Fate of Mercury in Synthetic Gypsum Used for Wallboard Production

Topical Report, Task 4 Wallboard Plant Test Results

Prepared by:

Jessica Marshall
USG Corporation

Gary M. Blythe and
Mandi Richardson
URS Corporation

November 2005

Cooperative Agreement No: DE-FC26-04NT42080

USG Corporation
125 South Franklin Street
Chicago, Illinois 60606-4678

Prepared for:

Charles Miller

National Energy Technology Laboratory
U.S. Department of Energy
626 Cochrans Mill Road
Pittsburgh, Pennsylvania 15236

DISCLAIMER

ABSTRACT

This report presents and discusses results from Task 4 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 also tested as part of this task, and has been or will be tested in Tasks 1 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 4 was conducted at a wallboard plant processing synthetic gypsum from a power plant that fires a Texas lignite fuel. The power plant has a dual-loop limestone forced oxidation FGD system, with the forced oxidation conducted in the reaction tank integral with the lower loop of the FGD absorber and in an external reaction tank for the upper loop. The FGD system has no gypsum fines blow down, and the power plant is not equipped with a selective catalytic reduction (SCR) system for NO_X emissions control.

The results of the Task 4 stack testing, as measured by the Ontario Hydro method, detected that less than 2% of the incoming mercury was emitted during wallboard production. These losses were distributed as less than 1% each across the dryer mill, kettle calciner, and board dryer kiln. Emissions were significantly lower than Task 1 through 3 results showed for gypsums produced by power plants firing bituminous coal, on both a percentage and a mass basis. As was seen in the Task 1 through 3 results, most of the mercury detected in the stack testing on the dryer mill and kettle calciner was in the form of elemental mercury.

TABLE OF CONTENTS

Page

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

This report presents and discusses results from Task 4 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 going to landfills. Establishing wallboard manufacturing plants near both power plants and population centers can reduce the quantity land filled, 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 SO_2 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 ($CaSO_4{\bullet}2H_2O$) 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 ($CaSO_3{\bullet}\frac{1}{2}H_2O$) byproduct. Most calcium sulfite byproducts are land filled, 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:

$$2\ CaSO_4{\bullet}2H_2O + \text{heat} \rightarrow 2\ CaSO_4{\bullet}\tfrac{1}{2}H_2O + 3\ H_2O$$

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, and 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^{o}F. The solids are dried by direct contact between the wet particles and the hot

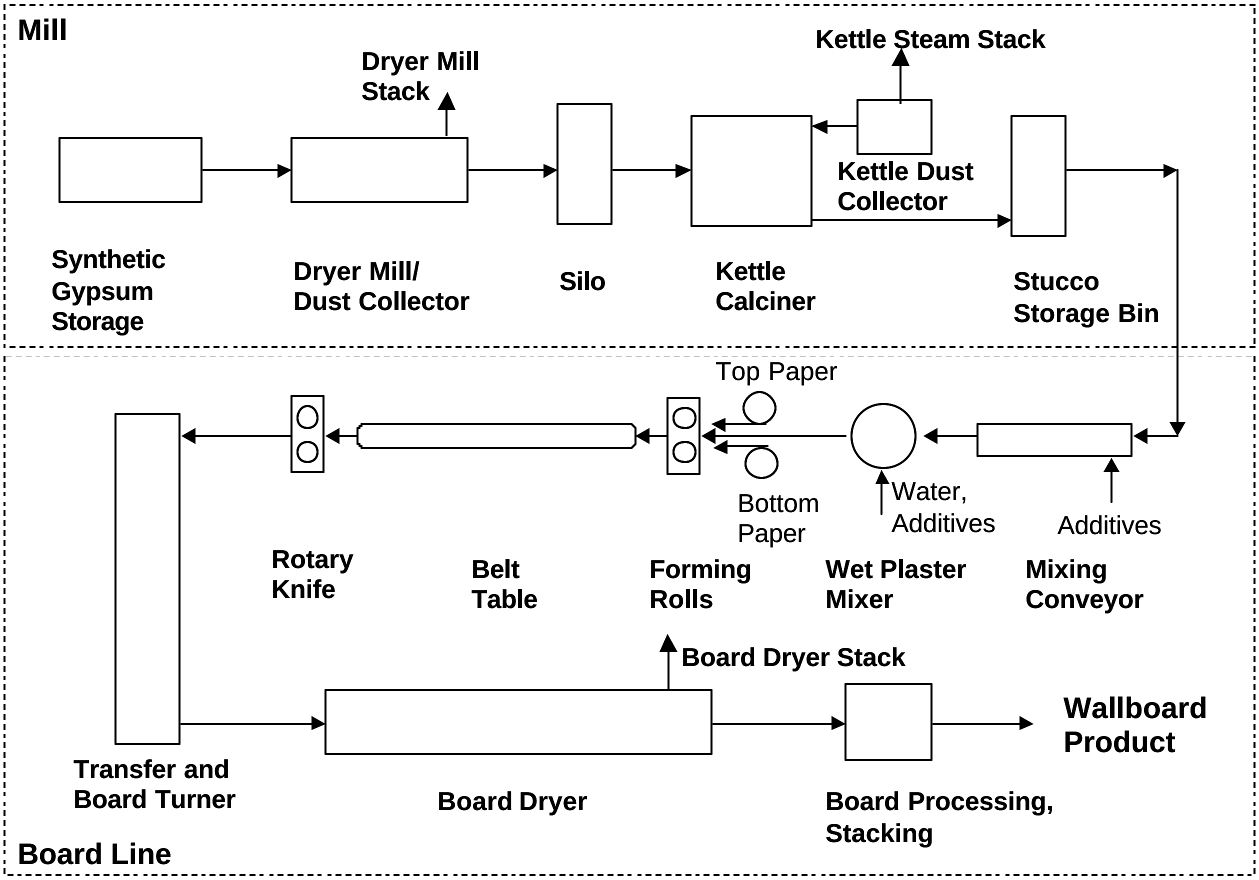

Figure 1. Simplified Schematic of the Wallboard Production Process Using Synthetic Gypsum Feedstock.

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 recycled to the kettle calciner feed. 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 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, to help confirm measured mercury loss rates.

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 TCLP test was chosen based on current regulations, however future studies may include a more comprehensive set of leachate procedures.

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 involves one commercial wallboard plant test. This report summarizes the results from Task 4, which investigated a synthetic gypsum feedstock produced by a power plant that fires Texas lignite fuel and that has a limestone, forced oxidation (LSFO) FGD system that produces a wallboard grade gypsum byproduct and that does not have an SCR for NO_X control. The FGD system does not incorporate a gypsum fines blow down, which tends to elevate the mercury content of the gypsum product compared to systems that do blow down fines.

