Field Testing of a Wet FGD Additive for Enhanced Mercury Control

Final Report

Prepared by:

Gary M. Blythe
MariJon Owens

March 2008

Cooperative Agreement No: DE-FC26-04NT42309

URS Corporation
9400 Amberglen Boulevard
Austin, Texas 78729

Prepared for:

Charles Miller

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

DISCLAIMER

ABSTRACT

This document is the final report for DOE-NETL Cooperative Agreement DE-FC26-04NT42309, "Field Testing of a Wet FGD Additive." The objective of the project has been to demonstrate the use of two flue gas desulfurization (FGD) additives, Evonik Degussa Corporation's TMT-15 and Nalco Company's Nalco 8034, to prevent the re-emission of elemental mercury (Hg^0) in flue gas exiting wet FGD systems on coal-fired boilers. Furthermore, the project was intended to demonstrate whether such additives can be used to precipitate most of the mercury (Hg) removed in the wet FGD system as a fine salt that can be separated from the FGD liquor and bulk solid byproducts for separate disposal.

The project involved pilot- and full-scale tests of the additives in wet FGD absorbers. The tests were intended to determine required additive dosages to prevent Hg^0 re-emissions and to separate mercury from the normal FGD byproducts for three coal types: Texas lignite/Powder River Basin (PRB) coal blend, high-sulfur Eastern bituminous coal, and low-sulfur Eastern bituminous coal.

The project team consists of URS Group, Inc., EPRI, Luminant Power (was TXU Generation Company LP), Southern Company, IPL (an AES company), Evonik Degussa Corporation and the Nalco Company. Luminant Power provided the Texas lignite/PRB co-fired test site for pilot FGD tests and project cost sharing. Southern Company provided the low-sulfur Eastern bituminous coal host site for wet scrubbing tests, the pilot- and full-scale jet bubbling reactor (JBR) FGD systems tested, and project cost sharing. IPL provided the high-sulfur Eastern bituminous coal full-scale FGD test site and cost sharing. Evonik Degussa Corporation provided the TMT-15 additive, and the Nalco Company provided the Nalco 8034 additive. Both companies also supplied technical support to the test program as in-kind cost sharing.

The project was conducted in six tasks. Of the six tasks, Task 1 involved project planning and Task 6 involved management and reporting. The other four tasks involved field testing on FGD systems, either at pilot or full scale. These four tasks included: Task 2 – Pilot Additive Testing in Texas Lignite Flue Gas; Task 3 – Full-scale FGD Additive Testing in High-sulfur Eastern Bituminous Flue Gas; Task 4 – Pilot Wet Scrubber Additive Tests at Plant Yates; and Task 5 – Full-scale Additive Tests at Plant Yates. The pilot-scale tests were completed in 2005 and the full-scale test using high-sulfur coal was completed in 2006; only the TMT-15 additive was tested in these efforts. The Task 5 full-scale additive tests conducted at Southern Company's Plant Yates Unit 1 were completed in 2007, and both the TMT-15 and Nalco 8034 additives were tested.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

EXECUTIVE SUMMARY

This document is the final report for DOE-NETL Cooperative Agreement DE-FC26-04NT42309, "Field Testing of a Wet FGD Additive." The objective of the project has been to demonstrate the use of two flue gas desulfurization (FGD) additives, Evonik Degussa Corporation's TMT-15 and Nalco Company's Nalco 8034, to prevent the re-emission of elemental mercury (Hg^0) in flue gas exiting wet FGD systems on coal-fired boilers. Furthermore, the project was intended to demonstrate whether such additives can be used to precipitate most of the mercury (Hg) removed in the wet FGD system as a fine salt that can be separated from the FGD liquor and bulk solid byproducts for separate disposal.

The project involved pilot- and full-scale tests of the additives in wet FGD absorbers. The tests were intended to determine required additive dosages to prevent Hg^0 re-emissions and to separate mercury from the normal FGD byproducts for three coal types: Texas lignite/Powder River Basin (PRB) coal blend, high-sulfur Eastern bituminous coal, and low-sulfur Eastern bituminous coal.

The project was conducted in six tasks. Of the six tasks, Task 1 involved project planning and Task 6 involved management and reporting. The other four tasks involved field testing on FGD systems, either at pilot or full scale. These four tasks included: Task 2 – Pilot Additive Testing in Texas Lignite Flue Gas; Task 3 – Full-scale FGD Additive Testing in High-sulfur Eastern Bituminous Flue Gas; Task 4 – Pilot Wet Scrubber Additive Tests at Plant Yates; and Task 5 – Full-scale Additive Tests at Plant Yates. The pilot-scale tests were completed in 2005 and the full-scale test using high-sulfur coal was completed in 2006; only the TMT-15 additive was tested in these efforts. The Task 5 full-scale additive tests conducted at Southern Company's Plant Yates Unit 1 were completed in 2007, and both the TMT-15 and Nalco 8034 additives were tested. Results from the pilot- and full-scale tests are discussed separately below.

Pilot-scale Test Results

The results of the pilot-scale TMT-15 additive tests conducted at the beginning of this project were not as conclusive as was hoped regarding the effects of adding TMT-15 to FGD slurries to enhance mercury capture by wet FGD systems. The primary objective of the additive is to prevent or limit mercury re-emissions from wet FGD systems.

The first pilot-scale additive parametric tests was conducted at Monticello Station in April 2005; no evidence was seen of re-emissions without the additive, so this objective could not be evaluated. A steady-state TMT-15 additive test was conducted at Monticello in September 2005 with the pilot wet FGD system operating downstream of a gold mercury oxidation catalyst; previous test results at Monticello without TMT-15 additive showed re-emissions when the pilot wet FGD was operated downstream of this catalyst. In September 2005 the Ontario Hydro method was used to measure re-emissions when operating the pilot wet FGD downstream of the gold catalyst and while adding TMT-15 at 20 mL/ton of coal fired. The units of mL of TMT-15 injected per ton of coal fired represent an Evonik Degussa dosing rate reporting convention. These results showed a mean re-emission level of 0.5 $\mu g/Nm^3$, which is about one fourth of the

re-emissions measured previously downstream of the gold catalyst at Monticello without TMT addition. Furthermore, when the 95% confidence intervals of these measurements are considered, it is possible that no re-emissions were occurring. This could be taken as evidence that TMT-15 addition greatly reduced re-emissions when operating the pilot wet FGD downstream of the gold catalyst. However, the oxidized mercury concentration at the wet FGD pilot inlet during the TMT test was only 25% of what the concentration had been for the previous test without TMT, which had been conducted several months earlier. When the mean re-emissions are expressed as a percentage of the mean FGD inlet oxidized mercury concentration, the percentages are the same for the two tests. This confounds the finding of whether or not TMT-15 was effective in limiting re-emissions.

Pilot jet bubbling reactor (JBR) FGD tests were conducted at Plant Yates in August 2005. In these tests, mercury SCEM data appear to be compromised by excessive scrubber liquor carryover from the pilot JBR into the outlet duct, and thus provided no useful information about re-emissions.

Other expected effects of TMT-15 addition were seen more clearly in these results. TMT-15 was very effective in lowering FGD liquor mercury concentrations in both sets of pilot-scale tests. For example, during the steady-state pilot FGD TMT-15 test at Monticello, the FGD liquor mercury concentrations were lowered by over an order of magnitude compared to baseline (no TMT addition) values from two days earlier. Liquid-phase reactions between oxidized mercury and sulfite ion (dissolved SO_2) are believed to produce re-emissions, so this suggests that TMT-15 would be effective at limiting re-emissions.

Results also show that TMT-15 addition can result in lower gypsum byproduct mercury concentrations if some form of gypsum fines separation is employed, such as using hydrocyclones for primary dewatering. Observed reductions in gypsum mercury concentration varied from 17% to 29% in the three series of pilot-scale tests.

The effectiveness of TMT-15 in lowering gypsum mercury concentrations appears to be limited by the ability of the FGD absorber blow down slurry dewatering equipment to remove fine particles. Hydrocyclones leave a percentage of fine particles in the underflow slurry, and these fine particles appear to account for much of the mercury that remains in the product gypsum. Other forms of solid separation equipment, that can make a sharper separation of fine particles from the coarser particles, may be able to produce a gypsum byproduct with a lower mercury concentration.

The addition of TMT-15 did not appear to have any adverse effect on the operation of either wet FGD pilot unit. Concentrations of species other than mercury in the FGD liquors, such as calcium, sulfate and chloride, did not appear to be affected; SO_2 removal percentages remained high; and gypsum byproduct purity and particle size distributions were not greatly impacted.

Full-scale Test Results

A full-scale test of TMT-15 addition to a limestone forced oxidation wet FGD system on a power plant that fires high-sulfur Indiana coal, IPL's Petersburg Unit 2, was conducted in July 2006.

This test showed mixed results. Consequently, relatively few conclusions can be made from the results of this test.

Flue gas measurements by the Ontario Hydro method showed a moderate reduction in re-emission levels after five days of TMT addition at a rate equivalent to 40 mL of TMT-15 added to the FGD reaction tank per ton of coal fired by Unit 2. Baseline (no TMT) re-emissions represented 49% of the FGD inlet oxidized mercury being re-emitted as elemental mercury in the outlet gas, while the TMT test re-emission result represented 35% of the inlet oxidized mercury. A greater reduction was expected. It is not clear whether the observed decrease was an effect of TMT-15 injection or merely represented day-to-day variation. The FGD absorber liquor samples from the TMT test showed little or no reduction in mercury concentrations due to TMT addition.

It was speculated that a component in the FGD liquor was interfering with the effectiveness of TMT in precipitating mercury from this liquor. Efforts were made as part of this project, although unsuccessfully, to identify such a component in the Petersburg FGD system. More work would be needed to try to identify what this component might be and how to counteract it.

Some data collected during the test remain unexplained. Mercury SCEM measurements at the Unit 2 stack showed that flue gas elemental mercury concentrations dropped significantly shortly after TMT-15 injection began at the lowest injection rate tested, equivalent to 10 mL of TMT-15 added per ton of coal fired in Unit 2. Since re-emissions cause elevated elemental mercury concentrations in the scrubbed flue gas, this drop in concentration was taken as evidence that TMT-15 was effective at controlling mercury re-emissions even at the lowest dosage tested. However, the stack elemental mercury concentrations continually increased as the TMT injection test progressed, to the point that the Ontario Hydro measurements at the end of the test showed only a moderate effect of TMT-15, as mentioned above. Furthermore, FGD liquor mercury analyses did not show the expected drop in mercury concentration that should correspond with the initial drop in stack elemental mercury concentration shortly after TMT-15 injection began. It was suspected that the observed drop in stack elemental mercury concentration shortly after TMT-15 injection began was due to lower coal mercury concentrations during this period. However, coal sample analyses show the coal mercury content to be relatively steady during the test period.

Other unexplained data came from follow-up TMT beaker tests were conducted at Petersburg Unit 2 in January 2007, six months after the full-scale tests were conducted. In those tests, TMT-15 dosing into beakers of FGD liquor showed that liquor mercury concentrations could be lowered through increasing TMT dosage, which is the expected effect. However, the baseline (no TMT addition) absorber liquor mercury concentration was measured in January 2007 at only 1 µg/L, whereas in July 2006 the concentrations ranged from 40 to 62 µg/L even with TMT-15 addition. One known difference between the Unit 2 operation between July 2006 and January 2007 is that the SCR was in operation in July and was not in operation (bypassed) in January. It was speculated that the SCR operating status was impacting the liquid phase mercury concentrations. However, follow-up measurements on the Unit 2 FGD absorber slurry, in April 2007 with the SCR bypassed and then in May 2007 with the SCR in service, did not show such a trend. It is also not known whether or not there were any mercury re-emissions from the Unit 2

wet FGD system during the January, April and May 2007 operations when the liquor mercury concentrations were much lower.

Two full-scale scrubber re-emission additive tests were conducted on the Unit 1 JBR at Plant Yates. The first was conducted in May 2007 using Evonik Degussa Corporation's TMT-15 and the second was conducted in August and September 2007 using the Nalco Company's additive Nalco 8034. Based on the success of TMT-15 in lowering pilot JBR slurry liquor mercury concentrations in the 2005 test at Plant Yates, similar success was expected in the full-scale test. However, neither the TMT-15 nor Nalco 8034 test conclusively demonstrated the ability of the additive to control mercury re-emissions across the JBR.

The results of the TMT-15 test were similar to those in the earlier test at Petersburg Unit 2; neither of the expected results of TMT addition was observed. Re-emission of elemental mercury across the JBR appeared to increase rather than decrease with TMT addition, and the mercury concentration in the JBR slurry liquor was not decreased to near detection limits. The concentration decreased by a maximum of 47% and the resulting liquor mercury concentration was still relatively high at >100 μg/L. This suggests that TMT-15 was ineffective in the JBR at the dosages tested, which were within the range recommended by the manufacturer. Higher dosage rates were not tested because of additive cost considerations, and because of concern over direct reduction of oxidized mercury by TMT if it were present at higher concentrations in the FGD liquor. However, the mercury concentrations in the JBR liquor were extremely high during this test period, and prior to adding TMT 92% of the mercury in the JBR slurry was found in the liquor. It is not known if this high liquor mercury concentration impacted the TMT-15 test.

There is a possible explanation for why TMT-15 was relatively ineffective in precipitating mercury from the JBR liquor, both at Petersburg Unit 2 and at Plant Yates Unit 1: it is possible that part of what was measured as liquor phase mercury was actually present as extremely fine particles. Slurry samples were filtered on site with filter membranes that have a 0.7-μm pore size; therefore, particles smaller than approximately 0.7 μm in diameter could pass through the filter. If much of the liquor mercury measured was actually present as sub-micron-diameter precipitates that were rich in mercury, this could explain the apparent lack of effectiveness of TMT-15 in removing all of the mercury measured in the liquor phase. However, this does not help explain why TMT-15 was also ineffective in controlling re-emissions at Plant Yates. Mercury in the solid phase should not participate in aqueous re-emission reactions. If TMT was effective at precipitating any mercury actually present in the liquor as ionic mercury and not as sub-micron-diameter particles, a corresponding decrease in mercury re-emissions would have been expected.

The Nalco 8034 test results were also inconclusive, primarily because the baseline (no additive) re-emissions across the JBR were low. During baseline measurements in August 2007, and during Nalco 8034 addition in September the measured JBR liquor mercury concentrations were very low (generally less than 1 μg/L), and mercury re-emission levels were also low (0.5 μg/Nm^3 @ 3% O_2). This re-emission level is difficult to measure by CEM or Ontario Hydro methods. Re-emissions are quantified as the difference between two measured flue gas mercury concentration values. When the re-emission level is low, the number is a small difference between two larger numbers. When using Ontario Hydro measurement results, each of the larger numbers is a mean

from two to three measurement runs, and the mean has a 95% confidence interval. In this case the 95% confidence interval of the means was of the same order of magnitude as the apparent re-emission level, so re-emissions could not be determined with certainty. That is, the actual re-emission levels could have been somewhere within the range of 0.0 to 1.0 $\mu g/Nm^3$ @ 3% O_2 instead of the mean value of 0.5 $\mu g/Nm^3$ @ 3% O_2. The Nalco additive needs to be re-tested on an FGD system that has greater re-emission levels that can be better quantified.

As mentioned above, the baseline (no additive) JBR liquor mercury concentrations were much higher in May 2007 during the TMT-15 test than at the beginning of the Nalco 8034 test in August 2007. Additional analyses were conducted in an attempt to explain why the apparent JBR liquor mercury concentrations were so much higher in May than in August. Of these additional analyses, only trace metals analyses of the JBR liquor and hydrocyclone overflow solids offered potential explanations for this phenomenon. The JBR liquor had nearly four times the apparent iron concentration in May compared to August. If some of this iron was actually present as sub-micron-diameter iron precipitates with high mercury content, this could explain the high apparent mercury concentration in the JBR liquor.

In August 2007 a much higher percentage of the JBR slurry mercury content was found in the solids. The hydrocyclone overflow solids were found to have significantly higher selenium content in August than in May. It could be possible that the higher proportion of mercury in the solids rather than the liquor in August was due to the formation of insoluble mercuric selenide precipitates. However, it seems unlikely that selenides could exist in the forced oxidizing environment of the JBR – the more highly oxidized selenate form seems more likely and would not tend to precipitate mercury.

The mercury-rich fines stream separated in the hydrocyclone overflow slurry could potentially be filtered out of this stream and disposed of separately, as a means of lowering the mercury content of the gypsum byproduct. SPLP leaching tests were conducted to determine how readily mercury might leach from this potential disposal stream if placed in a monofill. SPLP results from hydrocyclone overflow and absorber slurry solid samples from the IPL Petersburg test for both baseline and TMT-addition conditions showed no measurable mercury in the leachates. The results from Plant Yates showed a small amount of mercury leached out of the baseline sample from May 2007, but no mercury was detected in the leachates from the TMT-15 and Nalco 8034 addition period hydrocyclone overflow solids. This was an expected benefit from employing either of these additives. The mercury measured in the leachate from the baseline sample from May 2007 was very low, about twice the analytical detection limit, and may have reflected some contamination by FGD liquor adhering to the solids leached.

Recommendations

The results from this project were not as successful as hoped. In the pilot-scale tests with TMT-15, the expected result of lowering mercury concentrations in FGD absorber liquors was seen, but a corresponding decrease in re-emissions rates was not measured conclusively due to various flue gas mercury measurement issues. In the two full-scale tests with TMT-15, the absorber liquor mercury concentrations were not lowered as effectively as in the pilot-scale tests, and little or no reductions in re-emissions were measured. In the full-scale test with Nalco 8034 additive,

the JBR liquor mercury concentrations were already quite low prior to additive addition, and mercury re-emission levels were down around the lower measurement limit. Thus, the effectiveness of this additive was not clearly measured.

It was seen as this project progressed that the amount of mercury in a wet FGD absorber liquor and the level of re-emissions from a wet FGD absorber can vary significantly over time for any one particular FGD system. The parameters that control liquor mercury concentrations and re-emission levels are not well understood.

These results suggest that there is no "one size fits all" wet FGD re-emissions additive. There are apparently one or more factors that impact the effectiveness of mercury precipitation additives in wet FGD absorber liquors. Consequently, more testing is needed, over a range of wet FGD systems and with more additive types.

However, this represents an empirical approach to finding additives that might work for a particular application. More work is needed to determine how much mercury partitioning varies between the liquor and solids in the absorber slurry in a given FGD system, what controls this partitioning, and how this affects mercury re-emission levels. Similarly, developing an understanding of why additives work in one FGD system and not another would greatly improve on the current state of the art.

INTRODUCTION

This document is the final report for DOE-NETL Cooperative Agreement DE-FC26-04NT42309, "Field Testing of a Wet FGD Additive." The objective of the project has been to demonstrate the use of two flue gas desulfurization (FGD) additives, Evonik Degussa Corporation's TMT-15 and Nalco Company's Nalco 8034, to prevent the re-emission of elemental mercury (Hg^0) in flue gas exiting wet FGD systems on coal-fired boilers. Furthermore, the project was intended to demonstrate whether such additives can be used to precipitate most of the mercury (Hg) removed in the wet FGD system as a fine salt that can be separated from the FGD liquor and bulk solid byproducts for separate disposal.

The project involved pilot- and full-scale tests of the additives in wet FGD absorbers. The tests were intended to determine required additive dosages to prevent Hg^0 re-emissions and to separate mercury from the normal FGD byproducts for three coal types: Texas lignite/Powder River Basin (PRB) coal blend, high-sulfur Eastern bituminous coal, and low-sulfur Eastern bituminous coal.

The project team consists of URS Group, Inc., EPRI, Luminant Power (was TXU Generation Company LP), Southern Company, IPL (an AES company), Evonik Degussa Corporation and the Nalco Company. Luminant Power provided the Texas lignite/PRB co-fired test site for pilot FGD tests and project cost sharing. Southern Company provided the low-sulfur Eastern bituminous coal host site for wet scrubbing tests, the pilot- and full-scale jet bubbling reactor (JBR) FGD systems tested, and project cost sharing. IPL provided the high-sulfur Eastern bituminous coal full-scale FGD test site and cost sharing. Evonik Degussa Corporation provided the TMT-15 additive, and the Nalco Company provided the Nalco 8034 additive. Both companies also supplied technical support to the test program as in-kind cost sharing.

The project was conducted in six tasks. Of the six tasks, Task 1 involved project planning and Task 6 involved management and reporting. The other four tasks involved field testing on FGD systems, either at pilot or full scale. These four tasks included: Task 2 – Pilot Additive Testing in Texas Lignite Flue Gas; Task 3 – Full-scale FGD Additive Testing in High-sulfur Eastern Bituminous Flue Gas; Task 4 – Pilot Wet Scrubber Additive Tests at Plant Yates; and Task 5 – Full-scale Additive Tests at Plant Yates. The pilot-scale tests were completed in 2005 and the full-scale test using high-sulfur coal was completed in 2006; only the TMT-15 additive was tested in these efforts. The Task 5 full-scale additive tests conducted at Southern Company's Plant Yates Unit 1 were completed in 2007, and both the TMT-15 and Nalco 8034 additives were tested.

Previous Topical Reports presented results from the Task 2 and Task 4 pilot-scale additive tests,[1] from the Task 3 full-scale testing at IPL's Petersburg Station,[2] and from the Task 5 full-scale additive tests at Southern Company's Plant Yates Unit 1.[3] Results from all four tasks are presented and discussed in this Final Report. However, more detail may be found in the individual Topical Reports.

Background

Many utility mercury emission compliance plans for coal-fired power plants incorporate the co-benefits of mercury capture in wet FGD systems. In wet FGD absorbers, the oxidized form of mercury (Hg^{+2}) is absorbed from the flue gas into the FGD liquor, while water insoluble elemental mercury (Hg^0) is typically not removed. Once absorbed, the oxidized mercury 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 elemental mercury, which, being insoluble, is released and re-emitted into the FGD outlet flue gas; 2) being retained in the FGD liquor and leaving the system in FGD wastewater, which could require additional treatment; or 3) being retained in the FGD byproduct solids. This project is investigating the use of FGD additives 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 used for wallboard production or agricultural purposes. A second objective of the project is to determine whether this same additive can be used to lower mercury concentrations in reused FGD solid byproducts, through separation of the fine mercury-containing salts formed from the remainder of the byproduct.

One of the wet FGD additives tested is an Evonik Degussa Corporation product, TMT-15. The intent of the TMT-15 additive is to precipitate absorbed mercury as a stable salt to minimize re-emissions and lower liquid-phase mercury concentrations. It is also possible for the salt to be removed from the solid FGD byproducts to lower their mercury content. While TMT-15 is used in Europe in such applications, it has only recently seen increasing use in U.S. plants, primarily in wet FGD systems on municipal waste incinerators. This 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 following paragraphs provide further background on how TMT-15 has been used previously to control mercury emissions from FGD systems.

In some circumstances mercury and other heavy metals must be removed from FGD wastewater before it can be discharged. A two-stage treatment process is sometimes used, with hydroxide precipitation followed by precipitation of the complexed metals with additives such as trimercapto-s-triazine, tri-sodium salt (TMT). TMT is commercially available from Evonik Degussa Corporation as a 15-wt% aqueous solution, TMT 15. TMT is also reportedly used directly in some wet FGD systems on municipal waste incinerators in Europe and in the U.S. to control mercury re-emissions.[4]

Mercury re-emissions occur when soluble Hg^{+2} reacts with sulfite ion (absorbed SO_2) in wet FGD liquors and is reduced to the insoluble Hg^0 form, which is released back into the FGD outlet flue gas. Conversion of Hg^{+2} to a non-volatile TMT salt before re-emission reactions occur can improve the overall mercury capture by the wet FGD system. TMT has reportedly been proven successful in this application in a number of coal-fired power plants and municipal waste incinerators in Europe and worldwide. Besides its ability to chemically bind with mercury, TMT reportedly has favorable toxicological and ecological properties.[4]

The reaction of TMT with heavy metals is based on the soluble tri-sodium salt chemically binding to heavy metals via the 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 (1.5 oxidized mercury molecules). TMT reportedly reacts over a wide pH range, including acidic conditions, without decomposing or releasing toxic gases such as H_2S.[4]

From the FGD absorber blow down slurry, fine particles of mercury-TMT compound may be transferred to the wastewater/fines blow down, absorber recycle and/or partly to the byproduct gypsum. TMT-metal compounds are reportedly quite stable. Evonik Degussa reports that 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 that TMT-metal compounds easily meet the leachability limits of the TCLP.[4] It is anticipated that 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.

This project was originally intended to demonstrate the effectiveness of TMT-15 for these purposes in FGD systems installed on U.S. coal-fired power plants. As described above, the project has conducted two sets of pilot-scale additive tests and two full-scale additive trials. Prior to the Task 5 testing conducted in 2007, the pilot-scale tests and the Task 3 full-scale tests had been conducted with TMT-15 with mixed results. During Task 5 full-scale test at Plant Yates a second additive, Nalco Company's Nalco 8034, was also evaluated. Nalco Company products have been used successfully for removing metals in wastewater facilities, and their scrubber additive, Nalco 8034, was expected to act similarly to TMT-15 by precipitating mercury from the liquor through the formation of fine mercury salts. Results for both additives are presented and discussed in this report for the Plant Yates full-scale test.

Report Organization

The remainder of this report is organized into four sections: a section that describes Experimental procedures followed by sections for Results and Discussion, Conclusions, and References. The Experimental and Results and Discussion sections are subdivided to address the individual tasks in the project. Rather than discuss the tasks in numerical order, the pilot-scale tests are addressed first (Tasks 2 and 4) followed by the two full-scale tests (Tasks 3 and 5). Besides pairing up the testing and results at the two different scales, this order also matches the actual test chronology. The pilot-scale tests were conducted over the time period April through September 2005, while the full-scale tests were conducted in July 2006 at IPL Petersburg Station and in May through September 2007 at Plant Yates.

EXPERIMENTAL METHODS

Pilot Wet FGD Additive Tests at Monticello Station

Overview

In the first pilot-scale field effort, additive tests were conducted on a pilot wet scrubber treating flue gas from Unit 3 at Luminant Power's Monticello Steam Electric Station, which fires a blend of Texas lignite and PRB coal. Wet FGD additive parametric tests were conducted in April 2005 on a 0.5-MW spray/tray FGD pilot unit built as part of another DOE co-funded project, DE-FC26-04NT41992. The FGD pilot unit is further described below. The pilot FGD was operated in a limestone reagent, forced oxidation (LSFO) mode. TMT-15 solution was metered into the FGD slurry recycle pump discharge line with a small diaphragm pump.

Mercury semi-continuous emissions monitors (Hg SCEMs, also described below) were used to measure absorber inlet and outlet mercury concentrations and speciation, to quantify net mercury removal and mercury re-emissions under baseline (no TMT) and additive conditions. At baseline (no additive) test conditions, mercury re-emissions were not seen from the pilot wet FGD when treating the flue gas at Monticello Unit 3, so the ability of TMT-15 to prevent re-emissions could not be evaluated in these tests. Instead, the parametric tests focused on the ability to lower FGD liquor mercury concentrations and to produce a mercury-TMT salt that may be separated from the gypsum byproduct.

After conducting the parametric tests, it became apparent that to truly evaluate this latter objective, the pilot unit should have equipment to separate the fine mercury-containing salts from the byproduct gypsum. To accomplish this, EPRI funded the addition of a hydrocyclone dewatering loop to the FGD pilot unit. This dewatering loop is described below along with the pilot wet FGD description.

The dewatering loop was constructed during the summer of 2005, and a second week of TMT-15 additive tests was conducted on the pilot unit at Monticello at the end of September. This test was conducted at a single TMT-15 dosage, selected based on previous pilot test results, and was intended to operate for a long enough period for the FGD byproduct solids to come to steady state with respect to mercury concentration. A second change for the "steady state" test was that it was conducted downstream of a gold mercury oxidation catalyst. The gold catalyst was being operated as part of Cooperative Agreement DE-FC26-04NT41992, and previous pilot wet FGD test results at Monticello showed re-emissions when operating downstream of that catalyst. It was decided that operating downstream of this catalyst, where re-emissions were expected, would better allow the ability of TMT-15 to control re-emissions to be evaluated.

Description of Monticello Unit 3

Unit 3 at TXU Generation's Monticello Steam Electric Station is a 793-MW unit that fires a blend of Texas lignite and PRB coal. It has a horizontally opposed, pulverized-coal boiler with low NO_X burners. A cold-side electrostatic precipitator (ESP) is used for particulate control and a

LSFO, open spray tower wet FGD system is used for SO_2 control. The lignite/PRB coal blend contains 0.7 wt% sulfur, 0.14 ppm mercury, and 210 ppm chloride on average. The ESP outlet flue gas typically contains 25-50% oxidized mercury and the balance elemental mercury, with total mercury concentrations of about 20-30 $\mu g/Nm^3$. However, the Texas lignite has roughly four times the mercury content of the PRB on a mass basis, and the percentage of each fuel type fired cannot be closely controlled. Consequently, variations in the percentage lignite versus PRB fired can greatly influence the flue gas mercury concentration and oxidation percentage.

Pilot Wet FGD System

The DOE-NETL co-funded 41992 project provided the opportunity to build a wet FGD pilot unit that is used to determine the ability to scrub catalytically oxidized mercury. The wet FGD pilot unit is designed to treat the flue gas from one of the four catalyst chambers on the mercury oxidation catalyst pilot unit, about 2000 acfm. It can be operated with lime or limestone reagent (usually provided by the host site full-scale wet FGD system reagent preparation system) and with inhibited, natural or forced oxidation. The flue gas contactor includes a single spray nozzle and a perforated plate tray. There is a single mist eliminator stage after the gas absorption section. Figure 1 is a simplified piping and instrumentation diagram (P&ID) for the pilot wet FGD system.

The pilot FGD was installed to treat flue gas from downstream of the ESP on Monticello Unit 3. It could treat flue gas from either upstream or downstream of a mercury oxidation catalyst pilot unit also installed on Unit 3. The wet FGD pilot unit was operated using slurry from the full-scale FGD system at Monticello as the initial charge to the reaction tank; thus the testing started with near steady-state liquor and solids compositions. All of the testing was conducted in the LSFO mode, as the full-scale FGD system operates. Finely ground limestone reagent slurry from the full-scale system was used as makeup for the pilot FGD, so any impacts of limestone constituents on mercury capture should be the same for the pilot FGD as for the full-scale FGD system.

TMT-15 solution was metered into the FGD slurry recycle pump discharge line with a small diaphragm pump. The injection location is marked on the P&ID in Figure 1. The solution flow was introduced through an existing pressure gauge fitting on the line. The TMT-15 solution was diluted, then pumped out of a 5-gallon plastic container placed on a digital weighing scale. Diluted TMT solution flow rates were set by adjusting the pump stroke, and verified by periodically noting the change in weight of the container. The TMT-15 injection rates were so low that dilution below the normal 15 wt% was required to get the injection rate up to a measurable and controllable value.

