

Fate of Mercury in Synthetic Gypsum Used for Wallboard Production

Topical Report, Task 6 Wallboard Plant Test Results

Prepared by:

Jessica Sanderson
USG Corporation

Gary M. Blythe and
Mandi Richardson
URS Corporation

December 2006

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 Cochran's Mill Road
Pittsburgh, Pennsylvania 15236

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

This report presents and discusses results from Task 6 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 now includes six discrete tasks, each conducted at various USG wallboard plants using synthetic gypsum from different FGD systems. The project was originally composed of five tasks, which were to 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. However, Task 5, which was to include testing with an alternate FGD reagent, could not be conducted as planned. Instead, Task 5 was conducted at conditions similar to Task 3, although with gypsum from an alternate FGD system. Subsequent to conducting Task 5 under these revised conditions, an opportunity arose to test gypsum produced at the same FGD system, but with an additive (Degussa Corporation’s TMT-15) being used in the FGD system. TMT-15 was expected to impact the stability of mercury in synthetic gypsum used to produce wallboard, so Task 6 was added to the project to test this theory.

In this project, process stacks in the wallboard plant have been sampled using the Ontario Hydro method. For every task, the stack locations sampled have included a dryer for the wet gypsum as it enters the plant and a gypsum calciner. For Tasks 1, 4, 5 and 6, the stack of the dryer for the wet wallboard product was also tested. Also at each site, in-stream process samples were 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 were used to construct mercury mass balances across the wallboard plants.

Task 6 was conducted at a wallboard plant processing synthetic gypsum from a power plant that fires Eastern bituminous coal. The power plant has a single-loop, open spray tower limestone forced oxidation FGD system, with the forced oxidation conducted in the reaction tank integral with the FGD absorber. The FGD system has gypsum fines blow down as part of the dewatering step. The power plant is equipped with a selective catalytic reduction (SCR) system for NO_x emissions control, and the SCR was in service during the time period the gypsum tested was produced. Also, as mentioned above, Degussa additive TMT-15 was being added to the FGD system when this gypsum was produced.

The results of the Task 6 stack testing, as measured by the Ontario Hydro method, detected that an average of 55% of the incoming mercury was emitted during wallboard production. These losses were distributed as about 4% across the dryer mill, 6% across the board dryer kiln, and 45% across the kettle calciner. Emissions were similar to what Task 5 results showed on a percentage basis, but about 30% lower on a mass basis. The same power plant FGD system produced the synthetic gypsum used in Task 5 (with no use of TMT-15) and in Task 6 (with TMT-15 added to the FGD system). The lower emissions on a mass basis appeared to be due to lower average mercury content in the gypsum being processed. It is not certain whether the lower average mercury content in the gypsum was an effect of TMT-15 addition to the FGD system. As was seen in the Task 1 through 5 results, most of the mercury detected in the Ontario Hydro method stack testing was in the form of elemental mercury.

TABLE OF CONTENTS

	Page
Disclaimer	iii
Abstract	iv
Introduction	8
Background	8
The Wallboard Production Process	9
Project Overview.....	11
Report Organization.....	14
Experimental	15
Rationale for Selecting the Synthetic Gypsum Tested.....	15
Commercial Wallboard Plant Test Procedures	16
Results and Discussion	21
Gypsum and Process Sample Mercury Analysis Results	21
Ontario Hydro Stack Sampling Results.....	26
Plant Process Data	29
Mercury Balance Results.....	30
Summary of Mercury Loss Calculations	34
Conclusion	36
References	39

LIST OF FIGURES

Figure 1. Simplified Schematic of the Wallboard Production Process Using Synthetic Gypsum Feedstock.	10
Figure 2. Schematic of Wallboard Plant 4 Showing Sampling Locations	17

LIST OF TABLES

Table 1. Planned Project Test Matrix	12
Table 2. Revised Project Test Matrix.....	14
Table 3. Task 6 Raw Gypsum and Mill Process Sample Mercury and Moisture Analyses, URS Results	21
Table 4. Task 6 Mill Process Sample Characterization, USG Results.....	22
Table 5. Task 6 Board-line Process Sample Analyses, URS Results	23
Table 6. Task 6 Board-line Process Sample Characterization, USG Results.....	23
Table 7. Task 6 Ontario Hydro Results – Summary of Exhaust Gas Conditions	27
Table 8. Task 6 Ontario Hydro Results – Speciated Mercury Emissions Data	28
Table 9. Task 6 Mill Test Process Conditions	30
Table 10. Task 6 Board-line Test Process Conditions.....	30
Table 11. Task 6 Mercury Balance Results for the Mill Test	31
Table 12. Task 6 Mercury Balance Results for the Board-line Test	33
Table 13. Summary of Task 6 Overall Mercury Loss During Wallboard Production, Calculated by Two Methods.....	35

INTRODUCTION

This report presents and discusses results from Task 6 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 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 most of the mercury scrubbed from flue gases in most U.S. wet FGD systems ends up in the solid byproducts. 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 land filled, although some is reused as mine fill.

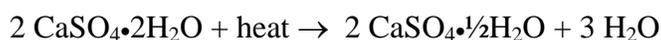
Approximately 70% of all of the FGD byproduct reuse in the U.S. is gypsum used as wallboard feedstock. During the year 2005, synthetic gypsum from FGD systems represented 30% of the U.S. wallboard plant feedstock.

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, 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°F. The solids are dried by direct contact between the wet particles and the hot

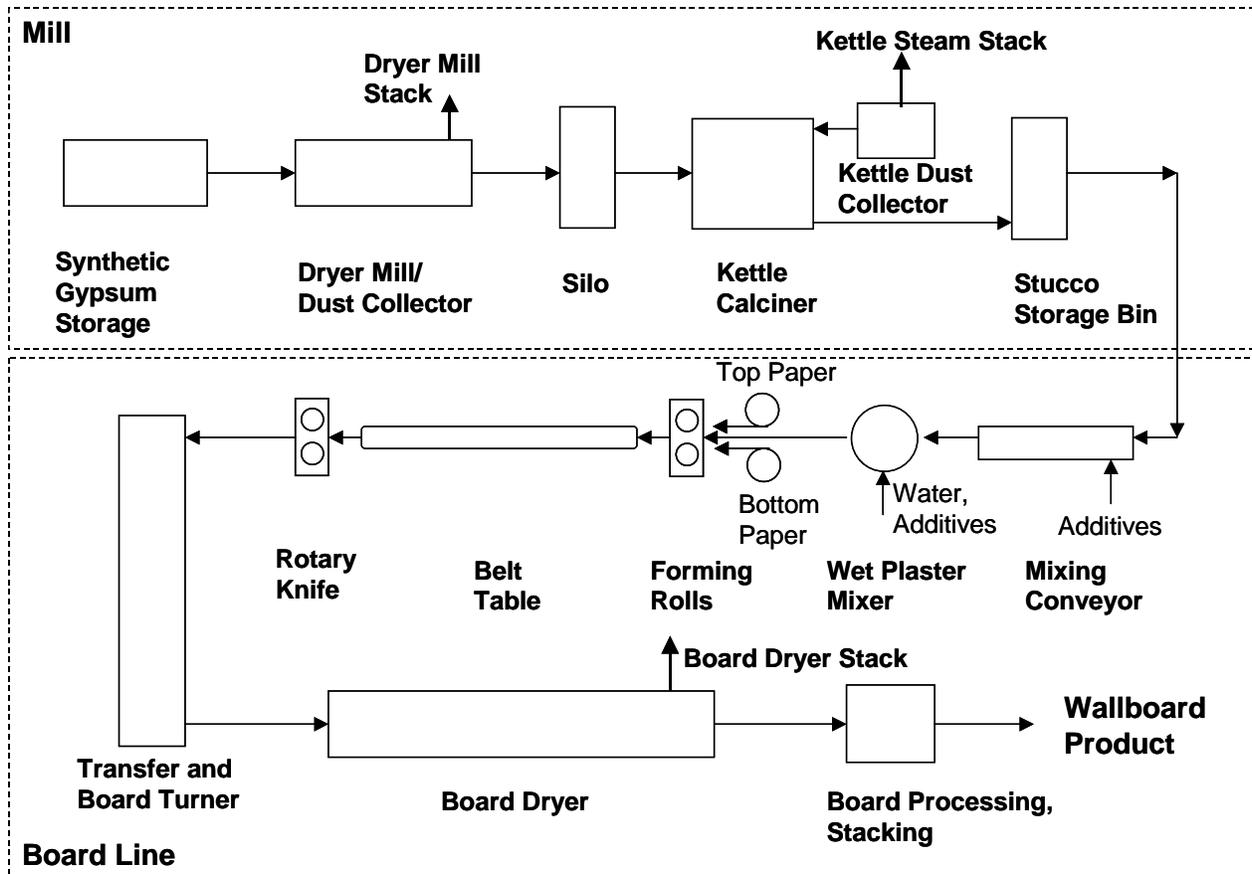


Figure 1. Simplified Schematic of the Wallboard Production Process Using Synthetic Gypsum Feedstock.