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

The Task 4 FGD system incorporates a dual-loop scrubbing process. The lower loop is the first to contact the flue gas to be scrubbed, and operates at a relatively low pH (<5). The lower loop has a reaction tank integral to the bottom of the absorber, and forced oxidation air is added there. The slurry blow down to dewatering, to produce the synthetic gypsum byproduct, is from the lower loop. The upper loop operates at higher pH (>5) and has a reaction tank external to the absorber. Forced oxidation air is also added in that reaction tank. The slurry from the upper loop flows to the lower loop, where higher limestone utilization is achieved.

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 high-sulfur, bituminous LSFO plant with SCR that employs gypsum fines blow down, 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.

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 4, including Ontario Hydro measurements in the dryer mill, kettle calciner, and board kiln, 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 through 3[1,2,3]. Planned laboratory evaluations, including simulated gypsum calcining tests and mercury leaching from wallboard product samples by TCLP, have not all been completed 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 4, 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 as a wallboard plant feedstock for a test condition. 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 testing in Tasks 1 through 3 was conducted at wallboard plants processing synthetic gypsum from high-sulfur, bituminous-coal-fired plants with FGD systems. Most synthetic gypsum processed in wallboard plants comes from bituminous coal sources. However, a growing amount of wallboard is produced from synthetic gypsum produced in scrubbed power plants that fire low rank coals such as Powder River Basin (PRB) or lignite fuels.

Low rank coals differ from high-sulfur bituminous coals in a number of manners that impact mercury in the synthetic gypsum. For example, low-rank coals typically have lower chloride content than bituminous coals, which results in lower mercury oxidation percentages in the FGD inlet flue gas. This could result in lesser amounts of mercury being removed in the FGD systems. However, from the standpoint of mercury concentrations in the synthetic gypsum, this effect is offset to some degree by the fact that the lower rank coals typically have lower sulfur content, and hence produce less gypsum per mass of coal or lignite fired.

There is evidence, at least from one laboratory evaluation, that synthetic gypsum from low-rank coals behaves differently when dried and calcined in a wallboard plant than gypsum from bituminous coal. In a laboratory study conducted for EPRI, calcining simulations were conducted on five different synthetic gypsum samples. In these studies, synthetic gypsum samples from a Texas lignite fired power plant and from a PRB plant showed measurably lower percentage mercury losses than three samples from high-sulfur, bituminous coal plants.[4] This observed difference may have been coincidental, since the number of samples from each coal type was small. However, these results suggested that coal rank would be an important variable to investigate as part of this project.

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.

For this test, the intent was for the wallboard plant to be operated on 100% feedstock from Power Plant C, as it would be more 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. However, only the first two of three sampling runs were completed with the wallboard plant processing only feedstock from Power Plant C. Because of equipment mechanical problems in the mill during the test and wallboard plant throughput issues, the third sampling run had to be completed while the plant was operating on a blend of about 70% material from Power Plant C and 30% from another power plant. Fortunately, the synthetic gypsum produced by the other power plant has a very low mercury content, so the processing of the material blend during the third sampling run is not thought to have greatly impacted the test results.

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 during any of the three sampling runs.

Three days of wallboard plant testing were conducted in USG Wallboard Plant 3, with the first and second days testing in the mill and the second and third days 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.

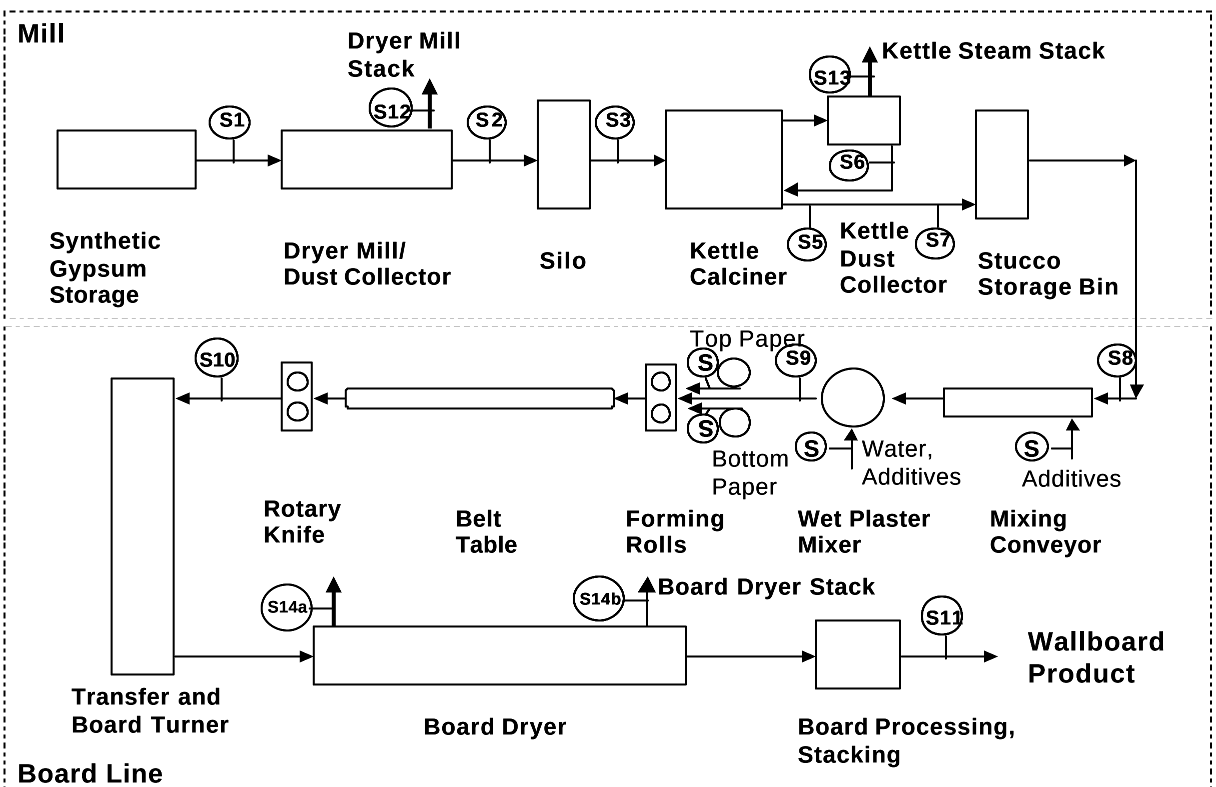

Figure 2. Schematic of Wallboard Plant 4 Showing Sampling Locations

Days 1 and 2 – 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 a downstream kettle calciner dust collector (steam) stack. Wallboard Plant 3 has one dryer mill and three kettle calciners. During this test period, though, only two of the three kettle calciners were operating and one of those two was sampled. As noted in the previous Topical Reports for this project, the Ontario Hydro method was modified slightly for sampling at the kettle calciner steam stack, as described below.