As mentioned above, a dewatering loop was added to treat the FGD absorber blow down slurry for the steady state TMT test, so that fine mercury-TMT salts could be separated from the bulk gypsum byproduct. The hydrocyclone loop includes a Krebs 2-inch polyurethane hydrocyclone, a magnetic flow meter to measure the slurry feed rate to the hydrocyclone, a hydrocyclone feed pressure indicator, and a 200-gallon hydrocyclone underflow tank. The hydrocyclone overflow can be directed to a plant sump or to the blow down holding tank on the pilot wet FGD skid. Figure 2 shows a schematic of the dewatering loop.
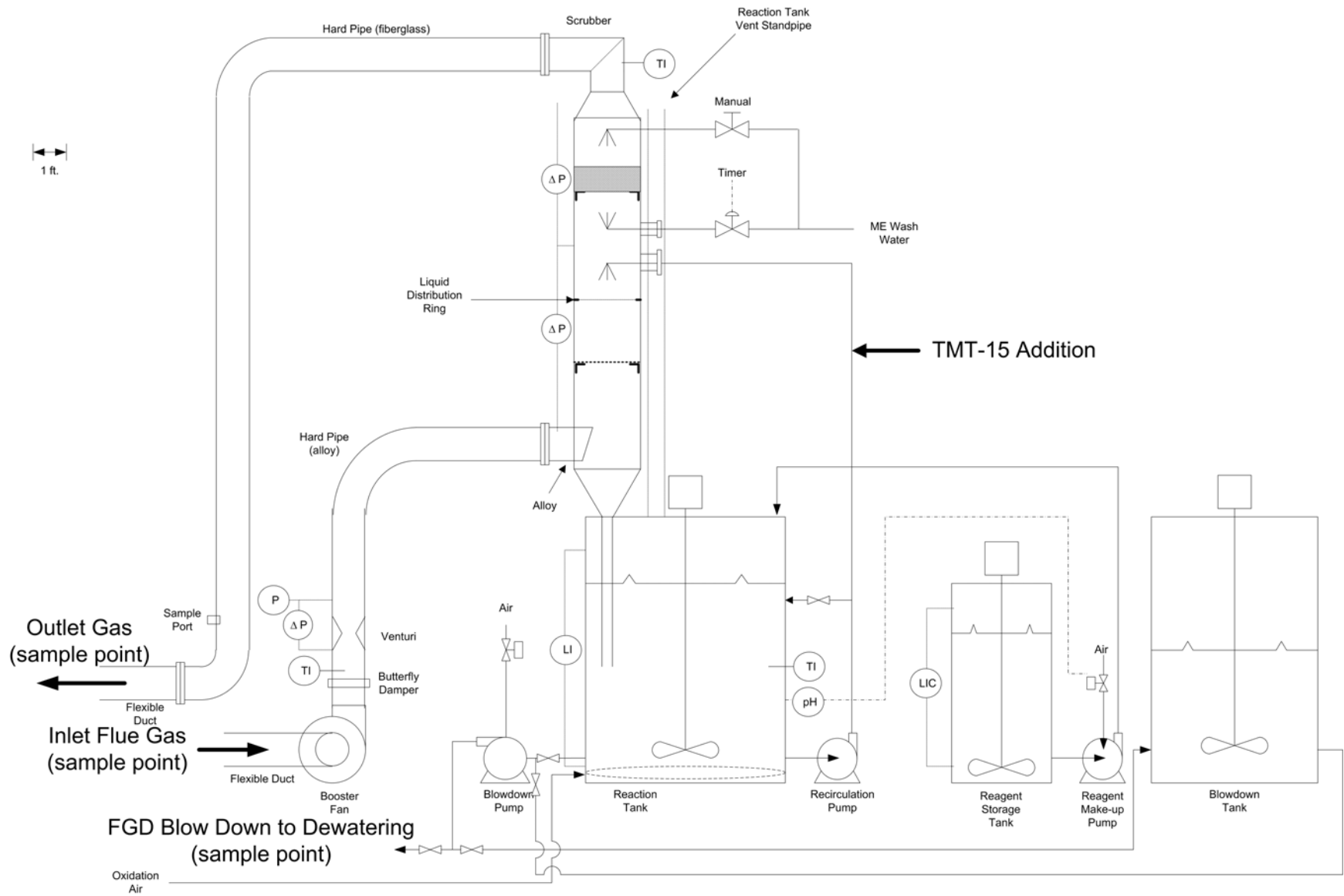
Figure 1. Simplified P&ID for Pilot Wet FGD System
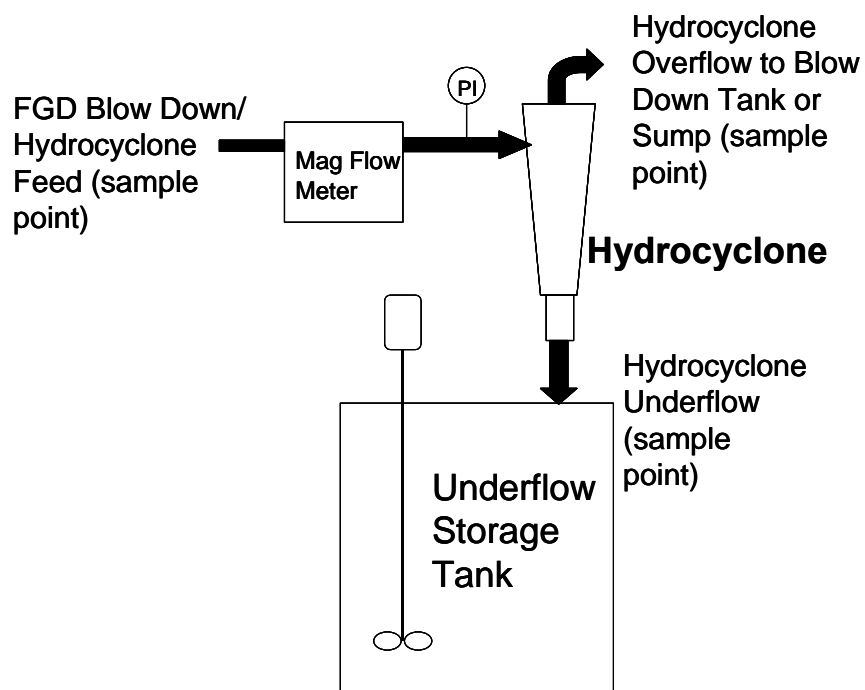
Figure 2. Schematic of Pilot Wet FGD Absorber Blow Down Slurry Dewatering

Mercury SCEM

During pilot FGD operation, flue gas mercury measurements were made using a mercury SCEM developed for EPRI, as illustrated in Figure 3. Flue gas was pulled from an inertial gas separator (IGS) filter installed at either the FGD absorber inlet or outlet location. The IGS filter consists of a heated stainless steel tube lined with sintered material. A blower is used to pull a flue gas sample at high velocity through the sintered metal section. A secondary sample stream is pulled across the sintered metal filter at a rate of about 1 L/min and then is directed to the mercury analyzer through a series of impinger solutions using a Teflon-lined pump.

To measure total mercury in the flue gas, the impinger solutions consist of stannous chloride ($SnCl_2$) followed by a sodium carbonate (Na_2CO_3) buffer and sodium hydroxide (NaOH). The $SnCl_2$ solution reduces all flue gas mercury species to elemental mercury. After passing through the $SnCl_2$ impinger, the gas flows through the Na_2CO_3 and NaOH solutions to remove acid gases, thus protecting the downstream, analytical gold surface.

Gas exiting the impinger solutions flows through a gold amalgamation column, where the mercury in the gas is adsorbed at less than 100°C. After adsorbing mercury onto the gold for a fixed period of time (typically 1 to 5 minutes), the mercury concentrated on the gold is thermally desorbed (>700°C) from the column into clean air. The desorbed mercury is sent as a concentrated stream to a cold-vapor atomic absorption spectrophotometer (CVAAS) for analysis. The total flue gas mercury concentration is measured semi-continuously, typically with a one- to five-minute sample time followed by a one- to two-minute analytical period.
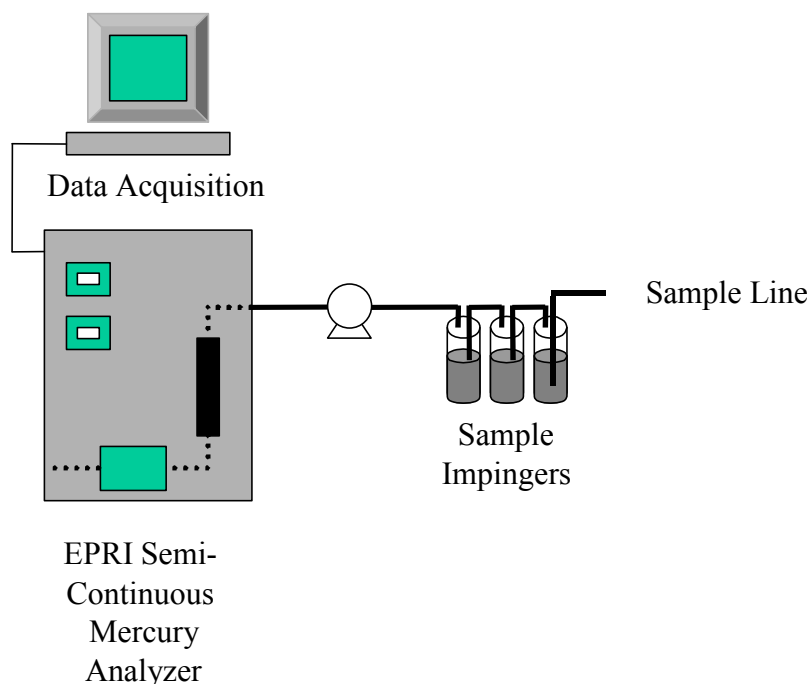
Figure 3. Schematic of Mercury SCEM

To measure elemental mercury in the flue gas, the stannous chloride impinger is replaced with an impinger containing either tris(hydroxymethyl)aminomethane (Tris) or potassium chloride (KCl) solution. The Tris solution has been shown in previous EPRI studies to capture oxidized mercury while allowing elemental mercury to pass through without being altered, while KCl is used to collect oxidized mercury in the Ontario Hydro train. Mercury passing through the Tris or KCl solution to the gold is analyzed as described above and assumed to be elemental mercury only. The difference between the total mercury concentration (stannous chloride solution) and elemental mercury concentration (Tris or KCl solution) is assumed to be the oxidized mercury concentration.

Two analyzers are typically used to semi-continuously monitor FGD inlet and outlet gas mercury concentrations. The analyzers are switched intermittently between sampling for elemental versus total mercury concentrations.

Test Plan

Table 1 summarizes sampling and analysis plan for this testing. During both the parametric and steady state test weeks, mercury removal and speciation data were collected across the pilot FGD on day shift using the Hg SCEM as described above. Over the last two days of the steady state test, triplicate Ontario Hydro method measurements were made at the pilot unit inlet and outlet.

Table 1. Sampling and Analysis Activities for Monticello Wet FGD Pilot Additive Tests

Location	Sample Type	Frequency	Planned Analyses*
FGD inlet/outlet	Flue gas	Daily, day shift	Hg concentration and speciation by Hg SCEM
		Triplicate runs, Thursday/Friday of week 2	Hg concentration and speciation by Ontario Hydro method
FGD reagent	Slurry	Once per week	Hg concentration
FGD makeup water	Liquor	Once per week	Hg concentration
FGD reaction tank/ blow down liquor	Filtered and preserved liquor	Daily	FGD chemistry, Hg concentration
FGD reaction tank/ blow down solids	Filtered and preserved slurry solids	Daily	Hg concentration
	Whole slurry sample	Daily	Wt% solids, Hg concentration, FGD chemistry
FGD reaction tank/ blow down fines	Whole slurry sample, wet sieved off site	Daily	Hg concentration, particle size, wt% of whole slurry, SPLP
FGD reaction tank/ blow down bulk solids	Whole slurry sample, wet sieved off site (multiple size fractions)	Daily	Hg concentration, particle size, wt% of whole slurry

*Only a selected subset of daily samples were analyzed

Each test day, one set of FGD reaction tank/absorber blow down liquor and reaction tank/absorber blow down solid/slurry samples was collected and preserved. Preservation techniques involved immediate filtering to separate the slurry liquor from the solids, then adding preserving solutions to the liquor portion to prevent precipitation, reduction, oxidation, or other chemical reactions of the analyte(s) of interest. No further preservation was required for the solids once separated from the liquor.

During the steady-state tests where dewatering equipment was available, hydrocyclone overflow and underflow samples were also collected. For the first week of parametric tests, dewatering equipment was not available on the pilot FGD system. The fine solids and bulk gypsum were size separated in the laboratory by settling, and mercury concentrations were measured by size fraction.

These samples were analyzed off site for mercury and FGD species concentrations, and for particle size distributions in the solids. These results were used to determine any impacts of the additive on FGD chemistry (e.g., reagent utilization or sulfite oxidation) and to construct cursory

mercury balances around the FGD system, including how the mercury phase separates between the liquor, fine solids and bulk gypsum.

Pilot JBR Additive Tests at Plant Yates

Overview

The second pilot-scale field effort was to conduct wet FGD additive tests at Southern Company's Georgia Power Plant Yates. Tests were conducted on a pilot-scale jet bubbling reactor (JBR) wet FGD absorber installed on Unit 1 at Plant Yates. Two weeks of pilot-scale additive screening tests were conducted in August 2005. Hg SCEMs were used to measure absorber inlet and outlet mercury concentrations and speciation to quantify net mercury removal and mercury re-emissions under baseline (no TMT) and additive conditions. The primary test variable was the TMT-15 dosage rate.

Description of Unit 1 at Plant Yates

Unit 1 at Plant Yates is rated at nominally 123-MW of generating capacity, although the unit load is typically no greater than 110 MW. It fires low sulfur (~ 1%) Eastern bituminous coal. The coal contains an average of 0.05 ppm of mercury and 220 ppm of chloride. The ESP outlet flue gas typically contains about 60% Hg^{+2} and 40% Hg^0 at a total concentration of 10 $\mu g/Nm^3$ or less. The host unit has a tangentially fired PC boiler and uses a small (design SCA of 173 ft^2/kacfm) cold-side ESP with gas conditioning for particulate control, and the CT-121 wet FGD process, which employs a JBR flue gas contactor, for SO_2 control. There is no selective catalytic reduction (SCR) unit installed on this unit.

Figure 4 shows a simplified schematic of a JBR. A JBR configuration is different than a conventional spray/tray absorber tower, such as was tested at Monticello, in that there is not a high-volume slurry recycle from a reaction tank to nozzles in the absorber vessel. Instead, in a JBR the flue gas is bubbled into the FGD slurry through downcomer tubes to result in intimate gas/slurry contacting. Limestone slurry is added in the upper, absorption zone of the JBR, and FGD byproduct slurry is withdrawn from a lower, reaction zone of the JBR. A small slurry recycle stream (not shown in the figure) is used to quench the flue gas before it enters the JBR.

Pilot JBR

Figure 5 is a schematic of the pilot JBR, which is trailer mounted. It is sized to treat a flue gas flow rate of 2,725 acfm at saturated gas (scrubber outlet) conditions. It was previously installed as a "polishing," clear solution (i.e., not a slurry) scrubber downstream of the full-scale JBR for another test program at Plant Yates. For the TMT-15 additive tests, the pilot JBR was reconfigured in parallel with the full-scale JBR to treat hot, SO_2-containing flue gas. That is, the pilot JBR inlet duct was re-routed to originate upstream of the full-scale JBR rather than downstream. The pilot JBR was also modified to add a slurry pump to feed slurry to the spray nozzles shown for flue gas quenching during LSFO operation. An existing spray liquor recycle vessel was blanked off, and the mist eliminator upstream of the pilot JBR was removed. These
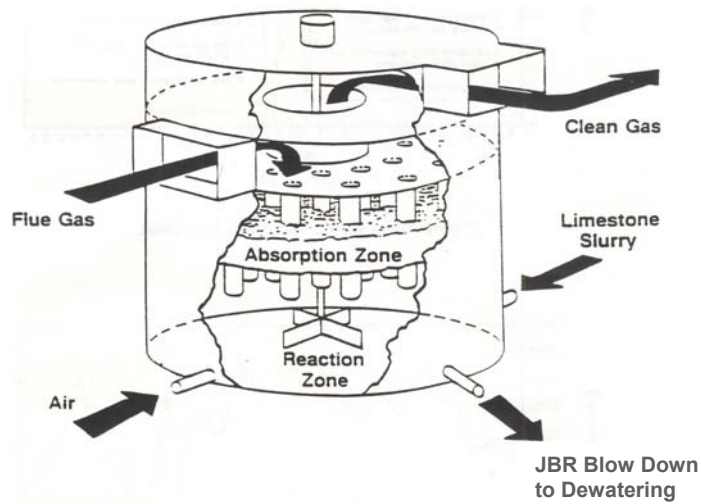
Figure 4. Simplified Schematic of a JBR

Source: Burford et al, "Plant Yates ICCT CT-121 Demonstration Results of Parametric Testing," 1993
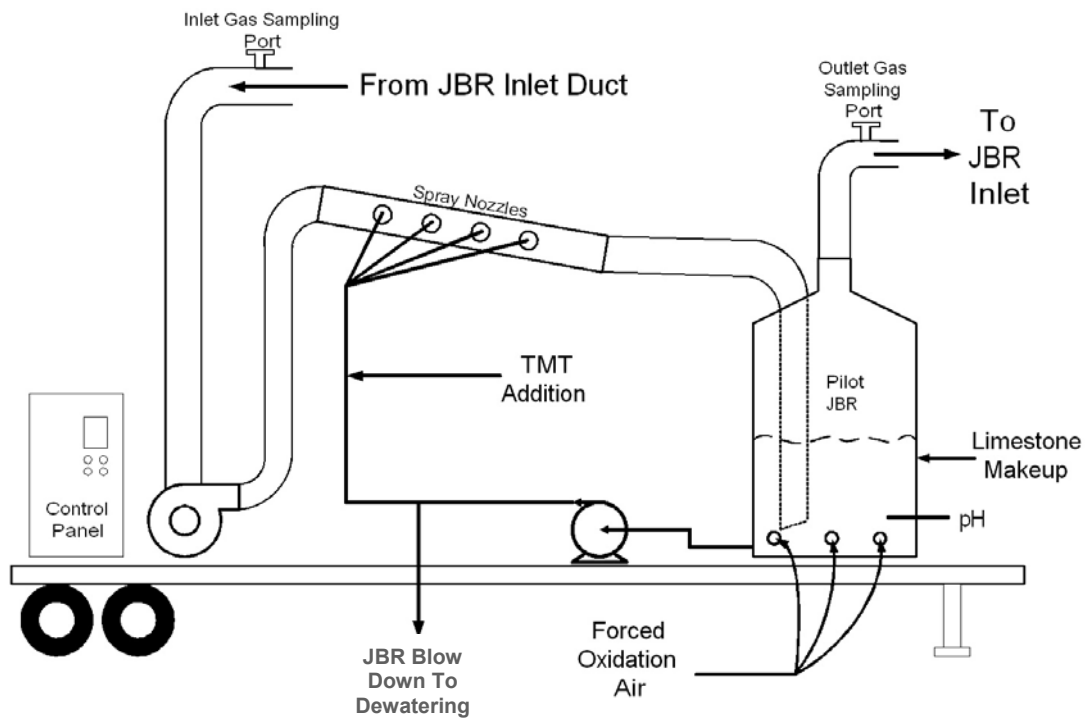
Figure 5. Schematic of 1-MW Pilot JBR Wet FGD

changes better simulate the configuration of the full-scale JBR. Finally, forced oxidation air was added at the bottom of the pilot JBR through spargers spaced around its circumference. Figure 5 reflects all of these modifications made to the pilot JBR prior to the TMT tests.

The EPRI hydrocyclone dewatering loop, as described above for the Monticello tests and illustrated in Figure 2, was also used to separate mercury-TMT fines from the gypsum byproduct in the pilot JBR blow down slurry. However, the magnetic flow meter was not available at the time of the Yates testing, so the hydrocyclone feed rate was adjusted to achieve a desired hydrocyclone inlet pressure reading.

As described above for the full-scale system, in a JBR there is not a high-volume recirculating slurry stream as in a spray/tray tower that would be an equivalent injection point for TMT. There is, however, a small slurry recycle stream used to quench the flue gas before it enters the JBR downcomer tubes. For these pilot tests, the TMT-15 was added with the small quench slurry stream.

Two equipment items were not included in the pilot JBR and had an adverse effect on pilot additive test results, as will be discussed in the following section. One item not included was a mechanical agitator in the reaction zone. It was thought by Southern Company personnel who readied the pilot unit for LSFO operation that the action of forced oxidation air, introduced through spargers around the circumference of the JBR reaction zone, would be adequate to keep the slurry well mixed. However, this did not prove to be the case, and evidence was seen of poor mixing of the JBR slurry during the tests.

For example, the slurry pH was measured with an insertion-style pH probe mounted through the side of the JBR up in the absorption zone. The measurement and control of slurry pH was quite sluggish during these tests, with the pH being slow to increase when fresh limestone slurry was made up, and slow to drop as the limestone was utilized. Also, blow down from the JBR was taken as a slipstream of the slurry being pumped from the reaction zone up to the flue gas quench nozzles in the duct upstream of the JBR. Samples taken from this stream showed inconsistent results with respect to pH, weight percent solids, and apparent limestone utilization.

Another item not included in the pilot JBR was a mist eliminator. It was felt that since the flue gas exiting the pilot JBR was being ducted directly into the full-scale JBR, removal of mist carryover would not be necessary. However, as described below, the high apparent mist loading in the pilot JBR outlet gas interfered with the ability to measure the outlet flue gas mercury concentration and speciation.

Mercury SCEM

The same mercury SCEMs as described above for the Monticello tests were used to measure mercury removal across the pilot JBR. One SCEM was used to monitor the pilot JBR inlet gas and the other to monitor the outlet gas. Please refer to the previous discussion for a description of these devices.

As mentioned above, the pilot JBR did not have a mist eliminator for the outlet gas, which led to a considerable amount of entrained mist in the flue gas being sampled at the outlet location by the SCEM. This, in turn, led to measurement problems with the pilot JBR outlet gas sample. Because the IGS filter used in the mercury SCEM sampling train is heated to minimize mercury adsorption by solids in the sample gas, it is speculated that this heating led to evaporation of mist

carryover liquor, releasing aqueous mercury, and desorption of mercury from mist carryover solids. As a result, the pilot JBR outlet flue gas Hg SCEM results from these tests are not believed to be representative.

Test Plan

Table 2 summarizes the sampling and analytical activities that were planned for the pilot JBR tests conducted at Plant Yates.

Table 2. Planned Sampling and Analysis Activities for Yates JBR Pilot Additive Tests

Location	Sample Type	Frequency	Planned Analyses*
JBR inlet/outlet	Flue gas	Daily, day shift	Hg concentration and speciation by Hg SCEM
Limestone reagent	Slurry	Once per week	Hg concentration
JBR makeup water	Liquor	Once per week	Hg concentration
JBR blow down to dewatering, liquor	Filtered and preserved liquor	Daily	FGD chemistry, Hg concentration
JBR blow down to dewatering, solids	Filtered and preserved slurry solids	Daily	Hg concentration
	Whole slurry sample	Daily	Wt% solids, Hg concentration, FGD chemistry
JBR blow down to dewatering fines (Hydrocyclone overflow)	Filtered and preserved liquor and solids; Whole slurry sample	Daily	Hg concentration by phase, particle size, wt% solids
JBR blow down to dewatering gypsum product solids (Hydrocyclone underflow)	Filtered and preserved liquor and solids; Whole slurry sample	Daily	Hg concentration by phase, particle size, wt% solids

*Only a selected subset of daily samples to be analyzed

Full-scale Additive Test at High-sulfur Eastern Bituminous Coal Site

Overview and Plant Description

In July 2006, a full-scale TMT-15 test was conducted at IPL's (an AES company) Petersburg Station, Unit 2. Unit 2 is rated at 455-MW of gross generating capacity, and has a tangentially fired boiler that fires Indiana high-sulfur coal. Air pollution control equipment includes SCR for NO_X control, a cold-side ESP, and a wet FGD system. The presence of an SCR in the flue gas path was expected to increase the mercury oxidation percentage in the FGD inlet flue gas; however, the predominant oxidized mercury form was still expected to be mercuric chloride. The wet FGD system operates in LSFO mode and produces wallboard-grade gypsum. A single, open spray tower module treats all of the flue gas from Unit 2 (no bypass).

IPL had previous data that indicated mercury re-emissions from the Unit 2 wet FGD system, and so was interested in testing TMT-15 for its effectiveness in controlling re-emissions. A test program was planned whereby baseline data were collected, then TMT-15 was added in increasing dosage rates of 10 mL/ton of coal, 20 mL/ton, and 40 mL/ton. The units of mL of TMT-15 injected per ton of coal fired is an Evonik Degussa dosing rate convention. After one day of operation at each TMT-15 rate, the "optimum" injection rate was selected and operation continued at that rate for nearly a week. FGD inlet and stack mercury concentrations were to be monitored by mercury SCEMs as described previously in this section. Also, triplicate Ontario Hydro runs were made at the FGD inlet and stack during baseline operation and after one week of operation with TMT injection. Periodically, FGD absorber slurry samples were collected and stabilized for off-site mercury analyses over the two-week test period.

Evonik Degussa recommends that TMT-15 be spiked into the FGD absorber slurry on a continuous basis, and injected into the slurry as it is being fed to the absorber nozzles. This minimizes the opportunity for TMT to precipitate with other divalent transition metals such as copper and zinc prior to coming into contact with freshly absorbed mercury in the absorber vessel. However, this was not possible at Petersburg Unit 2 because there were no available ports in the scrubber slurry piping through which TMT-15 could be injected, and the piping is all rubber-lined, making it nearly impossible to weld on new fittings. Consequently, after discussions between URS, IPL and Evonik Degussa, an alternate injection location was agreed upon.

Before describing the injection location, it is helpful to describe the FGD blow down slurry dewatering scheme at Petersburg Unit 2. The dewatering scheme, which is illustrated in Figure 6, consists of two stages of hydrocyclones followed by a vacuum belt filter. The first stage of hydrocyclones separates a low-weight-percent-solids slurry that is mostly returned to the absorber, while most of the underflow is sent to a secondary dewatering system located some distance from the absorber. At times the primary hydrocyclone underflow stream is returned to the Unit 2 FGD absorber to control wt% solids levels in the absorber recirculating slurry.
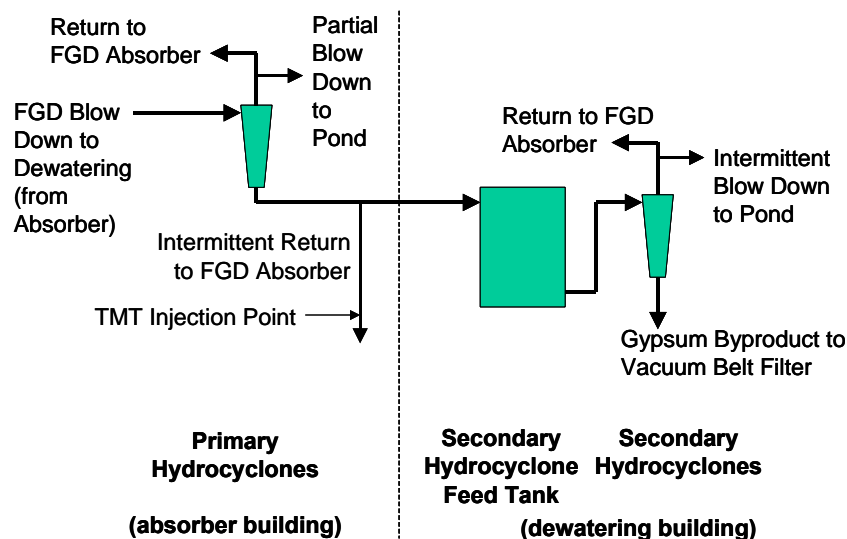
Figure 6. Schematic of Byproduct Slurry Dewatering Scheme for Petersburg Unit 2

In the secondary dewatering system, the primary hydrocyclone underflow stream is fed to a second stage of hydrocyclones that further concentrate the solids in their underflow. This stream is then sent to the vacuum belt filter to produce the wallboard grade gypsum byproduct. The secondary hydrocyclone overflow and the vacuum belt filter filtrate are returned to the FGD absorber.

TMT-15 was added to the underflow return line from the primary hydrocyclones to the absorber, at a location within the absorber building. When the primary hydrocyclone underflow was being sent to secondary dewatering (which was most of the time), the TMT-15 injection was the only flow in this line. When the primary hydrocyclone underflow was being recycled to the absorber to build wt% solids in the slurry, the TMT-15 was mixed with the underflow recycle. This cycling may have affected the TMT-15 addition rate to the absorber reaction tank.

The TMT injection was implemented with small, fractional-horsepower 120-V diaphragm pumps. TMT-15 was pumped through 3/8-in. tubing out of 65-kg plastic drums. The drums were changed as they were emptied. A total of 27 drums were used over the course of the test.

One of the planned measurements during the test, mercury SCEM measurements of absorber inlet total mercury and oxidized mercury concentrations, was not made successfully during the test program. The SCEM at the FGD inlet showed poor recovery of mercury spikes during the baseline test, which was speculated to be due to an interference present in the flue gas, possibly ammonia slip from the SCR. After several days of trying to troubleshoot and correct this problem, the atomic absorption spectrophotometer on the mercury SCEM in service at the stack failed. Because of the previous interference problem with measurements at the FGD inlet, it was decided to move the FGD inlet analyzer to the stack and not to replace the analyzer that failed at the stack. The test program was completed with only the stack SCEM in service. The SCEM was identical to the one described above for the pilot-scale testing at Monticello Station.

While the stack mercury SCEM measurements were conducted as planned, there was no indication of the effectiveness of TMT-15 at preventing mercury re-emissions during the conduct of the test; both scrubber inlet and stack elemental mercury concentrations are required to quantify mercury re-emissions. Since FGD liquor mercury analyses were conducted off site, neither was there an indication of the effectiveness of TMT in precipitating mercury from the FGD absorber liquor. Thus, there was no on-site, real-time indicator of TMT effectiveness during the conduct of the test. Instead, the effectiveness of TMT injection was determined later, from Ontario Hydro gas-phase mercury concentration data and FGD liquor and solids mercury analyses.

The test was completed as planned, with the screening for TMT dosage rate over the first several days. However, since there was no real-time feedback on the effectiveness of the three TMT-15 dosages tested, as a conservative measure it was decided to conduct the steady-state TMT injection test at the highest planned dosage rate of 40 mL/ton of coal.