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 recycled to the kettle calciner feed or added to the calciner product stream. 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, 5 and 6.

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 to 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 was originally structured in five tasks. As shown in Table 1, each involves one commercial wallboard plant test.

Table 1. Planned 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 five different synthetic gypsum feedstocks, testing was to 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 shown 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.

The first four tasks included 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 fires Texas lignite rather Eastern bituminous coal, and that does not have SCR.

Each of these variables was 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.

As shown in the table, the project plan was for the fifth task to investigate a synthetic gypsum feedstock produced by a power plant that fires Eastern high-sulfur bituminous coal and that has an SCR for NO_x control, but it was not certain whether the SCR would be in operation when the gypsum to be tested would be produced. The major variable to be evaluated in Task 5 was the effect of FGD reagent. While the other four tasks tested gypsums produced from FGD systems that use limestone reagent with in situ (in the FGD absorber reaction tank) forced oxidation, Task 5 was to test gypsum produced from an FGD system that uses lime reagent and forced oxidizes the byproduct in a tank external to the absorber loop.

However, the logistics for conducting Task 5 using gypsum from Power Plant D proved to be difficult. USG Wallboard Plant 1 normally processes a blend of gypsum from Power Plants A and D, with Power Plant D material comprising less than half. And, since the gypsum from Power Plant A was expected to have a higher mercury content than that from Power Plant D, a blend of the two was deemed to be inappropriate for Task 5. Because of space limitations at the wallboard plant, it proved very difficult to stockpile enough material to allow the wallboard plant to gradually transition to processing 100% material from Power Plant D. After an extended period over which the wallboard plant unsuccessfully attempted to achieve that goal, it was decided to modify the project plan for Task 5.

The highest mercury losses measured in the first four tasks were in Task 3, where the gypsum was produced by a power plant that fires high-sulfur Eastern bituminous coal, has an SCR in service, uses limestone FGD reagent, and incorporates gypsum fines blow down as part of the gypsum dewatering scheme. It was decided to test a second system with a similar configuration in Task 5, to see if similarly high mercury losses would be measured. One difference between Tasks 3 and 5 is that for Task 5, the SCR was not in service (bypassed) on the power plant that produced the gypsum. However, based on results from Tasks 1 and 2, this was not thought to be a significant factor.

After conducting Task 5, it was apparent that mercury losses were very similar to the Task 3 results, on both a percentage and mass basis, and thus higher than the losses measured as part of Tasks 1, 2 and 4. As part of another DOE Cooperative Agreement, DE-FC26-04NT42309, an additive is being tested that holds promise for improving net capture of oxidized mercury by wet FGD systems, lowering byproduct gypsum mercury concentrations, and possibly making the remaining mercury in the gypsum more stable during thermal processes such as wallboard production. This additive, Degussa Corporation's TMT-15, is further described in the following section of this report.

As part of the 42309 project, full-scale TMT-15 tests were being conducted at Power Plant E. This offered the opportunity to test synthetic gypsum from Power Plant E with TMT-15 addition at Wallboard Plant 4, for comparison to the previous Task 5 results without TMT addition. DOE-NETL agreed to co-fund this additional test, and Task 6 was added to the project.

The revised project test matrix is shown in Table 2, including the change to testing gypsum from Power Plant E in Task 5, and the addition of Task 6. One difference between Tasks 5 and 6 besides TMT-15 addition is that for Task 5, the SCR was not in service (bypassed) on the power plant that produced the gypsum, while for Task 6 it was in service. However, based on results from Tasks 1 and 2, and by comparison of Task 3 and Task 5 results, this was not thought to be a significant factor.

Table 2. Revised Project Test Matrix

Task	1	2	3	4	5	6
Synthetic Gypsum Source:						
Power Plant	A	A	B	C	E	E
Coal Type	High sulfur bituminous	High sulfur bituminous	High sulfur bituminous	Texas lignite	High sulfur bituminous	High sulfur bituminous
FGD Reagent	Limestone	Limestone	Limestone	Limestone	Limestone	Limestone
Forced Oxidation Mode	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ
Gypsum Fines Blow Down?	No	No	Yes	No	Yes	Yes
SCR Operating?	Yes	No	Yes	No	No	Yes
TMT-15 Addition to FGD?	No	No	No	No	No	Yes
USG Wallboard Plant Tested	1	1	2	3	4	4

This report presents and discusses the results of the wallboard plant testing conducted as part of Task 6, 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 5¹⁻⁵. 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 6, 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

In wet FGD absorbers, the oxidized form of mercury (Hg^{+2}) is absorbed from the flue gas into the FGD liquor, while water insoluble Hg^0 is typically not removed. Once absorbed, the Hg^{+2} can follow as many as three pathways for leaving the FGD system. These include: 1) Undergoing reduction reactions while in the FGD liquor to form Hg^0 , which, being insoluble is released and re-emitted into the FGD outlet flue gas; 2) Being retained in the FGD liquor, and potentially becoming a regulatory compliance issue in FGD blow down liquor; or 3) Being retained in the FGD byproduct solids. DOE Cooperative Agreement DE-FC26-04NT42309 is investigating the use of an FGD additive to rapidly precipitate mercury in FGD liquor as a solid salt, to minimize pathways 1 and 2. Pathway 3 may be the most desirable for FGD systems that landfill their FGD solid byproducts, but could become an issue if the byproducts are reused such as for wallboard production. A second objective of the 42309 project is to determine whether this same additive can be used to minimize mercury concentrations in reused FGD solid byproducts, through separation of the fine mercury-containing salts formed from the remainder of the byproduct gypsum stream.

The additive being tested is Trimercapto-s-triazine, tri-sodium salt (TMT), commercially available from Degussa Corporation as a 15-wt% aqueous solution (TMT-15). TMT-15 can be used to precipitate absorbed mercury as a stable salt to minimize re-emissions and lower liquid-phase mercury concentrations. The salt can be separated from the solid FGD byproducts to lower their mercury content.

While TMT-15 is used in Europe in such applications, it has not seen widespread use in U.S. plants. The 42309 project is providing an opportunity to evaluate the use of TMT-15 for these purposes on pilot- and full-scale wet FGD systems on U.S. coal-fired units.

The reaction of TMT with heavy metals is based on the soluble tri-sodium salt chemically binding to heavy metals via sulfur groups. In the process, high-molecular-weight organo-metallic compounds are produced which have a very low aqueous solubility. They precipitate as solid substances and can be separated from the liquor by filtration. The ionic reaction is nearly instantaneous and proceeds stoichiometrically. The active substance, trimercapto-s-triazine, reacts as a trivalent anion and can thus bind three cationic heavy metal equivalents. TMT reportedly reacts over a wide pH range, including acidic conditions, without decomposing or releasing toxic gases such as H_2S . Besides its ability to chemically bind with mercury, TMT reportedly has favorable toxicological and ecological properties.⁶

In the FGD blow down slurry, fine particles of mercury-TMT compound can be transferred to the wastewater/fines blow down, absorber recycle and/or partly to the byproduct gypsum. TMT-metal compounds are reportedly quite stable. According to Degussa, temperatures in excess of 210°C (which is well above the gypsum calcining temperature) are needed to begin to decompose the mercury-TMT salt, and TMT-metal compounds easily meet the leachability limits of the TCLP.