Triplicate runs were to be made at each of these two locations. However, on the third sampling run of the day, the kettle calciner being sampled was forced off line due to a mechanical problem. It was decided to continue the third sampling run for the dryer mill, but delay the third run for the kettle calciner until the next day.

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 ($CaSO_4 \bullet ½H_2O$) 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 coal flue gases, 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, by adding impinger volume 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 was appropriate for sampling this stream.

Also, as noted in the Experimental section of this Topical Report, due to mechanical difficulties, the third kettle calciner sampling run, conducted on Day 2, was conducted while the mill was processing a blend of 70% synthetic gypsum from Power Plant C and 30% synthetic gypsum from another source.

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, additional solid stream samples were collected: the solids collected from the kettle calciner dust collector, which are recycled back to the calciner feed (collected for the first two runs only); and the stucco as it is fed to the product stucco storage bin. The latter sample is slightly different than the calciner product stucco because an additional, proprietary process step is conducted on the product stucco before it is sent to the product stucco storage bin. These two additional sample types were analyzed for mercury concentration, but these data were not used for 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.

As previously explained, the third kettle calciner Ontario Hydro stack sampling run was delayed until Day 2 when operations required the processing of a blended gypsum material. In response, the process solid grab samples for the kettle calciner feed and all samples downstream of the kettle calciner were also postponed until the stack sampling was in progress the following day. In order to document how the mercury content of the raw feed through the dryer mill changed when processing the 30/70 percent blend rather than 100% gypsum from Power Plant C, an additional raw gypsum blend and dryer mill feed sample was collected on Day 2.

These 18 grab samples 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 periodically during the sampling periods.

Days 2 and 3 – Board-Line Testing

Stack Sampling

According to the original project plan, no stack sampling was to be conducted on the board dryer kiln stack as part of Task 4; only process samples were to be collected. However, because the mercury losses from the board dryer kiln stack measured as part of Task 1 were higher than expected,[1] it was decided to add board dryer kiln stack measurements to the scopes of Tasks 4 and 5.

On the second test day, the intent was to conduct triplicate Ontario Hydro Method measurements on the board dryer kiln stack gas. The timing of the second day measurements was to approximately correspond with the processing of stucco material calcined the previous day, taking into account the residence time in the stucco storage bin between the mill and board line. However, as mentioned above, on Day 2 the mill began processing a blend of 70% gypsum from Power Plant C and 30% gypsum from another power plant. The inventory of stucco produced from 100% gypsum from Power Plant C was depleted late in the second board kiln Ontario Hydro run (the run was stopped when this inventory was depleted). Because it was late in the day and it might take some time for the board line to reach steady state after converting to the different stucco feed, it was decided to conduct the third board dryer kiln Ontario Hydro sampling run the next morning, on Day 3.

The board dryer kiln at Wallboard Plant 3 is somewhat different than at Wallboard Plants 1 and 2 in that it has two flue gas stacks, one on the wet wallboard feed end (the “wet end”) and one on the wallboard product end (the “dry end”). Consequently, during each board dryer kiln sampling run, two Ontario Hydro measurement runs were conducted simultaneously, one on each stack.

Process Sampling

During each of the triplicate Ontario Hydro runs, samples were collected of the feed stucco, the slurry fed to the board forming machine, and the wet and dry product wallboard.

Water and a number of proprietary additives are added to the stucco when mixing the slurry prior to the board forming step. The water, each of these additives, and the paper used during board forming were also sampled once during the test, to evaluate their impact on the mercury content of the slurry and the wallboard. Triplicate samples of the additives and paper were not deemed to be necessary, as each is fed from a large silo, storage tank, or rolls that should have been relatively homogenous over the course of the three Ontario Hydro runs. Note that, because the composition and dosages of the additives are considered proprietary, the results from sampling additives and the paper are reported only as their percent contribution to the total mercury content in the wet board. No individual additive feed rate or mercury concentration data are reported, nor are the chemical compositions or names of these additives.

As for the mill testing effort, key process data were collected throughout each sampling run. These data were collected as screen prints from the process control software, intermittently during each of the three Ontario Hydro runs. For the board line, these data include the stucco feed rate, water and additive feed rates (not included in this report), paper thickness and weight, board production rate, and the dryer flue gas temperatures.

As the three-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 (where appropriate) 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 4 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 February 16 and 17, 2005. Table 3 shows results for additional characterization of these samples conducted by USG, including mercury and combined (water of hydration only) moisture content 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 February 17 and 18, 2005.

Table 2. Task 4 Raw Gypsum and Mill Process Sample Mercury and Moisture Analyses, URS Results (values in italics are for samples representing a blend of 70% gypsum from Power Plant C and 30% from another power plant)

Sample Number	Sample Description	Mercury Content, μg/g (dry basis)					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	0.52	0.52	0.54/ *0.40*[#]	0.53[#]	0.01[#]	11.8	12.9	13.3/ *10.2*	12.6[#]
S2	Land Plaster from Dryer Mill	0.56	0.52	0.53	0.54	0.03	<1	<1	<*1*	-
S3	Land Plaster to Kettle Calciner	0.50	0.52	*0.44*	-	-	<1	<1	<*1*	-
S5	Kettle Calciner Product, as measured	0.56	0.60	*0.42*	-	-	<1	<1	<*1*	-
	Kettle Calciner Product, dry gypsum basis	0.47	0.51	*0.36*	-	-	<1	<1	<*1*	-
S6	Kettle Calciner Dust Collector Solids, as measured	0.79	0.68	-	-	-	<1	<1	<*1*	-
	Kettle Calciner Dust Collector Solids, dry gypsum basis	0.67	0.59	-	-	-	<1	<1	<*1*	-
S7	Product Stucco, as measured	0.52	0.57	*0.40*	-	-	<1	<1	<*1*	-
	Product Stucco, dry gypsum basis	0.45	0.48	*0.34*	-	-	<1	<1	<*1*	-

*95% Confidence Interval of mean
[#]First value for Run 3 is for third Dryer Mill Ontario Hydro sampling time period, second is for Kettle Calciner Ontario Hydro sampling time period; mean and 95% confidence interval values are based on first value for Run 3

Table 3. Task 4 Raw Gypsum and Mill Process Sample Characterization Results, USG Results (values in italics are for samples representing a blend of 70% gypsum from Power Plant C and 30% from another power plant)