Test Plan

Table 3 shows the test sequence and Table 4 summarizes sampling and analysis plan for this testing. The test sequence involved an initial baseline measurement period followed by three days of successive increases in TMT-15 injection rates. With each increase in rate, the FGD reaction tank was spiked with TMT-15 to the calculated steady state dosage in the tank, then TMT-15 was continuously added to maintain that dosage. After the three days of increasing TMT-15 dosage, the system was operated for nearly a week at a steady TMT-15 injection rate, which was chosen as 40 mL/ton of coal fired.

Table 3. Test Sequence for Petersburg Full-scale TMT-15 Additive Tests

Date	TMT-15 Dosage Rate (mL/ton of coal fired)	Comment
7/11/2006	0	Set up
7/12/2006	0	Baseline
7/13/2006	10	Baseline, began injection after noon
7/14/2006	20	Changed to new rate after noon
7/15/2006	40	Changed to new rate after noon
7/16/2006	40	
7/17/2006	40	
7/18/2006	40	
7/19/2006	40	
7/20/2006	40	Stopped injection at 14:00

Table 4. Sampling and Analysis Plan for Petersburg Full-scale TMT-15 Additive Tests

Location	Sample Type	Frequency	Planned Analyses
FGD inlet/Stack	Flue gas	Daily, day shift	Hg concentration and speciation by Hg SCEM (stack only)
		Triplicate runs, baseline and end of steady-state TMT injection period	Hg concentration and speciation by Ontario Hydro method
FGD reagent	Slurry	Once per week	Hg concentration
FGD makeup water	Liquor	Once per week	Hg concentration
FGD reaction tank/ blow down to dewatering liquor	Filtered and preserved liquor	Daily	Hg concentration
		Baseline and end of steady-state TMT injection period	FGD chemistry

Table 4. (continued)

Location	Sample Type	Frequency	Planned Analyses
FGD reaction tank/ blow down to dewatering solids	Filtered slurry solids	Baseline and end of steady-state TMT injection period	Hg concentration, Wt% solids, FGD chemistry, particle size distribution
Primary hydrocyclone overflow	Filtered and preserved liquor	Daily	Hg concentration
Primary hydrocyclone overflow	Solids	Baseline and end of steady-state TMT injection period	Hg concentration, wt% solids, particle size distribution
Primary hydrocyclone underflow	Filtered and preserved liquor, solids	Baseline and end of steady-state TMT injection period	Hg concentration, wt% solids, particle size distribution
Secondary hydrocyclone feed	Filtered and preserved liquor, solids	Baseline and end of steady-state TMT injection period	Hg concentration, wt% solids, particle size distribution
Secondary hydrocyclone overflow	Filtered and preserved liquor, solids	Baseline and end of steady-state TMT injection period	Hg concentration, wt% solids, particle size distribution
Secondary hydrocyclone underflow	Filtered and preserved liquor, solids	Baseline and end of steady-state TMT injection period	Hg concentration, wt% solids, particle size distribution
Byproduct Gypsum	Solids	Baseline and end of steady-state TMT injection period	Hg concentration

Several times during the test, the line into which TMT-15 was spiked had to be taken out of service to repair leaks (that were unrelated to TMT-15 injection). During these periods, the TMT injection had to be shut down but the Unit 2 FGD system remained in operation. To account for these periods where TMT-15 could not be injected, the FGD reaction tank was spiked with TMT-15 in the amount that would have been injected during the down time as soon as the line was put back in service. Table 5 is an event log that shows TMT-15 dosing start and stop times.

During both the parametric and steady-state injection rate test periods, mercury removal and speciation data were collected at the Unit 2 stack on day shift using the Hg SCEM as described earlier in this section. During baseline operation prior to TMT-15 injection and over the last full day of the extended-duration test in the second test week, triplicate Ontario Hydro method measurements were made at the Unit 2 FGD inlet and outlet (stack) locations.

Each test day, one set of FGD reaction tank/absorber blow down liquor and solid samples was collected and preserved. Preservation techniques involved immediate filtering to separate the slurry liquor from the solids, then adding preserving solutions to the liquor portion to prevent precipitation, reduction, oxidation, or other chemical reactions of the analyte(s) of interest. No further preservation was required for the solids once separated from the liquor. Whole slurry samples were also retained for later measurement of weight percent solids levels.

Table 5. TMT-15 Dosing Event Log

Date/Time	Event
7/13/2006 14:20	Started initial spike for 10 mL/ton
7/13/2006 20:16	Stopped TMT injection due to leak
7/14/2006 2:43	Resumed injection
7/14/2006 15:50	Adjusted rate to 20 mL/ton
7/15/2006 14:53	Begin spike to 40 mL/ton
7/16/2006 7:53	Stopped TMT injection because of absorber box leak
7/16/2006 11:57	Resumed injection
7/17/2006 0:00	Stopped injection due to leak
7/17/2006 17:49	Resumed injection
7/18/2006 8:30	Stopped injection due to leak
7/19/2006 1:00	Resumed injection
7/20/2006 14:00	End TMT injection

During the baseline period and at the end of the steady-state test period, samples were collected and preserved from throughout the Unit 2 absorber blow down dewatering system, including the primary and secondary hydrocyclone overflow and underflow, horizontal belt filter feed slurry, and product gypsum.

These samples were analyzed off site for mercury and FGD species concentrations, and for particle size distributions in the solids. These results were used to determine any impacts of the additive on FGD chemistry (e.g., reagent utilization or sulfite oxidation) and to determine how the mercury phase separated between the liquor, fine solids and bulk gypsum.

Full-scale Additive Test at Plant Yates

Overview

Two full-scale scrubber additive tests were conducted at Southern Company's Plant Yates Unit 1, which was described above for the Task 4 pilot-scale tests conducted there. Figure 7 illustrates the Plant Yates flue gas configuration. The JBR on which the additive testing was conducted was also described earlier.

A test program was planned for evaluating TMT-15 for its effectiveness at controlling re-emissions at full scale whereby baseline data were collected, then TMT-15 would be added continuously at an "optimum" dosage rate for 30 days to allow for steady-state testing. FGD inlet mercury concentrations were monitored by a mercury semi-continuous emissions monitor (SCEM), while stack mercury concentrations were monitored by an installed plant continuous emissions monitor (CEM). The SCEM was described previously in this section, and the plant
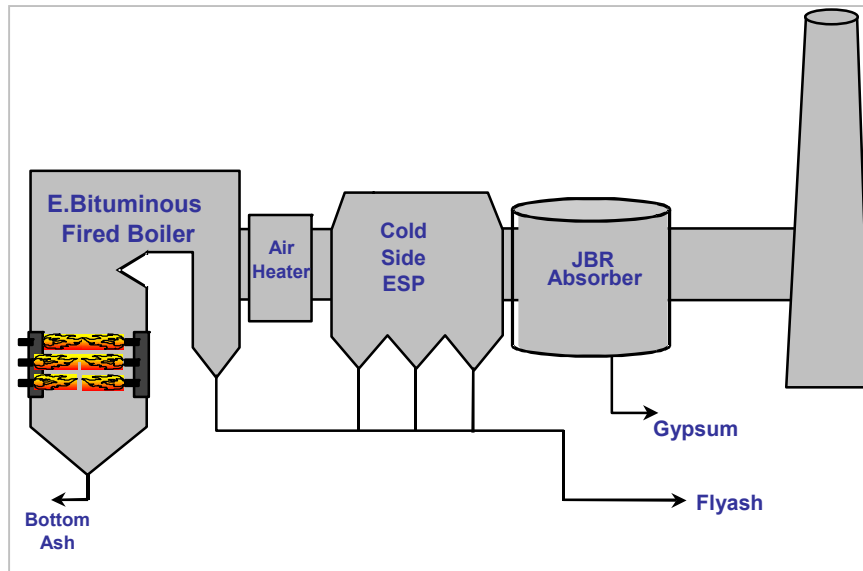
Figure 7. Plant Yates Flue Gas Configuration

mercury CEM is described below. Also, triplicate Ontario Hydro runs were made at the FGD inlet and stack during baseline operation and after steady-state operation conditions with TMT-15 injection were achieved.

The JBR on Yates Unit 1 is equipped with a hydrocyclone that separates a low-weight-percent, fine-solids slurry that is mostly returned to the JBR, while most of the underflow is sent to a gypsum stack/pond located some distance from the JBR. At times the hydrocyclone underflow stream is instead returned to the Unit 2 FGD absorber while the overflow is sent to the gypsum stack, to control weight percent solids levels in the absorber recirculating slurry. Figure 8 illustrates the Plant Yates dewatering scheme.
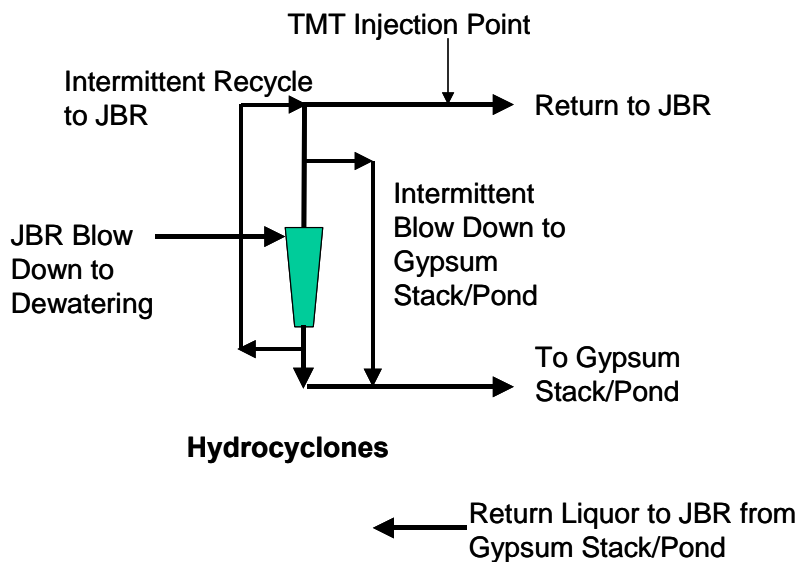
Figure 8. Illustration of Plant Yates JBR Slurry Dewatering Scheme

25

The planned 30-day test was begun in May 2007. TMT-15 was introduced to the JBR via the hydrocyclone return (which could be either underflow or overflow), allowing for continuous injection into the JBR slurry. The TMT-15 injection was implemented with small, fractional-horsepower 120-V diaphragm pumps. TMT-15 was pumped through 3/8-in. tubing out of 65-kg plastic drums. Drums were changed as they were emptied.

Periodically, FGD absorber slurry and hydrocyclone overflow and underflow samples were collected and stabilized for off-site mercury analyses. During baseline operation and after steady-state operation with TMT-15 injection was achieved, additional FGD absorber slurry and hydrocyclone overflow and underflow samples were collected and stabilized for off-site metals analyses. Samples of limestone reagent, makeup water and gypsum stack return liquor were also taken.

The effectiveness of TMT-15 at preventing mercury re-emissions during the test was observed by comparing inlet mercury SCEM elemental mercury concentrations to the stack total mercury concentration by CEM. The stack mercury CEM was not set up to speciate between oxidized and elemental mercury at the time. The JBR was expected to achieve greater than 90% removal of the inlet oxidized mercury, so the stack mercury was expected to be almost entirely in the elemental form. Since re-emissions are measured as an increase in flue gas elemental mercury concentration across a wet FGD system, comparison of inlet elemental mercury concentrations to stack total mercury concentrations should provide a reasonable indicator of the level of re-emissions, particularly on a relative basis.

However, the effectiveness of TMT-15 injection was ultimately determined by off-site analyses, from Ontario Hydro gas-phase mercury concentration data and FGD liquor and solids mercury analyses.

Due to an apparent lack of effectiveness at controlling re-emissions based on Ontario Hydro data, TMT-15 testing was stopped after 15 days. Subsequently, another scrubber additive, Nalco 8034, was substituted for TMT-15. A full 30-day test, plus baseline measurements, was conducted starting in August 2007 using Nalco 8034. The test measurements made during the Nalco 8034 test were the same as during the TMT-15 test as described above.

Plant Mercury CEM

The installed CEM unit on the Yates Unit 1 stack outlet location is a Thermo Mercury Freedom System (MFS). The MFS can determine elemental, oxidized, and total mercury in exhaust stacks of coal-fired boilers. The system uses a direct measurement atomic fluorescence method that precludes the use of argon tanks and gold amalgamation. The system extracts a small sample flow from the flue gas stream and immediately dilutes it inside the probe. Any oxidized mercury in the diluted sample is then converted to elemental mercury in a dry heated converter to obtain a total Hg measurement. This diluted, converted sample is continuously transported to the mercury analyzer where it is analyzed using atomic fluorescence technology developed specifically for measuring mercury vapor concentrations on a continuous, real-time basis. Continuous readings of the MFS can be averaged and reported at one-minute, six-minute or hourly intervals.

A "proprietary" dry scrubber component enables the the MFS to measure elemental mercury concentrations separately from total mercury, and the oxidized mercury concentration is derived by subtraction, like in the SCEM measurements described above.

The MFS consists of a sampling probe with an integrated converter, heated umbilical line, probe controller, saturated elemental mercury vapor calibrator, and an atomic fluorescence analyzer. The MFS can be audited by introduction of mercury calibration gas standards, which can be delivered directly to the probe inlet by the MFS umbilical. Figure 8 shows the Thermo MFS instrumentation and probe.

Figure 9. Thermo Mercury Freedom CEM Instrumentation and Probe

Test Plan

Table 6 shows the test sequence for the TMT-15 testing. The test sequence involved an initial baseline measurement period followed by continuous injection of TMT-15. Based on the results of previous pilot-scale testing at Plant Yates, a rate of 20 mL/ton of coal fired was selected to begin injection. The JBR was spiked with TMT-15 to a calculated steady-state dosage in the tank, then TMT-15 was continuously added to maintain that dosing rate. After four days at this rate with no apparent reduction in re-emissions, the rate was increased to a presumed maximum economic rate of 40 mL/ton of coal fired. Again, the JBR was spiked with TMT-15 to the calculated steady-state dosage in the tank, then continuously added to maintain the desired dosing rate. The system was operated for a further ten days at the higher steady TMT-15 injection rate.

During the baseline and TMT injection test periods, mercury speciation and removal data were collected using the Hg SCEM described above at the Unit 1 FGD inlet and using the plant CEM at the stack outlet location. During baseline operation prior to TMT-15 injection and during steady-state injection at the 40 mL/ton of coal fired rate, triplicate Ontario Hydro method measurements were made at the Unit 1 JBR inlet and outlet locations.

Table 6. Test Sequence for Yates Full-scale TMT-15 Additive Tests

Date	TMT-15 Dosage Rate, mL/ton of coal fired	Comment
5/14/2007	0	Set up
5/15 – 5/16/2007	0	Baseline
5/17/2007	20	Initial dosing spike ~10:00; began continuous injection
5/17 – 5/21/2007	20	
5/21/2007	40	Changed to new rate after noon
5/21 – 5/30/2007	40	Started injecting TMT-15 at a higher rate starting the afternoon of 5/29 to use up remaining inventory in drum
5/30/2007	40	Stopped injection ~18:00

Periodically during the baseline and injection test periods, a set of JBR reaction tank/absorber blow down liquor and solid samples and a set of hydrocyclone overflow and underflow liquor and solid samples were collected and preserved. Preservation techniques involved immediate filtering to separate the slurry liquor from the solids, then adding preserving solutions to the liquor portion to prevent precipitation, reduction, oxidation, or other chemical reactions of the analyte(s) of interest. No further preservation was required for the solids once separated from the liquor. Whole slurry samples were retained for later measurement of weight percent solids levels. Samples were also periodically collected and preserved from incoming streams to the Unit 1 JBR, including limestone reagent, makeup water and gypsum stack return liquor.

These samples were analyzed off site for mercury and FGD species concentrations, and for particle size distributions in the solids. These results were used to determine any impacts of the additive on FGD chemistry (e.g., reagent utilization or sulfite oxidation) and to determine how the mercury phase separated between the liquor, fine solids and bulk gypsum. Table 7 summarizes sampling and analysis events for this testing.

A 30-day test was performed using Nalco 8034 in August and September of 2007. The sampling and analysis plan for the Nalco 8034 testing remained the same as for the TMT-15 testing, as described in Table 2, with two exceptions. First, Yates plant personnel worked with the CEM vendor to provide speciated as well as total mercury concentration measurements at the stack location. Second, an additional SCEM analyzer was available during portions of the Nalco additive testing, so SCEM measurements were also performed at the stack location during the Ontario Hydro sampling periods.

Table 8 shows the test sequence for the Nalco 8034 testing. Because Nalco did not have an established dose rate reporting convention for the 8034 additive, URS chose to report the rates in units of grams of additive active ingredient injected per gram of FGD inlet Hg^{+2}. These units were chosen because it is the FGD inlet Hg^{+2} that is absorbed by the FGD system and that must be precipitated by the additive.

Table 7. Sampling and Analysis Events for Yates Full-scale Additive Tests

Location	Sample Type	Frequency	Planned Analyses
JBR inlet/outlet	Flue gas	Periodically, day shift, baseline and during additive injection	Hg concentration and speciation by Hg SCEM; Hg concentration by Plant CEM
		Triplicate runs, Baseline and during additive injection	Hg concentration and speciation by Ontario Hydro method
Limestone reagent	Slurry	Baseline and once per week of injection	Hg concentration
JBR makeup water	Liquor	Baseline and once per week of injection	Hg concentration
JBR blow down to dewatering slurry	Filtered and preserved liquor, whole slurry	Baseline and weekly during injection	FGD chemistry
JBR blow down to dewatering slurry	Filtered and preserved slurry liquor, solids	Baseline and weekly during injection	Hg concentration, metals
JBR blow down hydrocyclone overflow	Filtered and preserved slurry liquor, solids	Baseline and weekly during injection	Hg concentration, metals
JBR blow down hydrocyclone underflow	Filtered and preserved slurry liquor, solids	Baseline and weekly during injection	Hg concentration, metals
Gypsum stack return liquor	Liquor	Baseline and once per week of injection	Hg concentration
JBR blow down to dewatering slurry	Whole slurry, five 5-gallon buckets	Baseline and last week of injection	Ship to DOE contractor

Table 8. Test Sequence for Yates Full-scale Nalco 8034 Additive Tests

Date	Nalco 8034 Dosage Rate, g/g FGD Inlet Hg^{+2}	Comment
8/27/2007	0	Set up
8/28 – 8/29/2007	0	Baseline; scrubber pH 4.5
8/29/2007	400	Initial dosing spike ~ 15:00; began continuous injection
8/30 – 9/7/2007	875	Changed rate ~ 10:30 on 8/30
9/7 – 9/15/2007	525	Changed rate ~ 10:00 on 9/7
9/15 – 9/25/2007	525	Changed scrubber pH to 5.0 ~13:00
9/25 – 9/26/2007	525	Changed scrubber pH to 4.0 ~ 9:30
9/26/2007	>1000	Increased rate ~noon to empty additive container
9/27/2007		Stopped injection ~ 6:00

The values in the table should be considered nominal averages. The unit load varied during the test, with low load operation common overnight and on weekends. Also, the amount of oxidized mercury in the FGD inlet flue gas also varied over time. Because the test was not staffed with around-the-clock coverage to allow for hour-by-hour changes to dosing rates, the rate was periodically set to a value based on full-load operation and a typical FGD inlet Hg^{+2} concentration. For comparison of the Table 8 values for Nalco 8034 dosing rates with TMT-15 dosing rates, a TMT-15 rate of 40 mL/ton of coal fired is equivalent to approximately 200 g of TMT active ingredient per gram of Hg^{+2} in the JBR inlet gas.

Comparison of absorber inlet Hg measurements by SCEM with stack outlet Hg measurements by the plant CEM showed no decrease in re-emissions across the scrubber during the ten days of steady-state injection of TMT-15 at the 40 mL/ton of coal fired rate. This was confirmed by Ontario Hydro measurements. After 15 days of TMT-15 addition, testing was stopped so remaining project funds could be used to evaluate an alternative scrubber additive, Nalco 8034.

The test sequence for the Nalco 8034 portion of the test program involved an initial baseline measurement period followed by continuous injection of Nalco 8034. Nalco suggested an initial dosing rate of 250 g/g FGD inlet Hg^{+2}. Calculated quantities of Nalco 8034 injected were based on inlet baseline measurements of 3 $\mu g/Nm^3$ for Hg^{+2}. The JBR was spiked with Nalco 8034 to the calculated steady state dosage in the tank, then Nalco 8034 was continuously added to maintain that dosing rate. Due to unit load variation and fluctuations in inlet oxidized mercury concentration, the actual Nalco 8034 dosing rate averaged approximately 400 g/g FGD inlet Hg^{+2}. After a day at this rate with no clear reduction in re-emissions, the rate was increased to an average of 875 g/g FGD inlet Hg^{+2}. Again, the JBR was spiked with Nalco 8034 to the calculated steady-state dosage in the tank, then continuously added to maintain that dosing rate. The system was operated for a further eight days at the higher steady Nalco 8034 injection rate, still with no clear reduction in re-emissions.

As a higher injection rate was not economically desirable, and with concerns that a large surplus of Nalco 8034 in the JBR liquor may lead to reducing conditions, the injection rate was lowered to an average value of 525 g/g FGD inlet Hg^{+2}. No attempt was made to purge the additive from the reaction tank; when the change was implemented the Nalco 8034 addition rate was decrease to the new value and the concentration in the reaction tank was allowed to decay to the new steady-state value over time. The system was operated for a further eight days at this Nalco 8034 injection rate, although with no clear reduction in re-emissions based on SCEM/CEM data.

At the suggestion of Nalco Company technical representatives, the pH of the JBR slurry was raised from 4.5 to 5.0, as they felt this was more in the range of effectiveness for this additive. The system was operated at the higher pH for ten days with no apparent lowering of re-emissions.

Near the end of the end of the 30-day injection period, plant personnel altered the JBR operating conditions to prepare for a scheduled shutdown and maintenance outage. Slurry pH was reduced to 4.0, and the weight percent solids was reduced to facilitate cleanout of the JBR during the outage. These changes in FGD operating conditions may have influenced additive test results over the last few test days. Unit 1 was removed from service as planned on 9/28/07.

RESULTS AND DISCUSSION

This section provides details of technical results for the two pilot-scale TMT additive tests followed by results from the two full-scale additive tests. Results from each site are described in separate subsections.

Wet FGD Pilot Additive Tests at Monticello Station

Parametric Test Results

TMT-15 parametric test were conducted at Luminant Power's Monticello Unit 3 in April 2005, using the 0.5-MW pilot wet FGD system described in the previous section and operating in LSFO mode. The second week, consisting of a steady-state pilot TMT additive test, also in LSFO mode, was conducted at Monticello Unit 3 in late September 2005.

The one-week parametric test included baseline (no TMT) performance and four subsequent tests at increasing dosage rates of TMT-15. Evonik Degussa's reporting convention for TMT dosage is in "mL/ton of coal fired," where the mL dosage is as 15 wt% solution. The dosages tested included 0, 5, 10, 20 and 40 mL/ton of coal.

Mercury Removal Data

Baseline (no TMT addition) mercury removal data were measured for the pilot wet FGD system by mercury SCEM, using one analyzer each at the FGD inlet and outlet. These baseline results from April 25, summarized in Table 9, showed no evidence of mercury re-emissions (which would be seen as an increase in Hg^0 concentration across the FGD absorber). Instead, the results show significant removal of Hg^0, which was not expected since it is primarily Hg^{+2} that is removed by wet scrubbers. The results also show a lower than expected removal percentage of Hg^{+2}. Together, these two observations suggest that at the pilot FGD outlet location, the sample conditioning system for the mercury SCEM was oxidizing elemental mercury in the sample gas being delivered to the analyzer. This would produce a low bias for observed Hg^{+2} removal and a high bias for Hg^0 removal. Evidence of such a bias was seen in previous results for the outlet of this pilot wet FGD system when comparing Ontario Hydro method and SCEM results as part of another DOE-sponsored project.[5]

However, in spite of this suspected bias, it is apparent that the pilot wet FGD was removing some Hg^0. If only Hg^{+2} is removed by the wet FGD system, the inlet flue gas mercury oxidation percentage should represent an upper limit for the overall mercury capture percentage. The results in Table 9 show a higher overall mercury capture percentage across the pilot wet FGD than the inlet flue gas oxidation percentage, suggesting that some Hg^0 was being removed. Note that previous Ontario Hydro results for baseline (no TMT addition) testing, conducted with this pilot unit as part of another project mentioned above, also showed no evidence of re-emissions and a small percentage capture of Hg^0.[5] Therefore, these aspects of the SCEM results have been previously confirmed by another measurement method.

Table 9. Pilot FGD Mercury Removal Data, by SCEM

Date		TMT-15 Dose, mL/ton of coal fired	Pilot Unit Inlet Hg, μg/Nm³ @ 3% O_2		FGD Outlet Hg, μg/Nm³ @ 3% O_2		Hg Oxidation at Pilot Inlet, %	Total Hg Removal by FGD, %	Hg^{+2} Removal by FGD, %	Hg^0 Removal by FGD, %
			Total Hg	Hg^0	Total Hg	Hg^0				
4/25	Average	None	23.4	17.2	10.9	7.0	27%	53%	38%	59%
	Std. Dev.	-	2.2	2.1	1.2	0.7	-	-	-	-
4/26	Average	5	19.8	8.9	9.9	5.8	55%	50%	62%	35%
	Std. Dev.	-	3.9	1.5	3.6	0.6	-	-	-	-
4/27	Average	10	21.6	13.4	11.4	9.0	38%	47%	71%	33%
	Std. Dev.	-	3.6	1.6	2.5	1.1	-	-	-	-
4/28	Average	20	17.9	10.1	9.6	7.3	44%	47%	71%	28%
	Std. Dev.	-	7.4	0.8	3.8	2.5	-	-	-	-
4/29	Average	40	22.3	15.2	13.7	12.0	32%	39%	77%	21%
	Std. Dev.	-	3.4	4.2	2.8	1.4	-	-	-	-

With no measured re-emissions to be controlled, the test objectives were focused on other expected effects of TMT-15 injection, including reduced FGD liquor mercury concentration and the ability to form mercury salts that can be inertially separated from the byproduct gypsum. Tests were conducted at the four TMT dosage rates described above.

The pilot FGD mercury removal data for the TMT tests are also included in Table 9. Although there was some day-to-day variability, the results did not indicate any significant effect of the additive on FGD capture of mercury; no effect was expected since there was no evidence of re-emissions at baseline conditions. As did the baseline test results from April 25th, the results for all four TMT dosage tests showed no evidence of mercury re-emissions and showed some removal of elemental mercury.

Mercury Concentrations in FGD Liquor and Solids

The effects of the additive on FGD blow down liquor and byproduct solid mercury concentrations are shown in Figure 10 and Table 10 below, respectively. The FGD liquors were digested by EPA Method 7470 and analyzed by atomic fluorescence. The solids were digested by a modified version of EPA Method 3051 and also analyzed by atomic fluorescence. Results are shown as a function of TMT-15 dosage, in mL/ton of coal fired.
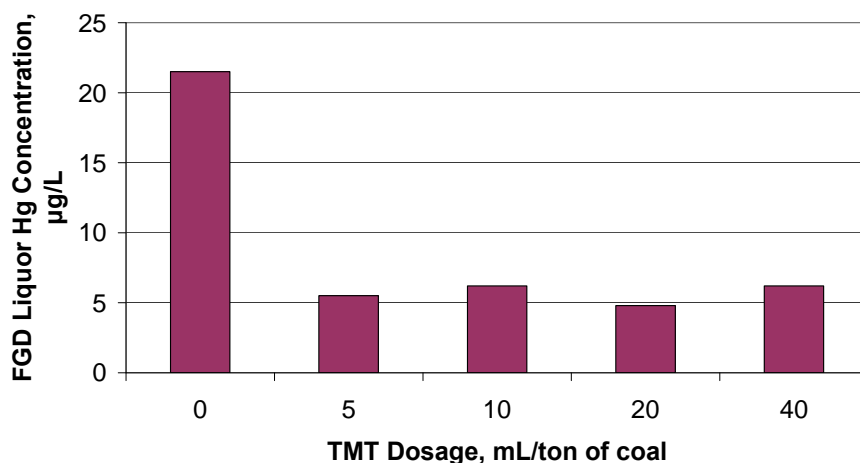
Figure 10. Effect of TMT Addition on FGD Blow Down Liquor Total Hg Concentration, μg/L

Table 10. Effect of TMT Addition on FGD Blow Down Solids Hg Concentrations

TMT Dosage (mL/ton of coal)	Wt% Gypsum Solids in Slurry	Gypsum Hg Content, μg/g (% of Hg in slurry)	Wt% Fines in Slurry	Fines Hg Content, μg/g (% of Hg in slurry)
0	11.6	1.7 (53%)	0.3	55 (44%)
5	9.2	1.2 (33%)	0.5	39 (65%)
10	10.7	1.2 (36%)	0.3	75 (62%)
20	10.0	1.0 (33%)	0.4	52 (63%)
40	9.3	1.2 (36%)	0.3	57 (61%)

The liquor mercury concentration results in Figure 10 show that the addition of TMT-15 lowered the mercury concentration by approximately a factor of four, but there was no apparent dosage effect. That is, the lowest dosage was nominally as effective as the highest dosage tested.

Regarding the solids mercury concentration results shown in Table 10, it was expected that adding TMT-15 would result in the formation of fine mercury-TMT salts that would be incorporated with the FGD solid byproducts. Some form of physical separation is required to separate the mercury-rich fine salts from the larger gypsum particles. While most LSFO FGD systems have hydrocyclones to dewater the byproduct slurry and separate fine solids, the pilot wet FGD system did not, at that time, include a hydrocyclone. Therefore, this separation had to be conducted in the laboratory, using gravity-based settling to allow the darker fines to be decanted from the rapidly settling and lighter colored gypsum solids.

The results in Table 10 show that after fines separation, the gypsum mercury concentration was reduced in the TMT addition tests from 1.7 μg/g for the baseline (no TMT) byproduct from April 25 to 1.0 to 1.2 μg/g during TMT injection. Again, there was no apparent effect of TMT injection

dosage on the result, indicating that a dosage even lower than 5 mL/ton of coal might have been adequate.

However, the reduction in gypsum mercury concentration of 30 to 40% seen with TMT addition was not as great as had been hoped. As can be seen in the data in Table 10, a small amount of fines was gravity separated from each slurry sample, and the fines contained a very high concentration of mercury. In the case of the TMT tests, the fines mercury content represented greater than 60% of the mercury content of the original FGD absorber blow down slurry. Even a small contamination of the byproduct gypsum with fines could markedly increase its measured mercury concentration.

FGD Solids Particle Size Analyses

These solids samples were sent out for subsequent measurement of particle size distribution, using a Leco "Lecotrac" particle size analyzer on solids dispersed in methanol. The results of these particle size analyses are summarized in Table 11. The results show that the settled gypsum phase had a mean particle size in the range of 40 to 45 μm, which is typical of gypsum sold for use in wallboard production. The fines have a much smaller particle size, with a mean of about 26 μm for the baseline (no TMT) test on April 25, and an even lower mean in the range of 15 to 20 μm for the TMT tests. Perhaps the formation of fine TMT-mercury salts tended to lower the mean particle size in the fines phase. Note that these particle size distribution measurements were made on solid samples that were filtered from the slurry on site, using 0.7-μm-pore-size filter media. Thus, these particle size distributions would not reflect the presence of any sub-micron-diameter solids (<0.7 μm diameter) that might have been present.

