

Fate of Mercury in Synthetic Gypsum Used for Wallboard Production

Topical Report, Task 3 Wallboard Plant Test Results

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ABSTRACT

This report presents and discusses results from Task 3 of the study “Fate of Mercury in Synthetic Gypsum used for Wallboard Production,” performed at a full-scale commercial wallboard plant. Synthetic gypsum produced by wet flue gas desulfurization (FGD) systems on coal-fired power plants is commonly used in the manufacture of wallboard. This practice has long benefited the environment by recycling the FGD gypsum byproduct, which is becoming available in increasing quantities, decreasing the need to landfill this material, and increasing the sustainable design of the wallboard product. However, new concerns have arisen as recent mercury control strategies involve the capture of mercury in FGD systems. The objective of this study is to determine whether any mercury is released into the atmosphere when the synthetic gypsum material is used as a feedstock for wallboard production. The project is being co-funded by the U.S. DOE National Energy Technology Laboratory (Cooperative Agreement DE-FC26-04NT42080), USG Corporation, and EPRI. USG Corporation is the prime contractor, and URS Group is a subcontractor.

The project scope includes five discrete tasks, each conducted at various USG wallboard plants using synthetic gypsum from different FGD systems. The five tasks will include 1) a baseline test, then variations representing differing power plant 2) emissions control configurations, 3) treatment of fine gypsum particles, 4) coal types, and 5) FGD reagent types. Process stacks in the wallboard plant are being sampled using the Ontario Hydro Method. The stack locations sampled for each task include a dryer for the wet gypsum as it enters the plant and a gypsum calciner. The stack of the dryer for the wet wallboard product was not tested in this task but has been or will be tested in Tasks 1, 4 and 5. Also at each site, in-stream process samples are being collected and analyzed for mercury concentration before and after each significant step in wallboard production. The Ontario Hydro results, process sample mercury concentration data, and process data are being used to construct mercury mass balances across the wallboard plants.

Task 3 was conducted at a wallboard plant processing synthetic gypsum from a power plant that fires a high-sulfur bituminous coal. The power plant has a limestone forced oxidation FGD system, with the forced oxidation conducted in the reaction tank integral with the FGD absorber, and gypsum fines blow down. During the production of the synthetic gypsum used during this test, a selective catalytic reduction (SCR) system was in service for NO_x emissions control.

The results of the Task 3 stack testing, as measured by the Ontario Hydro method, detected 42% of the incoming mercury was emitted in the mill portion of the wallboard production. These losses were distributed as 1% across the dryer mill and 41% across the kettle calciner.

Approximately 99% of the mercury detected in the stack testing on the kettle calciner was in the form of elemental mercury. Solids analysis measured an additional 4% loss across the board dryer kiln, based on the mercury content of the raw synthetic gypsum. The total mercury loss measured across the raw gypsum dryer and kettle calciner by the Ontario Hydro method, and estimated from feed and product sample mercury analyses for the wallboard product dryer represented 46% of the raw synthetic gypsum mercury content. Although emissions were significantly higher than Task 1 and 2 results on a percentage basis, the synthetic gypsum tested in this task contained a relatively low concentration of mercury; thus the amount of mercury released was not much greater when expressed on a mass basis.

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INTRODUCTION

This report presents and discusses results from Task 3 of the study “Fate of Mercury in Synthetic Gypsum used for Wallboard Production,” performed at a full-scale commercial wallboard plant. The objective of this project is to measure whether any mercury evolves from synthetic gypsum produced by wet flue gas desulfurization (FGD) systems on coal-fired power plants, when that material is used as a feedstock for wallboard production. The project is being co-funded by the U.S. DOE National Energy Technology Laboratory (Cooperative Agreement DE-FC26-04NT42080), USG Corporation, and EPRI. USG Corporation is the prime contractor, and URS Group is a subcontractor.

Background

To address concerns about air quality, the U.S. Congress passed the Clean Air Act Amendments of 1990, which placed significant restrictions on sulfur dioxide emissions from coal-fired power plants. To reduce sulfur dioxide emissions and meet the Clean Air Act standards, many electric utilities installed wet FGD systems on their coal-fired plants. These FGD systems combine the sulfur dioxide gases released during coal combustion with a sorbent such as limestone or lime. In many of these wet FGD systems, the resulting byproduct is oxidized to produce synthetic gypsum. The synthetic gypsum produced is commonly used as a feedstock for wallboard production. The reuse of the synthetic gypsum is environmentally beneficial and is also economically attractive for both the power and wallboard industries. The Clean Air Interstate Rule, signed by the U.S. EPA in March 2005, will further regulate sulfur dioxide emissions. Greater amounts of synthetic gypsum will be created, potentially causing a large increase in the volume of this material to go to landfills. Establishing wallboard manufacturing plants near both power plants and population centers can reduce the quantity landfilled, while increasing the sustainable design of the wallboard product by reducing transportation and use of fossil fuels.

A number of mercury control strategy plans for U.S. coal-fired power generating plants involve the capture of oxidized mercury from flue gases treated by wet FGD systems. For example, in finalizing the Clean Air Mercury Rule on March 15, 2005, the U.S. EPA recognized mercury emissions reduction “co-benefits” possible for coal-fired plants that are equipped with selective catalytic reduction (SCR) for NO_x control and wet FGD systems for SO₂ control. SCR systems on bituminous coal fired plants have been observed to oxidize most of the elemental mercury in the SCR inlet gas. Also, a number of proposed mercury control processes involve using low-temperature catalysts or injected chemicals to oxidize elemental mercury and promote increased mercury removal across FGD systems.

For these processes to be effective at overall mercury control, the mercury must stay in the FGD byproducts and not be re-emitted to the atmosphere or into ground water. Measurements by URS Group and others have indicated that nearly all of the mercury scrubbed from flue gases in most U.S. wet FGD systems ends up in the solid byproducts. Very little mercury is typically found in the FGD liquors. Thus, mercury stability in FGD solid byproducts is an important aspect of mercury capture in FGD systems.

Most FGD systems use lime or limestone reagent and employ forced oxidation to produce gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) as the solid byproduct. Much of the gypsum byproduct is reused, primarily as a feedstock for wallboard manufacturing. Those that do not produce gypsum instead produce a calcium sulfite hemihydrate ($\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$) byproduct. Most calcium sulfite byproducts are landfilled, although some is reused as mine fill.

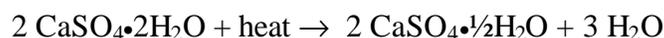
Approximately 70% of all of the FGD byproduct reuse in the U.S. is gypsum used as wallboard feedstock. During the year 2005, synthetic gypsum from FGD systems is expected to represent 30% of the U.S. wallboard plant feedstock.

This raises new technical questions: What is the fate of mercury in synthetic gypsum in the wallboard plant process? How much mercury is released into the atmosphere during the production of wallboard using synthetic gypsum? Is the amount of mercury released counterproductive to controlling mercury emissions from coal-fired power plants?

Even if mercury is not released in significant quantities during wallboard production, there remains a question as to the stability of mercury in the wallboard product. As an example, at the end of its product life cycle, most wallboard ends up in municipal landfills. What is the stability of mercury in wallboard produced from synthetic gypsum? Will the mercury leach into the acidic aqueous environment in a municipal landfill? This project is intended to collect data from commercial wallboard plants processing FGD synthetic gypsum to help answer these questions.

The Wallboard Production Process

Figure 1 shows an overview of the wallboard production process. In the process, synthetic gypsum is dried to produce “land plaster,” which is gypsum that contains no free moisture, only chemically bound waters of hydration. The land plaster is then calcined to produce the “beta” form of calcium sulfate hemihydrate according to the following chemical reaction:



The beta hemihydrate is also commonly called “stucco” or “plaster of Paris.” The stucco is subsequently mixed with water and a number of additives to form a slurry that is extruded between two sheets of paper to form the wallboard. The hemihydrate re-hydrates to form gypsum by the reverse of the reaction shown above. This re-hydration consumes much of the water in the slurry, and causes the gypsum formed to set up as a cohesive solid. The wet board travels down a conveyor belt while it is setting up. After adequate residence time to set up, the board is cut to approximate length, then dried to remove free moisture (excess water not consumed by the re-hydration reaction). The dried product is cut to final length then stack for shipping.