Sample	Run	Combined Moisture Content, wt%*	Mercury Content, μg/g		Particle Size Distribution (microns)				Blaine Surface Area, cm^2/gm
			As measured, dry basis	Dry Gypsum basis	Mean Diameter	Particle Size at % Less Than			
						1%	10%	95%	
S1 – Raw Gypsum Feed to Dryer Mill	1	20.3	0.49	0.49	55.3	11.0	25.8	103	1,079
	2	20.3	0.51	0.51	57.2	11.3	26.4	111	1,060
	3	20.3	0.51	0.51	55.5	10.2	24.6	111	1,144
S2 – Land Plaster from Dryer Mill	1	19.5	0.57	0.55	43.1	3.6	14.5	82.6	1,533
	2	19.9	0.52	0.51	49.9	5.2	19.3	97.0	1,255
	3	13.0	0.53	0.49	51.5	4.2	16.8	111	1,359
S3 – Land Plaster to Kettle Calciner	1	19.7	0.48	0.48	68.2	8.1	25.2	164	1,110
	2	19.8	0.51	0.51	50.7	5.2	19.5	99.8	1,229
	3	13.0	0.43	0.39	62.5	5.8	17.3	169	1,432
S5 – Kettle Calciner Product	1	6.4	0.55	0.46	48.8	6.9	19.2	94.1	2,252
	2	6.4	0.59	0.49	49.2	6.9	19.1	96.1	2,310
	3	6.5	0.40	0.34	74.5	6.9	19.2	200	2,569
S6 – Kettle Calciner Dust Collector Solids	1	6.7	0.73	0.62	40.4	3.1	11.5	84.6	2,957
	2	8.1	0.67	0.58	42.6	4.2	14.4	85.8	2,498
	3	-	-	-	-	-	-	-	-
S7 – Product Stucco	1	7.4	0.51	0.43	48.8	3.7	14.6	105	2,588
	2	6.5	0.55	0.47	47.2	3.5	13.9	99.7	2,787
	3	6.4	0.39	0.33	64.6	3.6	13.0	185	3,201
S8 – Stucco Feed to Board Line	1	6.5	0.57	0.48	30.4	1.2	3.6	77.4	5,633
	2	6.3	0.52	0.44	24.1	1.2	3.5	66.7	5,995
	3	6.3	0.35	0.29	32.4	1.2	3.8	99.9	6,822

*Values shown represent waters of hydration only – do not include free moisture content

Table 4. Task 4 Stucco, Wallboard Product and Intermediate Process Sample Mercury and Moisture Analyses, URS Results (values in italics are for samples representing a blend of 70% gypsum from Power Plant C and 30% from another power plant)

Sample Number	Sample Description	Mercury Content, μg/g (dry basis)			Moisture Content, wt% as received		
		Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
S8	Stucco Feed, as measured	0.57	0.55	*0.40*	<1	<1	*<1*
	Stucco Feed, dry gypsum basis	0.48	0.46	*0.34*	<1	<1	*<1*
S9	Slurry to Forming Rolls	0.51	0.50	*0.33*	29.6*	28.9*	*28.5**
S10	Wet Wallboard	0.48	0.47	*0.30*	28.2	26.9	*28.1*
S11	Dry Wallboard Product	0.48	0.47	*0.33*	<1	<1	*<1*

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

In the previous three Topical Reports produced as part of this project, a mean and a 95% confidence interval about that mean have been shown for key values in the tables. 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. However, for this Topical Report, the change in the feedstock for Run 3 for all but the dryer mill test meant that two runs were at one feedstock condition and the third was at a different feedstock condition. For this reason, it was decided not to show mean and 95% confidence interval values in this report except for the dryer mill results as shown in Table 2.

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 for the first two runs (all three runs for the dryer mill test). For the samples from the third kettle calciner test (S3 through S7), the mercury concentrations were significantly lower than the corresponding values in the first two tests.

For the three dryer mill tests, the raw gypsum feed contained an average of 0.53 µg/g (dry basis) and 13% moisture, the latter of which is at the high end of the typical range for FGD gypsum. The raw gypsum from Power Plant C is shipped to Wallboard Plant 3 in open rail cars, and rainy weather led to an increase in synthetic gypsum moisture content. Note that the mercury concentration in the gypsum from Power Plant C is about half of that from Power Plant A (tested in Tasks 1 and 2) but about 2.5 times greater than from Power Plant B (tested in Task 3).

For the third wallboard test, the mercury concentration of the raw gypsum feed to the dryer mill, 0.40 µg/g, was about 75% of the average value for the three dryer mill tests shown in Table 2. This reflects the feedstock consisting of about 70% gypsum from Power Plant C and 30% gypsum from another power plant that has a very low mercury content.

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, S6, and S7) on a dry gypsum basis. This accounts for the effects of the loss of waters of hydration by the stucco. Similarly, a column in Table 3 shows 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. No loss of mercury is seen across the dryer mill, as the average mercury concentration in the land plaster is nearly identical to the average mercury concentration in the raw gypsum feed.

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, small apparent losses of mercury across the kettle calciner are seen for the first two runs. The feed gypsum averaged 0.51 µg/g of mercury content on a dry basis (dry of free moisture only – not waters of hydration) while the product stucco averaged 0.49 µg/g (about 4% loss). For Run 3 on the kettle calciner, these two samples show a greater apparent mercury loss percentage (18%), with the land plaster feed showing 0.44 µg/g while the calciner product showed 0.36 µg/g. However, given that these values reflect only a single set of grab samples, there is a relatively high uncertainty in quantifying mercury losses by comparing the mercury analyses on these two samples. The Ontario Hydro stack sampling results for the kettle calciner will most likely provide a better measure of this loss percentage.

The results of USG analyses in Table 3 show mercury concentrations that are very similar 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 0.51 µg/g for the first two runs, while the USG analyses showed a mean of 0.50 µg/g. For the third run, the URS analyses showed 0.44 µg/g and the USG analyses showed 0.43 µg/g. For sample S5, the URS analyses showed a mean concentration of 0.58 µg/g for the first two runs, while the USG analyses showed a mean of 0.53 µg/g. For the third run, the URS analyses showed 0.42 µg/g and the USG analyses showed 0.40 µg/g. This is considered excellent agreement between two laboratories analyzing separate splits of the same sample, by two different methods.

The USG characterization of these samples generally shows expected trends. For example, the specific surface area of the land plaster is observed to increase from about 1100 to 1500 cm^2/g to over 2200 cm^2/g upon calcining, which would be expected due to the evolution of waters of hydration from the particles. One unexpected result is the combined moisture content (water of hydration content) of the land plaster from the dryer mill for the third run. A sample of 100% pure gypsum should have a combined moisture content of 20.9 wt%, while 100% stucco should have a combined moisture content of 6.2 wt%. The measured value of 13.0 wt% is indicative of partial dehydration of the raw gypsum in the dryer mill, which seems unlikely given the observed operating temperatures. These results remain unexplained.