Table 11. Results of Particle Size Analyses of Gravity Separated Solids from TMT Parametric Tests

Test Date	TMT Dosage, mL/ton of coal	Sample	D_{10}*, μm	D_{50}*, μm	D_{90}*, μm
4/25	0 (Baseline)	Product Gypsum	24.4	43.7	70.8
		Fines	7.7	26.0	37.7
4/26	5	Product Gypsum	24.2	42.3	66.9
		Fines	2.9	14.9	30.6
4/29	40	Product Gypsum	26.0	39.5	52.1
		Fines	6.0	19.4	29.7

*Particle size at which 10%, 50%, or 90% of the sample mass is smaller

Figure 11 illustrates the details of the particle size data, for the 5 mL/ton TMT additive test on April 26. The data show that although the two solids fractions have substantially different particle size distributions, there is a percentage of the gypsum phase in the same particle size range as the bulk of the fines phase (~14 to 30 μm). Even one or two percent of mass in these

particle size ranges could represent high mercury content fines that contribute significantly to the mercury content of the gypsum.
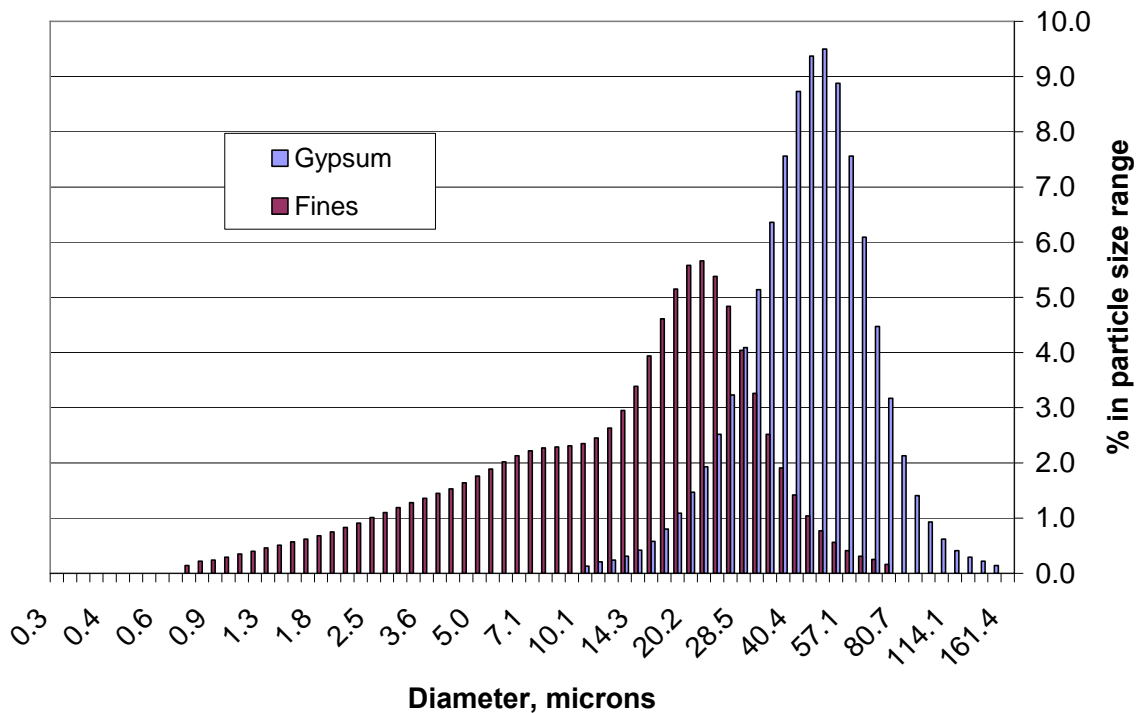
Figure 11. Comparison of Gypsum and Fines Particle Size Distributions for 5 mL/ton of coal TMT Additive Test

There was concern that gravity settling separation used in the laboratory may not have been as effective as hydrocyclones at separating fines from the bulk gypsum. Consequently, it was decided that for the subsequent steady-state TMT addition test, a hydrocyclone should be used to separate fines from the bulk gypsum in the field. EPRI funded the retrofit of a hydrocyclone to the pilot wet FGD system to provide for primary dewatering in the field. Follow-up TMT tests were conducted on the wet FGD pilot at Monticello in late September 2005 using this hydrocyclone to separate the fines from the bulk gypsum. The hydrocyclone was also used for primary dewatering of a slipstream of slurry from the pilot JBR test at Plant Yates. Results from that test are discussed later in this section.

FGD Operating Conditions

During the parametric tests, the reaction tank pH was typically controlled at a value of 5.7 to 5.8, and the reaction tank temperature was about 122 to 132°F. The lower temperatures typically corresponded with times after make up of cool fresh water to the reaction tank. Oxidation reduction potential (ORP) was checked with a hand-held instrument, and typically ranged from 250 to 325 mV. SO_2 removal was checked intermittently during the week with a Western Model 721 UV SO_2 Analyzer. Although the data are not reported here, the spot checks ranged from 85% to 97% SO_2 removal across the FGD system, with no apparent correlation with TMT dosage. Inlet SO_2 concentrations were around 300 ppmv (dry basis) at as-measured O_2 levels.

Samples of the wet FGD pilot reaction tank slurry were collected and preserved daily to determine FGD operating conditions during these tests. The results of those analyses are summarized in Table 12 for the FGD slurry liquor samples and Table 13 for the FGD slurry solid chemical analyses. They show that for all test days, the FGD system was operating as a highly oxidized forced oxidation system (>97% gypsum as the solid byproduct) with very high limestone reagent utilization. The liquor analyses show that concentrations of major species such as calcium, chloride and sulfate were relatively constant over the test week, although the TMT additions tests were about 10 to 20% more dilute in soluble species than the baseline test on April 25.

Table 12. Results of FGD Liquor Sample Analyses for the TMT Parametric Tests (mg/L)

TMT-15 Addition Rate (Date)	SO_3	SO_4	Cl^-	Mg	Ca	Na	CO_3
Baseline [no TMT] (4/25)	<8	5,807	1,779	1,363	623	951	144
5 mL/ton of coal (4/26)	<8	5,192	1,458	1,119	641	814	70
10 mL/ton of coal (4/27)	<8	5,390	1,506	1,152	639	840	74
20 mL/ton of coal (4/28)	<8	5,115	1,395	1,057	639	786	60
40 mL/ton of coal (4/29)	<8	5,305	1,446	1,184	639	811	47

Table 13. Results of FGD Solid Sample Analyses for the TMT Parametric Tests

TMT-15 Addition Rate (Date)	Slurry Wt% Solids	Solids Wt% Inerts*	Solids Analysis, mg/g					Solids Wt% Gypsum
			Ca	Mg	SO_4	SO_3	CO_3	
Baseline [no TMT] (4/25)	13.2	1.33	225	<1	544	<1	2	97.4
5 mL/ton of coal (4/26)	11.9	1.21	229	<1	549	<1	3	98.3
10 mL/ton of coal (4/27)	12.2	0.99	232	<1	550	<1	3	98.5
20 mL/ton of coal (4/28)	11.6	0.85	230	<1	556	<1	2	99.6
40 mL/ton of coal (4/29)	10.2	0.99	230	<1	552	<1	2	98.6

*Inerts are acid-insoluble solids that can include fly ash and mineral impurities from the limestone reagent

Steady-State Test Results

As described above, the steady-state TMT additive test at Monticello was delayed until the last week of September to allow time to specify, procure and set up a primary dewatering system to size separate the solids in the slurry blow down from the pilot wet FGD system.

Throughout this report the term absorber "blow down" is used to describe the slurry fed to the hydrocyclone for dewatering. However, because the FGD system uses a slurry pump to

continuously recirculate slurry from the reaction tank through the absorber and the blow down is a slipstream of that recirculating slurry, the blow down is identical to the reaction tank slurry. Also in this report, the term "fines" is often used to describe the solids in the hydrocyclone overflow, while the term "byproduct gypsum" is often used to describe the solids in the hydrocyclone underflow. In most LSFO FGD systems, the hydrocyclone underflow becomes the feed to the vacuum filter for secondary dewatering, and thus is the source of the gypsum byproduct.

In the original project plan, there was no need to conduct a baseline (no TMT addition) test during this second week of testing, as it was to have followed a weeklong parametric test effort that included a baseline test. However, because five months elapsed between the two weeks of TMT additive testing, a baseline (no TMT) test was conducted during the first part of the second week to measure mercury removal across the pilot FGD system with no TMT additive.

Also, the steady-state TMT additive test was conducted downstream of a gold-based mercury oxidation catalyst, whereas the previous parametric tests were conducted with no oxidation catalyst upstream. This change resulted in a higher percentage of oxidized mercury (rather than elemental mercury) in the FGD inlet flue gas for the steady-state test. The reason for conducting this test downstream of the gold catalyst was based on previous results from pilot wet FGD tests conducted downstream of four mercury oxidation catalysts being tested at Monticello as part of the NETL co-funded 41992 project. Those results showed significant mercury re-emissions when scrubbing the flue gas from downstream of the gold catalyst.[5] It was expected that conducting the TMT-15 steady-state test downstream of the gold catalyst would provide an opportunity to observe the effectiveness of TMT in preventing mercury re-emissions. It is believed that downstream of the gold oxidation catalyst, the predominant form of oxidized mercury present in the flue gas is still mercuric chloride, as in other flue gases.

The steady-state TMT additive test was conducted at a TMT-15 dosage of 20 mL/ton of coal fired. Although the parametric tests conducted earlier at Monticello showed virtually no effect of TMT-15 dosage over the range of 5 to 40 mL/ton of coal on FGD liquor mercury concentrations, it was decided to go with a dosage of 20 mL/ton for two reasons. One was concern that since this test was to be conducted downstream of the gold mercury oxidation catalyst, it might take a higher TMT dosage than in the parametric tests because of higher expected oxidized mercury concentrations in the FGD inlet flue gas. The other reason was that 20 mL/ton coincides with Evonik Degussa's "rule of thumb" for required TMT dosage to minimize mercury re-emissions, and it was felt that it would be best to test at their recommended dosage, rather than a lower dosage that might later prove to have been less effective.

Mercury Removal Data

Two mercury SCEMs were used to monitor mercury capture across the wet FGD during baseline operation (no TMT addition) and during TMT-15 addition. Unfortunately, the SCEM used to track FGD inlet mercury concentrations suffered a hard drive failure in the computer used to control analyzer operation and record analyzer results. This hard drive failure resulted in a complete loss of the inlet analyzer data up through the last day of the steady-state TMT-15 test. Although some raw data were recorded in a notebook by the SCEM operator as the data were produced, the data recorded were not complete enough to recreate the lost electronic data.

The flue gas at Monticello changes markedly in total mercury concentration and mercury speciation due to temporal variations in fuel quality, and variations in the percentage of lignite versus PRB fired in the unit. For this reason, FGD outlet data alone, which were not lost, are of little value in measuring mercury removal by species across the FGD system. On the last day of the steady-state test, the single remaining SCEM was cycled between analyzing the FGD inlet and outlet flue gases, and between measuring total and elemental mercury concentrations at each location. Again, because of significant temporal variations in mercury concentrations and oxidation percentage at Monticello, these single analyzer cycling data are of little use in quantifying FGD removal of mercury species. Since the SCEM data are of little use, they are not included in this report.

Fortunately, as planned, triplicate Ontario Hydro measurements were made at the FGD inlet and outlet on the last day of the TMT-15 steady-state test. These data provide information about mercury capture and re-emission levels across the pilot wet FGD system during the TMT-15 steady state tests. Previous "baseline condition" (no TMT) data are available from operation of the wet FGD pilot unit downstream of the gold catalyst in April 2005 as part of the NETL co-funded 41992 project. Results from both sets of Ontario Hydro measurements are shown in Table 14.

Table 14. Results of Ontario Hydro Method Measurements Across Wet FGD Pilot Unit for Operation Downstream of Gold Catalyst – with and without TMT-15 Addition (mean value for three runs $\pm$ the 95% confidence interval about the mean)

	Hg Concentration (μg/Nm^3 @ 3% O$_2$)*		Total Hg Oxidation at FGD Inlet (%)	Hg Removal Across FGD (%)	Hg Re-emissions (% of inlet Hg^{+2})
	FGD Inlet	FGD Outlet			
April 20, 2005 Baseline (no TMT addition) Results:					
Hg^{+2}	28.3 ± 2.3	3.8 ± 0.9	-	87 ± 3	-
Hg^0	1.1 ± 0.2	3.2 ± 1.7	-	-189 ± 95	7.5 ± 2.7
Total Hg	29.4 ± 2.5	7.0 ± 2.7	96 ± 1	76 ± 4	-
September 29-30, 2005 Steady-state TMT-15 Test Results (20 mL/ton of coal):					
Hg^{+2}	7.1 ± 0.6	0.2 ± 0.0	-	98 ± 1	-
Hg^0	3.5 ± 0.4	4.0 ± 0.4	-	-15 ± 17	7.5 ± 8.4
Total Hg	10.5 ± 0.8	4.2 ± 0.5	67 ± 2	61 ± 7	-

*Note: 1μg/Nm^3 @ 3% O$_2$ = 0.67 lb of Hg per 10^{12} Btu heat input

Comparing the April and September data, the FGD inlet total mercury concentrations are quite a bit different. The total in September is only about 36% of the April concentration. This suggests that in September, the unit was firing a higher percentage of PRB coal (which has a lower

38

mercury content than the Texas lignite) than in April, and/or that the fuels being fired had a lower mercury content. Mercury analyses on the PRB and lignite fired during the April and September tests confirmed both of these affects on the FGD inlet total mercury concentration.

Another thing to note in Table 14 is that the effectiveness of the gold catalyst for oxidizing elemental mercury in the FGD inlet flue gas was significantly lower in September than in April. The data show 96% total mercury oxidation at the FGD inlet in April, but only 67% in September. This is believed to be due to a buildup of fly ash in the horizontal gas flow channels of the catalyst, caused by malfunctions of the sonic horns that are meant to prevent fly ash buildup. As a result of these differences between total mercury concentration and oxidation percentage between the April and September data, the FGD inlet oxidized mercury concentration in September was only 25% of the April concentration.

The September data show considerably higher apparent percent removal of oxidized mercury than was measured in April, 98% versus 87%, respectively. The lower percentage in April is believed to be due to a mechanical problem (slurry recirculation pump cavitation) that lowered the FGD absorber liquid-to-gas ratio during that test. The apparent improvement in September is believed to be due to correcting the cavitation problem and not related to TMT addition.

The September data show considerably less mercury re-emissions across the wet FGD absorber than in April when expressed in terms of the increase in elemental mercury concentration across the absorber. This is an expected benefit of TMT addition. In the April data, the elemental mercury concentration increase across the wet FGD pilot was measured to be 2.1 μg/Nm^3 @ 3% O$_2$ (3.2 minus 1.1) whereas in September the increase was only 0.5 μg/Nm^3 @ 3% O$_2$. Furthermore, when the 95% confidence intervals of the September data are considered, the mean concentrations of elemental mercury at the FGD inlet and outlet overlap substantially, meaning it was not certain that any re-emissions were occurring during the September TMT test. As an example, the mean inlet elemental mercury concentration plus one 95% confidence interval ranges from 3.45 to 3.85 μg/Nm^3 @ 3% O$_2$, while the mean outlet concentration minus one 95% confidence interval ranges from 3.55 to 3.98 μg/Nm^3 @ 3% O$_2$. These ranges are almost identical, meaning there is a reasonable probability that the inlet and outlet elemental mercury concentrations were identical and there were no re-emissions during this test. This view of the data suggests that the TMT-15 addition was effective at reducing or eliminating re-emissions when operating the FGD system downstream of the gold catalyst.

However, the re-emissions level can also be expressed as a percentage of the FGD inlet oxidized mercury. This is a relevant way of expressing the re-emissions rate since it is the oxidized mercury that is absorbed and chemically reduced to produce re-emissions, and re-emissions levels might be expected to be a function of the amount of oxidized mercury absorbed. This term is used to express re-emission rates throughout this report. Because the FGD inlet oxidized mercury concentration in September was only 25% of that in April, when the re-emissions are calculated as a percentage of the inlet oxidized mercury concentration, the mean re-emission percentages are identical for the April and September data, at 7.5%.

This might call into question the effectiveness of TMT-15 in limiting re-emissions, except that the 95% confidence interval for the mean re-emissions percentage from the September data is

greater than the actual mean (8.4% versus a mean of 7.5%). This means the 95% confidence interval of the data includes zero re-emissions or less, so there is no certainty that re-emissions were actually occurring during the September measurements.

It should be noted that measurement of mercury re-emissions can be difficult, as it requires the simultaneous measurement of elemental mercury concentrations in both the FGD inlet and outlet flue gases. Re-emissions are quantified as the difference between the two values. If the re-emissions levels are relatively small, this measurement is prone to error because it involves subtracting one large number from another to quantify a small difference. The relative standard deviation for the Ontario Hydro method is cited as less than 11% for mercury concentrations greater than 3 $\mu g/Nm^3$ and less than 34% for concentrations less than 3 $\mu g/Nm^3$.[6] Subtracting two values with these levels of relative standard deviation can lead to errors in quantifying the difference. Furthermore, the FGD outlet location is difficult for measuring mercury concentrations because the flue gas is wet and can contain entrained FGD liquor droplet carryover. These droplets can contain absorbed mercury and can bias measurement results.

In summary, the Ontario Hydro data are not conclusive about the effectiveness of TMT-15 in limiting re-emissions from the pilot wet FGD system when operating downstream of the gold mercury oxidation catalyst. Uncertainty in the mean quantity of re-emissions measured by the Ontario Hydro method limits the conclusions that can be made from these data. In retrospect, it would have been better to collect a new set of "baseline" (no TMT-15 addition) mercury capture data for the pilot wet FGD system by the Ontario Hydro method in September 2005. This new set of baseline data should have accounted for changes in the pilot wet FGD inlet flue gas oxidized mercury concentration compared to the previous April data, and would have provided a better benchmark for measuring TMT-15 effectiveness. The plan had been to use mercury SCEM data for this new baseline, but the hard drive failure described above meant that baseline SCEM data were not available.

Mercury Concentrations in FGD Liquor and Solids

During the September tests, samples were collected and preserved of the FGD blow down slurry liquor and solids. These samples were analyzed to determine the effects of TMT addition on mercury concentrations in the slurry liquor and solids. The results of these analyses are shown in Table 15 below.

The results show that the FGD liquor mercury concentrations were reduced by over an order of magnitude by TMT-15 addition, comparing the baseline (no TMT) concentration from September 28 to the concentration during the second day of the steady-state test (32.2 versus 2.77 $\mu g/L$). Correspondingly, the absorber blow down slurry solids mercury concentration increased with the addition of TMT, as would be expected.

The data in the far right column of Table 15 show the mercury in the FGD liquor as a percentage of the total amount of mercury in the slurry. This percentage was calculated from the data in the three columns to the left in the table. TMT-15 addition at 20 mL/ton of coal fired was observed to lower this percentage from 13% in the baseline test on September 28 to 1% by September 30. Virtually all of the mercury absorbed by the FGD absorber was precipitated into the solid phase.

Table 15. FGD Blow Down Slurry Liquor and Solids Mercury Concentrations (solids concentrations based on samples filtered off site)

Sample	Liquor Hg Concentration (μg/L)	Wt% Solids	Solids Hg Concentration (μg/g)	% of FGD Blow Down Hg in Slurry Found in Liquor (calculated value)
Baseline [no TMT] (9/28/05):				
FGD Blow Down Slurry	32.2	13.2	1.42	13.0
Hydrocyclone Overflow	19.4	13.2*	1.52	-
Hydrocyclone Underflow	15.0	62.1	0.55	-
TMT-15 at 20 mL/ton of coal (9/29/05):				
FGD Blow Down Slurry	3.54	11.9	1.43	1.8
Hydrocyclone Overflow	3.34	3.3	3.76	-
Hydrocyclone Underflow	3.84	62.7	0.54	-
TMT-15 at 20 mL/ton of coal (9/30/05):				
FGD Blow Down Slurry	2.77	12.2	1.91	1.0
Hydrocyclone Overflow	1.90	4.1	4.61	-
Hydrocyclone Underflow	2.56	64.1	0.46	-

*It appears that the sample analyzed for wt% solids was a mislabeled FGD blow down slurry sample, since the wt% solids values are identical. For later mass balance calculations, a value of 4 wt% was assumed.

Also shown are liquor and solids mercury analysis results for overflow and underflow samples after the FGD slurry blow down was sent through the hydrocyclone for primary dewatering. The expected result was that the FGD liquor mercury concentrations would be approximately the same as in the blow down slurry, as the liquor should be homogenous, but that the solid mercury concentrations would be markedly different between the overflow and underflow. This is because previous results from a variety of sites have shown that slurry fines tend to be much richer in mercury than the larger gypsum byproduct solids.

Furthermore, most of the solids in the blow down slurry should report to the underflow, while most of the liquor should report to the overflow. Thus, the overflow should have a lower wt% solids concentration than the blow down slurry and a higher solids mercury concentration, while the underflow should have a higher wt% solids but a lower solids mercury concentration than the blow down slurry.

The liquor mercury concentration results were as expected for the days where TMT was being added – the scrubber blow down, hydrocyclone overflow and underflow liquor samples all have similar mercury concentrations. However, for the baseline (no TMT) test on September 28, the

hydrocyclone overflow and underflow liquor samples show lower mercury concentrations than the blow down slurry. This may be a residence time effect, as data from other sites has shown that liquid phase mercury concentrations can decrease after slurries leave the FGD absorber reaction tank, presumably due to adsorption on the solids in the slurry over time. The order in which these samples were filtered and preserved after they were collected may have impacted how much mercury remained with the liquor.

Discussion of the solid sample results is required. Solid samples were recovered from the slurry samples filtered on site, but after reviewing the mercury concentration data for these solids it was apparent that a bias was introduced when the samples were filtered and preserved. The sampling and preservation technique used at the time was to collect a sample of about 500 mL in volume, then filter a portion on site to recover a preserved liquor and solid aliquot. While filtering a portion of the sample should produce a representative liquor sample, it may bias the solid sample. It has been shown that FGD solids mercury concentrations vary significantly with particle size, with mercury concentrations being much higher in the fine particles. The sample particle size distribution data discussed below show that all samples had a significant percentage of fine particles. If only a portion of the sample is filtered, it is possible that some of the sample aliquots have had an over-represented fine particle fraction, and thus a high bias in the sample mercury concentration. Others may have an under-represented fine particle fraction and a low bias in measured mercury concentration.

The current procedure is to collect smaller sample volumes and filter the entire amount of sample to collect representative solids. During the September tests, additional slurry samples were collected that were not filtered on site. These samples were subsequently filtered off site and analyzed for mercury concentration in an attempt to resolve these apparent anomalies. Normally, a slurry sample that has been allowed to sit for some time before filtering, as were these additional slurry samples, could bias the solids mercury concentration high because of adsorption of mercury from the liquor in the slurry. However, particularly for the samples from the TMT test period, the liquor mercury represented such a small percentage of the total slurry mercury content that any such bias should be negligible.

The results of the mercury analyses on the solids from the slurries filtered off site are shown in Table 15, along with the FGD liquor sample analyses on the aliquots filtered on site. These solids analysis results reflect the expected trends from these tests. The FGD blow down slurry solids mercury concentration increases from baseline through the second day of TMT addition, an expected result of TMT addition that reflects the higher percentage of the mercury in the slurry in the solid phase. Furthermore, the hydrocyclone overflow solids mercury concentrations were observed to increase with TMT addition, while the underflow solids mercury concentrations were observed to decrease. This is also an expected effect of TMT, to concentrate the mercury in the slurry in fine TMT salts. For all three days, the hydrocyclone overflow solids mercury concentration was higher than the blow down slurry solids concentration, while the underflow solids concentration was lower. This was expected because the fines typically have higher mercury concentrations than the larger gypsum particles, with or without TMT addition.

A comparison of the baseline (no TMT) test samples from September 28 with those from the second day of the steady-state TMT test shows that expected benefits of TMT addition were

realized. The FGD liquor mercury concentrations were reduced by more than an order of magnitude, and the mercury concentration of the product gypsum (after fines removal) was reduced by a small margin (about 17%). With TMT addition, most of the mercury in the slurry was concentrated in the fine particles found in the hydrocyclone overflow stream. However, the use of TMT-15 to precipitate mercury as a fine salt and the use of a hydrocyclone to separate those fine salts did not result in a gypsum byproduct free of mercury. This is further discussed below with the FGD solids particle size analysis results.

FGD Solids Particle Size Analyses

Samples of the FGD blow down (hydrocyclone feed), hydrocyclone overflow and underflow were sent out for particle size analyses by the same technique used for the parametric tests. The results of those particle size analyses are summarized in Table 16. The particle size analyses all show the expected trend, that the hydrocyclone overflow solids were finer than the FGD blow down solids (hydrocyclone feed) while the underflow solids were coarser.

Table 16. Summary of Particle Size Analyses on Solid Samples from Steady-state TMT Additive Test

Test Date	TMT Dosage, mL/ton of coal	Sample	D_{10}*, µm	D_{50}*, µm	D_{90}*, µm
9/28	0 (Baseline)	Scrubber Blow Down	19.6	46.2	73.0
		Fines (HC Overflow)	17.5	44.1	69.9
		Product Gypsum (HC Underflow)	34.3	55.7	85.6
9/29	20	Scrubber Blow Down	16.4	39.9	64.6
		Fines (HC Overflow)	12.5	30.1	54.2
		Product Gypsum (HC Underflow)	34.7	53.9	80.8
9/30	20	Scrubber Blow Down	18.9	39.3	63.6
		Fines (HC Overflow)	13.8	30.8	52.4
		Product Gypsum (HC Underflow)	29.3	48.5	74.1

*Particle size at which 10%, 50%, or 90% of the sample mass is smaller

These data also show that there is quite a bit of overlap in the particle size distributions of the hydrocyclone overflow and underflow. Hydrocyclones typically do not make a sharp separation at a given particle size, but instead tend to produce two streams with overlapping "bell shaped" particle size distributions. For example, for the September 30 samples, the D_{10} for the product gypsum was 29.3 µm, while the D_{50} for the fines was slightly coarser at 30.8 µm. This says that more than 10% of the product gypsum was finer than the median particle size of the fines. Since the fines sample from September 30 had a considerably higher mercury concentration than the product gypsum (see Table 15), it is likely that the fine particles that remain in the product gypsum account for most of its mercury content.

This concept is further illustrated in Figure 12 below, which compares the particle size distributions of the FGD blow down solids (hydrocyclone feed) to the product gypsum solids. The data are plotted as cumulative percent smaller than the particle diameters shown on the "x" axis. The plot shows that the FGD blow down slurry solids have a higher percentage of fine particles than the hydrocyclone underflow solids. This is expected, as the difference represents the fines removed in the hydrocyclone overflow. However, the figure also shows that 10% of the hydrocyclone underflow consists of particles smaller than 30 μm in diameter, which most likely have a higher mercury concentration than the remaining 90% of the particles larger than 30 μm.
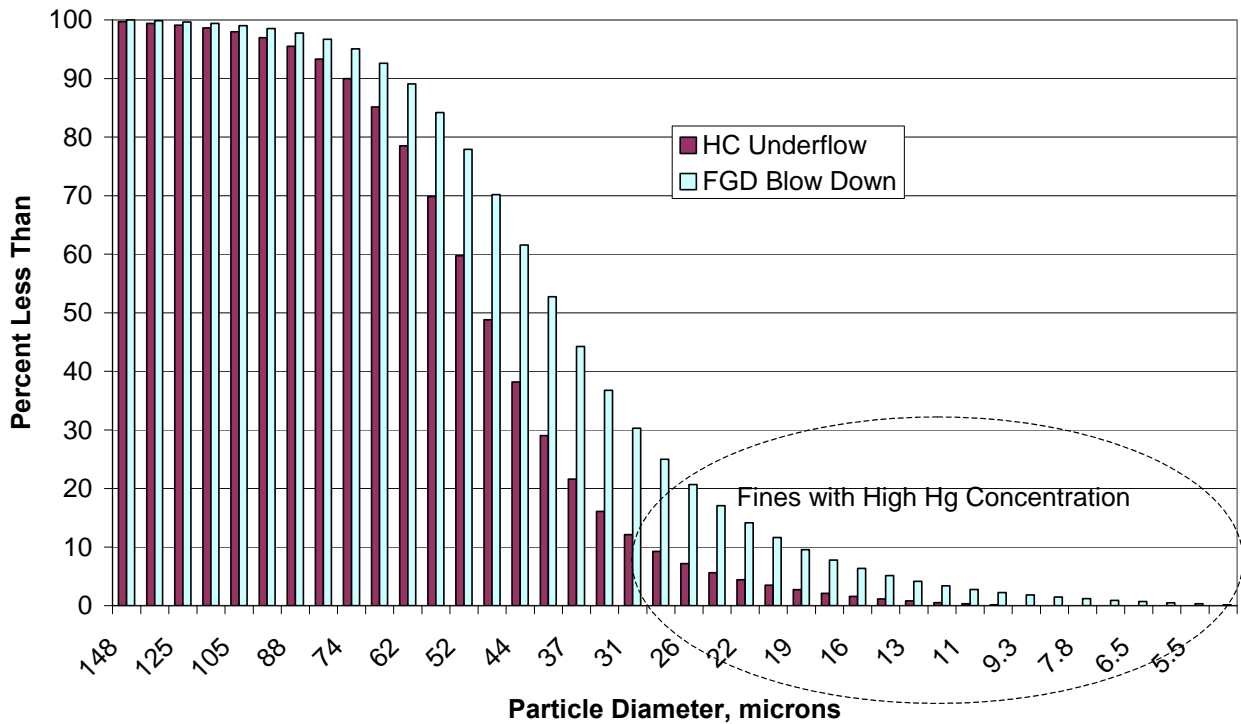
Figure 12. Comparison of Particle Size Distribution Data from 9/30/05

These data suggest that if hydrocyclones are used to separate fine TMT-mercury salts from the product gypsum, they will never be completely effective in removing all of the high-mercury-content fine solids from the gypsum. Perhaps another size separation technique that can provide a sharper size cut, such as wet sieving, would be more effective.

FGD Operating Conditions

During the September 2005 steady-state test, the pilot FGD system operated around the clock (other than a couple of brief outages) from the afternoon of September 27 through the afternoon of September 30. The reaction tank pH was controlled at a value of 5.8, and the reaction tank temperatures ranged from 116 to 122°F. Oxidation-reduction potential (ORP) was not measured because of an instrument problem.