The initial gypsum drying and calcining steps described above occur in a section of the plant called the mill. The dryers are typically direct gas fired. Their purpose is to remove the free moisture in the synthetic gypsum (typically 8 to 12% by weight of the raw material) prior to calcining. The dryers consequently operate at temperatures well below the gypsum calcining temperature of 262°F. The solids are dried by direct contact between the wet particles and the hot

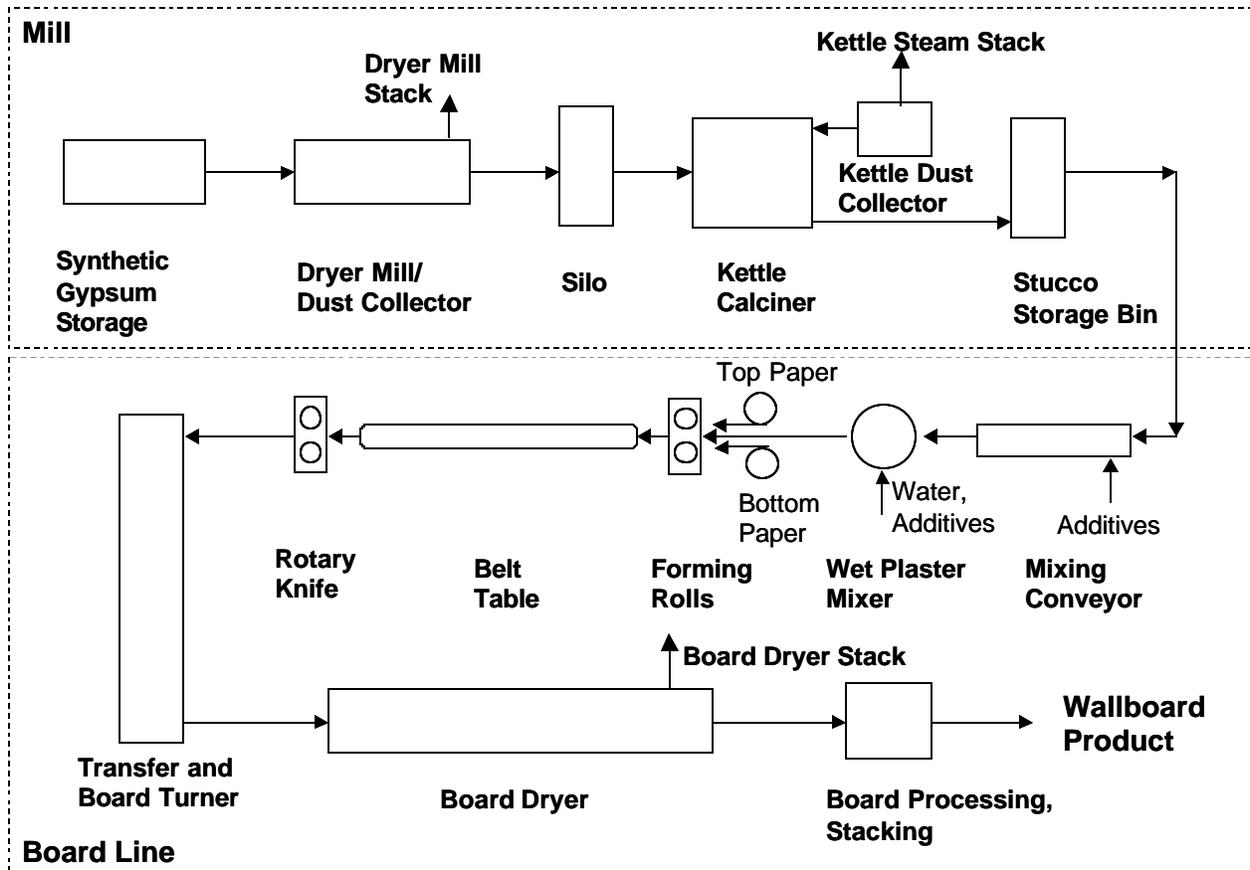


Figure 1. Simplified Schematic of the Wallboard Production Process Using Synthetic Gypsum Feedstock.

flue gas. The moisture-free synthetic gypsum (land plaster) is collected in mechanical collectors or a fabric filter and placed in intermediate storage silos prior to feeding to the calciners.

In the calcining step, the solids temperature must be raised above 262°F to promote release of 1-½ waters of hydration, but must be kept below 325°F to avoid forming anhydrous calcium sulfate (no remaining waters of hydration). The calciners used at the wallboard plant tested are indirect-fired kettle calciners, so the vent gas from the solids side of the kettle is primarily a mixture of steam and air. A kettle calciner dust collector removes fine stucco particles from this vent gas. The recovered fine particles are incorporated into the product stucco. The stucco leaving the kettle is cooled and placed in a bin for intermediate storage, to provide a buffer between the mill and board line.

In the board line, the cooled stucco from the silo is fed to a mixer, where “gauging” water is added to form a viscous slurry. The gauging water is typically of high quality (e.g., potable water). A number of proprietary additives are mixed with the wet slurry produced from the stucco.

This wet slurry is continuously extruded between two sheets of paper that are fed from rolls above and below the extruder. One type of paper is used for the face of the wallboard product

and another for the back. The dimensions of the formed board are set by rollers and edge shoes. The formed board travels down a long conveyor belt that provides residence time for the stucco to re-hydrate and take a set. At the end of this belt, the formed board is cut and inverted so the face paper is facing up.

The board then enters a dryer. The dryer is zoned to operate over a range of temperatures, typically over 400°F at the dryer entrance and about 200°F at the exit. However, the board residence time in the dryer is controlled to limit the temperature of the dried board. This temperature must be limited to avoid any of the set-up solids re-calcining to the hemihydrate form. Thus, the bulk of the rehydrated gypsum solids in the wallboard product stay well below 262°F in temperature. From the dryer, the dried board is cut to final size, has end tape applied, and is stacked for shipment.

Any potential mercury losses during the wallboard process are assumed to occur during the thermal processes, with losses most likely during the calcining step. The synthetic gypsum particles are raised to the highest temperature in the process during this step (above 262°F). Losses are also possible from the synthetic gypsum dryer and the finished wallboard dryer, although the maximum temperatures to which the gypsum is raised are lower in the dryers (approximately 170°F to 230°F).

Project Overview

This project is intended to provide information about the fate of mercury in synthetic gypsum produced by FGD systems on coal-fired power plants, when used as feedstock for wallboard production. Solid samples from various locations in the wallboard process, including the wallboard product, are being collected and analyzed for mercury content. Simultaneous flue gas measurements are being made using the Ontario Hydro method to quantify any mercury releases to the atmosphere during wallboard production. Most of the testing is concentrated in the mill processes where the synthetic gypsum is dried and calcined. Any potential mercury releases from the synthetic gypsum solids are thought to result from thermal desorption. It is in the mill portion of the process where the feedstock sees the highest process temperatures and where the evolution of waters of hydration may promote mercury desorption.

Initially, a limited amount of testing was to be conducted in the downstream board line, where the calcined gypsum is slurried, mixed with proprietary additives and formed into wallboard. The project plan was for the board dryer kiln stack flue gas to only be measured for mercury content at the first test site. Lesser mercury release was expected in the board dryer kiln because it is downstream of the mill, and the rehydrated gypsum solids typically see lower temperatures than in the mill. However, once results were available from Task 1, showing appreciable mercury loss from the board dryer kiln stack, stack testing for the board dryer kiln was added to the project scope for Tasks 4 and 5.

The solid and flue gas mercury concentration and plant process data are being used to calculate mercury balances around the operating wallboard plant.

Samples of each synthetic gypsum tested are being evaluated in laboratory simulated calcining tests to provide comparison data and evaluate a lab technique for screening synthetic gypsum

samples. Also, wallboard produced from synthetic gypsum will be leached according to the Toxicity Characteristic Leaching Procedure (TCLP) to provide an indication whether wallboard disposed of in municipal landfills will have a tendency to release mercury into groundwater.

The project will investigate wallboard produced from a variety of synthetic gypsum sources, all from FGD systems on coal-fired power plants, but from different coal types, power plant emissions control configurations and FGD conditions. The project is structured in five tasks. As shown in Table 1, each of which involves one commercial wallboard plant test. This report summarizes the results from Task 3, which investigated a commonly used synthetic gypsum feedstock, produced by a power plant that fires high-sulfur bituminous coal and that has a limestone, forced oxidation (LSFO) FGD system that produces a wallboard grade gypsum byproduct and that has an SCR for NO_x control. The FGD system incorporates a gypsum fines blow down, which tends to lower the mercury content of the gypsum product. The other four tasks include tests on synthetic gypsum feedstocks produced from:

- A power plant that fires medium- to high-sulfur bituminous coal and that has an SCR for NO_x control, an LSFO FGD system that produces wallboard grade gypsum byproduct, and does not have gypsum fines blow down.
- The same plant included in Task 1, but without the SCR operating (SCR catalyst bypassed). Since SCR catalysts have been observed to promote mercury oxidation, taking the SCR out of service may impact the amount of mercury captured in the FGD byproduct and could impact mercury losses during wallboard production,
- A plant that fires a low rank coal (Texas lignite) rather than bituminous coal, and
- A plant that uses lime rather than limestone FGD reagent, and employs external rather than in situ forced oxidation.

Each of these variables is thought to impact the amount of mercury in the synthetic gypsum feedstock and/or possibly impact the stability of that mercury in the wallboard production process.

Table 1. Project Test Matrix

Task	1	2	3	4	5
Synthetic Gypsum Source:					
Power Plant	A	A	B	C	D
Coal Type	High sulfur bituminous	High sulfur bituminous	High sulfur bituminous	Texas lignite	High sulfur bituminous
FGD Reagent	Limestone	Limestone	Limestone	Limestone	Lime
Forced Oxidation Mode	In Situ	In Situ	In Situ	In Situ	External
Gypsum Fines Blow Down?	No	No	Yes	No	Yes
SCR Operating?	Yes	No	Yes	No	TBD*
USG Wallboard Plant Tested	1	1	2	3	1

*To be determined later based on the time of the year of the test

To investigate all five of these synthetic gypsum feedstocks, testing will be conducted at three different USG wallboard plants, since no one plant uses all five as a feedstock. The relationship between synthetic gypsum types and USG plants proposed for investigation is summarized in Table 1. Note that the power plants and USG wallboard plants are not identified by name, only by letter or number codes, in accordance with an agreement for anonymity at the beginning of the project.