The results from the board line samples in Table 4 show that the mercury concentrations in the stucco feed to the wallboard plant (S8) were close to the values measured in the product stucco going to the stucco storage bin (S7). For example, for Runs 1 and 2, S7 averaged 0.55 µg/g of mercury content, while S8 averaged 0.56 µg/g. For Run 3, both samples were measured at 0.40 µg/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 reasonably successful.

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 1½ 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 less than 1% CO_2 and nearly 21% oxygen. The moisture content was relatively high at about 12% due to the free moisture from the gypsum that is evolved in the dryer. The dryer mill flue gas temperature was well below 200^{o}F, as would be expected because of the need to keep the dried gypsum below its initial calcination temperature of 262^{o}F.

The kettle calciner results for flue gas composition were consistent with a very wet air stream, containing no measurable CO_2 content and 21% oxygen. The measured moisture content of the stack gas was high, averaging 56%, due to the waters of hydration released from the gypsum. The measured moisture content was the same as was measured at Wallboard Plant 1 in Tasks 1 and 2, but lower than was measured at Wallboard Plant 2 (79%) in Task 3.

The board dryer kiln sampling results showed that the “wet end” stack flue gas flow rate is lower than the “dry end” flue gas rate. It is also hotter, as might be expected, but more dilute (higher measured oxygen concentration). The moisture content in the wet end flue gas was lower than in the dry end flue gas, which seems counterintuitive, but this may be because of the greater air dilution seen in this flue gas stream.

Table 6 summarizes the mercury concentration and mass rate data. The results show that for the dryer mill and kettle calciner stacks, the mercury is mostly in the elemental form (Hg^0). This 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. Alternatively, an unknown mechanism for the absorption of a small percentage of elemental mercury in the FGD system could provide another explanation as to the presence of the unexpected elemental mercury in the stack emissions. 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.[5]

For the board dryer kiln, the results showed closer to equal percentages of oxidized and elemental mercury in the stack flue gas. However, the measured concentrations in those stacks were extremely low, with the total mercury concentrations at or below the stated detection limit of the Ontario Hydro method of 0.5 $\mu g/Nm^3$, so the observed mercury speciation data may not be meaningful.[6]

The total mercury concentration data show that on a dry gas basis, the concentrations in the kettle calciner steam stack are in the range of 20 to 30 $\mu g/Nm^3$, while the dryer stack averaged 2 $\mu g/Nm^3$. The measured total mercury concentrations in the board dryer kiln stack were very low, around 0.5 $\mu g/Nm^3$.

Table 5. Task 4 Ontario Hydro Results – Summary of Exhaust Gas Conditions

Sample Number	Run No.	Date (2005)	Time (24-h)	Flow Rate		Temperature (°F)	H_2O (%)	CO_2 (%)	O_2 (%)
				acfm*	Dscfm#				
Dryer Mill (1 of 1)									
S12	1	2/16	0940-1140	42,600	32,400	149	10.7	<1	21
	2	2/16	1230-1430	40,700	30,500	150	11.8	<1	21
	3	2/16	1520-1805	41,200	31,100	137	13.1	<1	21
	Mean			41,500	31,300	145	11.9	-	-
Kettle Calciner (1 of 2 operating)									
S13	1	2/16	0940-1140	4,580	1,530	257	54.9	0	21
	2	2/16	1230-1430	4,570	1,350	265	59.6	0	21
	3	2/17	1524-1725	4,860	1,630	259	54.5	0	21
	Mean			4,670	1,500	260	56.3	-	-
Board Dryer Kiln (1 of 1)									
S14a (wet end)	1	2/17	1215-1415	31,000	19,300	244	17.9	<1	21
	2	2/17	1500-1620	30,500	18,700	246	19.0	<1	21
	3	2/18	0900-1100	32,200	17,900	284	22.6	<1	21
	Mean			31,200	18,600	-	-	-	-
S14b (dry end)	1	2/17	1215-1415	54,700	35,300	203	20.1	<1	18
	2	2/17	1500-1620	50,100	32,100	203	20.4	<1	18
	3	2/18	0900-1100	50,800	31,900	213	21.2	<1	18
	Mean			51,900	33,100	-	-	-	-

*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

Table 6. Task 4 Ontario Hydro Results – Speciated Mercury Emissions Data

<table>
<tr><th rowspan="2">Sample Number</th><th rowspan="2">Run No.</th><th rowspan="2">Date (2005)</th><th rowspan="2">Time (24-h)</th><th colspan="4">Concentration (μg/Nm^3)*</th><th rowspan="2">Total Mercury Emission Rate (lb/h)#</th></tr>
<tr><th>Particle-Bound, Hg^P</th><th>Oxidized, Hg^{+2}</th><th>Elemental, Hg^0</th><th>Total Hg</th></tr>
<tr><td colspan="9">Dryer Mill (1 of 2)</td></tr>
<tr><td rowspan="5">S12</td><td>1</td><td>2/16</td><td>0940-1140</td><td>0.08</td><td>0.34</td><td>1.80</td><td>2.22</td><td>2.51×10^{-4}</td></tr>
<tr><td>2</td><td>2/16</td><td>1230-1430</td><td>0.09</td><td>0.23</td><td>1.78</td><td>2.10</td><td>2.24×10^{-4}</td></tr>
<tr><td>3</td><td>2/16</td><td>1520-1805</td><td>0.09</td><td>0.18</td><td>2.46</td><td>2.73</td><td>2.97×10^{-4}</td></tr>
<tr><td colspan="3">Mean</td><td>0.09</td><td>0.25</td><td>2.01</td><td>2.35</td><td>2.57×10^{-4}</td></tr>
<tr><td colspan="3">95% Confidence Interval</td><td>0.01</td><td>0.09</td><td>0.44</td><td>0.38</td><td>0.42×10^{-4}</td></tr>
<tr><td colspan="9">Kettle Calciner (1 of 2)</td></tr>
<tr><td rowspan="3">S13</td><td>1</td><td>2/16</td><td>0940-1140</td><td>7.06</td><td>1.72</td><td>12.3</td><td>21.0</td><td>1.12×10^{-4}</td></tr>
<tr><td>2</td><td>2/16</td><td>1230-1430</td><td>7.35</td><td>2.32</td><td>19.5</td><td>29.2</td><td>1.37×10^{-4}</td></tr>
<tr><td>3</td><td>2/17</td><td>1524-1725</td><td>5.13</td><td>2.66</td><td>11.9</td><td>19.7</td><td>1.12×10^{-4}</td></tr>
<tr><td colspan="9">Board Dryer Kiln (1 of 1)</td></tr>
<tr><td rowspan="3">S14a (wet end)</td><td>1</td><td>2/17</td><td>1215-1415</td><td><0.03</td><td>0.14</td><td>0.15</td><td>0.37</td><td>2.48×10^{-5}</td></tr>
<tr><td>2</td><td>2/17</td><td>1500-1620</td><td><0.04</td><td>0.16</td><td>0.34</td><td>0.60</td><td>3.90×10^{-5}</td></tr>
<tr><td>3</td><td>2/18</td><td>0900-1100</td><td><0.03</td><td>0.17</td><td>0.29</td><td>0.55</td><td>3.42×10^{-5}</td></tr>
<tr><td rowspan="3">S14b (dry end)</td><td>1</td><td>2/17</td><td>1215-1415</td><td><0.03</td><td><0.11</td><td>0.29</td><td>0.43</td><td>5.29×10^{-5}</td></tr>
<tr><td>2</td><td>2/17</td><td>1500-1620</td><td><0.05</td><td>0.16</td><td>0.29</td><td>0.49</td><td>5.52×10^{-5}</td></tr>
<tr><td>3</td><td>2/18</td><td>0900-1100</td><td><0.03</td><td><0.11</td><td>0.41</td><td>0.55</td><td>6.17×10^{-5}</td></tr>
</table>