SO_2 removal was checked intermittently during the week with a Western Model 721 UV SO_2 Analyzer. Although the data are not reported here, the spot checks typically showed greater than 90% SO_2 removal across the FGD system, both during baseline operation on September 28 and during TMT addition the remainder of the week. As discussed later with the mass balance calculations, the average SO_2 removal during the last day of the TMT addition period was slightly above 95%.

Initial operation began by filling the pilot FGD reaction tank with slurry blow down from the Unit 3 full-scale FGD system. Samples of the wet FGD pilot reaction tank slurry were collected and preserved daily starting September 28 (after more than 24 hours of pilot FGD operation) to determine FGD operating conditions during these tests. The results of those analyses are summarized in Table 17 for the FGD slurry liquor samples and Table 18 for the FGD slurry solid chemical analyses. They show that for all test days, the FGD system was operating as a highly oxidized LSFO system ($\geq$95% gypsum as the solid byproduct) with very high limestone reagent utilization.

Table 17. Results of FGD Blow Down Liquor Sample Analyses for the TMT Steady State Test

TMT-15 Addition Rate (Date)	pH	Temp. °F	Liquor Concentration, mg/L						
			SO_3	SO_4	Cl^-	Mg	Ca	Na	CO_3
Baseline [no TMT] (9/28)	5.91	121	<1	11,611	4,945	2,738	650	2,048	11
20 mL/ton of coal (9/29)	5.66	119	1	6,223	1,864	1,365	647	1,028	12
20 mL/ton of coal (9/30)	5.82	120	3	6,151	1,699	1,271	612	971	14

Table 18. Results of FGD Blow Down Solid Sample Analyses for the TMT Steady State Test

TMT-15 Addition Rate (Date)	Slurry Wt% Solids	Solids Wt% Inerts	Solids Analysis, mg/g					Gypsum Purity, %	Limestone Utilization, %
			Ca	Mg	SO_4	SO_3	CO_3		
Baseline [no TMT] (9/28)	13.2	1.33	224	1	533	<1	4	95.5	98.8
20 mL/ton of coal (9/29)	11.9	1.21	228	1	530	<1	3	95.0	99.1
20 mL/ton of coal (9/30)	12.2	0.99	228	<1	540	<1	4	96.8	98.8

The liquor analyses show that concentrations of highly soluble species such as magnesium, sodium, and chloride dropped significantly from September 28 to September 29 and remained at the lower level through September 30. The reason for this drop is not clear. It is possible that the concentrations of these soluble species built up during the first 24+ hours of operation, where there was no blow down of slurry from the wet FGD pilot, then stabilized at the lower

concentrations once regular blow down of slurry and makeup of fresh water began. Note that the lower concentrations seen on September 29 and 30 are more in line with what was measured during the parametric tests in April, shown previously in Table 12.

Mercury Balance Calculations

The data presented and discussed above were used to calculate mercury balances around the wet FGD pilot unit. Two types of balances were calculated. One was to determine the extent to which the mercury in the flue gas was represented in the FGD blow down slurry. Since reliable flue gas mercury concentration data were only available for the last day of the steady-state TMT addition test, the mercury balance was calculated only for those data.

The second type of mercury balance was to calculate the extent to which the mercury in the FGD blow down slurry was recovered in the hydrocyclone overflow and underflow samples. Since samples were collected on three days (9/28, 9/29, and 9/30) the balances were calculated for all three days.

For the first type of mercury balance, the Ontario Hydro data were used to determine the flue gas flow rate to the wet FGD pilot and the amount of mercury removed from the flue gas across the FGD absorber. SO_2 analyzer spot-check data were used to determine the average FGD inlet and outlet SO_2 concentrations, and thus the amount of SO_2 removed and the amount of gypsum byproduct formed per unit time. These two sets of data were used to predict how much mercury should be present in the FGD blow down slurry per unit mass of gypsum byproduct in the slurry. The results are summarized in the following paragraph.

The SO_2 analyzer data showed that the FGD inlet concentration averaged about 318 ppmv (dry basis) while the outlet averaged 14 ppmv. This corresponds with just over 95% SO_2 removal. The flue gas flow rate to the wet FGD system was measured at 886 dscfm (at 68°F) during the Ontario Hydro measurements. These data were used to calculate a gypsum production rate of 3,390 g/hr. The Ontario Hydro data showed an average FGD inlet total mercury concentration of 6.3 µg/Nm^3 at the actual FGD inlet O_2 concentration, 10.2% (the same basis at which the SO_2 concentrations were measured), and 61% mercury removal (see Table 14). This corresponds with a mercury removal mass rate of 5,400 µg/hr. Combining these two rates results in an expected mercury content of the FGD blow down slurry of 1.6 µg/g of FGD solid byproduct, assuming all of the mercury removed reported to the solids. The value measured for the FGD blow down slurry for 9/30, as shown in Table 15, was about 20% higher at 1.9 µg/g (including a small contribution of mercury in the slurry liquor). Although the two values do not agree exactly, the agreement is within 20%, which generally represents acceptable mass balance closure. This minor discrepancy could easily be an artifact of small measurement errors in mercury or SO_2 concentrations, and/or in flow rate measurements.

Furthermore, there is a potential for mercury concentrations having varied somewhat during periods when Ontario Hydro measurements were not being conducted. The gas data represent actual measurements made late in the day on September 29 and in the morning and early afternoon of September 30. However, the FGD reaction tank residence time was estimated to cover a much longer period of 50 hours. Lignite and PRB coal mercury concentration data show

that the fuel mercury concentrations were decreasing over the period of September 28 through September 30. Thus, the absorber blow down slurry solids are representative of mercury capture over the previous two days, during periods that the fuel mercury concentrations were higher. Considering the residence time effect, an FGD blow down slurry mercury content of 1.9 μg/g would be expected even though the gas data predict a lower value of 1.6 μg/g.

In the second type of mercury balance, the FGD blow down and hydrocyclone overflow and underflow wt% solids data from Table 15 were used to solve for the percentages of the blow down liquor and solids that reported to the overflow and underflow. Once these percentages were calculated, the mercury concentrations of each stream were used to calculate the extent to which the mercury in the blow down slurry was accounted for in the hydrocyclone overflow and underflow streams. The results of the total mass distribution calculations are summarized in Table 19 and of the mercury balance calculations in Table 20.

Table 19. Summary of Hydrocyclone Overall Mass Balance Estimates

Date	TMT-15 Dosage (mL/ton of coal)	% of FGD Blow Down Slurry Liquor		% of FGD Blow Down Slurry Solids	
		HC Overflow	HC Underflow	HC Overflow	HC Underflow
9/28/2005	0 (baseline)	81	19	21	79
9/29/2005	20	83	17	20	80
9/30/2005	20	84	16	25	75

Table 20. Summary of Hydrocyclone Mercury Balance Calculations

Date	TMT-15 Dosage (mL/ton of coal)	% of FGD Blow Down Slurry Mercury Content				
		HC Over-flow Liquor	HC Over-flow Solids	HC Under-flow Liquor	HC Under-flow Solids	Total Hg Recovery
9/28/2005	0 (baseline)	6.3	20	1.2	27	54
9/29/2005	20	1.4	52	0.3	30	84
9/30/2005	20	0.6	59	0.2	18	78

The results in Table 19 show the expected distribution of solids and liquor in the hydrocyclone outlet streams: most of the solids end up in the underflow and most of the liquor ends up in the overflow. The results in Table 20 show reasonable recovery percentages for the mercury in the FGD blow down in the hydrocyclone product streams for the two TMT test day samples (84% and 78%), but poor recovery for the baseline sample (54%).

However, as stated in the footnote to Table 15, there was a question about the actual wt% solids concentration of the hydrocyclone overflow sample from the baseline test day. Because the originally measured value was believed to be in error, an assumed wt% value was used for the

mass balance calculations in Table 19 and may have contributed to the low mercury recovery in Table 20. Also, the solids mercury concentrations used for these calculations were from the samples filtered and analyzed off site. These samples had ample time for mercury in the liquor to adsorb onto the solids. For the TMT tests, there was little mercury in the liquor, so this possible bias on the solids mercury concentrations was insignificant. But for the baseline sample, where the mercury in the liquor accounted for 13% of the mercury in the whole slurry, adsorption of mercury from the liquor to the solids and/or to the sample container walls in the samples filtered off site may have biased the solid phase mercury concentration values reported in Table 15. Such a bias could have adversely affected the mercury recovery calculations in Table 19.

In summary, the mercury balance closures shown above for the comparison of slurry and flue gas data for September 30, and for the hydrocyclone product streams versus the FGD blow down for the two days of TMT addition show acceptable closure for pilot unit testing of this type.

Pilot JBR Parametric Additive Tests at Plant Yates

A series of parametric TMT-15 additive tests were conducted on the 1-MW pilot JBR at Plant Yates in August 2005, while operating in LSFO mode. The eight-day parametric test effort, including start up and shut down periods, measured baseline (no TMT) performance and included three subsequent tests at increasing dosage rates of TMT-15. The TMT-15 dosages tested included 2.5, 7.5, and 20 mL/ton of coal fired.

Mercury Removal Data

Mercury removal data were measured for the pilot JBR FGD system by mercury SCEM, using one analyzer each at the FGD inlet and outlet. The results are summarized in Table 21.

Table 21. Daily Average Mercury SCEM Data for Pilot JBR TMT-15 Tests

Date	TMT-15 Dose, mL/ton of coal fired	JBR Inlet Hg, $\mu g/Nm^3$ @ 3% O_2		JBR Outlet Hg, $\mu g/Nm^3$ @ 3% O_2		Hg Oxidation at Pilot FGD Inlet, %	Total Hg Removal by FGD, %	Hg^{+2} Removal by FGD, %	Hg^0 Removal by FGD, %
		Total Hg	Hg^0	Total Hg	Hg^0				
8/18/2005	0	2.3	0.3*	2.1	2.1	87*	11	103*	-632*
8/19/2005	2.5	3.8	1.6	4.5	2.8	58	-16	25	-72
8/20/2005	7.5	3.6	1.9	2.9	2.5	45	20	78	-32
8/21/2005	20	3.6	2.2	4.0	3.7	39	-11	80	-64

*It is suspected that solids buildup on the IGS filter at the inlet sample was causing oxidation of elemental mercury in the inlet flue gas sample, biasing these results; the IGS filter was replaced for subsequent days

In general, the pilot JBR outlet SCEM data are not believed to be reliable. As described in Section 2, the pilot JBR did not have a mist eliminator, which apparently led to significant slurry carryover into the pilot JBR outlet duct where the outlet SCEM sample was collected. The IGS

filters used to separate a gas sample to go to the SCEM are typically heated to greater than 400°F to minimize mercury adsorption on solids that collect on IGS filter surfaces. However, if there is significant FGD liquor and solids carryover in the gas sampled, the mercury in the liquor and/or on the solids can be evaporated and/or desorbed at the elevated operating temperature of the IGS filter. In this circumstance the JBR outlet total mercury concentrations are believed to be biased high, and the outlet mercury speciation (total versus elemental) not reliable.

As an example, the data for testing on August 19 and August 21 show negative overall mercury removal, which would require mercury to be desorbing from the JBR liquor at a higher rate than oxidized mercury is being absorbed from the inlet flue gas. Furthermore, the apparent removal percentage for oxidized mercury for August 19, 25% does not seem realistic, as the JBR represents an effective flue gas contactor that should absorb oxidized mercury at high efficiency even though some may be re-emitted. Even the apparent oxidized mercury removal efficiency values for August 20 and 21, at 78% and 80%, appear to be low.

Although the data from all four days show evidence of elemental mercury re-emissions from the JBR, these data are not seen as being reliable for the reasons described above. Therefore, the SCEM data cannot be used to reliably determine whether there was any re-emission from the pilot JBR under baseline (no TMT) conditions, or whether TMT-15 addition was effective in controlling re-emissions.

Mercury Concentrations in FGD Liquor and Solids

Because the gas-phase mercury concentration data were considered unreliable, data analysis from the pilot JBR TMT-15 additive tests focused on pilot JBR liquor and solid mercury concentration data. The results of these analyses are summarized in Table 22. Included in the table are the results of mercury analyses on blow down slurry samples from the full-scale JBR for August 18 and 21. Also shown are mercury analysis results for hydrocyclone overflow and underflow samples from treating blow down slurry from the pilot JBR. The JBR blow down slurry (pilot or full scale) is pumped from the reaction zone at the bottom of the JBR on a continuous basis, and thus is expected to be representative of the reaction zone slurry at the time the sample is collected.

The pilot-scale JBR had been charged with blow down slurry from the full-scale JBR the day before the baseline samples were collected on August 18, and the blow down slurry was diluted with makeup water. The results for the baseline test on August 18 show that the liquor mercury concentration in the pilot JBR was about half that of the full-scale JBR, and that the wt% solids in the pilot JBR slurry was a factor of 11 lower than the wt% solids in the full-scale JBR. This suggests that the pilot JBR was operating very dilute compared to the full-scale JBR.

However, analyses of highly soluble liquid phase species from the pilot- and full-scale JBR from August 18, presented later in this subsection, show that the pilot-scale JBR was only 10 to 20% more dilute than the full-scale JBR. The concentrations of these highly soluble species provide a better indication of the dilution of the slurry in the pilot JBR than mercury, which can be adsorbed on solids or re-emitted, or suspended solids, which can become stratified and poorly represented in a grab sample.

49

Table 22. Pilot JBR Blow Down Slurry Liquor and Solids Mercury Concentrations

Sample	Liquor Hg Concentration (µg/L)	Wt% Solids	Solids Hg Concentration (µg/g)	% of FGD Blow Down Hg in Slurry Found in Liquor
Baseline [no TMT] (8/18/05):				
Full-scale JBR Blow Down Slurry	14.6	12.1	0.10	52
Pilot JBR Blow Down Slurry	7.52	1.1	0.29	70
Hydrocyclone Overflow	7.95	0.44	0.42	-
Hydrocyclone Underflow	9.33	19.8	0.07	-
TMT-15 at 2.5 mL/ton of coal (8/19/05):				
Pilot JBR Blow Down Slurry	8.79	0.71	0.09	93
Hydrocyclone Overflow	9.84	0.29	0.52	-
Hydrocyclone Underflow	8.45	21.1	0.07	-
TMT-15 at 7.5 mL/ton of coal (8/20/05):				
Pilot JBR Blow Down Slurry	0.67	4.9	0.20	6.2
Hydrocyclone Overflow	0.48	3.2	0.55	-
Hydrocyclone Underflow	1.18	35.6	0.08	-
TMT-15 at 20 mL/ton of coal (8/21/05):				
Full-scale JBR Blow Down Slurry	13.3	10.9	0.08	56
Pilot JBR Blow Down Slurry	<0.25	4.9	0.15	<1.6
Hydrocyclone Overflow	<0.25	2.0	0.76	-
Hydrocyclone Underflow	<0.25	43.1	0.05	-

The comparison of soluble liquid-phase species concentrations, which show little dilution, and wt% solids levels in the pilot- and full-scale JBR, which show an order of magnitude difference in wt%, indicates that the pilot JBR blow down slurry sample was biased low in solids content. This was most likely caused by solids accumulation at the bottom of the pilot JBR. As indicated in Section 2, the pilot JBR did not have a mechanical agitator, and relied on the flow of forced oxidation air at the bottom of the reaction zone to keep solids suspended. The wt% solids data from August 18 suggest that the forced oxidation air was not effective at keeping the solids suspended, leading to the very low wt% solids levels measured in the slurry blow down sample.

The data in Table 22 show the effects of TMT-15 addition. In the baseline sample from August 18, 70% of the mercury in the pilot JBR slurry sample was found in the liquor, although this percentage may be biased by solids stratification as discussed above. At the lowest TMT-15 dosage, 2.5 mL/ton of coal fired, the percentage in the liquid phase actually went up, although this may also be an artifact of solids stratification. As the TMT-15 rate was increased, the percentage of the slurry mercury in the liquid phase decreased, with the percentage at the highest rate, 20 mL/ton of coal fired, dropping to less than 1.6% (the analytical detection limit). The corresponding liquid-phase mercury concentrations dropped from 7.5 µg/L at baseline August 18) to below the measurement detection limit of 0.25 µg/L at the highest TMT-15 dosage rate.

The data for the hydrocyclone overflow and underflow samples generally showed expected trends. The overflow tended to have lower wt% solids than the JBR blow down but higher solids mercury concentrations, while the underflow had higher wt% solids and lower solids mercury concentrations than the blow down. In spite of the fact that most of the absorbed mercury was shifted from the liquor to the solids by the addition of TMT, fines removal from the product gypsum resulted in the product from the highest TMT-15 dosage test having a 30% lower mercury concentration than the baseline (no TMT) product solids from August 18. Note that all of the product solids from the pilot JBR underflow had very low mercury concentrations (less than 0.1 µg/g).

FGD Solids Particle Size Analyses

Samples of the pilot JBR blow down, hydrocyclone overflow and underflow from the baseline test (August 18) and the 20 mL/ton of coal TMT test (August 21) were sent out for particle size analyses. The same technique was used as for the samples from the Monticello pilot FGD tests. The results of those particle size analyses are summarized in Table 23.

Table 23. Summary of Particle Size Analyses on JBR Blow Down Solid Samples from Steady-state TMT Additive Test

Test Date	TMT Dosage, mL/ton of coal	Sample	D_{10}*, µm	D_{50}*, µm	D_{90}*, µm
8/18	0 (Baseline)	JBR Blow Down Slurry Solids	16.1	37.7	72.0
		Fines (HC Overflow)	6.4	22.8	50.2
		Product Gypsum (HC Underflow)	11.5	34.2	67.8
8/21	20	JBR Blow Down Slurry Solids	14.5	44.6	89.6
		Fines (HC Overflow)	6.1	32.1	71.6
		Product Gypsum (HC Underflow)	24.3	54.8	99.7

*Particle size at which 10%, 50%, or 90% of the sample mass is smaller

The particle size analyses generally show the expected trend, that the hydrocyclone overflow solids were finer than the JBR blow down solids (hydrocyclone feed) while the underflow solids are coarser. An exception was the baseline test underflow solid sample (August 18), which was measured to have about the same particle size distribution as the feed (within experimental error). As did the Monticello steady-state TMT additive test results discussed above, these data show quite a bit of overlap in the particle size distributions of the hydroclone overflow and underflow.

Hydrocyclones typically do not make a sharp separation at a given particle size, but instead tend to produce two streams with overlapping "bell shaped" particle size distributions, as illustrated in Figure 13. For both sets of samples, the D_{10} of the underflow was smaller than the D_{50} of the overflow solids. This says that more than 10% of the product gypsum was finer than the median particle size of the fines. Since the fines samples had a considerably higher mercury concentration than the product gypsum (see Table 22), it is likely that fine particles which remain in the product gypsum account for most of its mercury content.
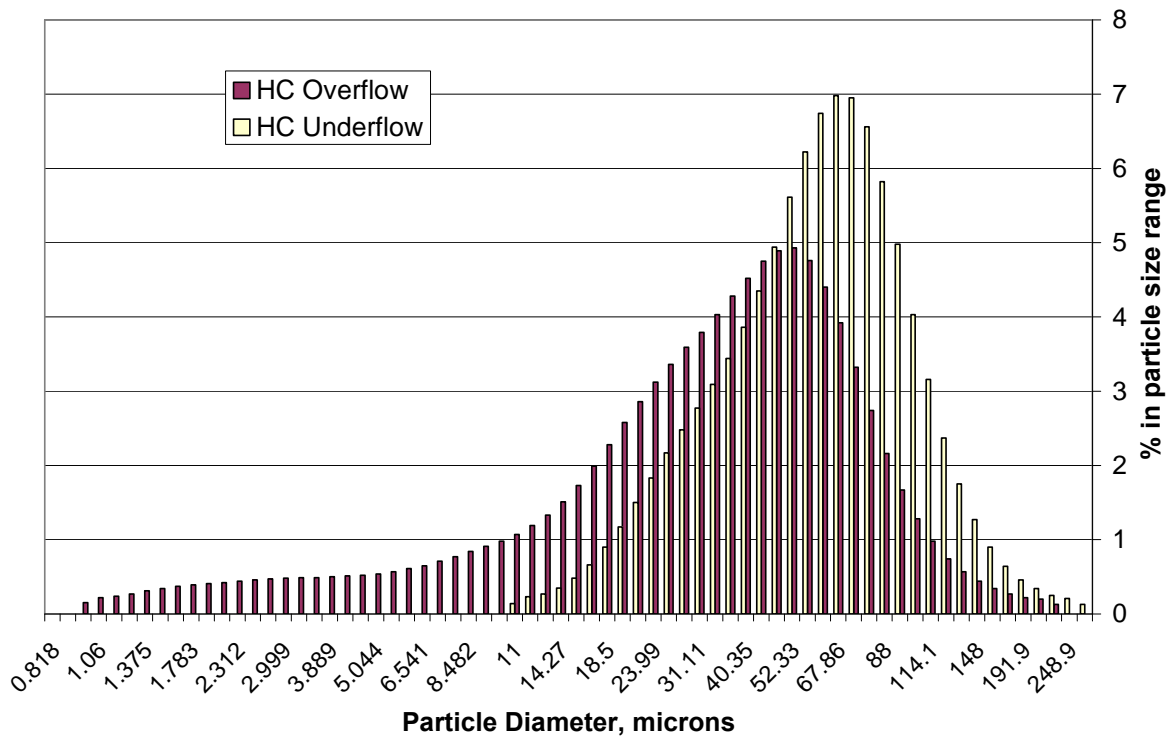
Figure 13. Hydrocyclone Overflow and Underflow Particle Size Data for the 20 mL/ton of Coal TMT-15 Test at Plant Yates

FGD Operating Conditions

The pilot JBR was operated on day shift only, typically from about 8:00 a.m. to 6:00 p.m. The desired operating conditions for the pilot JBR were for the pH in the absorption zone to be controlled at 4.0, and the JBR pressure drop be greater than 10 in. H_2O. The pressure drop was generally controlled above this level, but as discussed below, the pH measurement and control proved to be problematic, apparently due to inadequate mechanical agitation. The flue gas flow rate was intended to run as high as the pilot JBR fan would allow. However, the maximum fan

speed was limited by "tripping" the variable frequency drive (VFD) for the fan if the set point was raised too high or at high ambient temperature at the VFD. The observed flue gas flow rate varied from about 2000 to 4000 acfm at pilot JBR inlet conditions, as measured by the inlet multi-point pitot. However, some of this flow variation appeared to be in the flow measurement rather than in the actual flow rate. The flue gas inlet temperature upstream of the quench nozzles typically ran 270°F to 280°F after the pilot JBR had operated several hours. The forced oxidation air rate, which also provided slurry agitation (although apparently inadequately), was typically 25 to 30 scfm. The oxidation air rate tended to be limited by the forced oxidation air pressure available from the full-scale JBR forced oxidation air header on the side nearest the pilot JBR. The slurry level in the pilot JBR was varied between about 118 to 125 inches.

The CEM on the full-scale JBR typically showed the inlet SO_2 concentration to be about 650 ppmv, although there was an excursion the morning of August 19 up to 975 ppmv. The inlet SO_2 concentration at the pilot JBR was checked periodically with gas absorption tubes. These measurements ranged from 505 to 750 ppmv (wet basis). The pilot JBR outlet SO_2 concentrations were also checked periodically with gas absorption tubes. These showed widely varying SO_2 removal percentages, with outlet SO_2 concentrations varying from a high of 500 ppmv to as low as 10 ppmv (wet basis). The wide variation in outlet SO_2 concentration was apparently an adverse effect of poor agitation and pH control in the absorption zone of the JBR.

Samples were collected of the pilot JBR blow down slurry for the second day of the baseline test (August 18) and each of the three TMT-15 dosage tests. Samples were also collected from the full-scale JBR on the same days as the baseline pilot JBR test (August 18) and the final TMT-15 pilot JBR test (August 21).

The results of chemical analyses of these samples are summarized in Table 24 for the FGD liquor samples and Table 25 for the FGD solids. Looking at the concentrations of liquid-phase species, the concentrations of the highly soluble ions in the FGD liquors, chloride (Cl), magnesium (Mg) and sodium (Na), can be compared to determine how dilute the pilot JBR was operating compared to the full-scale JBR. For the August 18 data, the pilot JBR concentrations of Cl, Mg, and Na were 92%, 82%, and 88%, respectively, of the full-scale JBR results. This suggests that the pilot JBR was only 10 to 20% more dilute than the full-scale JBR.

As shown in Table 24, though, the wt% solids in the pilot JBR blow down slurry was only 1.1% versus 12.1 for the full-scale JBR. Since the soluble salts show only a 10 to 20% dilution in the pilot JBR, while the solids show a factor of 11 lower solids content, the conclusion can be made that solid were settling in the bottom of the pilot JBR and were not reflected in the blow down slurry. As discussed previously, this is most likely an effect of the pilot JBR not having a mechanical agitator.

The liquor analysis results show that the soluble species concentrations remained relatively constant over the pilot test period. At the time of the highest TMT-15 rate test on August 21, the pilot JBR soluble species concentrations were nearly identical to those of the full-scale JBR (within ± 7%).

Table 24. Results of JBR Blow Down Liquor Sample Analyses for the TMT Parametric Tests (mg/L unless noted otherwise)

TMT-15 Addition Rate (Date)	pH	Temp. $^\circ$F	ORP	SO_3	SO_4	Cl^-	Mg	Ca	Na	CO_3
Full-scale JBR (8/18)	4.72	124	430	5	3184	2636	659	1437	89	35
Pilot JBR Baseline [no TMT] (8/18)	4.02	125	457	2	2100	2435	516	1439	78	88
Pilot JBR 2.5 mL/ton of coal (8/19)	3.03	125	524	1	2003	3362	588	1824	91	94
Pilot JBR 7.5 mL/ton of coal (8/20)	5.15	125	266	2	1596	2864	579	1415	84	36
Pilot JBR 20 mL/ton of coal (8/21)	6.08	124	177	34	1711	2639	568	1408	88	157
Full-scale JBR (8/21)	4.38	124	433	7	1646	2841	583	1431	85	65

Table 25. Results of JBR Blow Down Solid Sample Analyses for the TMT Parametric Tests

TMT-15 Addition Rate (Date)	Slurry Wt% Solids	Solids Wt% Inerts	Solids Analysis, mg/g					Solids Wt% Gypsum
			Ca	Mg	SO_4	SO_3	CO_3	
Full-scale JBR (8/18)	12.1	1.7	227	<1	538	<1	2	96.4
Pilot JBR Baseline [no TMT] (8/18)	1.1	1.8	236	<1	493	<1	43	88.4
Pilot JBR 2.5 mL/ton of coal (8/19)	0.7	2.2	224	<1	527	<1	5	94.5
Pilot JBR 7.5 mL/ton of coal (8/20)	4.9	1.6	236	1	491	<1	53	88.0
Pilot JBR 20 mL/ton of coal (8/21)	4.9	1.9	251	1	443	1	98	79.4
Full-scale JBR (8/21)	10.9	2.0	223	<1	539	<1	2	96.5

The pH values for the pilot JBR showed the effects of the poor agitation on the ability to control limestone makeup rates. Because of the poor mixing, the pH in the pilot JBR varied over a wide range. The blow down slurry sample pH values ranged from 3.03 to 6.08. Generally, the pH of the blow down slurry showed poor correlation with the pH measured by the pH controller, located higher up in the reaction tank of the pilot JBR. Because of this poor correlation, as the testing progressed, pH control was done with manual limestone dosing to the pilot JBR rather than relying on the feedback signal from the pH controller.

The oxidation-reduction potential (ORP) readings from the pilot JBR were observed to correlate inversely with pH. At lower pH the ORP was higher and at higher pH the ORP trended lower. This indicates that the liquor was more highly oxidizing at lower pH, which is consistent with previous FGD experience that generally shows higher sulfite oxidation at lower pH, most likely due to increased solubility of metals that serve as oxidation catalysts.

The solid analyses show further adverse effects of the apparent poor mixing in the JBR reaction zone. Although all of the solids samples were highly oxidized (very little sulfite $[SO_3^=]$ in the solids) several of the samples showed high carbonate content and low gypsum purity (<90%), indicative of high pH excursions and/or poor mixing of carbonate-rich solids in the absorption zone of the JBR.

Mercury Balance Calculations

Given that the slurry solids in the JBR were apparently stratified by the lack of mechanical agitation, that the SCEM gas phase mercury concentration data were not considered to be reliable, and that the pilot JBR was not operated around the clock to achieve true steady state operation, no attempt was made to close a mercury balance around the pilot JBR. Overall mass and mercury balances were calculated around the hydrocyclone when blowing down slurry from the pilot JBR, though. Table 26 shows the overall mass balance estimate around the hydrocyclone, based on feed, overflow and underflow wt% solids values. Table 27 shows the mercury balances around the hydrocyclone based on the estimates from Table 26 and the mercury analysis results from Table 22.

Table 26. Summary of Hydrocyclone Overall Mass Balance Estimates for Pilot JBR

Date	TMT-15 Dosage (mL/ton of coal)	% of FGD Blow Down Slurry Liquor		% of FGD Blow Down Slurry Solids	
		HC Overflow	HC Underflow	HC Overflow	HC Underflow
8/18/2005	0 (baseline)	96	3.6	37	63
8/19/2005	2.5	98	2.0	40	60
8/20/2005	7.5	94	6.3	57	43
8/21/2005	20	92	7.6	36	64

Table 27. Summary of Hydrocyclone Mercury Balance Calculations for Pilot JBR

Date	TMT-15 Dosage (mL/ton of coal)	% of FGD Blow Down Slurry Mercury Content				
		HC Over-flow Liquor	HC Over-flow Solids	HC Under-flow Liquor	HC Under-flow Solids	Total Hg Recovery
8/18/2005	0 (baseline)	71	17	3.1	4.5	96
8/19/2005	2.5	102	16	1.8	3.4	123
8/20/2005	7.5	4.1	149	0.7	17	171
8/21/2005	20	1.5	175	0.1	21	197

The mercury balance results show reasonably close closures for the samples from August 18 and 19, but nearly 200% recovery of the mercury in the pilot JBR blow down slurry in the hydrocyclone overflow and underflow for the samples from August 20 and 21. For those two days, it appears that the amount of mercury in the hydrocyclone overflow solids is over-reported. This suggests that either the wt% solids values for those samples are biased high, and/or the mercury concentrations are biased high.

There are two possible reasons for the wt% solids and/or solids mercury concentration bias seen in the mercury balance closures for August 20 and 21. One is a possible sample filtering and preservation bias discussed previously for the Monticello steady-state TMT additive test. The other is a possible sample time bias. The JBR blow down (hydrocyclone feed) sample set typically takes several minutes to collect, because the preserved FGD liquor samples are pressure filtered at the point of sample collection into separate prepared bottles for the various analytes. Given the evidence of stratification of solids in the lower portions of the JBR where the recycle pump takes suction, it is possible that the hydrocyclone feed slurry composition varied during the time that elapsed between when the hydrocyclone feed samples were collected and when the overflow and underflow samples were collected.