This report presents and discusses the results of the wallboard plant testing conducted as part of Task 3, including Ontario Hydro measurements in the dryer mill and kettle calciner, process sample mercury content, process data, and mercury balance results. Previous reports have presented and discussed the results of the tests conducted at part of Tasks 1 and 2^{1,2}. Planned laboratory evaluations, including simulated gypsum calcining tests and mercury leaching from wallboard product samples by TCLP, have not been conducted yet and will be reported later in the project.

Report Organization

The remainder of this report is organized into four sections: Experimental, Results and Discussion, Conclusion, and References. The section entitled Experimental describes the experimental methods used to conduct the mercury testing at a commercial wallboard plant as part of Task 3, including stack testing, process sampling, and off-site chemical analyses. The Results and Discussion section presents results from the stack testing, process sample analyses, process data collected, and mercury balance calculations. The Conclusion section provides preliminary conclusions that can be made from the results of this commercial wallboard plant mercury test.

EXPERIMENTAL

A description of the project test matrix was provided in the Introduction section. This section begins with an explanation of the rationale used for choosing this particular FGD synthetic gypsum for the base case test conditions. The remainder of the section presents details of how the wallboard plant mercury test was conducted, including stack testing by the Ontario Hydro method, process sample collection and analyses, and process data collection.

Rationale for Selecting the Synthetic Gypsum Tested

The Task 1 wallboard plant test involved testing the fate of mercury in synthetic gypsum from a high-sulfur, bituminous-coal-fired power plant equipped an operating SCR and with an LSFO FGD system that does not employ fines blow down (Power Plant A). This combination was selected for the first test because the synthetic gypsum produced at Power Plant A has a relatively high mercury content. As explained below, higher mercury content should enhance the accuracy of the tests. Furthermore, previous laboratory testing funded by EPRI³ and initial full-scale tests by USG⁴ suggest that small measurable mercury losses could be expected from this feedstock during wallboard production. For these reasons, it was thought that testing this material as the first case might be a USG worst-case scenario for potential mercury losses during wallboard production.

Previous testing has shown that, at least for some plants that fire high-sulfur bituminous coal, having an SCR in service tends to increase the percentage oxidation of mercury in the flue gas upstream of an FGD system, and to increase the percentage capture of mercury in the FGD.^{5,6} Many plants that are equipped with SCR only operate them during the “ozone season,” from May 1 through September 30 each year, and bypass the SCR catalyst the remainder of the year. For such plants, one might expect that synthetic gypsum produced from their FGD systems would contain more mercury with the SCR operating during the ozone season than that produced during the remainder of the year.

Gypsum fines blow down is believed to be an important variable. Most synthetic gypsum used as a wallboard plant feedstock is subject to a number of quality control specifications by the wallboard manufacturer, including maximum moisture content, minimum gypsum content, maximum chloride content, and particle size distribution. A number of FGD variables affect the ability to meet the solids particle size distribution specification. These variables include the gypsum crystal residence time in the FGD absorber loop, FGD reagent chemical composition, and the amount of physical abrasion to which the crystals are exposed as they are recirculated and dewatered. Some FGD systems cannot meet the wallboard manufacturer’s particle size specification unless they separate a portion of the byproduct containing the smallest particle sizes. This separation is typically accomplished with hydrocyclones. The separated fines are either discarded or sold for other uses. Other plants need to purge a portion of the hydrocyclone overflow as a means of limiting chloride buildup in the FGD liquor. These plants blow down gypsum fines as part of the chloride purge. In still other plants, there is no need to separate the fines and/or purge chlorides, and the fines are included in the byproduct sent to the wallboard plant.

Laboratory testing conducted by URS for EPRI has indicated that the mercury concentration in gypsum fines can be as much as an order of magnitude higher than in the larger particles.³ This suggests that mercury precipitates and/or adsorbs at gypsum surfaces, since the fines have a much higher surface area to mass ratio than larger particles. It is also possible that mercury adsorbs on or precipitates with fine particles of impurities that enter the FGD system with fly ash in the flue gas for with the FGD reagent. Upwards of half of the mercury removed by the FGD system can be in the fines. Fines blow down therefore significantly lowers the mercury concentration in the synthetic gypsum byproduct going to the wallboard plant.

Since the plant providing the feedstock for the current, Task 3 test employs fines blow down, it was expected to have lower mercury content in the synthetic gypsum byproduct than would a similar plant without fines blow down (e.g., Power Plant A, whose byproduct was tested as part of Tasks 1 and 2). Because of this, the Power Plant B byproduct might thermally evolve less mercury in the wallboard plant than a byproduct with the fines included and a higher total mercury concentration. However, full-scale testing was required to confirm or deny such assumptions.

Commercial Wallboard Plant Test Procedures

Commercial wallboard plants often operate with a blend of feedstock from a number of FGD systems. Rarely does one power plant generate enough synthetic gypsum to feed the entire production of a modern wallboard plant, so most plants process synthetic gypsum from two or more power plants. Each synthetic gypsum has unique processing conditions within the wallboard plant process. Therefore, to minimize excessive swings in wallboard plant operating conditions, most plants blend the available feedstock to produce an “average” material for processing.

However, for this test, the wallboard plant was operated on 100% feedstock from Power Plant B. It would be difficult to elucidate the effects of power plant and FGD variables on mercury losses during wallboard production if synthetic gypsum blends were being processed during measurements. Also, the feedstock to the mill typically contains recycled material, which can include recycled wallboard, wallboard samples, material recycled from the calciner during shut downs, etc. Because recycle consists of material from a variety of sources, it was felt that recycle would add variability to the incoming feed mercury concentration and possibly its stability. Therefore, the wallboard plant test was conducted with no recycle feed to the plant and during the use of Power Plant B synthetic gypsum only.

Two days of wallboard plant testing were conducted in USG Wallboard Plant 2, with the first day in the mill and the second day in the board line as described below. Figure 2 illustrates the wallboard production process. Process streams that were sampled as part of the test, as described below, are marked with “S” followed by a number that represents a sample location. The sample numbers are used in the data tables later in the report.

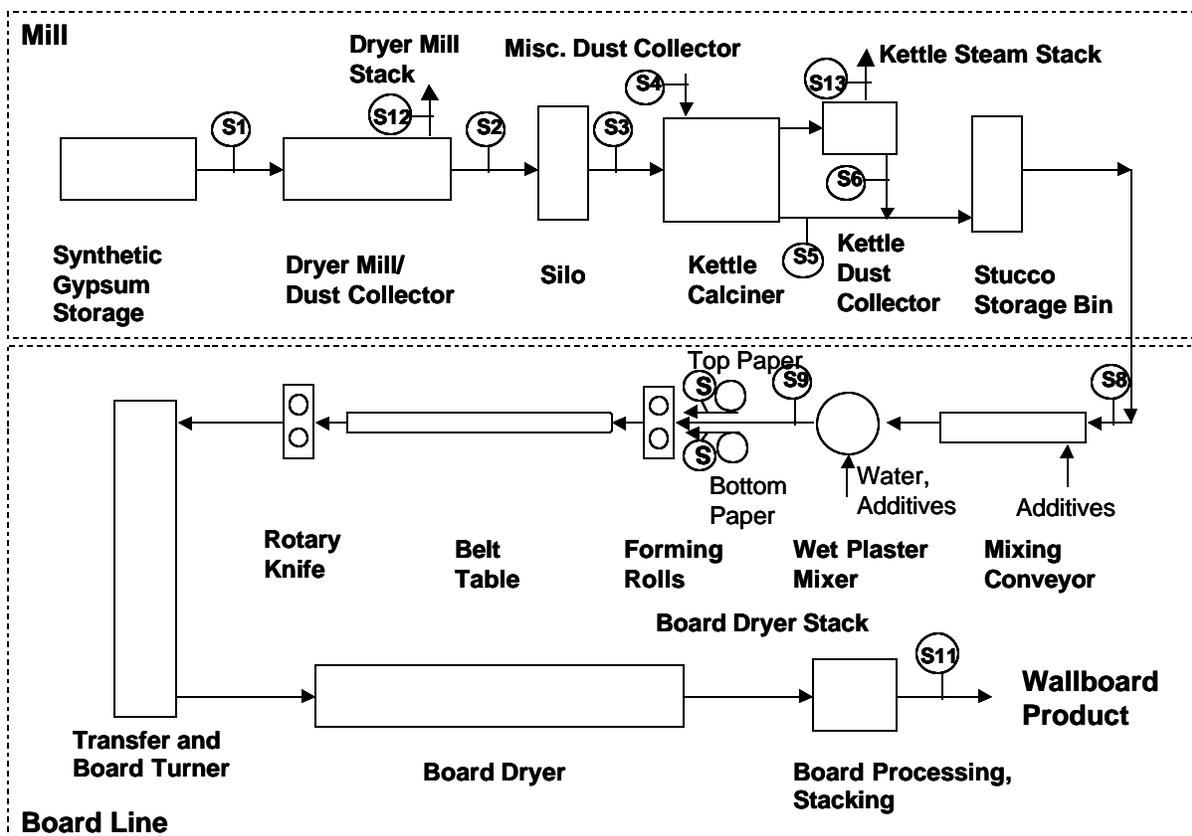


Figure 2. Schematic of a Wallboard Plant Showing Sampling Locations

Day 1 – Mill Testing

Stack Sampling

On the first test day, simultaneous gas measurements were conducted using the Ontario Hydro method (ASTM D6784-02) on a gypsum dryer (dryer mill) stack and the downstream kettle calciner steam stack on a single train of the plant. However, note that the method was modified slightly for sampling at the kettle calciner steam stack, as described below. Triplicate runs were made at each of these two locations.