*μg/Nm^3 = Micrograms per normal cubic meter (dry gas at 32°F, at as-measured O_2 concentration)

#lb/h = Pounds per hour

Compared to the mercury concentrations measured at Wallboard Plant 1 as part of Task 1, the dryer mill stack concentration at Wallboard Plant 3 was nearly four times lower, while the kettle calciner stack concentration were about five to seven times lower. In the board dryer kiln stacks, the mercury concentrations measured at Wallboard Plant 3 were 20 to 30 times lower than was measured at Wallboard Plant 1 as part of Task 1.

Comparing the mercury mass emission rate data in Table 6, the mercury losses from the dryer mill and kettle calciners were about equal, considering there is only one dryer mill and that two kettle calciners were operating. Considering the sum of the mercury losses from the two stacks on the board kiln, the mercury emissions from the board kiln were about one-half to one-third of those from either the dryer mill or kettle calciners.

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 4 Mill Test Process Conditions

Date	2/16/2005	2/16/2005	2/16/2005	2/17/2005	
Time	0940-1140	1230-1430	1520-1805	1524-1725	
Ontario Hydro Run	Run 1	Run 2	Run 3*	Run 3#	Average
Dryer Mill Syn Gyp Feeder Output, % of full scale	42	43	45	-	43
Dryer Mill Burner Output, % of full scale	37	41	41	-	40
Estimated Dryer Mill B Wet Feed Rate, tons/hr	36	36	36	-	36
Dryer Mill Dust Collector Outlet Temperature, ^oF	147	146	134	-	142
Kettle #1 Feeder Drive Load, % of full scale	45	43	-	41	-
Estimated Kettle Calciner Land Plaster Feed Rate, tons/hr	15	15	-	20	-
Kettle #1 North Stucco Temperature, ^oF	294	308	-	307	-
Kettle #1 South Stucco Temperature, ^oF	296	311	-	308	-
Kettle #1 Dust Collector Outlet Temperature, ^oF	276	287	-	281	-

*Run 3 for dryer mill only
#Run 3 for kettle calciner only

Table 8. Task 4 Board-line Test Process Conditions

Date	2/17/2005	2/17/2005	2/18/2005
Time	1215-1415	1500-1620	0900-1100
Board Width, in.	48	48	48
Board Thickness, in.	0.5	0.5	0.625
Kiln Wet Zone 1 Temperature, ^oF	490	493	524
Kiln End Temperature, ^oF	270	271	285

The rates shown in Table 7 for the dryer mill and kettle calciner were based on stucco usage on the board line and the relative change in level in the product stucco storage bins. The higher estimated rate in the third kettle calciner run is due to the higher firing rates that are possible when processing the blend of 70% synthetic gypsum from Power Plant C and 30% gypsum from another power plant, compared to what is possible when processing 100% of the wetter material from Power Plant C.

The process conditions shown in Tables 7 and 8 were used as the basis for mercury balance calculations, as discussed in the following subsection. Note that in board-line Run 3, the board line was producing fire code wallboard (5/8-in. thick) rather than the standard ½-in. thick product. This change led to the need to run higher temperatures in the board dryer kiln, which was also seen in the Ontario Hydro stack gas temperatures for Run 3 compared to Runs 1 and 2. The higher temperatures in the board dryer kiln may have impacted the measured mercury losses in Run 3.

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 losses across the dryer mill and kettle calciner were low, less than 1.0% of the mercury in the raw gypsum or land plaster, respectively, based on the Ontario Hydro stack results. For the dryer mill, the solids analysis actually did not indicate any mercury loss. For the kettle calciner, the percentage loss based on the solids analysis was between 4 and 7% for the first two runs, and 19% for the third run with the blend feedstock. The mercury losses measured by the Ontario Hydro method are believed to be more accurate than the losses indicated by solids analyses. The Ontario Hydro results represent a direct measurement of losses, integrated over a two-hour period, whereas the losses by solids analyses are based on the differences between analyses of one feed and product grab sample for each run period.

The mercury balances across the dryer mill 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%, and individual measurement run closures ranged from 99% to 109%. The mercury balance closures were good for the first two runs on the kettle calciner (94% to 97%), but not as good for the third run (82%). The lower level of agreement in the third run is related to the relatively larger difference between the percentage mercury loss measured by the Ontario Hydro method versus that indicated by the solids analyses. This discrepancy is likely due to the greater difficulty of collecting representative samples when a blend of two different feedstocks is being processed.