Full-scale Tests at IPL Petersburg Station

This subsection presents and discusses results for TMT additive tests conducted on the Petersburg Unit 2 full-scale wet FGD system, as previously described in Section 2.

Flue Gas Data

Mercury SCEM Results

As described in the Experimental section, the original project plan was to collect FGD absorber inlet and stack mercury concentration and speciation data to use as an indicator of TMT-15 effectiveness in controlling mercury re-emissions. However, measurement interferences at the FGD inlet location and failure of one of the analyzers led to SCEM measurements only being made at the stack location. Both total and elemental mercury concentrations were measured there, but the elemental mercury concentration data are of most relevance because the elemental mercury is present largely because of re-emissions. The stack elemental mercury concentration data from the test period are plotted below in Figure 14. Periods when TMT-15 injection to the reaction tank was interrupted are noted on the figure. The varied TMT-15 injection rates are noted by different data symbols, as identified in the legend.

At first it appeared that the TMT-15 injection was quite effective. After injecting at the lowest rate of 10 mL/ton of coal fired overnight (with one interruption) the stack elemental mercury concentrations were lowered to between 1.0 and 1.5 μg/Nm^3 (corrected to 3% O_2) on July 14, from earlier values in the range of 3 to 5 μg/Nm^3 on July 12 and 13. However, as the week went on, the stack elemental mercury concentrations increased back into the range of about 4 μg/Nm^3 in spite of the TMT-15 injection rate being increased up to 40 mL/ton of coal.

This observation could indicate that TMT-15 injection was most effective at the lowest injection rate tested, 10 mL/ton of coal fired. However, the FGD liquor mercury concentration data,
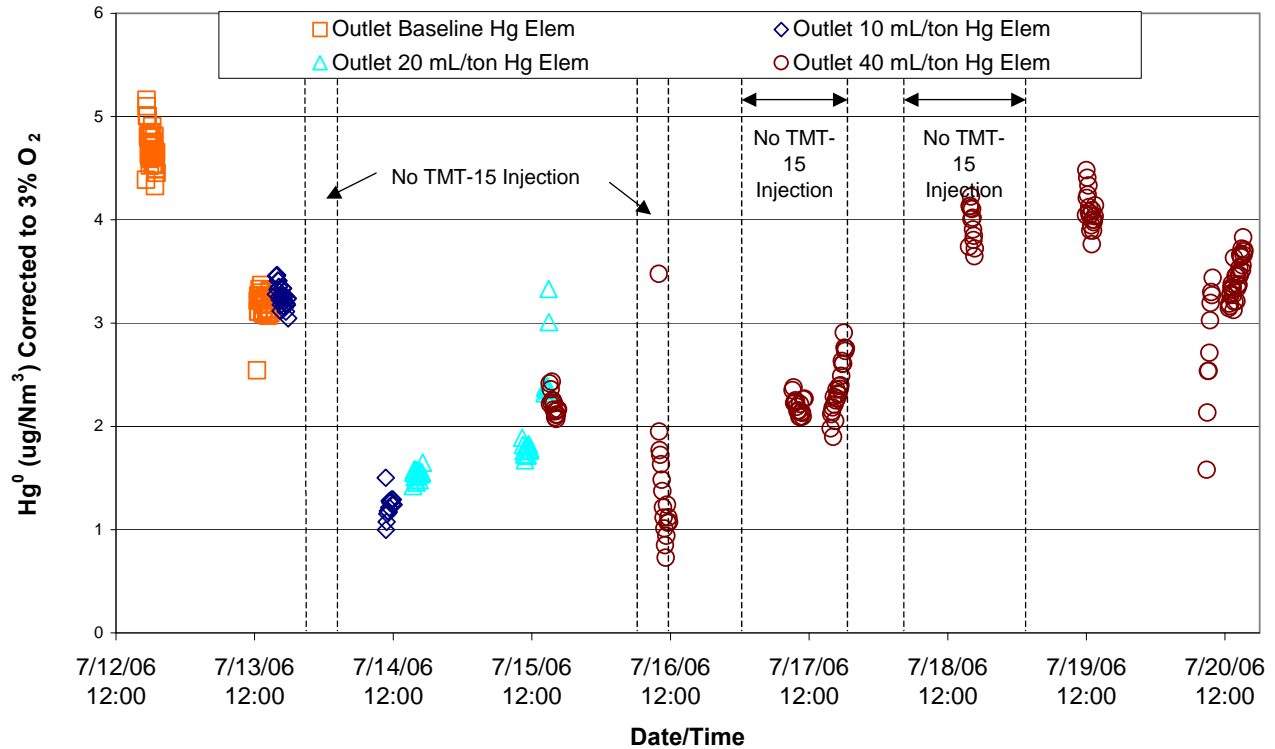
Figure 14. SCEM Results for the Petersburg Unit 2 Stack Flue Gas

discussed later in this report, do not indicate significant reductions in liquor mercury concentrations during this time period. It is likely that the drop in stack elemental mercury concentration seen around July 14 is due to other factors, which at this point remain unidentified.

Ontario Hydro Flue Gas Measurement Results

The most quantitative results from the test program are baseline and steady-state TMT injection period flue gas mercury concentration data measured by the Ontario Hydro method,[6] and FGD system liquor and solids mercury concentration data which are discussed later in this section. These results did not become available until after the field testing was completed. The Ontario Hydro results from the absorber inlet and stack for both the baseline and steady-state TMT injection condition are shown in Table 28.

The results do not show a reduction in elemental mercury re-emissions of the magnitude expected with TMT-15 addition. One row of the table expresses the level of re-emissions as a percentage of the FGD inlet oxidized mercury concentration, a re-emission level metric used throughout this report. At baseline, the re-emissions represented 49% of the FGD inlet oxidized mercury. With TMT addition, the re-emission level was somewhat reduced to 37% of the FGD inlet oxidized mercury based on the average of the three stack Ontario Hydro runs on July 20.

However, note that there are two columns of data for the stack concentrations for July 20, one that includes all three runs and one that does not include an apparent outlier run. For one of the three runs, the stack oxidized mercury concentration value was very high, measuring 2.2

57

Table 28. Results of Ontario Hydro Measurements During TMT-15 Test at Petersburg Unit 2 (mean values for three Ontario Hydro runs ± 95% confidence interval about mean)

Condition	Baseline		With TMT-15 @ 40 mL/ton coal		
Test Date(s)	7/12-7/13/2006		7/20/2006		
Parameter	FGD Inlet	Stack	FGD Inlet	Stack*	Stack**
Hg^0, μg/Nm^3 @ 3% O_2	2.3 ± 0.3	5.7 ± 0.4	2.0 ± 0.7	4.8 ± 0.6	4.6 ± 0.8
Hg^{+2}, μg/Nm^3 @ 3% O_2	6.9 ± 0.7	0.4 ± 0.1	7.6 ± 1.0	1.0 ± 1.1	0.5 ± 0.3
Total Hg, μg/Nm^3 @ 3% O_2	9.2 ± 1.0	6.1 ± 0.3	9.6 ± 1.3	5.8 ± 1.4	5.1 ± 0.5
Mercury Oxidation at FGD Inlet, %	75 ± 1	-	80 ± 6	-	-
Hg^{+2} Removal across Absorber, %	-	95% ± 2%	-	86% ± 18	94% ± 4
Hg^0 Re-emissions across Absorber, μg/Nm^3 @ 3% O_2	-	3.4 ± 0.4	-	2.8 ± 0.5	2.6 ± 0.4
Hg^0 Re-emissions, % of FGD inlet Hg^{+2}	-	49% ± 6%	-	37% ± 12%	35% ± 5%
Overall Hg Removal across Absorber, %	-	34% ± 5%	-	39% ± 23%	47% ± 1%

*Results including apparent outlier value for one of three runs
**Results for two runs, excluding apparent outlier value for one of three runs

μg/Nm^3, whereas the other two runs (other five runs considering the baseline measurements a week earlier) measured 0.6 μg/Nm^3 or less. This one run resulted in a calculated removal efficiency for oxidized mercury across the absorber of only 67%, while the results of the other five runs measured 92 to 96% removal. This seems like an obvious outlier, considering that oxidized mercury should be removed at high efficiency in a spray tower operating at a high liquid to gas ratio as does the Petersburg Unit 2 FGD absorber. While this one data point does not qualify as an outlier based on a "Q test" for three data points, it would be considered an outlier if all six data points are included.[7] Given that TMT-15 is not expected to impact oxidized mercury removal across the wet FGD system, and that the six stack oxidized mercury concentration measurements are at otherwise similar conditions, it seems reasonable to use Q test results for all six points to exclude the results of this one stack measurement run on July 20. Also, the SCEM data for the stack location indicated that the stack oxidized mercury concentration was less than 0.5 μg/Nm^3 during the second Ontario Hydro run period on July 20, much lower than the indicated value of 2.2 μg/Nm^3 for that Ontario Hydro run.

Although the data are presented both ways in Table 28, the remainder of the discussions of the Ontario Hydro results considers only the two stack runs for July 20. With the apparent outlier set of data excluded from the mean value for July 20, the re-emission level during TMT-15 addition was slightly lower at 35% rather than 37%. This represents a moderate improvement from the re-emission level of 49% measured during baseline testing on July 12-13. The overall mercury removal across the FGD was also moderately improved during TMT addition, from 34% of the FGD inlet total mercury being removed on July 12-13 to 47% on July 20. There is a small confounding effect on this observation, in that the FGD inlet mercury oxidation was higher

during the TMT-15 test period than during baseline (80% versus 75%). This alone would tend to increase the overall mercury removal across the absorber by two to three percentage points if re-emission percentages were otherwise unaffected.

Although these results show some improvement in net capture of mercury by the Unit 2 FGD system during TMT-15 injection, the decrease in elemental mercury re-emissions measured was not of the magnitude expected. It had been hoped that re-emissions levels would have been reduced to 5% or less of the FGD inlet flue gas oxidized mercury content. As will be discussed below, it is not clear whether the observed decrease in measured mercury re-emissions was an effect of TMT-15 injection or merely represented day-to-day variation, as little effect of TMT was seen on FGD liquor mercury concentrations.

FGD Liquor and Solid Byproduct Analysis Data

FGD Liquor Mercury Concentrations

As shown above in the pilot-scale TMT test results discussed above, an expected result of TMT-15 addition is a dramatic reduction in absorber liquor mercury concentrations. TMT is expected to precipitate oxidized mercury from the liquor before it has the opportunity to be reduced by sulfite ion. However, this effect was not seen at Petersburg. Absorber liquor and primary hydrocyclone overflow liquor (the return liquor to the absorber) were sampled and analyzed for mercury concentration almost daily over the test period. Table 29 summarizes the mercury concentration results.

Table 29. Results of Daily Absorber Blow Down and Primary Hydrocyclone Overflow Liquor Mercury Concentrations During Baseline and TMT Addition Periods

Date	Time	TMT-15 Dosage	Absorber Blow Down Liquor Mercury Concentration, µg/L	Primary Hydrocyclone Overflow Mercury Concentration, µg/L
7/12/2006	13:15	Baseline (0 mL/ton)	62.6	51.1
7/13/2006	8:50	Baseline (0 mL/ton)	61.7	52.5
7/14/2006	14:30	10 mL/ton	54.7	56.1
7/15/2006	14:15	20 mL/ton	62.7	57.7
7/16/2005	17:45	40 mL/ton	69.8	63.6
7/18/2006	10:15	40 mL/ton	45.7	-
7/19/2006	13:35	40 mL/ton	40.2	40.1
7/20/2006	8:03	40 mL/ton	60.4	57.0

The results show little or no reduction in liquor mercury concentrations after a week of TMT-15 injection. There was one period (the afternoon of July 19) where the liquor mercury concentrations were reduced to about two-thirds of the normal value. This sample was taken not long after a number of gallons of TMT-15 were spiked into the reaction tank. The spiking was required because the return line to the reaction tank, into which TMT was continuously added, was out of service for a number of hours. The spiking was done to return the reaction tank to a

59

steady state TMT dosage after the line was returned to service following repairs. This depression in liquor mercury concentrations not long after the TMT-15 spiking event suggests that higher TMT-15 dosages might have been more effective on the Unit 2 FGD system. However, at the time of the test the dosing rate of 40 mL/ton of coal fired was perceived to be an economic limit for TMT-15 dosage.

During baseline operation and at the end of the steady-state TMT spiking period, FGD liquor samples were taken throughout the Unit 2 FGD slurry blow down/byproduct dewatering system. The results of the mercury concentration analyses on these samples are summarized in Table 30. Figure 6 in Section 2 illustrates where these sampling points are located in the dewatering train. These results also show no significant effect of TMT addition in lowering liquor mercury concentrations.

Table 30. Results of Liquor Mercury Concentrations in Unit 2 FGD Blow Down Slurry Dewatering Train

Sample	7/12/2006 (Baseline), μg/L	7/20/2006 (after five days of TMT-15 Injection at 40 mL/ton), μg/L
Absorber Blow Down (from Table 5)	62.6	60.4
Primary Hydrocyclone Overflow (from Table 5)	51.1	57.0
Primary Hydrocyclone Underflow	49.9	57.9
Secondary Hydrocyclone Feed Tank	0.13	1.6
Secondary Hydrocyclone Overflow	<0.10	1.4
Secondary Hydrocyclone Underflow (Horizontal Vacuum Belt Filter Feed)	<0.10	1.6
Belt Filter Filtrate	<0.10	<0.20

FGD Byproduct Solids Mercury Concentrations

Solids samples from throughout the FGD system were also measured for mercury concentration. As shown above in the pilot-scale TMT test results, it was expected that the absorber solids mercury concentration would go up with TMT addition due to precipitation of mercury from the liquor. The hydrocyclone overflow solids mercury concentrations were also expected to go up, while the hydrocyclone underflow and byproduct gypsum mercury concentrations should go down. This was anticipated because of the relatively high concentration of mercury in fine TMT precipitates that would be removed with the hydrocyclone overflow.

The results of FGD solids mercury analyses are summarized in Table 31 for the daily absorber blow down and primary hydrocyclone overflow samples. Table 32 summarizes results for solids from throughout the Unit 2 byproduct dewatering system for the baseline and steady-state TMT addition Ontario Hydro flue gas test periods. Refer to Figure 6 in Section 2 for a review of these sample locations relative to the Unit 2 FGD dewatering scheme.

Table 31. Results of Daily Absorber Blow Down and Primary Hydrocyclone Overflow Solids Mercury Concentrations During Baseline and TMT Addition Periods

Date	Time	TMT-15 Dosage	Absorber Blow Down Solids Mercury Concentration, µg/g	Primary Hydrocyclone Overflow Solids Mercury Concentration, µg/g
7/12/2006	13:15	Baseline (0 mL/ton)	0.41	0.95
7/13/2006	8:50	Baseline (0 mL/ton)	0.37	0.90
7/14/2006	14:30	10 mL/ton	0.43	0.91
7/15/2006	14:15	20 mL/ton	0.35	0.76
7/16/2005	17:45	40 mL/ton	0.27	0.51
7/18/2006	10:15	40 mL/ton	0.44	-
7/19/2006	13:35	40 mL/ton	0.43	1.26
7/20/2006	8:03	40 mL/ton	0.33	0.74

Table 32. Results of FGD System Solids Mercury Concentration Data for Baseline and Steady-state TMT Addition Ontario Hydro Test Periods

Sample	7/12/2006 (Baseline), µg/g	7/20/2006 (after five days TMT-15 Injection at 40 mL/ton), µg/g
Absorber Blow Down (from Table 7)	0.41	0.33
Primary Hydrocyclone Overflow (from Table 6)	0.95	0.74
Primary Hydrocyclone Underflow	0.13	0.12
Secondary Hydrocyclone Feed Tank	0.19	0.13
Secondary Hydrocyclone Overflow	3.76	3.65
Secondary Hydrocyclone Underflow (Horizontal Vacuum Belt Filter Feed)	0.14	0.13
Dewatered Gypsum Byproduct	0.13	0.12

Comparison of the data from July 12-13 with those for July 20 shows a very small decrease in the mercury concentrations in the absorber solids, primary and secondary hydrocyclone underflow solids, and byproduct gypsum by the end of the TMT-15 injection period. The expected increase in hydrocyclone overflow solids mercury concentration was not seen during this period. Both the hydrocyclone underflow and overflow solid mercury concentrations went down by the end of the TMT injection test period (both primary and secondary hydrocyclones). This suggests an overall lowering in the mercury mass removal rate by the FGD system compared to the SO_2 mass removal rate, rather than indicating the expected TMT effect.

Coal sample analysis data from July 12 through July 20 are shown in Table 33 (coal moisture and mercury content only for July 13-19), and actually show a slightly higher rather than lower

coal mercury concentration on the 20th compared to the 12th. In fact, coal samples from July 13 through July 20 show a relatively constant coal mercury content, with a mean of 0.092 ppm and a standard deviation of 0.004 ppm. Unfortunately, there was not a coal sample from July 14, the day the mercury SCEM at the stack measured particularly low elemental mercury concentrations.

Table 33. Petersburg Unit 2 Coal Sample Data

Task Number, Power Plant	Heating Value (Btu/lb as received)	Total Moisture, wt %	Ash (Wt % as received)	Sulfur (Wt % as received)	Sulfur (lb SO$_2$/MM Btu)	Hg (Dry ppm)	Chlorine (Dry ppm)
7/12/2006 (Baseline)	12,488	13.0	8.84	3.12	5.0	0.078	70.9
7/13/2006 (Baseline)	-	11.7	-	-	-	0.088	-
7/13/2006(Baseline)	-	13.1	-	-	-	0.088	-
7/15/2006 (TMT-15 @ 20 mL/ton)	-	11.8	-	-	-	0.090	-
7/15/2006 (TMT-15 @ 20 mL/ton)	-	11.6	-	-	-	0.096	-
7/16/2006 (TMT-15 @ 40 mL/ton)	-	12.1	-	-	-	0.092	-
7/17/2006 (TMT-15 @ 40 mL/ton)	-	12.4	-	-	-	0.093	-
7/18/2006 (TMT-15 @ 40 mL/ton)	-	10.8	-	-	-	0.095	-
7/19/2006 (TMT-15 @ 40 mL/ton)	-	12.5	-	-	-	0.098	-
7/20/2006 (after five days TMT-15 Injection at 40 mL/ton)	12,575	12.3	9.26	3.13	5.0	0.087	66.3

The daily FGD solids mercury concentration data in Table 31 show that the absorber blow down and primary hydrocyclone overflow solids mercury concentrations varied up and down over the test period, perhaps reflecting variations in the coal sulfur and mercury content. There was only one day where the expected effect of TMT addition was seen – a significant increase in the mercury concentration in the primary hydrocyclone overflow solids mercury concentration – on July 19. This was shortly after TMT had been spiked into the reaction tank to make up for a period where TMT could not be injected. This solid sample corresponds with the same samples shown in Table 29 where the absorber liquor and primary hydrocyclone mercury concentrations were reduced on July 19. The stack mercury SCEM data plotted in Figure 14 do not show a corresponding decrease in stack elemental mercury concentration on July 19, though.

The absorber liquor and solids mercury concentration data are shown in Table 34. The absorber slurry weight percent solids level is also shown. These data were used to calculate the percentage of the mercury in the absorber slurry found in the FGD liquor. This percentage was expected to be significantly reduced by TMT injection. The data from the July 19 sample show the lowest percentage of the slurry mercury in the liquor, although the percentage was still not as low as was expected with TMT addition. This apparent effect of a spike addition of TMT-15 to the reaction tank on July 19 suggests that the TMT might have been more effective on the Unit 2 FGD system if it had been continually injected at a higher dosage rate.

62

Table 34. Daily Absorber Blow Down Slurry Mercury Concentrations During Baseline and TMT Addition Periods

Date	Time	TMT-15 Dosage	Absorber Blow Down Liquor Mercury Concentration, μg/L	Absorber Blow Down Solids Mercury Concentration, μg/g	Slurry wt% Solids	Percent of Total Mercury in Slurry in Liquor
7/12/2006	13:15	Baseline (0 mL/ton)	62.6	0.41	15.7	45
7/13/2006	8:50	Baseline (0 mL/ton)	61.7	0.37	16.1	47
7/14/2006	14:30	10 mL/ton	54.7	0.43	16.8	39
7/15/2006	14:15	20 mL/ton	62.7	0.35	15.5	49
7/16/2005	17:45	40 mL/ton	69.8	0.27	16.3	57
7/18/2006	10:15	40 mL/ton	45.7	0.44	15.1	37
7/19/2006	13:35	40 mL/ton	40.2	0.43	16.3	33
7/20/2006	8:03	40 mL/ton	60.4	0.33	16.3	48

FGD Byproduct Solids Particle Size Analyses

Samples from the baseline and steady-state TMT-15 injection periods were sent for particle size distribution analyses, to determine if TMT-15 addition had any impact on particle size, particularly in the fines fraction. The results of these analyses are summarized in Table 35.

Table 35. Results of Particle Size Analyses on Byproduct Solid Samples

Sample Location	D_{10}, μm*	D_{50}, μm*	D_{90}, μm*	Mean, μm
Baseline (no TMT injection) Samples, 7/12/2006:				
Absorber Blow Down Solids	20.2	36.8	59.6	39.1
Primary Hydrocyclone Overflow	10.0	27.7	45.1	28.4
Primary Hydrocyclone Underflow	28.2	41.7	63.7	44.6
Byproduct Gypsum	27.4	41.1	62.3	43.7
Steady-state TMT-15 Injection Period (40 mL/ton of coal), 7/20/2006:				
Absorber Blow Down Solids	19.2	34.0	55.1	36.3
Primary Hydrocyclone Overflow	11.5	25.4	41.0	26.4
Primary Hydrocyclone Underflow	27.8	41.4	62.0	43.9
Byproduct Gypsum	27.5	41.0	61.8	43.6

*Particle size at which 10%, 50%, or 90% of the particles (as noted in the subscript) are smaller.

The results do not show a significant change in particle size when comparing the baseline sample particle size distributions with those for the corresponding samples from the steady-state TMT injection period. The expected increase in the amount of fine particles in the hydrocyclone overflow, which would have reflected the formation of fine TMT-mercury salts, was not

63

observed. These data further support the observation that TMT addition did not show several of the expected impacts on the Unit 2 FGD system.

The results do show the expected effects of the dewatering system, though. The primary hydrocyclones separate the absorber blow down into a finer size fraction in the overflow versus a coarser size fraction in the underflow. The product gypsum particle size distributions are not much different than the primary hydrocyclone underflow solids size distributions, indicating that further dewatering and separation of fines in the secondary hydrocyclones does not have much impact on the byproduct particle size.

FGD Absorber Blow Down Slurry Chemistry

FGD absorber blow down slurry samples were collected and preserved for off-site analyses of typical FGD analytes during the baseline and steady-state TMT-15 injection periods, to observe whether TMT injection had any adverse effects on FGD chemistry. The results of these analyses are shown in Table 36. No adverse effects were expected, and the results show no significant TMT-15 addition effect on FGD chemistry. In particular, sulfite oxidation, limestone utilization, and gypsum purity did not appear to be affected.

Since the expected effects of TMT-15 addition on mercury removal by the wet FGD system were generally not seen during these tests, a number of hypotheses were proposed as to what limited its effectiveness. One was that, because the TMT-15 was injected into a return stream to the FGD reaction tank rather than to the feed stream to the absorber spray headers, other divalent transition metals may have precipitated with the TMT injected before it was able to precipitate mercury as it was absorbed. As a test of that hypothesis, FGD absorber liquor samples from the baseline and steady state TMT injection Ontario Hydro measurement periods were analyzed for other trace metals content.

These results are summarized in Table 37. The results again show no consistent effect of TMT-15 addition. The concentrations of three of the five metals analyzed actually increased during the TMT-15 injection period while the other two went down. It is apparent that some other effect was impacting the effectiveness of TMT-15 in precipitating mercury from the FGD liquor, and perhaps impacting the partitioning of these other metals between the FGD absorber slurry liquor and solids.

SPLP Analyses of Byproduct Solids

As part of the project plan for Task 3, samples of the gypsum byproduct and primary hydrocyclone overflow solids (fines blow down solids) were analyzed by the synthetic precipitation leaching procedure (SPLP), EPA Method 1312.[8] This method is intended to simulate the effects of rainfall in producing leachate from monofills of solid byproducts. The gypsum and the fines blow down solids are the two solid byproduct streams that leave the Unit 2 FGD system and might end up in a landfill at some power plants. The SPLP method was conducted on gypsum and hydrocyclone overflow solids from both the baseline (no TMT addition) and steady-state 40 mL/ton of coal TMT-15 injection rate test periods, on samples from July 12, 2006 and July 20, 2006, respectively.

Table 36. FGD Absorber Blow Down Slurry Analysis Results

Date	7/12/2006	7/13/2006	7/20/2006	7/20/2006
Time	13:15	08:56	08:03	16:00
TMT-15 Injection Rate, mL/ton of coal	0 (Baseline)	0 (Baseline)	40	40
pH	6.41	6.15	6.01	5.93
Temperature, ^{o}C	55.4	55	53.3	55.1
Slurry solids, wt%	15.70	16.09	16.33	15.53
Slurry Solids Analyses:				
Ca, mg/g	226	232	223	223
Mg, mg/g	1.6	1.3	1.1	1.1
SO_3, mg/g	<0.8	<0.8	<0.8	<0.8
SO_4, mg/g	511	531	525	524
CO_3, mg/g	16	14	10	10
Inerts, wt%	4.71	4.11	4.52	4.43
Gypsum Purity, wt% (based on sulfate analysis)	91.6	95.2	94.1	93.9
Sulfite oxidation, %	100.0	100.0	100.0	100.0
Limestone utilization, %	94.6	95.6	97.1	97.1
FGD Liquor Analyses:				
Ca^{++}, mg/L	1019	1133	1069	1034
Mg^{++}, mg/L	1166	1322	1550	1429
Na^+, mg/L	115	122	365	132
Cl^-, mg/L	481	431	463	425
$CO_3^=$, mg/L	91	464	698	656
$SO_3^=$, mg/L	<10	<10	<8	<8
$SO_4^=$, mg/L	3773	3297	3921	2016

Table 37. FGD Absorber Flow Down Solids Divalent Transition Metal Concentration Data for Baseline and Steady-state TMT Addition Ontario Hydro Test Periods

	Baseline (7/12/2006)	With TMT @ 40 mL/ton coal (7/20/2006)	Observed % Reduction (% Increase)
Ag, μg/g	1.2	0.82	32
Cd, μg/g	18	36	(100)
Cu, μg/g	75	57	24
Pd, μg/g	1.8	4.1	(128)
Zn, μg/g	94	191	(103)

The results from all four SPLP tests showed mercury concentrations below detection limits in the SPLP leachate (<0.25 µg/L). The toxicity characteristic limit for mercury in leachate is 200 µg/L. Thus, all four samples were approximately two orders of magnitude lower than the toxicity limit regardless of whether or not TMT-15 was added.

Follow-up Measurements at Petersburg Unit 2

After the test results from July 2006 became available, Evonik Degussa suggested a return to the site to conduct a more fundamental evaluation of the effectiveness of TMT-15 in precipitating mercury from the Unit 2 FGD liquor. They speculated on the presence of an interferent that may have prevented TMT from being effective. Evonik Degussa sometimes uses pH adjustment as a means of avoiding interferences when using TMT for wastewater treatment, and wanted to conduct beaker-scale tests on fresh liquor from the Unit 2 FGD system to see if there was a similar effect on mercury precipitation. Although pH adjustment is not a likely approach for application in FGD absorber recycle slurry, such an effect might provide insight to the mechanisms which prevented greater effectiveness of TMT-15 at Petersburg.

In January 2007, an Evonik Degussa engineer and a URS scientist returned to Unit 2 and conducted a series of beaker-scale TMT dosage tests. TMT-15 dosages equivalent to 10, 20 and 40 mL/ton of coal were tested at three conditions on liquor from the Unit 2 primary hydrocyclone overflow. The hydrocyclone overflow rather than the absorber reaction tank slurry was tested because some of the tests were to be conducted on clear liquors, and it was expected to be easier to filter the hydrocyclone overflow because of its lower solids content. The three conditions included treating whole hydrocyclone overflow slurry, filtered hydrocyclone overflow liquor, and filtered hydrocyclone overflow liquor with pH adjustment. The filtered liquor tests were conducted primarily because it was thought it would be easier to quantify TMT effectiveness if solids were not present (e.g., it might be possible to see the TMT precipitates in clear liquor). The results of these tests are summarized in Table 38.

Table 38. Results of TMT Addition Beaker Tests at Petersburg Unit 2, January 2007

TMT-15 Dosage, mL/ton of coal	Absorber Blow Down Liquor Mercury, µg/L	Hydrocyclone Overflow Slurry Mercury, µg/L	Hydrocyclone Overflow Liquor Mercury, µg/L	Hydrocyclone Overflow Liquor Mercury, µg/L (Nitric acid added to pH 2.89)
0	0.98	0.82	0.13	0.26
10	-	0.53	0.16	0.18
20	-	0.40	0.14	0.16
40	-	0.14	<0.12	0.14

The most surprising result was that the absorber liquor mercury concentration was over an order of magnitude lower than the baseline sample from July 2006 (0.98 µg/L versus 62.6 µg/L as shown in Table 29). However, the results of mercury analyses on the absorber solids from January (not shown in the table) showed higher mercury content than did the July baseline result

(0.83 μg/g versus 0.37-0.41 μg/g in July [Table 31]). After considering the weight percent solids in the absorber slurry (15-16% in both cases), the January sample actually had more mercury in the slurry than the July sample, but almost all of the mercury was in the solids (>99%).

Looking at the TMT beaker test results, other than the baseline 0 mL/ton TMT-15 dosage value for the filtered hydrocyclone overflow liquor mercury in the middle data set, the data show lower liquor mercury concentrations with continued increases in TMT-15 dosage. For the filtered hydrocyclone overflow liquor, the mercury concentrations are all near the analytical detection limit. At such low concentrations, it is hard to accurately quantify changes.

The biggest known difference between July 2006 and January 2007 is that the SCR was operating in July and was bypassed in January. It is not obvious that having the SCR out of service would change the FGD liquor mercury concentration so dramatically, and it cannot be concluded from this limited amount of data that this was an SCR-related effect. EPRI funded a return to Petersburg Unit 2 in April (SCR still bypassed) and May 2007 (SCR in service for ozone season), to measure baseline (no TMT) absorber mercury concentrations. These results did not show an SCR effect consistent with the comparison of July 2006 to January 2007 data. In April 2007, the absorber liquor mercury concentration was measured at 10.3 μL (6% of the slurry total mercury) while in May 2007 the liquor mercury concentration was only 0.2 μg/L (0.1% of the slurry total mercury). In this case the liquor mercury concentration was lower rather than higher with the SCR in service.