The kettle calciners are indirect-fired vessels. The gaseous stream from the calciner that could contain mercury from the synthetic gypsum is the “steam stack,” which is a mixture of the water calcined from the gypsum when forming stucco ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) and aeration air introduced at the bottom of the kettle. The other stack from the kettle calciner contains the flue gas from the burners, which are natural gas fired. This stream is not expected to have measurable mercury content.

The steam stack gas is significantly wetter than and typically does not contain species present in coal flue gases (e.g., CO_2 , SO_2 and HCl), for which the Ontario Hydro method was developed and validated. Consequently, the method was modified slightly to ensure proper sampling and speciation under these conditions.

As mentioned above, the kettle calciner steam stack gas is mostly water. Since the Ontario Hydro method measures mercury in a dry gas sample, it was speculated that the mercury content of the dry gas, which represents less than half of the total gas stream, could be greater than 100 $\mu\text{g}/\text{Nm}^3$, which is the stated upper measurement limit for which the method was developed.⁷ When sampling above this limit, there was concern that reagents in the collection impingers would be depleted. To avoid this issue and to reduce the quantity of water collected in the impingers during the run, the Ontario Hydro runs on the kettle calciner were reduced in duration from 120 minutes to 60-75 minutes. Also, additional impinger volume was added to the train to collect the large amount of condensed moisture expected.

The dryer mill is direct fired, so its stack gas is a true flue gas and the standard Ontario Hydro Method should be appropriate for sampling this stream. Therefore, the dryer mill Ontario Hydro sampling runs were for a full 120 minutes, as per the method. The kettle calciner sampling runs were started several minutes after the dryer mill runs began, so the kettle calciner sample would be collected in the middle of the dry mill sample collection period.

Process Sampling

During each of the three runs, process samples were collected from the dryer feed solids, dryer product solids (land plaster to intermediate silo), calciner feed (land plaster from intermediate silo), and calciner product stucco as it exits the calciner. While these four streams represent the feeds and products for the dryer mill and kettle calciner, two additional solid stream samples were collected: the solids collected in a “miscellaneous” dust collector from transfer points in the mill, which are added to the calciner feed solids; and the solids collected from the kettle calciner dust collector, which are incorporated into the product stucco. These two sample types were analyzed for mercury concentration, but these data were not used for any of the mercury balance or mercury loss calculations.

All six of these process solids samples were collected as “grab” samples collected during the middle part of each Ontario Hydro run. No attempt was made to collect time-integrated samples, e.g., by collecting small sample aliquots at periodic intervals throughout the Ontario Hydro sampling periods and compositing the aliquots into a single sample. It was felt that the incoming raw gypsum would be homogenous enough that one grab sample per run would adequately represent the feedstock and other process solids. These 18 grab samples (six locations times three Ontario Hydro runs) were subsequently analyzed for mercury content, moisture content, and other parameters.

Process data were collected for each of the three runs, including dryer and calciner feeder speeds and operating temperatures. These data were recorded as two-hour trend plots for each parameter.

Day 2 – Board-Line Testing

According to the project plan, no stack sampling was conducted on the board dryer kiln stack as part of Task 3; only process samples were collected. On the second test day, samples were collected of the feed stucco, the slurry fed to the board forming machine, and the dry product

wallboard. The timing of the second day measurements were coordinated with the plant to approximately correspond with the processing of stucco material calcined the previous day. This took into account the residence time in the stucco storage bin between the mill and board line, although such timing could not be exact. Triplicate sample sets were collected, spaced apart in time roughly corresponding with the elapsed time between the three Ontario Hydro measurement runs in the mill the previous day.

As for the Day 1 testing effort, key process data were collected for that test day. For the board line, these data include the stucco feed rate, board production rate, and the dryer gas temperatures.

As the two-day sampling effort was completed, all process and Ontario Hydro method samples were recovered, stabilized, and labeled, then shipped to URS and USG laboratories for analyses. Method blanks and reagent blanks for the Ontario Hydro method samples were included with the sample sets as a quality assurance/quality control measure.

Representative coal samples and power plant and FGD process data were also collected by the utility operating Power Plant B that produced the synthetic gypsum being evaluated. The coal samples will be analyzed for ultimate and proximate analyses, chlorine and mercury content. The coal data along with the power plant and FGD process data will be used to document typical conditions under which the synthetic gypsum evaluated was produced.

All of the mill and board-line process samples collected were analyzed for mercury content, by cold vapor atomic absorption after digestion in hydrofluoric acid. A number of samples were analyzed for other parameters, including gypsum moisture content, particle size distribution, specific surface area, and chloride content.

The mercury concentration analytical results, along with plant process data, were used to construct a mercury balance across the mill and the board line. The mercury balances show individual stream flow rates and mercury concentrations (except for the additives used in the board line), the amount of mercury entering and leaving the plant in each process stream, and overall mercury mass balance closures. Data are shown for individual sampling runs and as averages for the triplicate measurements.

The coal data, power plant data, and FGD process data from the power plant producing the synthetic gypsum evaluated have not yet been collected and tabulated. These data will be reported later in the project.

RESULTS AND DISCUSSION

This section provides technical results for the Task 3 wallboard plant test. Results presented include gypsum and process sample analysis results, Ontario Hydro flue gas measurement results, plant process data, and mercury balance results. Each type of result is discussed in a separate subsection below.

Gypsum and Process Sample Mercury Analysis Results

Table 2 summarizes the results of mercury and moisture content analyses conducted by URS on the raw gypsum, stucco product, and intermediate process samples collected during the mill test on September 21, 2004. Table 3 shows results for additional characterization of these samples conducted by USG, including mercury and moisture content (both free and combined [water of hydration] moisture) as well as other parameters. Table 4 shows the results for mercury and moisture content analyses conducted by URS on stucco, wallboard product, and intermediate process samples collected during the board-line test on September 22, 2004.

Table 2. Task 3 Raw Gypsum and Mill Process Sample Mercury and Moisture Analyses, URS Results

Sample Number	Sample Description	Mercury Content, mg/g (dry basis)					Free Moisture Content, wt% as received			
		Run 1	Run 2	Run 3	Mean	95% C.I.*	Run 1	Run 2	Run 3	Mean
S1	Raw Gypsum Feed to Dryer Mill	0.19	0.22	0.21	0.21	±0.02	13.3	10.3	10.2	11.3
S2	Land Plaster from Dryer Mill	0.22	0.22	0.20	0.21	±0.01	<1	<1	<1	-
S3	Land Plaster to Kettle Calciner	0.21	0.21	0.21	0.21	±0.01	<1	<1	<1	-
S4	Misc. Dust Collector Solids to Kettle Calciner	0.20	0.22	0.22	0.21	±0.01	<1	<1	<1	-
S5	Kettle Calciner Product, as measured	0.14	0.14	0.14	0.14	±0.00	<1	<1	<1	-
	Kettle Calciner Product, dry gypsum basis	0.11	0.12	0.12	0.12	±0.01	<1	<1	<1	-
S6	Kettle Calciner Dust Collector Solids, as measured	0.23	0.22	0.27	0.24	±0.03	<1	<1	<1	-
	Kettle Calciner Dust Collector Solids, dry gypsum basis	0.19	0.19	0.22	0.20	±0.02	<1	<1	<1	-

*95% Confidence Interval of mean

Table 3. Task 3 Raw Gypsum and Mill Process Sample Characterization Results, USG Results