It is anticipated that any mercury bound as a TMT salt that remains in FGD byproduct gypsum will remain stable and will not be volatilized into the flue gas in significant percentages when the gypsum is processed in a wallboard plant. Task 6 of this project was intended to demonstrate the effectiveness of TMT-15 for this purpose when added to an FGD system. The FGD system was the same whose byproduct gypsum was previously tested as part of Task 5.

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 wallboard 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 E, 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. 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.

Two days of wallboard plant testing were conducted in USG Wallboard Plant 4, with the first day testing 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.

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 raw gypsum dryer (called a Williams mill or dryer mill in this report) stack and a downstream kettle calciner dust collector (steam) stack. Wallboard Plant 4 has one dryer mill and two operating kettle calciners. Only one of the two kettle calciners was

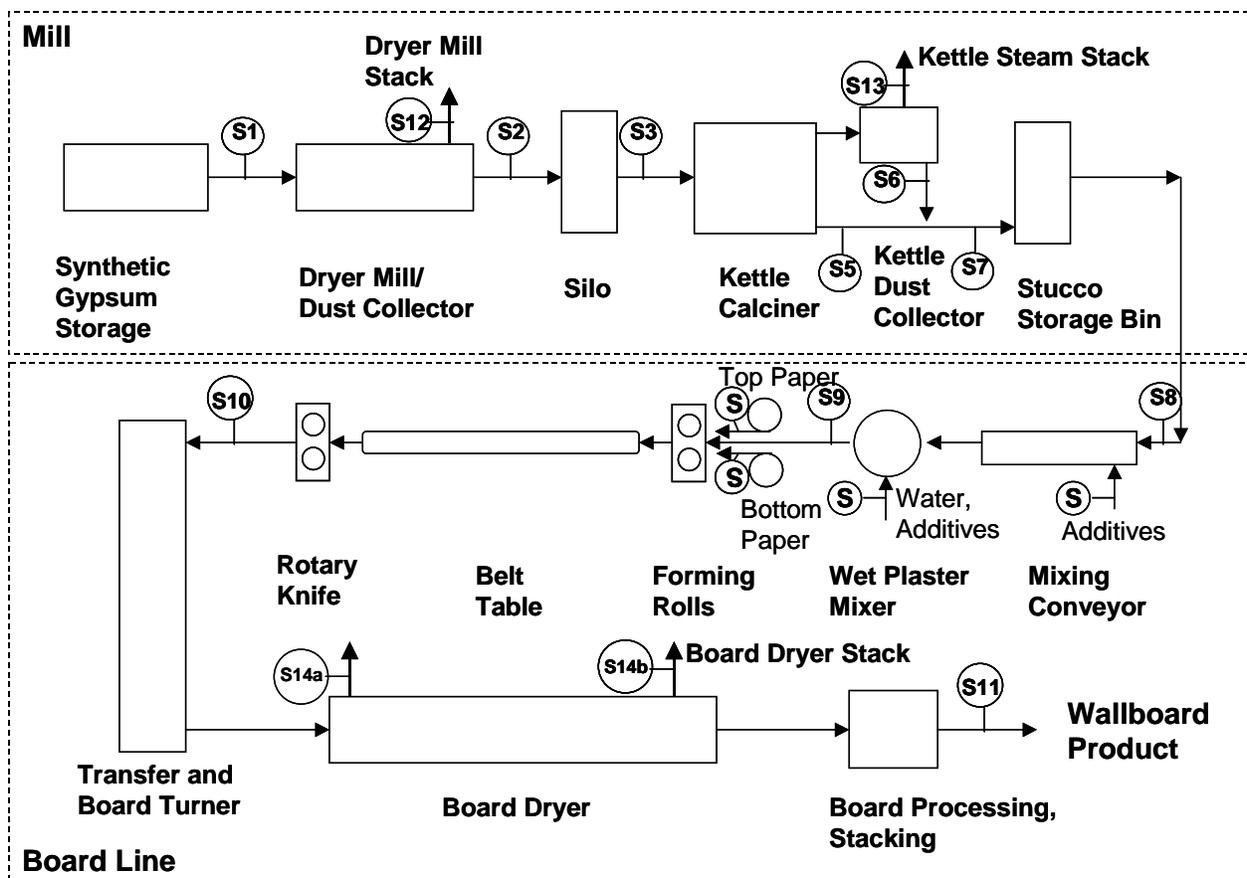


Figure 2. Schematic of Wallboard Plant 4 Showing Sampling Locations

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 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, nor would it be attributable to mercury in the land plaster feed.

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, and by reducing the run time to limit the total amount of water collected. 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.

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 the stucco as it is fed to the product stucco storage bin. 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 from the kettle calciner dust collector, which are blended with the calciner product, and calciner product stucco prior to having the dust collector solids added. These two additional sample types were analyzed and reported for mercury concentration, but these data were not used for mercury balance or mercury loss calculations because the relative proportions of each fed to the product stucco bin are not measured.

All six of these process solids samples were collected as “grab” samples 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. Based on results from the previous tasks, it was expected that the incoming raw gypsum would be homogenous enough that one grab sample per run would adequately represent the feedstock and other process solids. However, the samples were collected in the order according to the process flow through the mill, to at least partially account for residence time in each mill process vessel. The 18 grab samples were subsequently analyzed for mercury content, moisture content, and other parameters by URS and USG.

Process data were collected for each of the three runs, including dryer and calciner feeder speeds and operating temperatures. These data were recorded by mill operators periodically during the sampling periods.

Day 2 – Board-Line Testing

Stack Sampling

On the second test day, triplicate Ontario Hydro Method measurements were conducted 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.

The board dryer kiln at Wallboard Plant 4 (Tasks 5 and 6) is somewhat different than at Wallboard Plants 1 and 2 (Tasks 1 through 3), but similar to that at Wallboard Plant 3 (Task 4) 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. Only one sample of each was collected for each Ontario Hydro run, but the timing of when these samples

were collected was staggered to account for the residence time of the board line. The slurry fed to the board forming machine was sampled just after the feed stucco sample was collected, as there is little residence time between these two locations, but the wet wallboard product sample was collected several minutes later from board marked at the board forming area at the time the slurry sample was taken. Similarly, the time stamp on the wet board sampled was noted, and the dry product wallboard sample was taken from board with the same time stamp. Thus, all four samples were taken from material that passed through the board line within approximately a minute of the same time.

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 manually recorded from process control software screens, 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), board production rate, and the dryer flue gas temperatures. These data were consistent for all three Ontario Hydro runs.

As the second day of the sampling effort was completed, the process and Ontario Hydro method samples were recovered, stabilized, and labeled. The following day they were 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.

All of the mill and board-line process samples collected were analyzed by URS for mercury content, by cold vapor atomic absorption after digestion in hydrofluoric acid. USG analyzed separate aliquots of the same samples for mercury content with a direct mercury analyzer (thermal desorption followed by cold vapor atomic absorption). A number of samples were analyzed by USG for other parameters, including gypsum moisture content (free moisture and combined moisture, or waters of hydration), 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 means for the triplicate measurements.

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 in the final report for the project.

RESULTS AND DISCUSSION

This section provides technical results for the Task 6 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 3 summarizes the results of mercury and free moisture content analyses conducted by URS on the raw gypsum, stucco product, and intermediate process samples collected during the mill test on September 13, 2006. Table 4 shows results for additional characterization of these samples conducted by USG, including mercury, free and combined (water of hydration) moisture content, and other parameters. Table 5 shows the results for mercury and free moisture content analyses conducted by URS on stucco, wallboard product, and intermediate process samples collected during the board-line test on September 14, 2006, and Table 6 shows corresponding USG analysis results.