The Task 4 results show the lowest percentage mercury loss in the mill of the four tasks that have been completed to date. The previous lowest percentage losses had been measured in Task 1, for Wallboard Plant 1 and synthetic gypsum from Power Plant A (bituminous coal, LSFO, no fines blow down, SCR in service). Compared to the previous Task 1 results, the mercury loss percentages across the dryer mill are approximately the same at Wallboard Plant 3, but the percentage losses across the kettle calciner are less than half of those measured in Task 1. This observation tends to support the results of EPRI laboratory calcining simulations that showed lower mercury losses from synthetic gypsums produced by power plants that fire low-rank coals.[4]

Table 9. Task 4 Mercury Balance Results for the Mill Test (values in italics are for run representing a blend of 70% gypsum from Power Plant C and 30% from another power plant)

Run Number	Run 1	Run 2	Run 3	Mean	95% C.I.
Feed to Dryer Mill (Raw Gypsum):					
Feed rate, tons/hr	36	36	36	36	±0
Wt% moisture	11.8	12.9	13.3	12.6	±0.9
Hg content, µg/g, dry basis (from Table 2)	0.52	0.52	0.54	0.53	±0.01
Total Hg to dryer mill, g/hr	15	15	15	15	±0
Dryer Mill Product (Land Plaster):					
Dry rate, tons/hr	32	31	31	31	±0
Hg content, µg/g (from Table 2)	0.56	0.52	0.53	0.54	±0.03
Total Hg from dryer mill, g/hr	16	15	15	15	±1
Measured solids Hg loss rate, g/hr	-1.3	0.0	0.3	-0.3	±0.9
Measured Hg loss rate at stack, lb/hr (from Table 6)	2.51×10^{-4}	2.23×10^{-4}	2.96×10^{-4}	2.57×10^{-4}	$\pm 0.42 \times 10^{-4}$
Measured Hg loss rate at stack, g/hr	0.11	0.10	0.13	0.12	±0.02
% Hg loss across dryer mill, by solids analysis	-8.4%	-0.1%	1.7%	-2.3%	±6.1%
% Hg loss across dryer mill, by Ontario Hydro	0.8%	0.7%	0.9%	0.8%	±0.1%
Land Plaster Feed to Kettle Calciner:					
Feed rate, tons/hr	15	15	*20*	-	-
Hg content, µg/g (from Table 2)	0.50	0.52	*0.44*	-	-
Total Hg to kettle calciner, g/hr	6.9	7.1	*8.0*	-	-
Product Stucco:					
Product rate, tons/hr, calculated	12.6	12.6	*16.9*	-	-
Hg content, µg/g (from Table 2)*	0.56	0.60	*0.42*	-	-
Total Hg from kettle calciner, g/hr	6.4	6.9	*6.5*	-	-
Measured solids Hg loss rate, g/hr	0.5	0.3	*1.5*	-	-
Measured Hg loss rate at stack, lb/hr (from Table 6)	1.12×10^{-4}	1.38×10^{-4}	*1.12×10^{-4}*	-	-
Measured Hg loss rate at stack, g/hr	0.05	0.06	*0.05*	-	-
% Hg loss across kettle calciner, by solids analysis	6.6%	3.6%	*19%*	-	-
% Hg loss across kettle calciner, by Ontario Hydro	0.7%	0.9%	*0.6%*	-	-
Mass Balance Closures:					
Dryer mill Hg closure, output vs. input, %	109%	101%	99%	103%	±6%
Kettle Calciner Hg balance closure, output vs. input, %	94%	97%	*82%*	-	-
Overall Mill Hg balance closure, %*	-	-	-	-	-

*Overall mill mercury balance closures are not calculated because Run 3 was at different times for the dryer mill and kettle calciner, and even for Runs 1 and 2, the relative throughput of landplaster to the two calciners in service was not measured.

The results of mercury balance calculations across the board line are shown in Table 10. Fewer details about feed rates are shown in Table 10 than in Table 9 due to the proprietary nature of the wallboard forming process. The results show that mercury losses across the board dryer kiln are relatively low compared to the total mercury content of the wet board, with values of 0.2% to 0.4% loss shown in the Ontario Hydro stack results. The solids analyses results show a much wider range of results, from –4% loss (4% gain) to +6% loss. As described above for the mill results, the Ontario Hydro results are believed to be more accurate than the loss percentages estimated from grab sample mercury analyses.

Table 10. Task 4 Mercury Balance Results for the Board-line Test (values in italics are for run representing a blend of 70% gypsum from Power Plant C and 30% from another power plant)

Run Number	Run 1	Run 2	Run 3
Hg in Feed to Board Line:			
Relative Stucco Feed Rate, % of highest value during tests	88	89	*100*
Hg Concentration in Stucco, µg/g (dry) (from Table 4)	0.57	0.55	*0.40*
Hg in Stucco Feed, % of total Hg into Board Line	99.3	99.3	*99.4*
Hg in Water Added, % of total Hg into Board Line	0.0	0.0	*0.0*
Hg in Additives, % of total Hg into Board Line	0.4	0.4	*0.3*
Hg in Paper, % of total Hg into Board Line	0.3	0.3	*0.3*
Hg in Slurry to Board Forming:			
Hg Concentration in slurry, µg/g (dry) (from Table 4)	0.51	0.50	*0.33*
Moisture in Set Up Slurry, wt%	29.6	28.9	*28.5*
Hg in Slurry, % closure with stucco + water + additives	118%	121%	*107%*
Hg in Wet Wallboard:			
Hg Concentration in Wet Wallboard, µg/g (dry) (from Table 4)	0.48	0.47	*0.30*
Moisture in Wet Wallboard, wt%	28.1	26.9	*28.1*
Hg in Wet Wallboard, % closure with stucco + water + additives + paper	111%	116%	*99%*
Hg in Wallboard Product:			
Hg Concentration in Wallboard Product, µg/g (dry) (from Table 4)	0.48	0.47	*0.33*
Hg Loss and Balance Closures:			
Measured Hg loss rate at stack, lb/hr (from Table 6)	7.79×10^{-5}	9.40×10^{-5}	*9.55×10^{-5}*
% Hg Loss Across Board Dryer Kiln, by solids analysis	4.6%	6.1%	*-3.5%*
% Hg Loss Across Board Dryer Kiln, by Ontario Hydro	0.2%	0.3%	*0.4%*
Hg Balance Across Board Dryer Kiln, %	96%	95%	*104%*
Overall Board-line Hg Balance, output vs. input, %	107%	110%	*103%*

The observed mercury balances across the board kiln show very good closure, ranging from 95% to 104% for the individual test runs, as do the closures across the overall board line, which range from 103% to 110%.

At this point in the project, mercury losses across the board kiln have been measured by the Ontario Hydro method twice, as part of Task 1 and the current task. The mercury losses measured during the current task are considerably lower than were measured at Wallboard Plant 1 as part of Task 1, which showed a mean loss percentage of 1.9%.

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. 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. Note that no calculation is shown by the first method for Run 3, because the Ontario Hydro measurements for the dryer mill were conducted on a different feed material than was being processed during Run 3 for the kettle calciner and for the board dryer kiln.