Sample	Run	Moisture Content, wt%		Mercury Content, mg/g		Soluble Salts, ppm		Particle Size Distribution (microns)			Blaine Surface Area, cm ² /gm	
		Free	Com-bined	As measured, dry basis	Dry Gypsum basis	Total	Cl ⁻	Mean Dia.	Particle Size at % Less Than			
									10%	50%		95%
S1 – Raw Gypsum Feed to Dryer Mill	1	13.8	19.5	0.19	0.19	118	79	44.1	23.1	41.2	79.4	1413
	2	10.7	19.5	0.20	0.20	122	63	44.9	23.0	41.8	81.9	1436
	3	10.5	19.5	0.19	0.19	127	63	45.2	23.5	41.9	82.5	1373
Mean		11.7	19.5	0.19	0.19	122	68	44.7	23.2	41.6	81.3	1407
95% C.I.*		±2.0	±0.0	±0.01	±0.01	±5	±11	±0.7	±0.3	±0.4	±1.8	±36
S2 – Land Plaster from Dryer Mill	1	0.07	19.3	0.21	0.21	113	63	45.1	22.9	42.0	82.2	1374
	2	0.05	19.1	0.21	0.21	158	75	44.3	21.5	41.3	82.0	1454
	3	0.04	19.2	0.19	0.19	149	81	44.6	22.7	41.6	81.1	1410
Mean		0.05	19.2	0.20	0.20	140	73	44.6	22.4	41.6	81.8	1413
95% C.I.		±0.02	±0.1	±0.01	±0.01	±27	±10	±0.4	±0.9	±0.4	±0.7	±45
S3 – Land Plaster to Kettle Calciner	1	0.05	18.9	0.20	0.20	140	68	43.6	21.4	40.7	80.2	1497
	2	0.09	19.1	0.19	0.19	157	80	46.0	22.4	41.7	85.8	1406
	3	0.05	19.0	0.19	0.19	145	71	44.6	22.5	41.6	81.6	1420
Mean		0.06	19.0	0.20	0.20	147	73	44.7	22.1	41.3	82.6	1441
95% C.I.		±0.03	±0.1	±0.01	±0.01	±10	±7	±1.3	±0.7	±0.6	±3.3	±55
S4 – Misc. Dust Collector Solids to Kettle Calciner	1	0.12	14.5	0.19	0.19	302	112	41.6	18.7	38.5	78.6	1870
	2	0.10	14.4	0.21	0.21	239	106	37.1	13.7	34.9	72.9	2045
	3	0.11	14.2	0.21	0.21	125	78	36.7	13.2	34.5	72.5	2104
Mean		0.11	14.4	0.20	0.20	222	99	38.5	15.2	36.0	74.7	2006
95% C.I.		±0.01	±0.2	±0.01	±0.01	±101	±20	±3.1	±3.5	±2.4	±3.9	±138
S5 – Kettle Calciner Product	1	0.13	6.2	0.14	0.12	137	90	43.1	20.2	40.1	80.4	2097
	2	0.13	6.3	0.14	0.12	124	83	43.5	20.7	40.4	81.5	2018
	3	0.15	6.3	0.14	0.11	156	84	43.9	21.4	40.8	81.3	2097
Mean		0.14	6.2	0.14	0.12	139	86	43.5	20.8	40.5	81.1	2071
95% C.I.		±0.01	±0.0	±0.00	±0.00	±18	±4	±0.4	±0.6	±0.4	±0.7	±52
S6 – Kettle Calciner Dust Collector Solids	1	0.11	6.1	0.20	0.17	203	102	29.5	6.8	27.6	62.4	3180
	2	0.08	6.1	0.22	0.18	502	102	29.2	6.9	27.3	61.6	3214
	3	0.05	6.4	0.23	0.19	230	101	30.2	8.0	28.4	62.2	3155
Mean		0.08	6.2	0.21	0.18	312	102	29.6	7.2	27.8	62.1	3183
95% C.I.		±0.03	±0.2	±0.02	±0.01	±187	±0	±0.6	±0.7	±0.7	±0.5	±34
S8 – Stucco Feed to Board Line	1	0.08	6.3	0.09	0.08	220	102	47.5	16.3	40.2	109	2800
	2	0.15	6.3	0.09	0.08	207	105	48.9	17.3	41.0	114	2704
	3	0.08	6.3	0.09	0.08	256	109	48.9	17.5	40.8	114	2711
Mean		0.10	6.3	0.09	0.08	228	106	48.5	17.0	40.6	112	2738
95% C.I.		±0.05	±0.0	±0.00	±0.00	±29	±4	±0.9	±0.7	±0.5	±4	±61

*95% Confidence Interval of mean

Table 4. Task 3 Stucco, Wallboard Product and Intermediate Process Sample Mercury and Moisture Analyses, URS Results

Sample Number	Sample Description	Mercury Content, mg/g (dry basis)					Free Moisture Content, wt% as received			
		Run 1	Run 2	Run 3	Mean	95% C.I.	Run 1	Run 2	Run 3	Mean
S8	Stucco Feed, as measured	0.10	0.10	0.09	0.10	±0.00	<1	<1	<1	<1
	Stucco Feed, dry gypsum basis	0.08	0.08	0.08	0.08	±0.00	<1	<1	<1	<1
S9	Slurry to Forming Rolls	0.10	0.10	0.09	0.10	±0.00	30.4*	30.7*	31.8*	31.0*
S11	Dry Wallboard Product	0.07	0.08	0.08	0.07	±0.00	<1	<1	<1	<1

*Moisture content measured after sample set up, consuming some free moisture to rehydrate the stucco

In each of these three tables and throughout this section of the report, a mean and a 95% confidence interval about that mean are shown for key values in the table. The mean values represent the arithmetic average of the results from three runs, while the 95% confidence interval is a measure of observed variability of that value during the three runs. Specifically, the 95% confidence interval represents a range above and below the mean for the three runs over which we have a 95% confidence level that the true average for these three measurements would lie. The 95% confidence interval values were all calculated using the “CONFIDENCE” worksheet function in Microsoft Excel 2003[®] spreadsheet software.

The results from the URS analyses in Table 2 show that the raw gypsum feedstock, product stucco, and intermediate samples were relatively consistent in mercury content from run to run. The raw gypsum feed contained an average of 0.21 ppm (dry basis) and 11% moisture, which is within the typical range for FGD gypsum. Note that the mercury concentration in this gypsum was only 22% of the concentration in the gypsum tested in Task 1, which supports the expectation that the mercury content would be lower in gypsum from a plant with fines blow down. However, it is most likely that not all of this difference is due to the effects of fines blow down. The coal fired at Power Plant B likely has a lower mercury content than the coal fired at Power Plant A.

As at Wallboard Plant 1, the kettle calciner dust collector solids showed significantly higher mercury concentrations than the other process streams. This is likely because it is the finer gypsum particles with greater surface area, and stucco formed from these particles, that are collected in the dust collector.

Also, note that, notwithstanding potential mercury losses in the kettle calciner, mercury should be more concentrated in the kettle calciner product and in the product stucco than in the upstream samples, because of the evolution of 1½ waters of hydration in the calciner. For this reason, additional rows of data are shown in Table 2 expressing the mercury content in the stucco samples (S5 and S6) on a dry gypsum basis. This accounts for the effects of the loss of waters of

hydration by the stucco. Similarly, a column has been added to Table 3 showing all of the solids analysis results on a dry gypsum basis.

The corrected values can be compared directly to see apparent mercury losses across the dryer mill and kettle calciner. When comparing the mercury concentrations in the land plaster feed to the kettle calciner (S3) to the mercury concentrations in the kettle calciner product (S5) expressed on a dry gypsum basis, an apparent loss of mercury across the kettle calciner is clearly seen. The feed gypsum averaged 0.21 ppm of mercury content on a dry basis (dry of free moisture only – not waters of hydration) while the product stucco averaged only 0.12 ppm.

The results of USG analyses in Table 3 show mercury concentrations almost identical to those measured by URS on splits of the same samples. Perhaps the most important samples for this test are S3, the kettle calciner feed, and S5, the kettle calciner product, as those provide an indication of any mercury losses across the kettle calciner. For sample S3, the URS analyses showed a mean concentration of $0.21 \pm 0.01 \mu\text{g/g}$, while the USG analyses showed a mean of $0.20 \pm 0.01 \mu\text{g/g}$. For sample S5, both sets of analyses showed a mean concentration of $0.14 \pm 0.01 \mu\text{g/g}$.

The URS and USG sample moisture analyses also agree well. For sample S1, the dryer mill feed, the URS analyses show a mean moisture content of 11.3 wt%, while the USG analyses show a mean of 11.7%. The USG analyses on all of the samples from downstream of the dryer mill show free moisture content of 0.1 wt% or less, while the URS analyses just report these as less than 1%.

Otherwise, the USG characterization of these samples shows expected trends. For example, the particle size distributions of the two dust collector samples (S4 and S6) show smaller particles and higher specific surface areas than the other samples, as would be expected, as it should be the finer particles that are entrained in the flue gas going to the dust collectors. Also, the specific surface area of the land plaster is observed to increase from about $1400 \text{ cm}^2/\text{g}$ to over $2000 \text{ cm}^2/\text{g}$ upon calcining, which would be expected due to the evolution of waters of hydration from the particles.

The results from the board line samples in Table 4 show that the average mercury concentration in the stucco feed to the wallboard plant was lower than the average for the product stucco going to the stucco storage bin the day before ($0.10 \mu\text{g/g}$ vs. $0.14 \mu\text{g/g}$). This suggests that the attempt to time-phase the wallboard plant sampling to reflect the stucco produced in the mill the day before was not successful, and that the stucco mercury concentration was somewhat variable for this feedstock. Note that the USG analysis results in Table 3 show a similar disparity in mercury concentrations.

Conversely to what was described for the kettle calciner, in the board line the slurry and wallboard should have lower mercury concentrations than the feed stucco, due to the $1\frac{1}{2}$ waters of hydration gained on rehydration of the stucco. To account for this effect, a row has been added to Table 4 showing the feed stucco mercury concentration on a dry gypsum basis. This allows any loss of mercury from the feed stucco to be observed directly by comparing mercury concentrations of the feed and product on a common dry gypsum basis. However, the effects of mercury in the additives, water, and paper added in the board line on the mercury content of the

wallboard product must also be considered, as discussed later in this section in the mercury mass balance discussion.