Table 3. Task 6 Raw Gypsum and Mill Process Sample Mercury and Moisture Analyses, URS Results

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	0.13	0.13	0.12	0.13	±0.00	6.6	6.3	6.0	6.3
S2	Land Plaster from Dryer Mill	0.13	0.13	0.13	0.13	±0.00	NA**	NA	NA	
S3	Land Plaster to Kettle Calciner	0.13	0.13	0.13	0.13	±0.00	NA	NA	NA	
S5	Kettle Calciner Product, as measured	0.09	0.10	0.10	0.09	±0.00	NA	NA	NA	
	Kettle Calciner Product, dry gypsum basis	0.08	0.08	0.08	0.08	±0.00	-	-	-	-
S6	Kettle Calciner Dust Collector Solids, as measured	0.12	0.11	0.11	0.11	±0.01	NA	NA	NA	
	Kettle Calciner Dust Collector Solids, dry gypsum basis	0.10	0.09	0.09	0.10	±0.01	-	-	-	-
S7	Product Stucco, as measured	0.11	0.10	0.10	0.10	±0.01	NA	NA	NA	
	Product Stucco, dry gypsum basis	0.09	0.08	0.08	0.09	±0.01	-	-	-	-

*95% Confidence Interval of mean

**NA – not analyzed; expected value is 0.1 wt% or less

Table 4. Task 6 Mill Process Sample Characterization, USG Results

Sample	Run	Moisture Content, wt%		Mercury Content, $\mu\text{g/g}$		Soluble Salts, ppm		Mean Particle Diameter (microns)
		Free	Com-bined*	As measured, dry basis	Dry Gypsum basis	Total	Cl ⁻	
S1 – Raw Gypsum Feed to Dryer Mill	1	6.5	20.3	0.12	0.12			39.4
	2	6.0	20.3	0.12	0.12			39.2
	3	6.1	20.3	0.11	0.11			39.2
Mean		6.2	20.3	0.12	0.12	81	26	39.3
95% C.I.*		± 0.3	± 0.0	± 0.00	± 0.00			± 0.1
S2 – Land Plaster from Dryer Mill	1	0.0	20.2	0.11	0.11			39.8
	2	0.0	20.1	0.11	0.11			39.8
	3	0.0	20.2	0.11	0.11			40.3
Mean		0.0	20.1	0.11	0.11	78	23	40.0
95% C.I.		± 0.0	± 0.0	± 0.00	± 0.00			± 0.3
S3 – Land Plaster to Kettle Calciner	1	0.0	20.0	0.12	0.12			39.6
	2	0.0	20.1	0.12	0.12			39.8
	3	0.0	20.0	0.12	0.12			39.7
Mean		0.0	20.0	0.12	0.12	79	24	39.7
95% C.I.		± 0.0	± 0.0	± 0.00	± 0.00			± 0.1
S5 – Kettle Calciner Product	1	0.0	6.6	0.08	0.07			-
	2	0.0	6.5	0.08	0.07			44.0
	3	0.1	6.6	0.08	0.07			45.1
Mean		0.0	6.6	0.08	0.07	111	48	44.6
95% C.I.		± 0.1	± 0.1	± 0.00	± 0.00			± 0.9
S6 – Kettle Calciner Dust Collector Solids	1	0.0	7.0	0.10	0.09			33.0
	2	0.2	7.2	0.10	0.09			34.5
	3	0.2	7.2	0.10	0.09			34.5
Mean		0.1	7.1	0.10	0.09	123	46	34.0
95% C.I.		± 0.1	± 0.1	± 0.00	± 0.00			± 1.0
S7 – Stucco to Product Bin	1	0.4	7.0	0.09	0.08			-
	2	0.2	7.0	0.09	0.08			-
	3	0.4	10.0	0.09	0.08			33.5
Mean		0.4	8.0	0.09	0.08	160	49	-
95% C.I.		± 0.1	± 2.0	± 0.00	± 0.00			-

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

Table 5. Task 6 Board-line Process Sample Analyses, URS Results

Sample Number	Sample Description	Mercury Content, µg/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	0.11	0.11	0.12	0.11	±0.00	NA*	NA	NA	-
	Stucco Feed, dry gypsum basis	0.09	0.09	0.10	0.09	±0.00	-	-	-	-
S9	Slurry to Forming Rolls	0.08	0.09	0.08	0.08	±0.00	30.5*	31.3*	31.2*	31.0*
S10	Wet Wallboard	0.07	0.07	0.07	0.07	±0.00	33.7*	32.3*	30.7*	32.2*
S11	Dry Wallboard Product	0.08	0.09	0.09	0.09	±0.00	NA	NA	NA	-

*NA-not analyzed; expected value is 0.1% or less for stucco feed and 1% or less for wallboard product

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

Table 6. Task 6 Board-line Process Sample Characterization, USG Results

Sample	Run	Moisture Content, wt%		Mercury Content, µg/g		Soluble Salts, ppm		Particle Size Distribution (microns)
		Free	Com-bined*	As measured, dry basis	Dry Gypsum basis	Total	Cl ⁻	Mean Dia.
S8 – Stucco Feed to Board Line	1	0.1	6.8	0.09	0.08	-	-	43.5
	2**	0.1	6.8	0.10	0.08	-	-	41.9
	3	0.1	6.8	0.10	0.09	-	-	43.6
Mean		0.1	6.8	0.10	0.08	136	48	43.0
95% C.I.		±0.0	±0.0	±0.00	±0.00			±1.1
S9 – Slurry Feed	1	NA	20.2	0.08	0.08	-	-	-
	2**	NA	20.2	0.08	0.08	-	-	-
	3	NA	20.2	0.08	0.08	-	-	-
Mean		-	NA	0.08	0.08	-	-	-
95% C.I.		-	NA	±0.00	±0.00	-	-	-
S10 – Wet Wallboard	1	NA	20.1	0.08	0.08	-	-	-
	2**	NA	20.2	0.08	0.08	-	-	-
	3	NA	20.2	0.08	0.08	-	-	-
Mean		-	NA	0.08	0.08	-	-	-
95% C.I.		-	NA	±0.00	±0.00	-	-	-
S11 – Dry Product Wallboard	1	0.1	19.7	0.08	0.08	-	-	-
	2**	0.1	19.5	0.08	0.08	-	-	-
	3	0.2	19.6	0.08	0.08	-	-	-
Mean		0.1	19.6	0.08	0.08	-	-	-
95% C.I.		±0.0	±0.1	±0.00	±0.00	-	-	-

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

** Mean value for two samples, one from beginning and one from end of run

NA – not analyzed

As in previous 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 over the three runs.

The results from the URS analyses in Table 3 show that the raw gypsum feedstock, product stucco, and intermediate samples were relatively consistent in mercury content for all three runs. For the three dryer mill tests, the raw gypsum feed contained an average of 0.13 µg/g (dry basis) and 6.3% free moisture. Both the mercury content and free moisture content of this gypsum is the lowest in the six tasks that have been conducted as part of this project. The mercury concentration in the gypsum from Power Plant E tested as part of Task 6 is only 12 to 14% of that from Power Plant A (Tasks 1 and 2), 60% of that from Power Plant B (Task 3), 25% of that from Power Plant C (Task 4), and only 65% of the value previously seen from Power Plant E in Task 5.

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 3 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 4 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 indicated across the dryer mill based on the average mercury concentration in the land plaster compared to the average mercury concentration in the raw gypsum feed. However, when comparing the mercury concentrations in the land plaster feed to the kettle calciner (S3) to the mercury concentrations in the product stucco (S7) expressed on a dry gypsum basis, significant losses of mercury are apparent across the kettle calciner. The feed land plaster (gypsum) averaged 0.13 µg/g of mercury content on a dry basis (dry of free moisture only – not waters of hydration) while the product stucco averaged 0.09 µg/g when expressed on a dry gypsum basis (about 35% loss). However, given that these values reflect only single sets of grab samples per run, and analytical uncertainties in the results of mercury analyses on solid samples, there is uncertainty in quantifying mercury losses by comparing mercury analyses on feed and product samples. The Ontario Hydro stack sampling results for the kettle calciner are thought to provide a better measure of this loss percentage.

