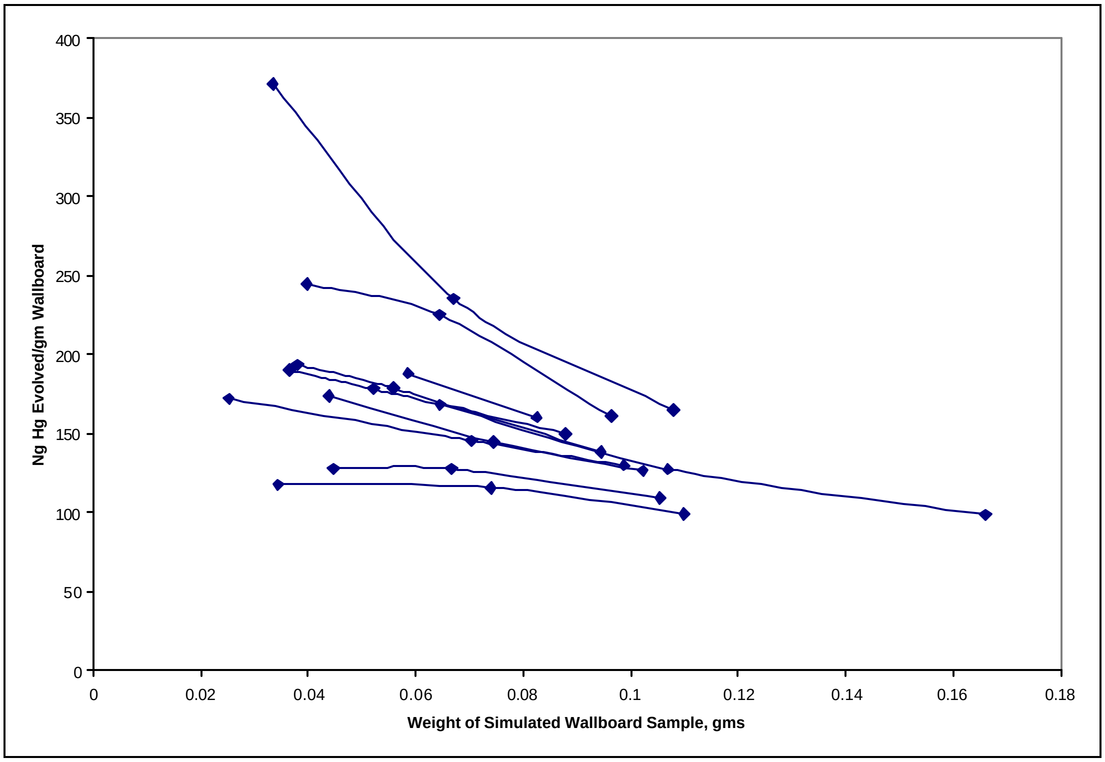


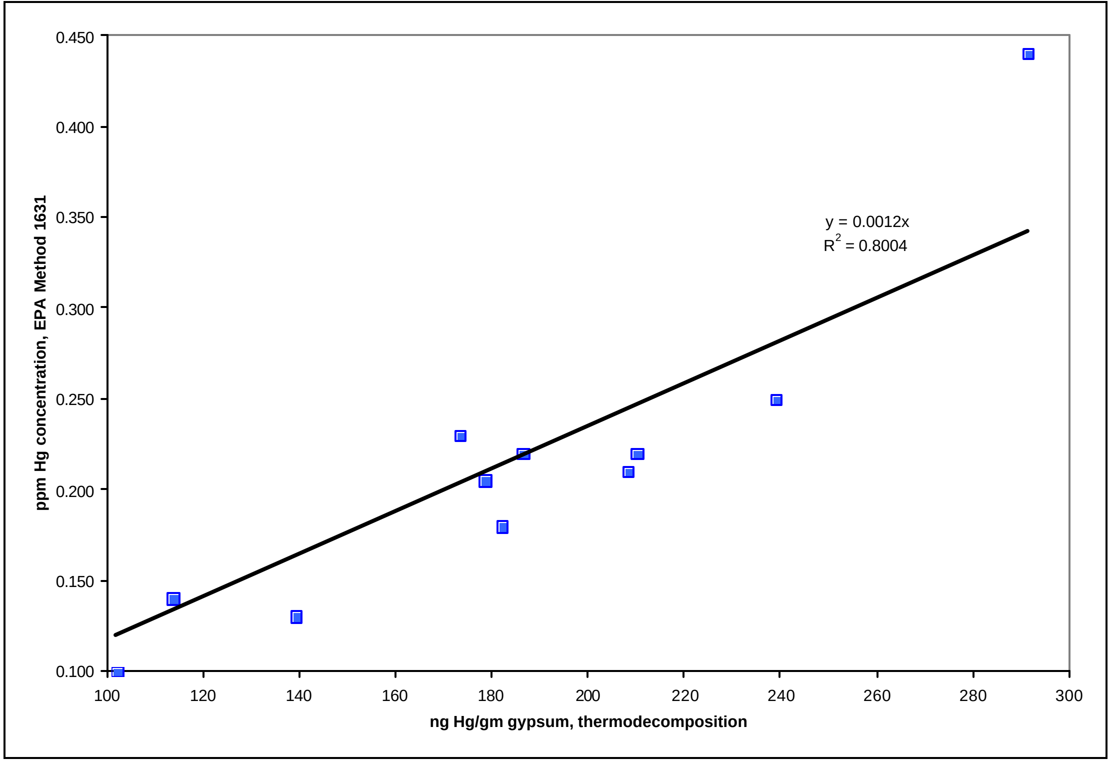
Figure 12 Ten Simulated Wallboard Samples - Decrease in Mercury Evolved as Weight of Wallboard Increased



Mercury evolved in 10 minutes at 600°F

As a note, a comparison of mercury analysis results by EPA Method 1631 to the mercury release from each sample during ramping thermodecomposition profile was calculated. That comparison data is shown in Figure 13. It was concluded that QA/QC for a high constant temperature thermodecomposition with CVAFS mercury detection should be further evaluated as a quick analysis method for solid samples containing ppb mercury concentrations. No preparation of solid samples would be required and analysis could take about 30 minutes. The only chemical required is a stannous chloride solution to insure all mercury is in the reduced form. A thermodecomposition method is simpler and may be more accurate for small samples.

Figure 13: Comparison of EPA Method 1631 of FGD Gypsum Analysis with Rough Calculation of Mercury Content from Ramped Thermodecomposition



Conclusions

Several conclusions were drawn from this work. A significant finding is that the form of mercury in FGD gypsum is probably not a distinct mercury compound but tightly associated with the calcium sulfate matrix. The preferred coordination is such that mercury leaching and thermal decomposition is limited compared to a discrete mercury compound. And as a preferred mercury form in gypsum, rearrangement of another mercury configuration can occur in the gypsum solid phase. Mercury chemistry is unique and complex and determining predictive behavior for mercury is a challenge.

The sensitive CVAFS technique demonstrated that no mercury evolves from FGD at 140°F, supposing this is a possible maximum temperature at a disposal site. At a wallboard drying temperature of 400°F mercury evolution from FGD gypsum peaks in 10 minutes while at 600°F peak mercury evolution is from 6 to 8 minutes. Thermodecomposition of prepared wallboard chips shows that mercury evolution per gram of material decreases with an increase in weight of the chip. The effect is more pronounced the higher the concentration of mercury in the chip. The overall effect on wallboard manufacture could be that reducing drying temperature to around 380°F could alleviate mercury evolution if a problem. However, because of the small surface area of the wallboard edges which is the only exposed gypsum during drying, mercury evolution may not be a problem. To assess this hypothesis, mercury content and evolution around a large sheet of papered wallboard should be monitored during drying to determine ratio of evolution to exposed gypsum surface area.

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