Full-scale Additive Tests at Plant Yates

This subsection provides details of technical results for TMT-15 and Nalco 8034 additive tests conducted on the Yates Unit 1 full-scale wet FGD system, which was described in Section 2. The TMT-15 test results are discussed first, then the Nalco 8034 test results. Also, as discussed below there were significant differences in JBR liquor mercury concentrations between the TMT-15 test period in May 2007 and the beginning of the Nalco 8034 test in August 2007. Additional analyses were conducted to investigate what might have caused these changes. The results of these additional analyses are presented and discussed at the end of this subsection.

TMT-15 Test Results

Flue Gas Data

As described in the Experimental section, JBR inlet mercury concentrations were periodically monitored by mercury SCEM, while stack mercury concentrations were continuously monitored by a plant CEM. Both total and elemental mercury concentrations were measured at the JBR inlet, but the CEM at the stack location measured only total mercury concentrations. Because the JBR removes nearly all of the oxidized mercury from the flue gas, the mercury was expected to be predominantly in the elemental mercury form at the stack location.

As summarized in Table 39, baseline (no TMT-15 addition) mercury removal data were measured on May 15 and showed 23% mercury re-emissions, seen as an increase in Hg^0 concentration across the JBR. (Actually the re-emissions were seen as the stack total mercury concentration being higher than the inlet elemental mercury concentration). As elsewhere in this

report, the re-emissions percentage shown is the apparent increase in elemental mercury concentration across JBR divided by the JBR inlet oxidized mercury concentration. This provides an indication of how much of the oxidized mercury that can get removed across the JBR is re-emitted instead.

Table 39. JBR Mercury Removal Data, by SCEM and CEM during the May 2007 TMT-15 Additive Portion of the Test Program

Date	Time Averaged	TMT-15 Dose Rate, mL/ton of coal fired	JBR Inlet Hg, $\mu g/Nm^3$ @ 3% O_2		JBR Outlet Total Hg, $\mu g/Nm^3$ @ 3% O_2	Hg Oxidation at Inlet, %	Total Hg Removal by FGD, %	Hg^{+2} Capture by FGD, %	Hg^0 Re-emission, % of inlet Hg^{+2}
			Total Hg	Hg^0					
5/15 2007	6:00 – 17:00	0 (baseline)	5.7	1.5	2.4	26	57	(assumed 100%)	23
5/18 2007	8:00 – 16:00	20	7.6	2.1	3.2	28	57	(assumed 100%)	21
5/24 2007	6:00 – 20:00	40	7.4	1.7	3.2	23	36	(assumed 100%)	53
5/29 2007	4:00 – 14:00	40	3.9	1.1	4.7	29	-8.2	(assumed 100%)	112

On three subsequent representative days of TMT-15 addition, no reduction in re-emission was observed. Although there was some day-to-day variability throughout the test program, these results did not indicate any significant effect of the additive in controlling mercury re-emissions. The extremely high re-emission rate shown for 5/29/2007 may be an anomaly of the operating mode at the end of the test period. When the decision was made to end the test after 15 days of TMT-15 injection, the injection rate was increased dramatically to use up the remaining inventory in the TMT-15 drum in use. At this high injection rate, it is possible that TMT-15 served as a reductant to directly reduce dissolved oxidized mercury to the elemental form.

Flue gas mercury concentration data measured by the Ontario Hydro method[6] were used as the determining factor in quantifying the effect of TMT-15 addition on re-emissions. Although the Ontario Hydro and SCEM/CEM results showed general agreement, the Ontario Hydro results were given the most weight because it is a reference method. Baseline and steady-state additive injection period mercury concentration data for the JBR slurry solids and liquor were also used to determine any TMT-15 effects. The solids and liquor results are discussed later in this section.

The Ontario Hydro results from the JBR inlet and stack for both the baseline and steady-state TMT-15 injection condition are shown in Table 40. There are two columns of data for the stack concentrations for May 24, one that includes results from all three Ontario Hydro measurement runs and one that does not include an apparent outlier run. For one of the three runs, the stack elemental mercury concentration value was very high, measuring 11.9 $\mu g/Nm^3$, whereas the

other two runs (other five runs considering the earlier baseline measurements) measured 7.9 μg/Nm^3 or less. This one run resulted in a negative calculated removal efficiency for mercury across the absorber, while the results of the other five runs measured 6 to 37% removal. While this one data point does not qualify as an outlier based on a "Q test" for three data points, it does seem to be an unreasonably high elemental mercury value. The stack CEM data during the questionable Ontario Hydro run period on May 24 show an average total mercury concentration of 6.0 μg/Nm^3 with a single maximum value of 7.8 μg/Nm^3, significantly less than the 11.9 μg/Nm^3 elemental mercury concentration value measured for that Ontario Hydro run. The remainder of the discussions of the Ontario Hydro results considers only the two stack runs for May 24.

Table 40. Results of Ontario Hydro Measurements During TMT-15 Test at Yates Unit 1 (mean values for three Ontario Hydro runs ± 95% confidence interval about mean)

| | Baseline | | With TMT-15 @ 40 mL/ton coal | | |
| | 5/15/07 | | 5/24/07 | | |
Condition	JBR Inlet	Stack	JBR Inlet	Stack*	Stack**
Hg^0, μg/Nm^3 @ 3% O$_2$	3.6 ± 0.6	4.6 ± 0.2	4.7 ± 0.7	8.9 ± 2.9	7.5 ± 0.9
Hg^{+2}, μg/Nm^3 @ 3% O$_2$	3.4 ± 0.7	0.2 ± 0.1	4.8 ± 0.2	0.7 ± 0.2	0.5 ± 0.1
Total Hg, μg/Nm^3 @ 3% O$_2$	7.0 ± 0.4	4.8 ± 0.2	9.5 ± 0.5	9.6 ± 3.1	8.0 ± 0.9
Mercury Oxidation at JBR Inlet, %	52 ± 9	-	49 ± 5	-	-
Hg^{+2} Removal across Absorber, %	-	95% ± 2%	-	87% ± 5%	89% ± 1%
Hg^0 Re-emissions across Absorber, μg/Nm^3 @ 3% O$_2$	-	1.0 ± 0.7	-	4.2 ± 2.7	3.0 ± 1.9
Hg^0 Re-emissions, % of JBR inlet Hg^{+2}	-	29% ± 17%	-	88% ± 59%	60% ± 34%
Overall Hg Removal across Absorber, %	-	31% ± 6%	-	-1% ± 31%	15% ± 16%

*Results including apparent outlier value for one of three runs
**Results for two runs, excluding apparent outlier value for one of three runs

The results do not show a reduction in elemental mercury re-emissions as was expected with TMT-15 addition. One row of the table expresses the level of re-emissions as a percentage of the FGD inlet oxidized mercury concentration, the same basis as was previously shown in Table 39 for the SCEM and CEM data. At baseline, the re-emissions represented 29% of the FGD inlet oxidized mercury, which agrees reasonably well with the SCEM/CEM data in Table 39 for this date (23%). With TMT-15 addition, the re-emissions level actually increased to 60% of the FGD inlet oxidized mercury based on the average of the two stack Ontario Hydro runs on May 24. The SCEM/CEM data in Table 39 show a similar re-emission level of 53%. In addition, the overall mercury removal across the scrubber was measured to decrease significantly with the addition of TMT-15 (15% by Ontario Hydro versus 36% by SCEM/CEM).

FGD Liquor and Solid Byproduct Analysis Data

As shown previously in the pilot-scale TMT test results, an expected result of TMT-15 addition is a dramatic reduction in absorber liquor mercury concentrations. TMT is expected to precipitate oxidized mercury from the liquor before it has the opportunity to be reduced by sulfite ion. During the TMT-15 test, JBR liquor and hydrocyclone overflow and underflow liquors were sampled and analyzed for mercury concentration periodically. Table 41 summarizes these mercury concentration results, which show a maximum of 47% reduction in liquor mercury concentration after two weeks of TMT-15 injection. A much greater reduction in liquor mercury was expected. Also, the baseline (no additive) JBR slurry liquor mercury concentrations were much higher than expected based on previous sampling at Plant Yates during the pilot-scale TMT test there in 2005. As shown previously in this section, during that testing the liquor in the full-scale JBR on Unit 1 was measured to have only 13 to 15 µg/L mercury content.

Table 41. Results of JBR Blow Down and Hydrocyclone Overflow and Underflow Liquor Mercury Concentrations During Baseline and TMT-15 Addition Periods

Date	TMT-15 Dosage	JBR Blow Down Liquor Hg Conc., µg/L	Hydrocyclone Overflow Liquor Hg Conc., µg/L	Hydrocyclone Underflow Liquor Hg Conc., µg/L
5/15/07	Baseline (0 mL/ton)	196	205	197
5/18/07	20 mL/ton	156	162	156
5/24/07	40 mL/ton	140	135	135
5/25/07	40 mL/ton	111	132	129
5/30/07	40 mL/ton	103	104	106

Solids samples from the JBR system were also measured for mercury concentration. As shown previously in the pilot-scale TMT test results, it was expected that the absorber solids mercury concentration would go up with TMT addition, due to precipitation of mercury from the liquor. The hydrocyclone overflow solids mercury concentrations were also expected to go up, while the hydrocyclone underflow concentrations were expected to go down. This was expected due to the concentration of mercury in fine TMT precipitates that would be removed in the hydrocyclones.

The results of FGD solids mercury analyses are summarized in Table 42. The results show very low mercury concentrations in the JBR solids, as might be expected based on the very high JBR liquor concentrations. The JBR slurry solids mercury concentrations did not go up as expected with TMT addition, nor was there a consistent increase in mercury concentration in the hydrocyclone overflow solids. The hydrocyclone underflow solids mercury concentrations did trend downward during the TMT-15 addition period, but of course the solids concentrations were very low even before TMT addition began.

Table 42. Results of JBR Blow Down and Hydrocyclone Overflow and Underflow Solids Mercury Concentrations During Baseline and TMT-15 Addition Periods

Date	TMT-15 Dosage	JBR Blow Down Solids Hg Conc., μg/g	Hydrocyclone Overflow Solids Hg Conc., μg/g	Hydrocyclone Underflow Solids Hg Conc., μg/g
5/15/07	Baseline (0 mL/ton)	0.072	1.07	0.063
5/18/07	20 mL/ton	0.049	0.60	<0.053
5/25/07	40 mL/ton	0.065	1.58	<0.053
5/30/07	40 mL/ton	0.064	0.97	0.041

The JBR liquor and solids mercury concentration data from Tables 41 and 42 are repeated in Table 43 along with the JBR slurry weight percent solids levels. These data were used to calculate the percentage of the mercury in the JBR slurry found in the FGD liquor. This percentage was expected to be significantly reduced by TMT-15 injection.

Table 43. JBR Blow Down Slurry Mercury Concentrations During Baseline and TMT Addition Periods

Date	TMT-15 Dosage	JBR Liquor Mercury Concentration, μg/L	JBR Solids Mercury Concentration, μg/g	Slurry wt% Solids	Percent of Total Mercury in Slurry Liquor
5/15/07	Baseline (0 mL/ton)	196	0.072	19.7	92
5/18/07	20 mL/ton	156	0.049	20.3	93
5/25/07	40 mL/ton	111	0.065	19.8	87
5/30/07	40 mL/ton	103	0.064	22.7	85

As shown in the table, mercury was predominantly found in the liquor phase of the slurry at baseline (no additive) conditions, with 92% of the slurry mercury found in the liquor. After two weeks of TMT-15 addition, this was reduced by only a modest amount, to 85%. Thus, the slurry analysis results show only a minor impact of TMT-15 on the mercury partitioning in the JBR slurry, and support the flue gas data that show TMT-15 was not effective at controlling mercury re-emissions from the JBR.

JBR FGD Slurry Chemistry

JBR slurry samples were collected and preserved for off-site analyses of typical FGD analytes during the baseline and steady-state scrubber additive injection periods, to observe whether scrubber additive injection had any adverse effects on FGD chemistry. The results of these analyses are shown for the TMT-15 test in Table 44. No adverse effects were expected, and the results show no significant scrubber additive effect on FGD chemistry. Key parameters such as sulfite oxidation, limestone utilization, and gypsum purity did not appear to be affected.

Table 44. JBR Blow Down Slurry Analysis Results from TMT-15 Test Period

Date	5/15/07	5/15/07	5/24/07	5/25/07
TMT-15 Injection Rate, mL/ton of coal	0 (Baseline)	20	40	40
pH	4.02	4.96	5.17	5.15
Temperature, ^{o}C	49.2	44.5	46.9	50.5
Slurry solids, wt%	19.7	20.3	21.1	19.8
Slurry Solids Analyses:				
Ca, mg/g	227	231	232	231
Mg, mg/g	0.3	0.5	0.4	0.4
SO_3, mg/g	<0.7	<0.7	<0.7	<0.7
SO_4, mg/g	543	535	541	541
CO_3, mg/g	1.9	16	13	15
Inerts, wt%	1.68	1.16	1.20	1.03
Gypsum Purity, wt% (based on sulfate analysis)	97.3	95.8	96.9	96.9
Sulfite oxidation, %	100	100	100	100
Limestone utilization, %	99.4	95.7	96.5	96.2
FGD Liquor Analyses:				
Ca^{++}, mg/L	1057	1104	1003	1000
Mg^{++}, mg/L	2,348	1,985	2,142	2,217
Na^+, mg/L	476	423	442	442
Cl^-, mg/L	4,890	4,540	4,247	4,263
$CO_3^=$, mg/L	51.6	58.8	77.2	70.3
$SO_3^=$, mg/L	7.0	<9	<3	<2
$SO_4^=$, mg/L	4,884	4,261	4,485	4,541

Nalco 8034 Test Results

As described in the Experimental section, the Nalco 8034 additive test began with baseline operation in late August 2007, and continued for a full 30 days of additive injection. The test results are described below.

Flue Gas Data

Mercury speciation and removal data as measured by SCEM at the JBR inlet and by CEM at the stack (JBR outlet) are shown in Table 45. As discussed previously, during the Nalco additive test the CEM at the stack was set up to speciate whereas it measured only total mercury during the TMT-15 test.

Table 45. JBR Mercury Removal Data, by SCEM and CEM during the August and September 2007 Nalco 8034 additive portion of the test program

	Time Averaged	Nalco 8034, g/g FGD Inlet Hg^{+2}	JBR Inlet Hg, μg/Nm^3 @ 3% O$_2$		JBR Outlet Hg, μg/Nm^3 @ 3% O$_2$		Hg Oxidation at Inlet, %	Total Hg Removal by FGD, %	Hg^{+2} Removal by FGD, %	Hg^0 Re-emissions, %
			Total Hg	Hg^0	Total Hg	Hg^0				
8/28 2007	10:00 – 21:00	0	4.6	2.4	2.9	2.8	53	36	94	18
9/8 2007	6:00 – 16:00	875	3.8	2.0	3.5	4.0	51	9	132	113
9/18 2007	6:00 – 20:00	525	5.7	1.5	3.1	2.4	27	46	84	22
9/26 2007	11:00 – 21:00	525	6.4	2.2	3.8	3.6	35	41	96	33

As summarized in the table, baseline (no Nalco 8034 addition) mercury removal data were measured in late August 2007 and showed 18% mercury re-emissions across the JBR. As previously defined in this report, this percentage represents the increase in elemental mercury concentration across the JBR divided by the JBR inlet oxidized mercury concentration.

On three subsequent representative days of Nalco 8034 addition, no reduction in re-emissions was observed relative to the baseline measurement. In fact, re-emission levels appeared to increase significantly at the highest additive injection rate. The overall concentrations of mercury measured in the flue gas during the Nalco 8034 testing in August and September 2007 were significantly lower than those measured during the TMT-15 test in May 2007.

The Ontario Hydro results from the JBR scrubber inlet and stack for both the baseline and steady-state Nalco 8034 injection condition are shown in Table 46. For the September 18, steady-state Nalco 8034 testing, there was one outlier run. Plant personnel adjusted the sulfur burners for the Unit 1 flue gas conditioning system to increase SO$_3$ levels in the flue gas shortly after the third Ontario Hydro run began. While it is not obvious how this change might have affected the Ontario Hydro measurements, the inlet oxidized mercury concentration value was very low, measuring below detection limits at <0.53 μg/Nm^3. The other two runs that day averaged 3.4 μg/Nm^3. This data point qualifies as an outlier based on a "Q test" for three data points, with a 98+% degree of confidence.[7] Also, the SCEM data for the JBR inlet location indicated a similar drop in oxidized mercury concentrations, making the results of the third Ontario Hydro run not comparable to those of the first two runs on September 18.

Table 46. Results of Ontario Hydro Measurements During Nalco 8034 Test at Yates Unit 1 (mean values for three Ontario Hydro runs ± 95% confidence interval about mean)

Condition	Baseline		With Nalco 8034 @ 525 g/g FGD Inlet Hg^{+2}	
	8/28/07		9/18/07	
	JBR Inlet	Stack	JBR Inlet*	Stack*
Hg^0, μg/Nm^3 @ 3% O$_2$	3.7 ± 0.9	4.2 ± 1.1	4.5 ± 0.3	5.0 ± 0.3
Hg^{+2}, μg/Nm^3 @ 3% O$_2$	2.9 ± 0.3	<0.3	3.4 ± 0.3	<0.5
Total Hg, μg/Nm^3 @ 3% O$_2$	6.6 ± 1.2	4.2 ± 1.1	8.0 ± 0.1	5.0 ± 0.3
Mercury Oxidation at JBR Inlet, %	56 ± 4	-	56 ± 5	-
Hg^{+2} Removal across JBR, %	-	>90%	-	>86%
Hg^0 Re-emissions across JBR, μg/Nm^3 @ 3% O$_2$	-	0.5 ± 0.9	-	0.5 ± 0.1
Hg^0 Re-emissions, % of JBR inlet Hg^{+2}	-	18% ± 32%	-	15% ± 1%
Overall Hg Removal across JBR, %	-	36% ± 13%	-	38% ± 4%

*Results for two runs, excluding outlier value for one of three runs

The remainder of the discussions of the Ontario Hydro results consider only two runs for September 18. The results do not show a significant reduction in elemental mercury re-emissions as was expected with Nalco 8034 addition. At baseline, the re-emissions represented 18% of the FGD inlet oxidized mercury. With Nalco 8034 addition, the re-emissions level remained nearly unchanged, decreasing only to 15% of the FGD inlet oxidized mercury. The overall mercury removal across the scrubber also remained basically unchanged, increasing from 36% at baseline conditions to 38% with the addition of Nalco 8034.

However, note that when expressed on an absolute concentration basis, the re-emissions levels averaged 0.5 μg/Nm^3 (corrected to 3% O$_2$) for both the baseline and Nalco 8034 test periods. This difference is relatively small, particularly when compared to the 95% confidence intervals for the mean inlet and outlet elemental mercury concentrations (0.1 to 0.9 μg/Nm^3 corrected to 3% O$_2$). This means that the re-emissions levels for both cases were low enough to be practically not measurable by the Ontario Hydro method.

FGD Liquor and Solid Byproduct Analysis Data

As during the TMT-15 test as described above, during the Nalco 8034 portion of the testing program JBR liquor and hydrocyclone overflow and underflow liquors were sampled and analyzed for mercury concentration periodically. The JBR slurry liquor was sampled more frequently than were the hydrocyclone overflow and underflow.

Table 47 summarizes the liquor mercury concentration results for the Nalco 8034 test. The baseline mercury concentrations were more than two orders of magnitude lower than those measured during the TMT-15 portion of the testing program. At such low concentrations, it is hard to accurately quantify changes. The results show an apparent reduction of approximately 50% at the highest injection rate of 875 g/g FGD inlet Hg^{+2}, but the concentrations subsequently

increased during continued operation at the 525 g/g FGD inlet Hg^{+2} injection rate. The concentrations particularly increased after the plant lowered the JBR pH set point to 4.0 near the end of the test, and began lowering the weight percent solids content in the JBR slurry.

Table 47. Results of JBR Blow Down and Hydrocyclone Overflow and Underflow Liquor Mercury Concentrations During Baseline and Nalco 8034 Addition Periods

Date	Nalco 8034 Dosage, g/g FGD Inlet Hg^{+2}	JBR Blow Down Slurry pH	JBR Blow Down Liquor Hg Conc., µg/L	Hydrocyclone Overflow Liquor Hg Conc., µg/L	Hydrocyclone Underflow Liquor Hg Conc., µg/L
8/28/07	Baseline (0)	4.5	0.34	0.39	0.29
8/30/07	875	4.5	0.26	-	-
8/31/07	875	4.5	0.20	-	-
9/7/07	875	4.5	0.16	-	-
9/8/07	525	4.5	<0.16	<0.16	-
9/17/07	525	5.0	0.84	-	-
9/18/07	525	5.0	0.76	<0.16	0.48
9/26/07	525	4.0	13.2	7.6	8.6
9/27/07	525	4.0	1.6	-	-

FGD solids mercury analysis results for the Nalco 8034 portion of the testing program are summarized in Table 48. The JBR slurry solids were analyzed a number of times during the test period; the hydrocyclone overflow and underflow solids were analyzed only for the baseline and steady-state Nalco 8034 addition test periods.

The JBR liquor and solids mercury concentration data from Tables 47 and 48 are repeated in Table 49, along with the JBR slurry weight percent solids, and used to calculate the percentage of the mercury in the JBR slurry found in the FGD liquor. This percentage was expected to be significantly lowered by Nalco 8034 addition. The results do not show a significant change from baseline conditions, although the baseline percentage was already extremely low. There was one significant increase in liquor mercury percentage on September 26, but this may have been a transient effect due to the plant lowering the JBR pH set point from 5.0 to 4.0. The percentage of mercury in the liquor was down considerably by the following day.

JBR FGD Slurry Chemistry

JBR slurry samples were collected and preserved for off-site analyses of typical FGD analytes during the baseline and steady-state scrubber additive injection periods, to observe whether scrubber additive injection had any adverse effects on FGD chemistry. No adverse effects were expected.

Table 48. Results of JBR Blow Down and Hydrocyclone Overflow and Underflow Solids Mercury Concentrations During Baseline and Nalco 8034 Addition Periods

Date	Nalco 8034 Dosage, g/g FGD Inlet Hg^{+2}	JBR Blow Down Slurry pH	JBR Blow Down Solids Hg Conc., µg/L	Hydrocyclone Overflow Solids Hg Conc., µg/L	Hydrocyclone Underflow Solids Hg Conc., µg/L
8/28/07	Baseline	4.5	0.28	12.8	0.16
8/30/07	875	4.5	0.38	-	-
8/31/07	875	4.5	0.36	-	-
9/17/07	525	5.0	0.42	-	-
9/18/07	525	5.0	0.44	13.6	0.31
9/26/07	525	4.0	0.31	-	-
9/27/07	525	4.0	0.55	-	-

Table 49. Daily JBR Blow Down Slurry Mercury Concentrations During Baseline and Nalco Addition Periods

Date	Nalco 8034 Dosage (g/g FGD Inlet Hg^{+2})	JBR Liquor Mercury Concentration, µg/L	JBR Solids Mercury Concentration, µg/g	Slurry wt% Solids	% of Slurry Mercury in Liquor
8/28/07	Baseline	0.34	0.28	18	0.6
8/30/07	875	0.26	0.38	16	0.4
8/31/07	875	0.20	0.36	18	0.3
9/17/07	525	0.84	0.42	17	1.0
9/18/07	525	0.76	0.44	18	0.8
9/26/07	525	13.2	0.31	17	17
9/27/07	525	1.55	0.55	17	1.4

The results of these analyses for the Nalco 8034 test are shown in Table 50, and show no significant scrubber additive effect on FGD chemistry. Sulfite oxidation, limestone utilization, and gypsum purity did not appear to be affected.

Additional Analyses

Because the baseline partitioning of mercury in the JBR liquor changed dramatically between the May TMT-15 test and the beginning of the Nalco 8034 test in August, additional chemical and data analyses were conducted to determine it there were significant changes in other parameters that might have had an influence. Other analyses were conducted to determine effect of the additives, such as on FGD slurry particle size and on leaching of mercury from fine solids. The results of these various additional analyses are presented and discussed in this subsection.

Table 50. JBR Slurry Analysis Results from Nalco 8034 Test Period

Date	8/28/07	9/8/07	9/18/07	9/26/07
Nalco 8034 Inj. Rate, g/g FGD Inlet Hg^{+2}	0 (Baseline)	525	525	525
pH	4.59	4.72	5.33	4.13
Temperature, ^{o}C	52.7	50.1	50.7	47.8
Slurry solids, wt%	17.7	16.9	17.8	7.3
Slurry Solids Analyses:				
Ca, mg/g	229	255	241	241
Mg, mg/g	0.2	0.2	0.2	0.1
SO_3, mg/g	<0.7	<0.7	<0.7	<0.7
SO_4, mg/g	539	538	540	559
CO_3, mg/g	1	3	10	2
Inerts, wt%	0.84	1.24	0.56	1.84
Gypsum Purity, wt% (based on sulfate analysis)	96.6	96.5	96.7	100
Sulfite oxidation, %	100	100	100	100
Limestone utilization, %	99.1	95.5	95.8	98.5
FGD Liquor Analyses:				
Ca^{++}, mg/L	986	919	1026	898
Mg^{++}, mg/L	2,087	1,778	2,332	1,266
Na^{+}, mg/L	441	397	526	310
Cl^{-}, mg/L	4,223	3,541	5,245	2,507
$CO_3^{=}$, mg/L	61	77	53	55
$SO_3^{=}$, mg/L	<8	10	17	4
$SO_4^{=}$, mg/L	4,900	4,568	4,949	3,931

Coal Analyses

Coal samples were collected periodically during both test programs. Coal samples from the baseline testing of both the TMT-15 and Nalco 8034 portions of the test program were analyzed, along with a sample from the steady-state Nalco 8034 addition test. Results of the coal sample analyses are shown in Table 51. The coal chlorine varied some in the two samples during the Nalco 8034 test period, which may help explain the variation in JBR inlet mercury oxidation seen in Table 45. Higher coal chlorine concentrations would be expected to promote higher mercury oxidation percentages, and vice versa. Also, the coal mercury concentration was about 30% higher in May than in August.

Table 51. Unit 1 Coal Sample Data

Condition	Heating Value, dry Btu/lb	Total Moisture, wt %	Ash, wt% dry	Sulfur, wt% dry	Chlorine, wt% dry	Hg, ppm dry
5/15/07 (Baseline)	13,201	3.31	11.68	1.74	0.0359	0.140
8/28/07 (Baseline)	13,072	5.51	13.13	1.71	0.0456	0.109
9/18/07 (Nalco 8034 addition @ 525 g/g FGD Inlet Hg^{+2}	13,308	3.69	11.45	1.83	0.0233	0.103

Metals Analyses

One theory for why the mercury partitioning had changed so dramatically between May and August 2007 was that a limestone supply change from dry-ground limestone prepared off site to wet ground limestone prepared in the Unit 1 FGD ball mill had changed the metal composition in the JBR slurry. In particular, iron is thought to adsorb or co-precipitate mercury in FGD liquors. The change back to the wet-ground limestone in August after the ball mill was repaired in May might have influenced the amount of iron present due to attrition of the steel ball grinding media and/or differences in the limestones themselves. However, other plant input streams such as the coal fired may have changed somewhat and also could have influenced the metals concentrations present in the JBR.

To investigate this theory, baseline samples from May and August were analyzed for metal concentrations. The samples analyzed included limestone solids, the liquor from the JBR feed limestone slurry, JBR slurry liquor and solids, hydrocyclone overflow slurry solids, and hydrocyclone underflow slurry solids. Besides the limestone samples, the hydrocyclone overflow solids were of particular interest because they represent the smallest particles in the JBR slurry solids, and mercury is known to be found in higher concentrations in fine particles. If the change in speciation were due to adsorption of mercury on metal solids, that metal should be concentrated in the hydrocyclone overflow solids.

The results of these analyses do not show many large differences in metals concentrations for a given sample type when comparing the May and August sample results. In general, most metal concentrations were higher in the May samples. The results were reviewed and sample analyses were identified where a significant difference in concentration was observed. Significant was defined as where the concentration of a given metal on one date was at least three times the concentration of that metal in that process stream and phase on the other date. These analyses are summarized in Table 52. None of the limestone solids or hydrocyclone underflow solids met these criteria; only certain metals from the JBR liquor and solids, limestone slurry liquor, and hydrocyclone overflow solids show greater than a threefold difference in concentration.

There is no metal result that clearly might explain the difference in mercury partitioning between the solids and liquor during these two time periods. The high selenium value in the hydrocyclone overflow solid sample from August could be indicative of mercury precipitation as mercuric selenide, but it is not likely that selenium would be present in this form in a forced oxidation

78

Table 52. Concentrations of Metals Where at Least a Threefold Difference in Concentration Was Seen Between May and August Samples of the Same Type

Analyte	JBR Liquor		Limestone Liquor		JBR Solids		Hydrocyclone Overflow Solids	
	5/15/07	8/29/07	5/15/07	8/29/07	5/15/07	8/29/07	5/15/07	8/29/07
Ag, µg/L	2.28	<0.17	-	-	-	-	-	-
Al, µg/L	210,500*	8,050	-	-	-	-	-	-
Be, µg/L	23.2	2.84	-	-	-	-	-	-
Co, µg/L	354	78.3	-	-	-	-	-	-
Cr, µg/L	57.0	0.48	2.07	<0.48	-	-	-	-
Cu, µg/L	756	108	-	-	-	-	-	-
Fe, µg/L	608	158	-	-	-	-	-	-
Mn, µg/g	-	-	-	-	8.45	1.32	-	-
Mo, µg/L	89	488	-	-	-	-	-	-
Ni, µg/L	-	-	72.3	229	-	-	-	-
Pb, µg/L	27.3	0.72	-	-	-	-	-	-
Se, µg/g	-	-	-	-	-	-	20.7	222
Ti, µg/L	86.2	15.2	-	-	-	-	-	-

*Based on comparison of these results with aluminum concentrations in other FGD liquors, this value is suspect, possible high by an order of magnitude

FGD system. Selenium in higher oxidation states would not form mercury precipitates. Fine iron particles had been considered as a possible factor in affecting the mercury partitioning, but none of the solid samples showed significant differences in iron concentrations. The limestone solids from August had about a 20% higher iron concentration than the sample from May, but the corresponding hydrocyclone overflow solids sample from August had about 20% less iron content than the May sample.

The JBR liquor iron concentration was nearly four times higher in May than in August. As discussed in the Conclusion section, it is possible that some of this iron may actually be present as sub-micron-diameter solids that passed through the filter media when the solids and liquor in the slurry were separated. Such particles would then be reported as liquor concentrations when the liquor was digested and analyzed. If this is the case, the higher iron concentration in May might correlate with the higher liquor mercury concentrations at that time. However, a reason why more sub-micron-diameter iron solids might have been present in May versus August remains unexplained.