The results of USG analyses in Table 4 show mercury concentrations that are slightly lower than 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 S7, the product stucco, as those provide an indication of any mercury losses across the kettle calciner. For sample S3, the URS analyses showed a mean concentration of 0.13 µg/g while the USG analyses showed a mean of 0.12 µg/g. For sample S7, the URS analyses showed a mean concentration of 0.10 µg/g (as measured), while the USG analyses showed mean of 0.09 µg/g. This is considered good agreement between two laboratories analyzing separate splits of the same sample by two different methods, though.

The USG characterization of these samples generally shows trends noted in previous task results. One interesting result is a comparison of the combined moisture content (water of hydration content) of the samples collected downstream of the calciner (S5 through S7). 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 average value of 6.6 wt% in the kettle calciner overflow product is indicative of near 100% calcining efficiency. However, the dust collector solids (S6) were measured to have a higher combined moisture content of 7.1%. This may be an indication that the fine particles collected in the dust collector are entrained out of the kettle calciner more rapidly and are not calcined as efficiently, or perhaps that the dust collector solids partially rehydrate on the dust collector bags while contacting humid flue gas. The stucco to the product bin (S7), which is a mixture of these two streams, would be expected to have an intermediate combined moisture content. However, the samples collected for S7 showed a higher mean moisture content than either of the streams that are combined to form this stream. The S7 sample is difficult to collect because the stream is hot, dusty, and at positive pressure relative to ambient. It is speculated that the S7 samples collected are not representative with respect to moisture content because of sample collection biases.

The results from the board line samples in Table 5 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) the previous day. S7 averaged 0.10 µg/g of mercury content, while S8 samples from the day before averaged 0.11 µg/g.

Conversely to what was described above 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 5 showing the feed stucco mercury concentration on a dry gypsum basis, and a corresponding column has been added to Table 6. 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. These results give no indication of mercury loss across the board line, as the product wallboard was measured to have the same average mercury content as the stucco feed when expressed on a dry gypsum basis (both averaged 0.09 µg/g). 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.

Also, the URS analyses of the intermediate samples in the board line showed lower mercury concentrations than either the stucco feed or product wallboard – the slurry to the forming rolls averaged 0.08 µg/g while the wet wallboard samples averaged 0.07 µg/g. The lower values measured for these intermediate samples were repeatable, having been seen in all three samples of each, and in later repeat analyses conducted to investigate this observation.

As for the mill samples, a comparison of the results of USG analyses for mercury content, summarized in Table 6, agree reasonably well with the URS results, at least for the feed stucco and dry wallboard product. On an as-measured basis, the stucco feed (S8) mercury concentration

was measured at an average of 0.11 µg/g by URS and 0.10 µg/g by USG. The wallboard product mercury content was measured as 0.09 µg/g by URS and 0.08 µg/g by USG.

The USG analyses of the intermediate samples – slurry to forming rolls (S9) and wet wallboard (S10) – do not show lower mercury concentrations than the stucco feed or product wallboard as did the URS results. In the USG results, all four sample types (S8 through S11) averaged 0.08 µg/g when reported on a dry gypsum basis. The reason for the slightly lower concentrations seen in the URS analyses of samples S9 and S10 remains unknown. However, one theory is that these wet samples tend to “lose” mercury through diffusion processes even though they are stored in sealed plastic bags (mercury may diffuse to the air in the bag and be lost when the bag is opened). The USG analyses were completed sooner than the URS analyses after the test date, and thus may have been less influenced by such a phenomenon.

Ontario Hydro Stack Sampling Results

The Ontario Hydro method stack sampling results are summarized in tables that follow. Table 7 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 dilute flue gas from natural gas firing, with about 1% CO₂ and nearly 20% oxygen. The moisture content was relatively high at about 9% due to the free moisture from the gypsum that is evolved in the dryer. The moisture content was lower than was measured during Task 5 (12%) because the gypsum tested as part of Task 6 was drier. The dryer mill flue gas temperature was well below 200°F, as would be expected because of the need to keep the dried gypsum below its initial calcination temperature of 262°F.

The kettle calciner results for flue gas composition were consistent with a very wet air stream, containing a trace CO₂ content of 0.2% and nearly 21% oxygen. The measured moisture content of the stack gas was high, averaging 49% due to the waters of hydration released from the gypsum. The measured moisture content was equal to that measured previously as part of Task 5.

The board dryer kiln sampling results showed that the “wet end” stack flue gas flow rate is slightly lower than the “dry end” flue gas rate. It is also hotter, slightly more concentrated (lower average measured oxygen concentration), and wetter. All of these comparisons between the wet end and dry end stack would be expected, and were seen previously in Task 5 results

Table 8 summarizes the mercury concentration and mass rate data. The results show that for the kettle calciner stack, the mercury is mostly in the elemental form (Hg⁰). This was generally seen at the wallboard plants previously tested in Tasks 1 through 5. 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 not a clear explanation for this phenomenon. 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.⁷

Table 7. Task 6 Ontario Hydro Results – Summary of Exhaust Gas Conditions

Sample Number	Run No.	Date (2006)	Time (24-h)	Flow Rate		Temperature (°F)	H ₂ O (%)	CO ₂ (%)	O ₂ (%)
				acfm*	Dscfm [#]				
Dryer Mill (1 of 1)									
S12	1	9/13	0750-1000	28,600	22,700	137	7.2	0.6	20.2
	2	9/13	1105-1313	26,300	19,500	157	10.3	0.9	19.6
	3	9/13	1419-1627	25,600	19,200	154	9.7	0.9	19.6
	Mean			26,900	20,500	149	9.1	0.8	19.8
Kettle Calciner (1 of 2 operating)									
S13	1	9/13	0825-0942	5,350	2,040	251	48.9	0.2	20.8
	2	9/13	1152-1305	5,300	2,000	251	49.4	0.2	20.8
	3	9/13	1458-1609	5,220	1,960	252	49.5	0.2	20.8
	Mean			5,290	2,000	251	49.2	0.2	20.8
Board Dryer Kiln (1 of 1)									
S14a (wet end)	1	9/14	1045-1252	21,500	12,600	238	23.1	1.5	18.1
	2	9/14	1330-1600	22,900	13,700	227	22.6	1.6	17.9
	3	9/14	1630-1837	21,900	12,800	241	22.4	0.1	20.7
	Mean			22,100	13,100	235	22.7	1.1	18.9
S14b (dry end)	1	9/14	1046-1250	28,800	22,400	165	8.7	0.5	19.9
	2	9/14	1330-1550	29,800	23,200	164	8.5	0.5	19.9
	3	9/14	1632-1832	30,000	23,400	163	8.2	0.5	20.0
	Mean			29,600	23,000	164	8.5	0.5	19.9

*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 8. Task 6 Ontario Hydro Results – Speciated Mercury Emissions Data

Sample Number	Run No.	Date (2006)	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	9/13	0750-1000	0.039	0.73	0.99	1.76	1.50×10^{-4}
	2	9/13	1105-1313	0.085	1.86	3.03	4.97	3.63×10^{-4}
	3	9/13	1419-1627	0.030	1.49	1.05	2.56	1.84×10^{-4}
	Mean			0.051	1.36	1.69	3.10	2.32×10^{-4}
	95% Confidence Interval			± 0.031	± 0.29	± 1.14	± 1.43	$\pm 1.05 \times 10^{-4}$
Kettle Calciner (1 of 2)								
S13	1	9/13	0825-0942	4.89	1.04	167	173	1.32×10^{-3}
	2	9/13	1152-1305	6.37	2.24	177	185	1.39×10^{-3}
	3	9/13	1458-1609	5.93	5.07	169	180	1.32×10^{-3}
	Mean			5.73	2.79	171	179	1.34×10^{-3}
	95% Confidence Interval			± 0.86	± 2.34	± 6	± 7	$\pm 0.05 \times 10^{-3}$
Board Dryer Kiln (1 of 1)								
S14a (wet end)	1	9/14	1045-1252	<0.070	<0.24	0.42	0.42	0.20×10^{-4}
	2	9/14	1330-1600	<0.060	<0.22	6.48	6.48	3.33×10^{-4}
	3	9/14	1630-1837	<0.060	<0.22	0.49	0.49	0.23×10^{-4}
	Mean			<0.063	<0.22	2.46	2.46	1.25×10^{-4}
	95% Confidence Interval			-	-	± 3.94	± 3.94	$\pm 2.04 \times 10^{-4}$
S14b (dry end)	1	9/14	1046-1250	<0.059	<0.17	1.98	1.98	1.66×10^{-4}
	2	9/14	1330-1550	<0.054	<0.16	1.04	1.04	0.90×10^{-4}
	3	9/14	1632-1832	<0.053	<0.16	0.44	0.44	0.38×10^{-4}
	Mean			<0.056	<0.16	1.15	1.15	0.98×10^{-4}
	95% Confidence Interval			-	-	± 0.88	± 0.88	$\pm 0.73 \times 10^{-4}$

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

lb/h = Pounds per hour

For the dryer mill, there is closer to an equal percentage of elemental and mercury in the stack flue gas. This has been seen in some of the previous task results, particularly when the total stack flue gas mercury concentrations are relatively low, as they were from Task 6.