Ontario Hydro Stack Sampling Results

The Ontario Hydro Method stack sampling results are summarized in tables that follow. Table 5 summarizes gas flow rate, temperature, and major component concentrations. The results in the table show that the mill dryer stream composition was consistent with a very dilute flue gas from natural gas firing, with only 1% CO₂ and 19% oxygen. The moisture content was relatively high at 11% due to the free moisture from the gypsum that is evolved in the dryer. The dryer mill flue gas temperature was below 200°F, as would be expected because of the need to keep the dried gypsum below its initial calcination temperature of 262°F.

Table 5. Task 3 Ontario Hydro Results – Summary of Exhaust Gas Conditions

Run No.	Date (2004)	Time (24-h)	Flow Rate		Temperature (°F)	H ₂ O (%)	CO ₂ (%)	O ₂ (%)
			acfm*	dscfm**				
Dryer Mill (1 of 2)								
1	9/21	1145-1345	67,400	49,300	165	10.5		
2	9/21	1445-1645	67,300	48,100	170	11.9		
3	9/21	1800-2000	65,200	46,500	170	12.0		
Mean			66,600	48,000	168	11.5	1	19
Kettle Calciner (1 of 2)								
1	9/21	1145-1319	8,370	1,270	264	79		
2	9/21	1450-1607	8,370	1,340	266	77		
3	9/21	1800-1917	7,720	984	263	82		
Mean			8,160	1,200	264	79	0	20

*acfm = Actual cubic feet per minute at stack conditions

**dscfm = Dry standard cubic feet per minute; standard conditions are 68°F, 29.92 in.Hg, and 0 percent moisture

The kettle calciner results for flue gas composition were consistent with a very wet air stream, containing no measurable CO₂ content and 20% oxygen. The measured moisture content of the stack gas was quite high, averaging 79%, due to the waters of hydration released from the gypsum. The measured moisture content was considerably higher than was measured at Wallboard Plant 1 (56%) in Tasks 1 and 2. There, evidence was seen of a flue gas leak into the indirect-fired side of the calciner, which likely increased the dry stack gas rate and correspondingly lowered its moisture content.

Table 6 summarizes the mercury concentration and mass rate data. The results show that for the dryer mill stack, the mercury was mostly in the oxidized form, while for the kettle calciner stack, the mercury almost entirely in the elemental form (Hg⁰). The latter was also seen at Wallboard Plant 1 in Tasks 1 and 2. This phenomenon remains somewhat surprising, given that it is predominantly water-soluble oxidized mercury (Hg⁺²) that is removed in wet FGD systems, while elemental mercury is virtually insoluble and not removed at significant percentages. There still is no clear explanation for this phenomenon. One possibility is that a portion of the oxidized

mercury absorbed in the FGD system undergoes reduction reactions after the mercury is deposited in the byproduct solids, to reduce a portion of the oxidized mercury to the elemental form. Note that in the elemental form, mercury is not expected to readily deposit near the point of emission but ascends into the atmosphere and contributes to the overall global cycle.⁸

Table 6. Task 3 Ontario Hydro Results – Speciated Mercury Emissions Data

Sample Number	Run No.	Date (2004)	Time (24-h)	Concentration ($\mu\text{g}/\text{Nm}^3$)*				Total Mercury Emission Rate (lb/h) [#]
				Particle-Bound, Hg^{P}	Oxidized, Hg^{+2}	Elemental, Hg^0	Total Hg	
Dryer Mill (1 of 2)								
S12	1	9/21	1145-1345	0.01	0.70	0.28	1.06	1.82×10^{-4}
	2	9/21	1445-1645	0.01	0.77	0.42	1.12	1.88×10^{-4}
	3	9/21	1800-2000	0.01	0.79	0.31	1.11	1.80×10^{-4}
	Mean			0.01	0.75	0.34	1.10	1.83×10^{-4}
	95% Confidence Interval			± 0.00	± 0.05	± 0.08	± 0.04	$\pm 0.05 \times 10^{-4}$
Kettle Calciner (1 of 2)								
S13	1	9/21	1145-1319	4.1	14.7	1725	1744	7.72×10^{-3}
	2	9/21	1450-1607	<0.10	15.1	1587	1602	7.47×10^{-3}
	3	9/21	1800-1917	0.16	16.4	2293	2309	7.93×10^{-3}
	Mean			1.4	15.4	1868	1885	7.71×10^{-3}
	95% Confidence Interval			± 2.6	± 1.1	± 423	± 423	$\pm 0.26 \times 10^{-3}$

* $\mu\text{g}/\text{Nm}^3$ = Micrograms per normal cubic meter (dry gas at 32°F, at as-measured O_2 concentration)

[#] lb/h = Pounds per hour

The total mercury concentration data show that on a dry gas basis, the concentrations in the kettle calciner steam stack are much higher, nominally 1700 to 2300 $\mu\text{g}/\text{Nm}^3$, than the dryer stack which averaged closer to 1 $\mu\text{g}/\text{Nm}^3$. Compared to the mercury concentrations measured at Wallboard Plant 1 as part of Task 1, the mean dryer mill stack concentration at Wallboard Plant 2 was nearly an order of magnitude lower but the kettle calciner stack concentration was greater than an order of magnitude higher. At Wallboard Plant 2, although the dry flue gas rate at the kettle calciner stack was much lower than in the dryer mill stack, when the mercury emissions from each are expressed as a mass rate, the losses at the kettle calciner steam stack are 40 times greater than in the dryer mill stack.

There might be concerns that the mercury concentration measurements at the kettle calciner steam stack would be inaccurate, because the measured concentrations are well outside the stated range of applicability of the Ontario Hydro method (1 to 100 $\mu\text{g}/\text{Nm}^3$).⁷ However, the Ontario Hydro method was developed for measuring mercury concentrations in flue gases that contain acid gases such as SO_2 , which tend to consume much of the permanganate solution used to capture elemental mercury in the sampling train. Since acid gases are not present in significant concentration in the kettle calciner steam stack gas, there appeared to be ample permanganate

available in those impingers to collect all of the elemental mercury in the sample gas, even at such high concentrations.

It should also be noted that because the measured flue gas moisture content in the kettle calciner steam stack was much higher than had been measured at Wallboard Plant 1, the Ontario Hydro measurements were not made at an “acceptable” percentage of the isokinetic sampling rate of 100% ±10%. This value represents the sample gas velocity as it enters the sampling nozzle on the Ontario Hydro sampling probe as a percentage of the flue gas velocity in the stack gas. The actual percent isokinetic for the three sampling runs on the kettle calciner steam stack ranged from 190% to 235%. However, poor isokinetic percentages would only affect the particulate-bound mercury measurement, most likely biasing this value high in this case. Since the particulate-bound mercury concentrations measured corresponded with 0.2% of the total mercury concentration or less, this sampling rate error is not thought to have impacted the measurement results. In future testing, the moisture content of the flue gas will be measured in a separate sampling run before setting Ontario Hydro Method sampling rates.

On the dryer mill, where the moisture content of the flue gas represents a relatively small percentage of the dry flue gas rate, the percent isokinetic was within the acceptable range, with values of 92 to 93%.

Plant Process Data

Plant process data are summarized in Table 7 for the mill tests and Table 8 for the board-line sampling. Some of the process data collected during the tests have not been reported here due to their proprietary nature. Note that in the mill, solids feed rates are not measured directly, but are controlled on a relative basis by the speed of the solids feeders and expressed as a percentage of full feeder speed. However, the mill supervisor can estimate feed rates based on the rate of level change in the stucco storage bins compared to wallboard production rates.

Table 7. Task 3 Mill Test Process Conditions

Date	9/21/2004	9/21/2004	9/21/2004	
Time	1145-1345	1445-1645	1800-2000	
Ontario Hydro Run	Run 1	Run 2	Run 3	Average
Dryer Mill B Feeder Output, % of full scale	42*	55	55	51
Estimated Dryer Mill B Wet Feed Rate, tons/hr	42	55	55	51
Dryer Mill B Dust Collector Inlet Temperature, °F	140	143	143	142
Dryer Mill B Dust Collector Outlet Temperature, °F	160	169	166	165
Kettle B Feed Set Point, % of full scale	67	67	69	68
Estimated Kettle Calciner Land Plaster Feed Rate, tons/hr	44	44	46	45
Kettle A #3 (Mid-kettle) Thermocouple, °F	300	300	300	300

*Includes one period of about 10 minutes during which a burner trip occurred – no solids feed during that period

Table 8. Task 3 Board-line Test Process Conditions

Date	9/22/2004
Time	0900-1300 Average
Board Width, in.	48
Board Thickness, in.	0.5
Kiln Wet Zone 1 Temperature, °F	450
Kiln End Temperature, °F	341

The rates shown in Table 7 for the dryer mill and kettle calciner are based on an estimated 51 ton/hr average dryer mill feed rate for the day-long test, adjusted for the percent moisture to produce a land plaster feed rate to the kettle calciner of 45 tons/hr. The average feed rate for each individual run was adjusted linearly based on percentage feed rate values recorded during that test period, so the averages for the three runs would come to 51 tons/hr wet and 45 tons/hr dry. The process conditions shown in Tables 7 and 8 were used as the basis for mercury balance calculations, as discussed in the following subsection. The dryer mill rate for runs 2 and 3, calciner feed rate for all three runs, and the board speed in the board dryer (not shown in Table 8) represent typical plant operation. For Ontario Hydro run 1, the dryer mill average rate was reduced by a burner trip mid-way through the run.