FGD Byproduct Solids Particle Size Analyses

Samples from the baseline periods for both the TMT-15 test and the Nalco 8034 test were analyzed for particle size distribution, to see if differences in particle size may have impacted the baseline mercury partitioning. Also, a sample from the steady-state Nalco 8034 injection period

was analyzed to determine if Nalco 8034 addition had any impact on particle size in the fines fraction.

The results of these particle size analyses are summarized in Table 53. The results show that the bulk gypsum had a mean particle size in the range of 48 to 51 μm, which is typical of gypsum sold for use in wallboard production. The fines (hydrocyclone overflow solids) have a much smaller particle size, with a mean ranging from 10 to 15 μm.

Table 53. Results of Particle Size Analyses on JBR Byproduct Solid Samples

Sample Location	D_{10}, μm*	D_{50}, μm*	D_{90}, μm*	Mean, μm
Baseline (no TMT-15 injection) Samples, 5/15/07:				
JBR Blow Down Slurry Solids	28.8	45.8	69.8	48.2
Hydrocyclone Overflow	1.32	7.13	21.7	9.80
Hydrocyclone Underflow	29.9	46.0	68.8	48.3
Baseline (no Nalco injection) Samples, 8/28/07:				
JBR Blow Down Slurry Solids	32.3	47.4	70.3	50.0
Hydrocyclone Overflow	1.63	9.47	32.9	14.6
Hydrocyclone Underflow	33.5	48.1	70.9	50.9
Steady-state Nalco 8034 Injection Period (525 g/g FGD Inlet Hg^{+2}), 9/18/07:				
JBR Blow Down Slurry Solids	30.6	47.6	73.9	50.9
Hydrocyclone Overflow	1.20	5.61	24.7	10.1
Hydrocyclone Underflow	29.2	46.4	72.0	49.4

*Particle size at which 10%, 50%, or 90% of the particles (as noted in the subscript) are smaller.

The results do not show a significant change in JBR solids particle size when comparing between baseline samples or comparing the baseline sample particle size distributions with those for the corresponding samples from the steady-state Nalco 8034 injection period. There was expected to be an increase in the amount of fine particles in the hydrocyclone overflow for the Nalco 8034 injection period. This may have been observed to some extent, as the hydrocyclone overflow solids were generally finer for the September 18 sample than in the baseline, August 28 sample.

Note that these particle size distribution measurements were made on solid samples that were filtered from the slurry on site, using 0.7-μm-pore-size filter media. Thus, these particle size distributions would not reflect the presence of sub-micron-diameter solids (<0.7 μm diameter) that might contribute to elevated liquor mercury concentration measurements.

Mercury Balance Calculations

Mercury Balance Across Hydrocyclones

A mercury balance was calculated to determine the extent to which the mercury in the FGD blow down slurry was recovered in the hydrocyclone overflow and underflow samples. The ability to

close a mercury balance around hydrocyclones is a good indicator of how effectively the partitioning of mercury between the solids and liquor was preserved in the samples and measured. Good closure of a mass balance across the hydrocyclones would tend to confirm the relative measurements of liquor and solid mercury concentrations during the May and August time periods, and confirm that the mercury partitioning was much different for these time periods.

JBR and hydrocyclone overflow and underflow weight percent solids data were used to solve for the percentages of the blow down liquor and solids that reported to the overflow and underflow. Once these percentages were calculated, the mercury concentrations of each stream were used to calculate the extent to which the mercury in the JBR blow down slurry was distributed between the hydrocyclone overflow and underflow streams.

The results of the total mass distribution calculations are summarized in Table 54, and results of the mercury balance calculations are shown in Table 55. These results show that the liquor blow down from the JBR splits almost equally between the hydrocyclone overflow and underflow, but 98 to 99% of the solids report to the underflow. The mercury balance numbers show that, as expected, most of the mercury in the JBR blow down slurry was found in the liquor during the May test period, and thus was split nearly equally between the hydrocyclone overflow and underflow streams. In the August samples, the mercury in the slurry was predominantly found in the solids. Because the hydrocyclone overflow solids tend to be higher in mercury concentration than the underflow solids, 30% to 40% of the total mercury in the JBR slurry reported to the hydrocyclone overflow solids in spite of this stream representing only 1% to 2% of the solids mass.

Table 54. Summary of Hydrocyclone (HC) Overall Mass Balance Estimates

Date	Scrubber Additive	% of JBR Blow Down Slurry Liquor		% of JBR Blow Down Slurry Solids	
		HC Overflow	HC Underflow	HC Overflow	HC Underflow
5/15/07	0 (baseline)	42	58	2	98
5/25/07	TMT-15 @ 40 mL/ton coal	44	56	1	99
8/28/07	0 (baseline)	43	57	1	99
9/18/07	Nalco 8034 @ 525 g/g FGD Inlet Hg+2	32	68	1	99

Table 55. Summary of Hydrocyclone (HC) Mercury Balance Calculations

Date	Scrubber Additive	% of JBR Blow Down Slurry Mercury Content				
		HC Over-flow Liquor	HC Over-flow Solids	HC Under-flow Liquor	HC Under-flow Solids	Total Hg Recovery
5/15/07	0 (baseline)	40	1.9	53	7.1	103
5/24/07	TMT-15 @ 40 mL/ton coal	46	3.8	57	<10	106 – 116*
8/28/07	0 (baseline)	0.3	39	0.3	57	96
9/18/07	Nalco 8034 @ 525 g/g FGD Inlet Hg^{+2}	<0.1	31	0.3	69	101

*A range is shown to reflect the possible impact of a "less than" value for the mercury content of the hydrocyclone underflow solids

The mercury recoveries across the hydrocyclones were good, ranging from 96% to <116% recovery of the mercury in the JBR blow down slurry. These good mass balance closures tend to support the accuracy of the much different mercury partitioning measurement results for the JBR slurry samples in May and August/September.

However, as discussed later in the Conclusion section, there is a possibility that some of the mercury that is reported as being in the liquor may have actually been present as sub-micron-diameter solids that passed through the filter media used to separate slurry solids and liquor. Such particles would tend to behave like dissolved solids in the hydrocyclones, so these mass balances cannot be used to distinguish between dissolved, ionic mercury and mercury present in sub-micron-diameter solids.

Mercury Balance Across JBR

An attempt was also made to close a mercury balance across the JBR, taking into account the coal sulfur and mercury concentrations and the mercury removal across the ESP. However, the calculation of the amount of mercury leaving the JBR in the blow down slurry is confounded by the fact that the blow down alternates between the hydrocyclone underflow and overflow streams. Since the concentrations of mercury in the liquor and solid phases, and the relative amounts of liquor and solid phases in these two streams are significantly different, the relative amounts of each going to blow down greatly impacts the mercury balance. The percentage of time the hydrocyclone overflow versus underflow is sent to blow down is not recorded at Plant Yates.

To account for this, two mercury balances were calculated, one assuming 100% hydrocyclone underflow going to blow down, and the other assuming that the cumulative blow down has a composition equal to that of the JBR slurry. However, depending on the water balance for the

JBR at any particular time, the cumulative blow down could be "richer" in hydrocyclone overflow slurry than is reflected by the assumption that the blow down composition is equal to that of the JBR slurry.

The results of this mercury balance are shown in Table 56. Four cases are shown, representing baseline operation in May and August 2007, and steady state operation with TMT-15 and Nalco 8034. However, the material balance input data are more complete for the Nalco test period.

Table 56. Results of Overall Mercury Balances Across JBR.

Date	5/15/2007	5/25/2007	8/28/2007	9/18/2007
Coal Heat Content, Btu/lb (dry basis)	13,201	*	13,072	13,308
Coal Sulfur, wt% (dry basis)	1.74	*	1.71	1.83
Coal Hg, ppm (dry basis)	0.14	*	0.109	0.103
Coal Ash, wt% (dry basis)	11.68	*	13.13	11.45
Ash sample Hg concentration, µg/g	**	**	0.34	0.34
Wt% solids, JBR blow down	19.7	19.8	17.7	17.8
Wt% solids, HCUF	41.7	43.7	37.2	31.6
Wt% solids, HCOF	0.9	0.7	0.4	0.7
Sulfate in JBR slurry solids, mg/g	543	541	539	540
JBR blow down liquor Hg, µg/L	196	111	0.34	0.76
HCUF liquor Hg, µg/L	197	129	0.29	0.48
HCOF liquor Hg, µg/L	205	131.7	0.39	0.16
JBR blow down solids Hg, µg/g	0.072	0.065	0.28	0.44
HCUF solids Hg, µg/g	0.063	0.053	0.16	0.31
HCOF solids Hg, µg/g	1.07	1.58	12.8	13.6
Apparent Hg removal, %:				
- Based on 100% JBR slurry blow down	73%	44%	35%	60%
- Based on 100% HCUF slurry blow down	29%	19%	20%	42%
Ontario Hydro result, % Hg removal	31%	15%	36%	38%

*Coal sample not analyzed, assumed concentration was equal to 5/15/2007 sample
**Ash sample not analyzed, assumed concentration was equal to August 2007 samples

Rather than calculate a true mercury balance, the input data were used to calculate an apparent mercury removal percentage across the JBR based on the two assumptions for the composition of the blow down slurry. As can be see in the bottom rows of the table, the apparent mercury removal across the JBR varies considerably depending on the assumption for the composition of the cumulative blow down slurry. In the May samples the range between the two mass balance estimates of mercury removal was particularly wide because there was so much mercury in the liquor, and the amount of liquor versus solids blow down varied substantially depending on the assumption.

In the cases of the May 15, May 25, and September 18 samples, the Ontario Hydro result was in reasonable agreement with the estimate based on mass balances that assume the JBR blow down was 100% hydrocyclone underflow. For the August 28 samples, the Ontario Hydro result was in better agreement with the estimate based on assuming the blow down was equal to the JBR slurry composition. However, besides the fact that the cumulative composition of the JBR blow down was not known, there are other potential errors associated with these mass balance calculations. For example, the coal and ash samples were simple grab samples, while the JBR slurry samples represent slurry with an average residence time in the JBR greater than 24 hours. Thus, the coal and ash samples may not have been representative of those streams over the entire period the JBR solids were produced. Similarly, the Ontario Hydro data represent mercury removal percentages over only a fraction of the time the JBR solids were produced. Also, the September samples were from the day after the Ontario Hydro runs while the other samples were from the day of the runs.

Given all of these issues affecting the mass balance calculations, the strongest conclusion that can be made from the results in Table 56 is that these mass balance calculations generally confirm the order of magnitude of the JBR mercury removal percentages observed by gas analyses.

SPLP Analyses of Byproduct Solids

As part of the project plan for Task 5, samples of the hydrocyclone overflow solids were analyzed by the synthetic precipitation leaching procedure (SPLP), EPA Method 1312.[8] This method is intended to simulate the effects of rainfall in producing leachate from monofills of solid byproducts. The hydrocyclone overflow solids are the solid byproduct stream with the highest mercury content that leave the Unit 1 FGD system, and might end up in a landfill at some power plants.

The SPLP method was conducted on hydrocyclone overflow solids from the baseline (no TMT-15 addition) portion of the May 2007 testing, from steady-state 40 mL/ton of coal TMT-15 injection rate test periods, and from steady-state 525 g/g FGD inlet Hg^{+2} Nalco 8034 injection rate test periods. Unfortunately, there was not enough sample remaining of the baseline hydrocyclone overflow solids from August 2007 to conduct SPLP analyses. Table 57 identifies the sample collection dates and shows results for the six samples analyzed.

Table 57. SPLP Leachate Results for Hydrocyclone Overflow Solids Samples from Yates Unit 1

Sample Date	Condition	Mercury Concentration in Leachate, µg/L
5/15/07	Baseline	0.83
5/18/07	TMT-15 @ 40 mL/ton coal	<0.50*
5/24/07	TMT-15 @ 40 mL/ton coal	<0.32
5/30/07	TMT-15 @ 40 mL/ton coal	<0.50
9/8/07	Nalco 8034 @ 525 g/g FGD inlet Hg^{+2}	<0.50
9/26/07	Nalco 8034 @ 525 g/g FGD inlet Hg^{+2}	<0.32*

*These results are in question due to low sample spike recoveries

Only the result from the May baseline (no additive) test showed a measurable mercury concentration in the SPLP leachate, at 0.83 µg/L. Even this result in question because the concentration is only about twice the method detection limit. Also, this sample was collected during a period of very high mercury concentration in the hydrocyclone overflow slurry liquor (about 200 µg/L). Even a small amount of liquor remaining adhered to the solid sample tested in the SPLP procedure could have led to a "false positive" result.

The results from all five SPLP tests for samples from FGD additive periods showed mercury concentrations below detection limits in the SPLP leachate (<0.32 to <0.50 µg/L), although two results are of questionable accuracy due to poor sample spike recovery. The toxicity characteristic limit for mercury in leachate is 200 µg/L. Thus, like in the samples from TMT-15 addition at IPL Petersburg, the samples from the Yates additive test periods were approximately two orders of magnitude lower than the toxicity limit, whether TMT-15 or Nalco 8034 was added at the FGD system.

These results indicate that even without the use of additives in the JBR, the mercury in the hydrocyclone overflow solids (a potential waste disposal stream) appears to be quite stable and likely to leach at relatively low concentrations into groundwater, if at all. With the use of either TMT-15 or Nalco 8034 the leachate mercury concentrations will be near zero.

CONCLUSION

Pilot-scale Tests

The results of the pilot-scale TMT-15 additive tests conducted at the beginning of this project were not as conclusive as was hoped regarding the effects of adding TMT-15 to FGD slurries to enhance mercury capture by wet FGD systems. The primary objective of the additive is to prevent or limit mercury re-emissions from wet FGD systems.

However, in the first pilot-scale additive parametric tests conducted at Monticello Station, no evidence was seen of re-emissions without the additive, so this objective could not be evaluated. The steady-state TMT-15 additive test conducted later at Monticello had the pilot wet FGD system operating downstream of a gold mercury oxidation catalyst, as previous test results without TMT-15 additive showed evidence of FGD re-emissions when downstream of this catalyst. The Ontario Hydro method was used to measure re-emissions when operating the pilot wet FGD downstream of the gold catalyst and while adding TMT-15 at 20 mL/ton of coal fired. These results showed a mean re-emission level of 0.5 $\mu g/Nm^3$, which is about one fourth of the re-emissions measured previously downstream of the gold catalyst at Monticello without TMT addition. Furthermore, when the 95% confidence intervals of these measurements are considered, it is possible that no re-emissions were occurring. This could be taken as evidence that TMT-15 addition greatly reduced re-emissions when operating the pilot wet FGD downstream of the gold catalyst. However, the oxidized mercury concentration at the wet FGD pilot inlet during the TMT test was only 25% of what the concentration had been for the previous test without TMT, which had been conducted several months earlier. When the mean re-emissions are expressed as a percentage of the mean FGD inlet oxidized mercury concentration, the percentages are the same for the two tests. This confounds the finding of whether or not TMT-15 was effective in limiting re-emissions.

Pilot jet bubbling reactor (JBR) FGD tests were conducted at Plant Yates in August 2005. In these tests, mercury SCEM data appear to be compromised by excessive scrubber liquor carryover from the pilot JBR into the outlet duct, and thus provided no useful information about re-emissions.

Other expected effects of TMT-15 addition were seen more clearly in these results. TMT-15 was very effective in lowering FGD liquor mercury concentrations in both sets of pilot-scale tests. For example, during the steady-state pilot FGD TMT-15 test at Monticello, the FGD liquor mercury concentrations were lowered by over an order of magnitude compared to baseline (no TMT addition) values from two days earlier. Liquid-phase reactions between oxidized mercury and sulfite ion (dissolved SO_2) are believed to produce re-emissions, so this suggests that TMT-15 would be effective at limiting re-emissions.

Results also show that TMT-15 addition can result in lower gypsum byproduct mercury concentrations if some form of gypsum fines separation is employed, such as using hydrocyclones for primary dewatering. Observed reductions in gypsum mercury concentration varied from 17% to 29% in the three series of pilot-scale tests.

86

The effectiveness of TMT-15 in lowering gypsum mercury concentrations appears to be limited by the ability of the FGD blow down slurry dewatering equipment to remove fine particles. Hydrocyclones leave a percentage of fine particles in the underflow slurry, and these fine particles appear to account for much of the mercury that remains in the product gypsum. Other forms of solid separation equipment, that can make a sharper separation of fine particles from the coarser particles, may be able to produce a gypsum byproduct with a lower mercury concentration.

The addition of TMT-15 did not appear to have any adverse effect on the operation of either wet FGD pilot unit. Concentrations of species other than mercury in the FGD liquors did not appear to be affected, SO_2 removal percentages remained high, and gypsum byproduct particle size distributions were not greatly impacted.

Several lessons were learned from these tests that should be reflected in any future testing related to mercury control by wet FGD systems. One is that mist carryover from wet FGD systems can greatly affect mercury concentration measurements by SCEMs that use IGS filters to extract a particulate-free flue gas sample. Pilot wet FGD systems should be equipped with mist eliminators that are as efficient as modern full-scale FGD absorbers to allow accurate mercury concentration measurements in the FGD outlet flue gas by SCEM methods. Also, as a result of these findings a modified method of separating a particulate-free sample to better deal with mist carryover has been developed. The modified method involves using two IGS filters in series, and operating them at lower temperatures to avoid mist evaporation. A second lesson for using SCEMs to evaluate mercury control performance is a reminder that the SCEM computer hard drive needs to be backed up frequently, and/or the complete SCEM output must be recorded elsewhere as it is produced to avoid excessive loss of data on computer failures.

A third lesson learned has to do with FGD slurry sampling to determine solid and liquid phase mercury concentrations. It is clear that liquor samples should be filtered and preserved as soon as possible after sample collection, to avoid biasing the liquor mercury concentration by adsorption on or desorption from solids in the slurry before this separation is made. However, it has also become clear that the only way to get a representative solid sample from slurry sample is to filter the entire sample to recover its solid content. Any partial filtering of the slurry sample may result in a biased mercury concentration in the solids, due to the significant variation in mercury concentration by solid particle size.

Full-scale Tests

The full-scale test of TMT-15 addition to a LSFO wet FGD system on a power plant that fires high-sulfur Indiana coal, IPL's Petersburg Unit 2, showed mixed results. Consequently, relatively few conclusions can be made from the results of this test.

Flue gas measurements by the Ontario Hydro method showed a moderate reduction in re-emission levels after five days of TMT addition at a rate equivalent to 40 mL of TMT-15 added to the FGD reaction tank per ton of coal fired by Unit 2. Baseline (no TMT) re-emissions represented 49% of the FGD inlet oxidized mercury being re-emitted as elemental mercury in the outlet gas, while the TMT test result represented 35% of the inlet oxidized mercury. A greater

reduction was expected. It is not clear whether the observed decrease was an effect of TMT-15 injection or merely represented day-to-day variation. The FGD absorber liquor samples from the TMT test showed little or no reduction in mercury concentrations due to TMT addition.

It was speculated that a component in the FGD liquor was interfering with the effectiveness of TMT in precipitating mercury from this liquor. Efforts were made as part of this project, although unsuccessfully, to identify such a component in the Petersburg FGD system. More work would be needed to try to identify what this component might be and how to counteract it. It is also possible that some of the mercury measured to be in the liquor at Petersburg was actually present on sub-micron-diameter (<0.7 μm) particles that passed through the filter membrane used to separate solids from the liquor. This possible effect is further discussed below.

Some data collected during the test remain unexplained. Mercury SCEM measurements at the Unit 2 stack showed that flue gas elemental mercury concentrations dropped significantly shortly after TMT-15 injection began at the lowest injection rate, equivalent to 10 mL of TMT-15 added per ton of coal fired in Unit 2. This was taken as evidence that TMT-15 was effective at controlling mercury re-emissions even at the lowest dosage tested. However, the stack elemental mercury concentrations continually increased as the TMT injection test progressed. The Ontario Hydro measurements at the end of the test showed only a moderate effect of TMT-15, as mentioned above. Furthermore, FGD liquor mercury analyses did not show the expected drop in mercury concentration that should correspond with the initial drop in stack elemental mercury concentration shortly after TMT-15 injection began. It was suspected that the observed drop in stack elemental mercury concentration shortly after TMT-15 injection began was due to lower coal mercury concentrations during this period. However, coal sample analyses show the coal mercury content to be relatively steady during the test period.

Other unexplained data came from follow-up TMT beaker tests conducted at Petersburg Unit 2 in January 2007, six months after the full-scale tests were conducted. In those tests, TMT-15 dosing into beakers of FGD liquor showed that liquor mercury concentrations could be lowered through increasing TMT dosage, which is the expected effect. However, the absorber liquor mercury concentration was measured in January at only 1 μg/L, whereas in July the concentrations ranged from 40 to 62 μg/L, even with TMT-15 addition. One known difference between the Unit 2 operation between July and January is that the SCR was in operation in July and was not in operation (bypassed) in January. It was speculated that the SCR operating status was impacting the liquid phase mercury concentrations. However, follow-up measurements on the Unit 2 FGD absorber slurry, with the SCR bypassed and then in service, did not show such a trend. It is also not known whether or not there were any mercury re-emissions from the Unit 2 wet FGD system during the January and May 2007 operations when the liquor mercury concentrations were much lower. Bench-scale testing as part of DOE-NETL Cooperative Agreement DE-FC2604NT42314 have shown that for a given absorber liquor composition, re-emission levels are generally proportional to the amount of mercury in the liquor.[9]

Two full-scale scrubber re-emission additive tests were conducted on the Unit 1 JBR at Plant Yates, the first using Evonik Degussa Corporation's TMT-15 and the second using the Nalco Company's additive Nalco 8034. Based on the success of TMT-15 in lowering pilot JBR slurry liquor mercury concentrations in the 2005 test at Plant Yates, similar success was expected in the

full-scale test. However, neither the TMT-15 nor Nalco 8034 test conclusively demonstrated the ability of the additive to control mercury re-emissions across the JBR.

The results of the first test with TMT-15 were similar to those in the earlier test at Petersburg Unit 2; neither of the expected results of TMT addition was observed. Re-emission of elemental mercury across the JBR appeared to increase rather than decrease with TMT addition, and the mercury concentration in the JBR slurry liquor was not decreased to near detection limits. The concentration decreased by a maximum of 47% and the resulting liquor mercury concentration was still relatively high at >100 µg/L. This suggests that TMT-15 was ineffective in the JBR at the dosages tested, which were within the range recommended by the manufacturer. Higher dosage rates were not tested because of additive cost considerations, and because of concern over direct reduction of oxidized mercury by TMT if it were present at higher concentrations in the FGD liquor.

There is a possible explanation for why TMT-15 was measured to be relatively ineffective in precipitating mercury from the JBR liquor, both at Petersburg Unit 2 and at Plant Yates Unit 1: it is possible that part of what was measured as liquor with the sampling and analytical protocol was actually present as extremely fine particles. Slurry samples were filtered on site with filter media that have a 0.7-µm pore size, so particles smaller than approximately 0.7 µm in diameter could pass through the filter. Such particles would be digested and analyzed as mercury in subsequent liquor analyses. DOE researchers have reported that mercury is often found in FGD solid byproducts in a solid phase that is rich in iron,[10] and trace metals analyses from the Yates test show about four times greater iron concentration in the JBR liquor in May 2007 than in August 2007. If a portion of this iron was present as sub-micron-diameter precipitates that are rich in mercury, this could explain the apparent lack of effectiveness of TMT-15 in removing all of the mercury from the liquor phase. However, this does not help explain why TMT-15 was also ineffective in controlling re-emissions at Plant Yates. Mercury in the solid phase should not participate in aqueous re-emission reactions. If TMT was effective at precipitating the mercury that was actually in the liquor as ionic mercury and not present as sub-micron particles, a corresponding decrease in mercury re-emissions would have been expected.

The Nalco 8034 test results were also inconclusive. However, at the beginning of this test and during Nalco 8034 addition the apparent JBR liquor mercury concentrations were very low (generally less than 1 µg/L), and mercury re-emission levels were also low (0.5 µg/Nm^3 @ 3% O$_2$). This re-emission level is difficult to measure by CEM or Ontario Hydro methods. Re-emissions are quantified as the difference between two measured values. When the re-emission level is low, the number is a small difference between two larger numbers. When using Ontario Hydro measurement results, each of the larger numbers is a mean from two to three measurement runs, and the mean has a 95% confidence interval. In this case the 95% confidence interval of the means was of the same order of magnitude as the apparent re-emission level, so re-emissions could not be determined with certainty. That is, the actual re-emission levels could have just as well been 0.0 or 1.0 µg/Nm^3 @ 3% O$_2$ instead of the measured value of 0.5 µg/Nm^3 @ 3% O$_2$. The Nalco additive needs to be re-tested on an FGD system that has greater re-emission levels that can be better quantified.

Additional analyses were conducted in an attempt to explain why the apparent JBR liquor mercury concentrations were so much higher in May than in August. Of these additional analyses, only trace metals analyses of the JBR liquor and hydrocyclone overflow solids offered potential explanations for this phenomenon. As mentioned above, the JBR liquor had nearly four times the apparent iron concentration in May compared to August. If some of this iron was actually present as sub-micron-diameter iron precipitates with high mercury content, this could explain the high apparent mercury concentration in the JBR liquor.

In August much more of the JBR slurry mercury content was found in the solids. The hydrocyclone overflow solids were found to have significantly higher selenium content in August than in May. It could be possible that the higher proportion of mercury in the solids rather than the liquor in August was due to the formation of insoluble mercuric selenide precipitates. However, it seems unlikely that selenides could exist in the forced oxidizing environment of the JBR.

The mercury-rich fines stream separated in the hydrocyclone overflow slurry could potentially be filtered out of this stream and disposed of separately, as a means of lowering the mercury content of the gypsum byproduct. SPLP leaching tests were conducted to determine how readily mercury might leach from this potential disposal stream if placed in a monofill. SPLP results from hydrocyclone overflow and absorber slurry solid samples from the IPL Petersburg test for both baseline and TMT-addition conditions showed no measurable mercury in the leachates. The results from Plant Yates showed a small amount of mercury leached out of the baseline sample from May 2007, but no mercury was detected in the leachates from the TMT-15 and Nalco 8034 addition period hydrocyclone overflow solids. This was an expected benefit from employing either of these additives. The mercury measured in the leachate from the baseline sample from May 2007 was very low, about twice the analytical detection limit, and may have reflected some contamination by FGD liquor adhering to the solids leached.

Recommendations

The results from this project were not as successful as hoped. In the pilot-scale tests with TMT-15, the expected result of lowering mercury concentrations in FGD absorber liquors was seen, but a corresponding decrease in re-emissions rates was not measured conclusively due to various flue gas mercury measurement issues. In the two full-scale tests with TMT-15, the absorber liquor mercury concentrations were not lowered as effectively as in the pilot-scale tests, and little or no reductions in re-emissions were measured. In the full-scale test with Nalco 8034 additive, the JBR liquor mercury concentrations were already quite low prior to additive addition, and mercury re-emission levels were down around the lower measurement limit. Thus, the effectiveness of this additive was not clearly measured.

It was seen as this project progressed that the amount of mercury in a wet FGD absorber liquor and the level of re-emissions from a wet FGD absorber can vary significantly over time for any one particular FGD system. The parameters that control liquor mercury concentrations and re-emission levels are not well understood.

These results suggest that there is no "one size fits all" wet FGD re-emissions additive. There are apparently one or more factors that impact the effectiveness of mercury precipitation additives in wet FGD absorber liquors. Consequently, more testing is needed, over a range of wet FGD systems and with more additive types. As this project has progressed over the past several years, additional wet FGD re-emissions additives have been identified in the literature or in press releases. Vosteen Consulting and Solucorp both have wet FGD additives that are candidates for testing. Babcock and Wilcox's additive, sodium hydrosulfide, has apparently been tested at a number of full-scale sites with more success than in a previous, DOE co-funded project. These three additives as well as the two tested as part of this project could be considered as candidates for testing at any wet FGD system that is experiencing re-emissions. Also, where possible, every effort should be made to inject the additive into the slurry just as it is fed to the absorber rather than adding it directly to the reaction tank, where the active ingredient has residence time to precipitate with other metals.

However, the multi-additive testing approach described above represents an empirical approach to finding additives that might work for a particular application. More work is needed to determine how much mercury partitioning varies between the liquor and solids in the absorber slurry in a given FGD system, what controls this partitioning, and how this affects mercury re-emission levels. Similarly, developing an understanding of why additives work in one FGD system and not another would greatly improve on the current state of the art.

Also, as the project was nearing its end, speculation was made that some mercury that is measured as being in the FGD liquor phase may actually be present as sub-micron-diameter particles (<0.7-μm) that pass through the filter media used to separate slurry solids from the liquor. Mercury present in filtered slurry as ultra-fine particles would not be affected by mercury precipitation additives such as TMT-15 or Nalco 8034. The role of any such ultra-fine particles on re-emissions is not known, but presumably they would not participate in the aqueous reactions that produce re-emissions. More work is needed with ultra-fine filtration at future test sites to see how much, if any, of what is measured to be liquid phase mercury is really present as sub-micron particles that contain mercury. Improved understanding here may also improve the understanding of why additives are, or are not effective in a given FGD system, as discussed in the previous paragraph.

REFERENCES

1. Blythe, Gary M. *Field Testing of an FGD Additive for Enhanced Mercury Control, Task 2 and 4 Pilot-scale Test Results.* Topical Report. Cooperative Agreement No. DE-FC26-04NT42309, URS Corporation, Austin, Texas 78729. May 2006.

2. Blythe, Gary M. *Field Testing of an FGD Additive for Enhanced Mercury Control, Task 3 Full-scale Test Results.* Topical Report. Cooperative Agreement No. DE-FC26-04NT42309, URS Corporation, Austin, Texas 78729. May 2007.

3. Blythe, Gary M. and MariJon Owens. *Field Testing of an FGD Additive for Enhanced Mercury Control, Task 5 Full-scale Test Results.* Topical Report. Cooperative Agreement No. DE-FC26-04NT42309, URS Corporation, Austin, Texas 78729. February 2008.

4. 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.

5. Blythe, Gary M. "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems," Quarterly Technical Progress Report, March 1, 2005 – June 30, 2005. Cooperative Agreement No. DE-FC26-04NT41992, URS Corporation, Austin, Texas 78729. July 2005.

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

7. Skoog, Douglas A., Donald M. West and F. James Holler. *Fundamentals of Analytical Chemistry*, Seventh Edition, Saunders College Publishing, Philadelphia, PA, 1996. pp 57-58.

8. Method 1312, Synthetic Precipitation Leaching Procedure, U.S. EPA, www.epa.gov/sw-846/pdfs/1312.pdf

9. Gary M. Blythe and David W. DeBerry, Ph.D. "Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors, Semiannual Technical Progress Report, April 1, 2007 – September 30, 2007," DOE/NETL Cooperative Agreement No: DE-FC26-04NT42314, October 2007.

10. Schroeder, Karl, et al. "Leach Testing of FGD Materials," paper presented at the DOE/NETL Mercury Control Technology Conference, Pittsburgh, PA, December 11-13, 2006.