For the board dryer kiln, the results showed mostly elemental mercury in both the wet end and dry end stack. The measurements during Task 5 showed closer to equal percentages of oxidized and elemental mercury in the dry end stack flue gas. However, in the dry end stack flue gas the measured concentrations for Task 5 were extremely low, mostly below the stated detection limit of the Ontario Hydro method of $0.5 \mu\text{g}/\text{Nm}^3$, so the observed mercury speciation data may not have been meaningful.⁸

The total mercury concentration data show that on a dry gas basis, the concentrations in the kettle calciner steam stack were approximately $180 \mu\text{g}/\text{Nm}^3$, while the dryer stack averaged $3 \mu\text{g}/\text{Nm}^3$. The measured total mercury concentrations in the board dryer kiln stacks were low, averaging around $2.5 \mu\text{g}/\text{Nm}^3$ in the wet end stack and $1 \mu\text{g}/\text{Nm}^3$ in the dry end stack.

Compared to the total mercury concentrations measured in the previous wallboard plant tests, the mercury concentrations measured in the dryer mill stack in Task 6 were in the middle of the range (a mean value of $3 \mu\text{g}/\text{Nm}^3$ compared to a range of 1 to $7 \mu\text{g}/\text{Nm}^3$). For the kettle calciner stack, the concentrations measured were about 6 to 9 times higher than were measured at Wallboard Plant 3 as part of Task 4, 6% to 34% higher than were measured at Wallboard Plant 1 as part of Tasks 1 and 2, but an order of magnitude lower than the concentration measured at Wallboard Plant 2 as part of Task 3 (a mean of $1885 \mu\text{g}/\text{Nm}^3$ dry basis). The Task 6 measurements for the kettle calciner stack total mercury concentration were also about 30% lower than were measured as part of Task 5 at the same wallboard plant and processing gypsum from the same FGD system.

In the board dryer kiln stacks, the mercury concentrations measured at Wallboard Plant 4 were lower than was measured at Wallboard Plant 1 as part of Task 1 (a mean of approximately $12 \mu\text{g}/\text{Nm}^3$), but higher than was measured at Wallboard Plant 3 as part of Task 4 (approximately $0.5 \mu\text{g}/\text{Nm}^3$). They were also somewhat higher than were measured at Wallboard Plant 4 previously as part of Task 5 (0.4 to $1.4 \mu\text{g}/\text{Nm}^3$).

Comparing the mercury mass emission rate data in Table 8, the mercury losses from the kettle calciners were 12 times those from the dryer mill, considering there is only one dryer mill and two kettle calciners operating. Considering the sum of the mercury losses from the two stacks on the board kiln, the mercury emissions from the kettle calciners were also about 12 times those from the board kiln. The mercury mass emissions rates from the dryer mill and the board kiln were measured to be about equal.

Plant Process Data

Plant process data are summarized in Table 9 for the mill sampling and Table 10 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. However, the mill supervisor can generally estimate feed rates based on the rate of level change in the stucco storage bins compared to wallboard production rates. The time required to fill a surge bin of known capacity is another method used to estimate kettle calciner production rates.

The rates shown in Table 9 for the dryer mill and kettle calciner were based on the amount of time it took to fill a stucco surge bin with a reported capacity of 30 tons of product. The process conditions shown in Tables 9 and 10 were used as the basis for mercury balance calculations, as discussed in the following subsection.

Table 9. Task 6 Mill Test Process Conditions

Date	9/13/2006	9/13/2006	9/13/2006	
Time	0750-1000	1105-1313	1419-1627	
Ontario Hydro Run	Run 1	Run 2	Run 3*	Average
Dryer Mill Syn Gyp Feeder Output, % of full scale	53	50	50	51
Dryer Mill Burner Output, % of full scale	32	31	31	31
Estimated Dryer Mill B Wet Feed Rate, tons/hr	24	24	24	24
Dryer Mill Dust Collector Outlet Temperature, °F	165	167	162	165
Kettle #2 Feeder rpm	800	750	850	800
Estimated Kettle Calciner Stucco Production Rate, tons/hr	9.5	9.5	9.5	9.5
Kettle #2 Stucco Temperature, °F	300	300	300	300

Table 10. Task 6 Board-line Test Process Conditions

Date	9/14/2006	9/14/2006	9/14/2006
Time	1045-1250	1330-1600	1630-1837
Board Width, in.	48	48	48
Board Thickness, in.	0.5	0.5	0.5
Kiln Nozzle Temperature, °F	476	475	475

Mercury Balance Results

Table 11 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 were low, at about 4% of the mercury in the raw gypsum, based on the Ontario Hydro stack results. The solids analyses indicated no loss across the dryer mill (0% mean loss). For the kettle calciner, the percentage loss based on the Ontario Hydro stack results averaged 45%, while the loss calculated from the solids analyses averaged only 35%. 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 one- to two-hour period,

Table 11. Task 6 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	24	24	24	24	±0
Wt% moisture	6.6	6.3	6.0	6.3	±0.3
Hg content, µg/g, dry basis (from Table 3)	0.13	0.13	0.12	0.13	±0.00
Total Hg to dryer mill, g/hr	2.6	2.6	2.6	2.6	±0.7
Dryer Mill Product (Land Plaster):					
Dry rate, tons/hr	23	22	23	22	±0
Hg content, µg/g (from Table 3)	0.13	0.13	0.13	0.13	±0.00
Total Hg from dryer mill, g/hr	2.7	2.6	2.6	2.6	±0.1
Measured solids Hg loss rate, g/hr	-0.1	0.1	0.0	0.0	±0.1
Measured Hg loss rate at stack, lb/hr (from Table 8)	1.50×10^{-4}	3.63×10^{-4}	1.84×10^{-4}	2.32×10^{-4}	$\pm 1.29 \times 10^{-4}$
Measured Hg loss rate at stack, g/hr	0.07	0.16	0.08	0.105	±0.05
% Hg loss across dryer mill, by solids analysis	-2.8%	3.5%	-0.8%	0.0%	±3.2%
% Hg loss across dryer mill, by Ontario Hydro	2.6%	6.2%	3.3%	4.1%	±1.9%
Land Plaster Feed to Kettle Calciner:					
Feed rate, tons/hr	11	11	11	11	±0
Hg content, µg/g (from Table 3)	0.13	0.13	0.13	0.13	±0.00
Total Hg to kettle calciner, g/hr	1.4	1.4	1.3	1.3	±0.0
Product Stucco:					
Product rate, tons/hr, calculated	9.5	9.5	9.5	9.5	±0.0
Hg content, µg/g (from Table 3)*	0.11	0.10	0.10	0.10	±0.01
Total Hg from kettle calciner, g/hr	1.0	0.8	0.9	0.9	±0.1
Measured solids Hg loss rate, g/hr	0.4	0.5	0.5	0.5	±0.1
Measured Hg loss rate at stack, lb/hr (from Table 8)	1.32×10^{-3}	1.39×10^{-3}	1.32×10^{-3}	1.34×10^{-3}	$\pm 0.05 \times 10^{-3}$
Measured Hg loss rate at stack, g/hr	0.60	0.63	0.60	0.61	±0.02
% Hg loss across kettle calciner, by solids analysis	30%	39%	35%	35%	±5%
% Hg loss across kettle calciner, by Ontario Hydro	44%	46%	46%	45%	±1%
Mass Balance Closures:					
Dryer mill Hg closure, output vs. input, %	105%	103%	104%	104%	±1%
Kettle Calciner Hg balance closure, output vs. input, %	115%	107%	110%	111%	±4%
Overall Mill Hg balance closure, %*	123%	117%	117%	119%	±4%

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 an average of 104% recovery of the mercury in the wet gypsum feed being accounted for in the land plaster product and stack flue gas. This recovery of greater than 100% is directly related to the mercury loss by solids analyses being less than was measured by the Ontario Hydro method. If the two percentage losses were equal, the mass balance would show 100% closure. Similarly, the balances across the kettle calciner show

an average of 111% recovery of the mercury in the land plaster feed in the sum of the mercury in the product stucco plus that in the stack flue gas. Again, the recovery of greater than 100% is a direct result of the percent loss by solids analyses being less than was indicated by the Ontario Hydro stack results. However, any mercury balance closure within $\pm 20\%$ of 100% across an operating, full-scale plant is considered acceptable. The overall mercury balance closure across the mill of 119% is still within that acceptable range.