Mercury Balance Results

Table 9 summarizes the mercury balance data for the mill testing. Details are shown on the mercury balance intermediate calculation results, based on input data taken from previous tables in this report.

The mercury balance data are shown in several ways. First, the percentage mercury loss from the gypsum solids being processed is calculated with that percentage being calculated in two ways: one based on the apparent loss by comparing inlet and outlet solids mercury concentrations, and the other based on the inlet concentration versus the Ontario Hydro measurement results for mercury losses from the stacks. The other form of presenting the data is an actual mercury balance, with individual balance closure percentages shown across the dryer mill, kettle calciner, and overall mill. These mercury balances were calculated from the inlet solids mercury concentrations and flow rates, outlet solids mercury concentrations and flow rates, and mercury losses in the flue gases based on the Ontario Hydro results.

The results show that the percentage mercury loss across the dryer mill was low while the percentage loss across the kettle calciner was relatively high. The average loss across the dryer mill was 1.0% of the mercury in the raw gypsum based on the Ontario Hydro stack results. The solids analysis actually did not indicate any mercury loss. For the kettle calciner, the percentage loss was 43% based on the solids analysis and 41% based on the Ontario Hydro stack results. The mercury loss measured across the entire mill totaled 42% by both methods (Ontario Hydro results vs. solids analyses).

Table 9. Task 3 Mercury Balance Results for the Mill Test

Run Number	Run 1	Run 2	Run 3	Mean	95% C.I.
Feed to Dryer Mill (Raw Gypsum):					
Feed rate, tons/hr	42	55	55	51	±9
Wt% moisture	13.3	10.3	10.2	11.3	±2.0
Hg content, µg/g, dry basis (from Table 2)	0.19	0.22	0.21	0.21	±0.02
Total Hg to dryer mill, g/hr	6.3	10	9.4	8.6	±2.2
Dryer Mill Product (Land Plaster):					
Dry rate, tons/hr	36	49	49	45	±8
Hg content, µg/g (from Table 2)	0.22	0.22	0.20	0.21	±0.01
Total Hg from dryer mill, g/hr	7.4	9.6	9.1	8.7	±1.3
Measured solids Hg loss rate, g/hr	-1.0	0.4	0.3	-0.1	±0.9
Measured Hg loss rate at stack, lb/hr (from Table 6)	1.82×10^{-4}	1.88×10^{-4}	1.80×10^{-4}	1.83×10^{-4}	$\pm 0.05 \times 10^{-4}$
Measured Hg loss rate at stack, g/hr	0.083	0.085	0.082	0.083	±0.002
% Hg loss across dryer mill, by solids analysis	-16%	3.6%	2.9%	-1.5%	±13%
% Hg loss across dryer mill, by Ontario Hydro	1.3%	0.9%	0.9%	1.0%	±0.3%
Land Plaster Feed to Kettle Calciner:					
Feed rate, tons/hr	44	44	46	45	±1
Hg content, µg/g (from Table 2)	0.21	0.22	0.21	0.21	±0.01
Total Hg to kettle calciner, g/hr	8.5	8.6	8.6	8.6	±0.0
Product Stucco:					
Product rate, tons/hr, calculated	37	37	39	38	±1
Hg content, µg/g (from Table 2)*	0.14	0.14	0.15	0.14	±0.00
Total Hg from kettle calciner, g/hr	4.6	4.8	5.1	4.9	±0.3
Measured solids Hg loss rate, g/hr	3.9	3.8	3.4	3.7	±0.3
Measured Hg loss rate at stack, lb/hr (from Table 6)	7.72×10^{-3}	7.47×10^{-3}	7.93×10^{-3}	7.71×10^{-3}	$\pm 0.26 \times 10^{-3}$
Measured Hg loss rate at stack, g/hr	3.5	3.4	3.6	3.5	±0.1
% Hg loss across kettle calciner, by solids analysis	46%	44%	40%	43%	±3%
% Hg loss across kettle calciner, by Ontario Hydro	41%	39%	42%	41%	±2%
Mass Balance Closures:					
Dryer mill Hg closure, output vs. input, %	117%	97%	98%	103%	±13%
Kettle Calciner Hg balance closure, output vs. input, %	95%	95%	102%	97%	±4%
Overall Mill Hg balance closure, %	130%	83%	94%	98%	±28%

*Assumes the product stucco is comprised of 97.5 wt% kettle calciner product and 2.5 wt% kettle calciner dust collector solids based on data collected as part of Task 1

On average, the mercury balances show excellent closures, particularly considering the measurements were made across a full-scale, commercial plant and that the solids samples were “grab” samples rather than composites over the test durations. The average mercury balance closure was 103% across the dryer mill and 97% across the kettle calciner. Individual measurement run closures showed wider variation, from +17% to -5% of 100%.

The average mercury mass balance closure across the entire mill was excellent, at 98%, but the individual run mercury balance closures showed wider variability, from +30% to -17% of 100%. This may be because there is an intermediate storage silo between the dryer mill and kettle calciner, so there is a time delay between when solids are processed by the dryer mill and when those same solids are processed in the kettle calciner. This effect is most pronounced for the individual runs, since the dryer mill and kettle calciner were sampled simultaneously rather than staggered to account for the intermediate storage silo residence time. However, on the average for the day, this storage silo residence time had less of an effect on results, as might be expected, with an overall mercury balance closure across the mill of 98%.

Compared to the results of the wallboard tests reported previously for Wallboard Plant 1 and Power Plant A, the mercury losses across the kettle calciner reported in Table 9 are nearly four times those reported in Task 1 and three times the results from Task 2 on a mass basis. Thus, although the raw gypsum tested from Power Plant B had only about 20% of the mercury content of the gypsum from Power Plant A, the considerably higher mercury loss percentage across the calciner at Wallboard Plant 2 (41% vs. 2 to 3%) resulted in a mercury loss three to four times greater on a mass basis.

The results of mercury balance calculations across the board line are shown in Table 10. It was not possible to calculate a rigorous mercury mass balance across the board line because, in accordance with the test plan, no flue gas mercury concentration measurements were made on the board dryer kiln stack. It was possible to compare the mercury concentration of the stucco feed to the board line to the mercury concentration of the wet slurry going to board forming, although the mercury concentrations of the additives and water added to the stucco to produce the slurry were not measured (also according to the test plan). However, by using the additive mercury concentrations and dosages measured previously at Wallboard Plant 1, the effect of these additives on the mercury concentration in the wet slurry was estimated. As shown in Table 10, using these estimates the amount of mercury in the wet slurry to board forming showed acceptable closure with the amount of mercury in the incoming stucco, with mass closures averaging 109%. This suggests that the estimates used for the mercury content in the additives and paper were reasonably accurate.

Mercury losses across the board dryer kiln were estimated from the measured decrease in mercury concentration in the wallboard product relative to the feed streams. When comparing the product to the original stucco feed, after accounting for the estimated mercury added by the additives and paper going into the wet wallboard, the mercury loss across the board dryer kiln averaged 14%. When compared to the wet slurry to board forming, after accounting for the paper also going into the wet wallboard, the loss was 21%.

These percentage loss estimates in the board line are considerably higher than were measured by flue gas Ontario Hydro measurements at Wallboard Plant 1, Task 1 (2%) and estimated from solids analyses for Task 2 (5%). However, because of the lower mercury content in the gypsum from Power Plant B, and the higher percentage mercury losses in the mill at Wallboard Plant 2, the estimated mass rate of mercury loss across the board line (not shown in Table 10) was lower at Wallboard Plant 2 than in either test at Wallboard Plant 1.

Table 10. Task 3 Mercury Balance Results for the Board-line Test

Run Number	Run 1	Run 2	Run 3	Mean	95% C.I.
Hg in Feed to Board Line:					
Relative Stucco Feed Rate, % of test average	100	100	100	100	NA*
Hg Concentration in Stucco, µg/g (dry) (from Table 4)	0.10	0.10	0.09	0.10	±0.00
Hg in Stucco Feed, % of total Hg into Board Line	89	89	89	89	±0.0
Hg in Water Added, % of total Hg into Board Line (estimated)	0	0	0	0	±0.0
Hg in Additives, % of total Hg into Board Line (estimated)	5	6	6	5	±0.0
Hg in Paper, % of total Hg into Board Line (estimated)	5	6	6	5	±0.0
Hg in Slurry to Board Forming:					
Hg Concentration in slurry, µg/g (dry) (from Table 4)	0.10	0.10	0.09	0.10	±0.00
Moisture in Set Up Slurry, wt%	30.4	30.7	31.8	31.0	±0.5
Hg in Slurry, % closure with Hg stucco + estimated in water + estimated in additives	106%	112%	109%	109%	±3%
Hg in Wallboard Product:					
Hg Concentration in Wallboard Product, µg/g (dry) (from Table 4)	0.07	0.08	0.08	0.07	±0.00
Hg Loss and Balance Closures:					
% Hg Loss Across Board Dryer Kiln, by solids analysis (wallboard product compared to stucco feed, with estimated mercury in additives and paper added)	20%	13%	8.2%	14%	±6%
% Hg Loss Across Board Dryer Kiln, by solids analysis (wallboard product compared to slurry to board forming plus estimated mercury in paper)	24%	22%	16%	21%	±5%

Summary of Mercury Loss Calculations

The data collected as part of this test were used to calculate an observed, overall percentage mercury loss from the raw gypsum feed during the wallboard production process by two methods. One was to sum the measured losses from the process stacks, as measured by the Ontario Hydro Method, and compare that total to the amount of mercury coming into the wallboard plant in the raw gypsum feed. The data on which this calculation was based are found in Tables 6 and 9 for the mill process stacks. However, because in accordance with the test plan, the board dryer kiln stack was not sampled by the Ontario Hydro Method, the losses across the board line had to be estimated from the change in solids concentration across the board line. The second method was to compare the mercury concentrations in the raw gypsum feed to the concentrations in the dry wallboard product. Data on which this calculation was based are found in Tables 2 and 4. Results from these two types of calculations are shown in Table 11.