Table 11. Summary of Task 4 Overall Mercury Loss During Wallboard Production, Calculated by Two Methods (values in italics are for run representing a blend of 70% gypsum from Power Plant C and 30% from another power plant)

	Run 1	Run 2	Run 3
Total Hg Loss from Process Stacks by Ontario Hydro Method, g/hr*	0.25	0.27	-
Total Hg to Wallboard Plant, g/hr#	15	15	-
Observed Overall Percentage Hg Loss based on Ontario Hydro Method	1.7%	1.8%	-
Hg Concentration in Raw Gypsum Feed to Wallboard Plant, µg/g	0.52	0.52	*0.40*
Hg Concentration in Wallboard Product, µg/g	0.48	0.47	*0.33*
Observed Percentage Hg Loss Across Wallboard Plant based on solids analyses	7.6%	8.5%	*17.1%*
Observed Percentage Hg Loss Across Wallboard Plant based on solids analyses, corrected for Hg added with additives and paper in board line	8.2%	9.2%	*17.5%*

*Assumes one dryer mill and two kettle calciner stacks, includes both board dryer kiln stacks
#Includes mercury in raw gypsum feed plus mercury added by additives and paper in the board line

The overall lost percentage by the first method shows 1.7 to 1.8% of the plant input mercury out the three process stacks as measured by the Ontario Hydro method. The apparent loss measured by the second method, the change in mercury concentration from the mill feed to the wallboard product is much higher, ranging from 8% to nearly 18% after correcting for 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. For reasons discussed earlier in this report, it is believed that the mean value of 1.7 to 1.8% mercury loss across the wallboard plant calculated by the first method, based on Ontario Hydro results, better reflects the actual losses from this feedstock. The mercury loss percentages based on solids analyses can be adversely impacted by two effects. One is the fact that the feed and product samples represent grab samples taken at a single point in time during each sampling run. This possible error is particularly a concern for Run 3, where the mill feed material was a blend of solids from two sources and it is difficult to collect a grab sample that reflects the proper percentages of the two sources. The second possible adverse impact is the effect of analytical variability when comparing two concentration measurements to quantify small mercury percentage losses.

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 land filled. 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 SO_2 (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 4 evaluated the use of synthetic gypsum from a limestone forced-oxidation FGD system on a plant that fires Texas lignite, does not have an SCR, and does not employ fines blow down. These results indicated that 1.7 to 1.8% of the incoming mercury was emitted during wallboard production, as measured by the Ontario Hydro method. These losses were distributed as less than 1% each across the dryer mill, kettle calciner, and board dryer kiln.

The measured mercury losses from Wallboard Plant 3 totaled approximately 0.3 grams per hour, considering the operation of one dryer mill, two kettle calciners, and one board dryer kiln. Of this total loss, about 40% was from the dryer mill, 40% from the kettle calciners, and 20% from the board dryer kiln. The total mercury losses measured amount to only 0.01 lb of mercury emitted per million square feet of wallboard produced or 0.01 grams of mercury per ton of dry gypsum processed. Based on Task 4 results and approximate industry production rates, the wallboard industry would emit less than 200 lb 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 0.2% of current power industry emissions. Previous results from Tasks 1 through 3 of this project would predict higher mercury emissions from the wallboard industry, though, ranging from 1 to 2% of current power industry emissions. However, the results from Tasks 1 through 4 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 4 results.

The mercury mass balance results from this Task 4 wallboard plant test validate the testing procedures employed, as good mercury mass balance closures were calculated in most instances. For the dryer mill, the mean mercury balance closure was within ±3% of 100%. For the kettle calciner, mercury balance closures were within ±6% of 100% for the first two runs where the feedstock was 100% synthetic gypsum from Power Plant C. For the third run, where a blend of material was being processed, the closure was not as good. For the board-line testing, a very good mercury balance closure of ±5% of 100% was realized across the board dryer kiln, and ±10% of 100% for the overall board line.

Of the flue gas streams measured for mercury content by the Ontario Hydro Method, the kettle calciner steam stack showed the highest mercury concentrations, with concentrations of 20 to 30 µg/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 content of 56%. 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. The mercury concentrations in the flue gas from the dryer mill and board dryer kiln were considerably lower, ranging from 2 to 3 µg/Nm^3 in the dryer mill stack and less than 1 µg/Nm^3 in the two board kiln stacks.

Results are now available from four full-scale wallboard plant tests, conducted as parts of Tasks 1 through 4 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 FGD 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 tested gypsum from a power plant configuration similar to that tested in Task 1, although with fines blow down from the gypsum byproduct. Finally, Task 4 tested gypsum from a power plant that fires Texas lignite, has a limestone forced oxidation FGD system, no SCR, and no gypsum fines blow down.

The gypsum processed during the Task 4 test had mercury content lower than those tested during Tasks 1 and 2, but higher than that tested during Task 3. The percentage mercury losses across the mill and across the board line were lower for the gypsum tested in Task 4 than were measured in Tasks 1 through 3. The resulting mercury loss mass rate across the entire wallboard plant was about an order of magnitude lower than was measured as part of Tasks 1 through 3 when expressed in terms of pounds of mercury released per million square feet of wallboard produced. This observation supports the results of previous laboratory gypsum calcining tests conducted by EPRI, which showed lower mercury losses from synthetic gypsums produced from FGD systems on plants that fire low-rank coals than from systems on plants that fire bituminous coal.[4] There is no current explanation for why this should be the case, though. Future testing as part of Task 5 in this project will determine how the mercury loss percentages and mass rates vary for gypsum produced from lime versus limestone FGD reagent.

In the Task 4 results, as was seen in the Task 1 through 3 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. The cause of this phenomenon has not yet been determined either.

REFERENCES

1. Marshall, Jessica, Gary Blythe and Mandi Richardson. *Fate of Mercury in Synthetic Gypsum Used for Wallboard Production, Topical Report, Task 1 Wallboard Plant Test Results,* U.S. Department of Energy, Pittsburgh, PA. Cooperative Agreement Number DE-FC26-04NT42080, April 2005.

2. Marshall, Jessica, Gary Blythe and Mandi Richardson. *Fate of Mercury in Synthetic Gypsum Used for Wallboard Production, Topical Report, Task 2 Wallboard Plant Test Results,* U.S. Department of Energy, Pittsburgh, PA. Cooperative Agreement Number DE-FC26-04NT42080, August 2005.

3. Marshall, Jessica, Gary Blythe and Mandi Richardson. *Fate of Mercury in Synthetic Gypsum Used for Wallboard Production, Topical Report, Task 3 Wallboard Plant Test Results,* U.S. Department of Energy, Pittsburgh, PA. Cooperative Agreement Number DE-FC26-04NT42080, August 2005.

4. *Mercury Stability in FGD Byproducts*, EPRI, Palo Alto, CA: 2004. 1004711.

5. *Mercury Study Report to Congress Volume III: Fate and Transport of Mercury in the Environment*, United States Environmental Protection Agency, EPA-452/R-97-005, December 1997.

6. *Standard Test Method for Elemental, Oxidized, Particulate-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method)*, ASTM International, West Conshohocken, PA, June 2002. D 6784 – 02.