The Task 6 Ontario Hydro method results show a similar percentage mercury loss across the mill to what was measured during Task 5 (~50%); these task results represent the highest percentage mercury losses in the mill of the six tasks conducted.

These results suggest the addition of TMT-15 to the FGD system had little impact on the stability of mercury in the synthetic gypsum when it is used for wallboard production. The results also reinforce the Task 3 and 5 findings that mercury remaining in gypsum from systems that have a significant fines blow down may be more susceptible to loss in a wallboard mill than gypsum from systems with little or no fines blow down.

However, it should be noted that results from DOE Cooperative Agreement DE-FC26-04NT42309 indicate a possible interference in the effectiveness of TMT-15 in the Power Plant E FGD liquor.⁹ For example, expected results such as reduced mercury concentrations in the FGD slurry liquid phase, increased mercury concentrations in the gypsum fines, and reduced mercury concentrations in the bulk gypsum solids were not seen. Furthermore, an expected reduction in concentration of other divalent transition metals that should be precipitated by TMT-15 was not seen. Further investigation is under way as part of the 42309 project to determine why TMT-15 was not effective in the Power Plant E FGD liquor. Consequently, the results of Task 6 should not be interpreted as conclusively indicating that TMT-15 cannot improve the stability of mercury in treated gypsum when that material used for wallboard manufacturing feedstock.

The results of mercury balance calculations across the board line for Task 6 are shown in Table 12. Fewer details about feed rates are shown in Table 12 than in Table 11 due to the proprietary nature of the wallboard forming process. The results show that mercury losses across the board dryer kiln are relatively low, with values averaging 5.8% loss shown in the Ontario Hydro stack results. However, there is considerable variability in the Ontario Hydro method results for the board dryer kiln stacks. The 95% confidence interval for the mean percent loss by the Ontario Hydro method is $\pm 5.6\%$, or nearly as large as the mean loss percentage. This calls into question the accuracy of the mean loss percentage as measured by the Ontario Hydro method. The solids analyses results show a much lesser loss, averaging essentially zero loss when comparing the dry wallboard to the feed stucco.

As described above for the mill results, Ontario Hydro results are generally believed to be more accurate than the loss percentages estimated from grab sample mercury analyses. However, in this case, the 95% confidence intervals for the mean values measured by the two methods are relatively large ($\pm 5\%$ to 6%) and substantially overlap. Thus, it is not clear which of the two methods represents a better measure of mercury losses across the board line.

Table 12. Task 6 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 highest value during tests	100	100	100	100	±0
Hg Concentration in Stucco, µg/g (dry) (from Table 5)	0.11	0.11	0.12	0.11	±0.00
Hg in Stucco Feed, % of total Hg into Board Line	99	99	9	99	±0
Hg in Water Added, % of total Hg into Board Line	0	0	0	0	-
Hg in Additives, % of total Hg into Board Line	1*	1*	1*	1*	-
Hg in Paper, % of total Hg into Board Line	0*	0*	0*	0*	-
Hg in Slurry to Board Forming:					
Hg Concentration in slurry, µg/g (dry) (from Table 5)	0.08	0.09	0.08	0.08	±0.00
Moisture in Set Up Slurry, wt%	30.5	31.3	31.2	31.0	±0.5
Hg in Slurry, % closure with stucco + water + additives	93%	98%	89%	93%	±5%
Hg in Wet Wallboard:					
Hg Concentration in Wet Wallboard, µg/g (dry) (from Table 5)	0.07	0.07	0.07	0.07	±0.00
Moisture in Wet Wallboard, wt%	33.7	32.3	30.7	32.2	±1.7
Hg in Wet Wallboard, % closure with stucco + water + additives + paper	82%	80%	80%	81%	±1%
Hg in Wallboard Product:					
Hg Concentration in Wallboard Product, µg/g (dry) (from Table 5)	0.08	0.09	0.09	0.09	±0.00
Hg Loss and Balance Closures:					
Measured Hg loss rate at stack, lb/hr (from Table 8)	1.86×10^{-4}	4.23×10^{-4}	0.62×10^{-4}	2.24×10^{-4}	$\pm 2.08 \times 10^{-4}$
% Hg Loss Across Board Dryer Kiln, by solids analysis (wet vs. dry wallboard)	-16.8%	-23.7%	-17.1%	-19.2%	±4.4%
% Hg Loss Across Board Dryer Kiln, by solids analysis (feed stucco vs. dry wallboard)	-1.4%	4.9%	-3.5%	-0.1%	±4.9%
% Hg Loss Across Board Dryer Kiln, by Ontario Hydro	4.9%	11.3%	1.5%	5.8%	±5.6%
Hg Balance Across Board Dryer Kiln, % (wet vs. dry wallboard)	126%	145%	123%	131%	±14%
Overall Board-line Hg Balance, feed stucco vs. dry wallboard, %	104%	116%	98%	106%	±11%

*The mercury concentrations in all but one additive and in paper sampled were less than method detection limits, thus only limited contribution of additives or paper to total mercury in board line could be calculated

This is further complicated by the observation that the URS analyses of the wet slurry to board forming (S9) and wet wallboard (S10) showed lower mercury concentrations than either the feed stucco (S8) or dry wallboard product (S11) when compared on a dry gypsum basis. As shown in Table 12, when calculating observed mercury losses by comparing the wet versus dry wallboard mercury concentrations, a relatively high percentage mercury gain is actually shown.

The observed mercury balances across the overall board line show good closure, averaging 106% recovery of the mercury in the feed stucco in the dry wallboard product and the two kiln stacks. The closures across the board dryer kiln are not good, ranging from 123% to 145% and averaging 131%. This poor closure is due to the low bias in the wet wallboard sample mercury analyses as conducted by URS, which may be due to mercury loss from these wet samples before they were analyzed for mercury content.

At this point in the project, mercury losses have been measured across a board kiln by the Ontario Hydro method four times, as part of Tasks 1, 4, 5, and 6. The mercury losses measured during the current task are higher than the range of the previous measurements based on the mean of the three sets of Ontario Hydro runs (5.8% loss). The losses measured at Wallboard Plant 1 as part of Task 1 showed a mean loss percentage of 1.9%, the losses measured at Wallboard Plant 3 as part of Task 4 showed a mean loss percentage of 0.5%, and the losses measured at the same Wallboard Plant 4 as part of Task 5 showed a mean loss percentage of 1.4%.

However, the high standard deviation for the three Ontario Hydro measurement sets on the board kiln stacks raises some question about the accuracy of the Task 6 result. One run (Run 2) showed particularly high measured mercury losses, which tended to skew both the mean and 95% confidence interval values.

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 8 and 11. 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 3 and 5 (URS results). Results from these two types of calculations are shown in Table 13.

The mean overall lost percentage by the first method shows 55% of the plant input mercury out the four 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 considerably lower, with a mean loss percentage of 32%.