Table 11. Task 3 Summary of Overall Mercury Loss During Wallboard Production, Calculated by Two Methods

	Run 1	Run 2	Run 3	Mean	95% C.I.
Total Hg Loss from Mill Process Stacks by Ontario Hydro Method and from Board Line by solids analyses, g/hr*	8.7	7.9	8.0	8.2	±0.5
Total Hg to Wallboard Plant, g/hr [#]	13	21	20	18	±4
Observed Overall Percentage Hg Loss based on Ontario Hydro Method for Mill Losses	64%	38%	41%	46%	±16%
Hg Concentration in Raw Gypsum Feed to Wallboard Plant, µg/g	0.19	0.22	0.21	0.21	±0.02
Hg Concentration in Wallboard Product, µg/g	0.07	0.08	0.08	0.07	±0.00
Observed Percentage Hg Loss Across Wallboard Plant based on solids analyses	63%	66%	63%	64%	±2%
Observed Percentage Hg Loss Across Wallboard Plant based on solids analyses, corrected for estimated Hg added with additives and paper in board line	65%	68%	65%	66%	±2%

*Assumes two dryer mill and kettle calciner stacks, one board dryer kiln stack

[#]Includes mercury in raw gypsum feed plus mercury added by additives and paper in the board line

The results in Table 11 show a mean loss of 46% of the plant input mercury out the two mill process stacks measured by the Ontario Hydro Method, including estimated losses from the board dryer kiln stack. Comparing the mercury concentrations in the raw gypsum feed to those in the dry wallboard product, a higher, 64% loss percentage was calculated (66% after correcting for the estimated amount of mercury added with additives and paper in the board line). The two methods do not agree well with respect to the percentage mercury loss from the wallboard plant feed. The overall mercury loss percentage by the second method appears to be biased high, though. On the day the mill was sampled, the kettle calciner product stucco had a mercury concentration averaging 0.14 µg/g. However, when the board line was sampled the next day, the stucco going to the board line was measured to have a lower average mercury concentration of 0.10 µg/g. Although the timing of the board line sampling was intended to account for the residence time in the product stucco bin, it is apparent that the material being processed when the board line samples were collected had a lower mercury concentration. The second calculation includes this difference of 0.04 µg/g in the overall mercury loss calculation, whereas the Ontario Hydro-based calculation does not (losses across the board line were calculated based on the lower, 0.10 µg/g average stucco feed concentration).

For this reason, it is believed that the mean value of 46% mercury loss across the wallboard plant calculated by the first method better reflects the actual losses from this feedstock. In fact, if the mercury loss by the second, solids analyses method is amended to consider the lower mercury content in the stucco feed to the board line during the second day of testing, the two methods agree quite well (46% vs. 50%).

CONCLUSION

The use of synthetic gypsum in making wallboard has long benefited the environment by recycling the FGD gypsum byproduct, decreasing the need to landfill and increasing the sustainable design of the wallboard product. In the future, increasing numbers of FGD systems will be operating in the U.S. in response to EPA's Clean Air Interstate Rule, signed on March 10, 2005, which calls for further reductions in sulfur dioxide emissions from coal-fired power plants. Correspondingly, greater amounts of synthetic gypsum will be produced to either be recycled or landfilled. The Clean Air Mercury Rule, signed by EPA on March 15, 2005, takes into account the expectation that significant mercury emissions reductions will be obtained as a "co-benefit" of increased control of SO₂ (and NO_x) emissions. This study investigates the potential for mercury to be released in the atmosphere when synthetic gypsum material is used as a feedstock for wallboard production.

Task 3 evaluated the use of synthetic gypsum from a limestone forced-oxidation FGD system on a plant that fires high-sulfur bituminous coal, with an SCR in service, and that employs fines blow down. These results indicated an average of 46% of the incoming mercury was emitted during wallboard production. These losses were distributed as 1% across the dryer mill and 41% across the kettle calciner, both as measured by the Ontario Hydro Method at their respective stacks, with the remaining 4% across the board dryer kiln (as measured by solids analyses). The measured mercury losses from Wallboard Plant 2 totaled approximately 8 grams per hour, considering the operation of two dryer mills, two kettle calciners, and one board dryer kiln.

Although the overall percentage loss is significant, the synthetic gypsum feedstock had a relatively low mercury concentration of approximately 0.2 ppm. Consequently, the total mercury losses measured amount to less than 0.2 lb of mercury emitted per million square feet of wallboard produced or 0.09 grams of mercury per ton of dry gypsum processed. Based on Task 3 results and approximate industry production rates, the wallboard industry would emit less than one ton of mercury compared to the current power industry emissions of 48 tons reported by the Environmental Protection Agency. According to this calculation, the estimated wallboard industry emissions would be less than 2% of current power industry emissions. Previous results from Tasks 1 and 2 of this project would predict even lower mercury emissions from the wallboard industry, less than 1% of current power industry emissions based on Task 1 results. However, the results from Tasks 1 through 3 represent a relatively small subset of the power plants, coal types, FGD conditions and wallboard plant conditions corresponding with synthetic gypsum use for wallboard production. Actual U.S. wallboard industry mercury emissions may vary from the estimates made from Task 1 through 3 results.

The mercury mass balance results from this Task 3 wallboard plant test validate the testing procedures employed, as good mercury mass balance closures were calculated. For the mill, the mean mercury balance closures across the dryer mill and kettle calciner were within $\pm 3\%$ of 100%. Solids analyses of the raw gypsum feed and the stucco product from the mill showed an overall mercury loss of 42%, which was identical to the percentage loss calculated from the Ontario Hydro results. For the board-line testing, a similar comparison could not be made because according to the test plan, no Ontario Hydro measurements were conducted.

Of the two flue gas streams measured for mercury content by the Ontario Hydro Method, the kettle calciner steam stack showed the highest mercury concentrations, with a mean concentration of almost $1900 \mu\text{g}/\text{Nm}^3$ when reported on a dry gas basis at actual flue gas oxygen concentrations. Because of differences in mass flow rate and moisture content, this mercury concentration cannot be compared to typical concentrations in coal-fired power plant stack flue gases. The kettle steam stack gas was measured to have a very high moisture concentration of 79%. The mercury concentrations are considerably lower when expressed on a wet flue gas basis, which is the condition under which it is actually released into the atmosphere. Furthermore, the flow rate from this kettle calciner steam stack was quite low, over two orders of magnitude lower than the flue gas flow rate from a typical power plant firing bituminous coal.

Results are now available from three full-scale wallboard plant tests, conducted as parts of Tasks 1 through 3 of this project. Task 1 tested gypsum from a power plant that fires medium- to high-sulfur bituminous coal, has an SCR and a limestone forced oxidation system, and does not employ gypsum fines blow down (the fines remain with the bulk gypsum byproduct). Task 2 tested gypsum from the same power plant but produced while the SCR was not in service (catalyst bypassed). Task 3, discussed in this report, tested gypsum from a power plant configuration similar to that tested in Task 1, although with fines blow down from the gypsum byproduct.

In the Task 3 results, as was seen in the Task 1 and 2 results, most of the mercury emissions from the mill were measured to be in the elemental form (Hg^0). These results are contrary to what was expected at the beginning of this project given that it is predominantly water-soluble oxidized mercury (Hg^{+2}) that is removed in wet FGD systems, while elemental mercury is virtually insoluble and not removed at significant percentages.

As expected, the gypsum processed during the Task 3 test had considerably lower gypsum content than those tested during Tasks 1 and 2. However, a surprising result was that the percentage mercury losses across the kettle calciner and board dryer kiln were higher for the gypsum tested in Task 3 than were measured in Tasks 1 and 2. The resulting mercury loss mass rate across the entire wallboard plant was about double that measured as part of Task 1 and about 15% higher than that measured as part of Task 2 when expressed in terms of pounds of mercury released per million square feet of wallboard produced.

It is not apparent that gypsum fines blow down would cause a doubling of mercury loss mass rates during wallboard production compared to a gypsum that contains fines, particularly considering that the gypsum representing fines blow down contained only about 20% of the mercury content of the gypsum with fines included. The higher loss rate is more likely an impact of coal and/or FGD conditions that influenced the mechanism by which liquid-phase mercury was deposited into the synthetic gypsum byproduct in the FGD system and how tightly it was bound.

Future testing as part of Tasks 4 and 5 in this project will determine how the mercury loss percentages and mass rates vary for gypsum representing other conditions. These other conditions include low rank coal versus bituminous coal, and lime versus limestone FGD reagent.

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