The loss percentage based on solids analyses has typically been corrected for mercury added with additives and paper in the board line in previous task results. However, for Task 6 most of the additive and paper sample mercury concentrations were below method detection limits. Because the mercury concentration in the raw synthetic gypsum feed for Task 6 was quite low, these un-quantified mercury additions could have produced a small change of approximately one percentage point to observed losses based on solids analyses, had the additive and paper concentrations been near detection limits.

Table 13. Summary of Task 6 Overall Mercury Loss During Wallboard Production, Calculated by Two Methods

	Run 1	Run 2	Run 3	Mean	95% C.I.
Total Hg Loss from Process Stacks by Ontario Hydro Method, g/hr*	1.4	1.6	1.3	1.4	±0.2
Total Hg to Wallboard Plant, g/hr [#]	2.6	2.6	2.6	2.6	±0.1
Observed Overall Percentage Hg Loss based on Ontario Hydro Method	52%	61%	51%	55%	±6%
Hg Concentration in Raw Gypsum Feed to Wallboard Plant, µg/g	0.13	0.13	0.12	0.13	±0.00
Hg Concentration in Wallboard Product, µg/g	0.08	0.09	0.09	0.09	±0.00
Observed Percentage Hg Loss Across Wallboard Plant based on URS solids analyses	34%	32%	30%	32%	±2%
Observed Percentage Hg Loss Across Wallboard Plant based on solids analyses, corrected for Hg added with additives and paper in board line	34%	32%	30%	32%	±2%

*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 two methods do not agree very well with respect to the percentage mercury loss from the wallboard plant feed. As discussed in the paragraphs above, it is believed that the mean value of 5.8% mercury loss across the board line calculated from Ontario Hydro results could be overstated due to the unusually high loss percentage indicated by the second of the three sampling runs. Thus, the true mean loss across the entire wallboard plant as measured by the Ontario Hydro results could have been as low as 49% rather than 55%, considering the 95% confidence interval of the mean.

Also, it is known that quantifying 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. Minor variations in process sample mercury content can adversely affect the percent mercury loss calculations. The second possible adverse impact is the effect of analytical variability when comparing two concentration measurements to quantify small mercury percentage losses. Considering the inherent error possibilities of measuring mercury losses by solid sample analyses, it is likely that the true mean mercury loss percentage across Wallboard Plant 4 was closer to 50% than the 32% mean indicated from solid sample analyses.

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 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 6 evaluated the use of synthetic gypsum from a limestone forced-oxidation FGD system on a plant that fires Eastern bituminous coal, has an SCR in service, employs gypsum fines blow down, and was using Degussa Corporation's additive TMT-15 in an attempt to reduce elemental mercury re-emissions from the wet FGD system. These results indicated that as much as 55% of the incoming mercury was emitted during wallboard production, as measured by the Ontario Hydro method. These losses were distributed as approximately 4% across the dryer mill, 45% across the kettle calciners, and 6% across the board dry kiln. However, there is some question that the losses measured across the board dry kiln may have been skewed high by an exceptionally large loss result for one of three Ontario Hydro measurement runs.

The measured mercury losses from Wallboard Plant 4 totaled approximately 1 gram per hour, considering the operation of one dryer mill, two kettle calciners, and one board dryer kiln. Of this total loss, about 7% was from the dryer mill, 86% from the kettle calciners, and 7% from the board dryer kiln. The total mercury losses measured amount to about 0.1 lb of mercury emitted per million square feet of wallboard produced or 0.06 gram of mercury per ton of dry gypsum processed. Based on Task 6 mercury emission 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 1 to 2% of current power industry emissions.

The individual results from Tasks 1 through 6 of this project would predict mercury emissions from the wallboard industry ranging from 0.2 to 2% of current power industry emissions. However, the results from Tasks 1 through 6 still 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 estimates made based on Task 1 through 6 results.

Of the flue gas streams measured for mercury content by the Ontario Hydro Method in Task 6, the kettle calciner steam stack showed the highest mercury concentrations, with concentrations of 170 to 190 µg/Nm³ 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 49%. 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 5 $\mu\text{g}/\text{Nm}^3$ in the dryer mill stack and from 6.5 $\mu\text{g}/\text{Nm}^3$ down to less than 0.5 $\mu\text{g}/\text{Nm}^3$ in the two board kiln stacks.

Results are now available from six full-scale wallboard plant tests, conducted as Tasks 1 through 6 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, while 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. Finally, Task 5 tested gypsum from a power plant configuration similar to that tested in Task 3, in that the FGD system employs gypsum fines blow down, while Task 6 tested the same gypsum source but while the plant was using TMT-15 additive.

The results from Task 6 proved to be similar to those from Tasks 3 and 5. The Task 6 gypsum mercury concentrations were about one-third lower, at about 0.13 versus 0.2 $\mu\text{g}/\text{g}$, but the overall mercury loss percentages were similar. The loss percentages measured were 46% for Task 3, based on an estimate for the mercury loss across the wallboard dryer kiln since that was not measured by the Ontario Hydro method, 51% for Task 5, and 55% for Task 6. The results from these three tasks also showed the highest percentage mercury losses across the wallboard process of the six gypsum/wallboard plant configurations tested. The similarity in results for gypsum from two FGD systems employing gypsum fines blow down suggests a relationship between this aspect of FGD system operation and mercury emissions from the wallboard process. However, it remains a possibility that it is merely coincidence that these test results are so similar.

In the Task 6 results, as was seen in the Task 1 through 5 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.

Finally, the hypothesis that led to the addition of Task 6 to the scope of this project was that an additive such as TMT-15 could precipitate mercury from the wet FGD liquor as a fine, thermally stable salt. This was expected to produce benefits such as reduced elemental mercury re-emissions from the wet FGD system, lowered synthetic gypsum mercury concentrations due to

an increased amount of mercury in the fines blow down stream, and reduced mercury release when the synthetic gypsum is used to produce wallboard. The results from Task 6 did show a lower gypsum mercury concentration than had been seen during Task 5 without the TMT-15 additive. However, based on information presented in Reference 8, this does not appear to have been an effect of TMT-15 addition.

The results from Task 6 clearly did not show the third potential benefit of TMT-15 addition, reduced mercury release when the synthetic gypsum is used to produce wallboard. The percentage mercury loss of mercury from the synthetic gypsum across the wallboard plant was measured to be very similar in Tasks 5 and 6, indicating no effect of TMT-15. It should be noted that information presented in Reference 8 showed that TMT-15 did not produce many expected results when added to the wet FGD system at Power Plant E. It appears that there was an interfering species in the Power Plant E wet FGD system that prevented the TMT-15 additive from performing as intended. Unfortunately, these results did not become available until the Task 6 wallboard test was underway. Thus, the results from Task 6 should not be interpreted as conclusively indicating that TMT-15 has no effect on mercury release during wallboard production from synthetic gypsum. Under better circumstances, the anticipated effects of TMT-15 on mercury release during wallboard production may be realized.

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. Marshall, Jessica, Gary Blythe and Mandi Richardson. *Fate of Mercury in Synthetic Gypsum Used for Wallboard Production, Topical Report, Task 4 Wallboard Plant Test Results*, U.S. Department of Energy, Pittsburgh, PA. Cooperative Agreement Number DE-FC26-04NT42080, November 2005.
5. Marshall, Jessica, Gary Blythe and Mandi Richardson. *Fate of Mercury in Synthetic Gypsum Used for Wallboard Production, Topical Report, Task 5 Wallboard Plant Test Results*, U.S. Department of Energy, Pittsburgh, PA. Cooperative Agreement Number DE-FC26-04NT42080, June 2006.
6. Tarabocchia, John and Ruediger Peldszus, “Mercury Separation from Flue Gas and Scrub Water with Trimercapto-s-triazine (TMT),” paper presented at the Combined Power Plant Air Pollutant Control Mega Symposium, Washington, D.C., May 19-22, 2003.
7. *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.
8. *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.
9. Blythe, Gary, et al. “Wet FGD Additive for Enhanced Mercury Control,” paper presented at the DOE/NETL Mercury Control Technology Conference, Pittsburgh, PA, December 11-13, 2006.