

Field Testing of a Wet FGD Additive for Enhanced Mercury Control – Task 5 Full-scale Test Results

Topical Report

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ABSTRACT

This Topical Report summarizes progress on Cooperative Agreement DE-FC26-04NT42309, “Field Testing of a Wet FGD Additive.” The objective of the project is 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 intends to demonstrate whether the additive 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 is conducting pilot- and full-scale tests of the additives in wet FGD absorbers. The tests are 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 has provided the Texas lignite/PRB co-fired test site for pilot FGD tests and cost sharing. Southern Company has provided the low-sulfur Eastern bituminous coal host site for wet scrubbing tests, as well as the pilot- and full-scale jet bubbling reactor (JBR) FGD systems tested. IPL provided the high-sulfur Eastern bituminous coal full-scale FGD test site and cost sharing. Evonik Degussa Corporation is providing the TMT-15 additive, and the Nalco Company is providing the Nalco 8034 additive. Both companies are also supplying technical support to the test program as in-kind cost sharing.

The project is being conducted in six tasks. Of the six project tasks, Task 1 involves project planning and Task 6 involves management and reporting. The other four tasks involve field testing on FGD systems, either at pilot or full scale. The four tasks include: 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 and the full-scale test using high-sulfur coal were completed in 2005 and 2006 and have been previously reported. This topical report presents the results from the Task 5 full-scale additive tests, conducted at Southern Company’s Plant Yates Unit 1. Both additives were tested there.

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INTRODUCTION

This project is being conducted as part of NETL Cooperative Agreement DE-FC26-04NT42309, “Field Testing of a Wet FGD Additive.” The objective of the project is to demonstrate the use of flue gas desulfurization (FGD) additives to prevent the re-emission of elemental mercury (Hg^0) in flue gas exiting wet FGD systems on coal-fired boilers. Furthermore, the project intends to demonstrate whether the additive 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 is conducting pilot- and full-scale tests of additives in wet FGD absorbers. The tests are intended to determine additive dosage requirements to prevent Hg^0 re-emissions 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. as the prime contractor, EPRI, Luminant Power (was TXU Generation Company LP), Southern Company, IPL (an AES company), Evonik Degussa Corporation and the Nalco Company. EPRI is providing technical input and co-funding. Luminant Power has provided the Texas lignite/PRB co-fired test site for pilot FGD tests, Monticello Steam Electric Station Unit 3, and is providing EPRI tailored collaboration project co-funding. Southern Company has provided the low-sulfur Eastern bituminous coal host site for wet scrubbing tests, as well as the pilot- and full-scale jet bubbling reactor (JBR) FGD systems tested. They are also providing on-site test support and management, and project co-funding through a tailored collaboration project with EPRI. A third utility, IPL, an AES company, has provided the high-sulfur Eastern bituminous coal full-scale FGD test site and project co-funding. Finally, Evonik Degussa Corporation is providing their TMT-15 additive and the Nalco Company is providing their Nalco 8034 additive. Both companies have supplied the additives as well as technical support to the test program as in-kind cost sharing.

The project is being conducted in six tasks. Of the six project tasks, Task 1 involves project planning and Task 6 involves management and reporting. The other four tasks involve field testing on FGD systems, either at pilot or full scale. The four tasks include: 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. A previous Topical Report presented results from the Task 2 and Task 4 pilot-scale additive tests, which were completed in 2005.¹ Results from the Task 3 full-scale testing at IPL’s Petersburg Station, which were completed in 2006, were also presented in a previous Topical Report.²

This report presents the results from the Task 5 full-scale additive tests at Southern Company’s Plant Yates Unit 1. Both additives were tested at this site.

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 the FGD blow down liquor, 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 reused such as for wallboard production. 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 being 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 is only now seeing increased use in U.S. plants, primarily in 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 blow down liquor before it can be discharged. A two-stage treatment has reportedly proven successful using hydroxide precipitation followed by precipitation of the complexed metals with 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 used directly in some wet FGD systems on municipal waste incinerators in Europe and in the U.S. to control mercury re-emissions.

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.³

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 H₂S.

In the FGD 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.³ 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 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 reported here, the pilot-scale tests and one of the full-scale tests had been conducted with mixed results. During this second full-scale test 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, is expected to act similarly to TMT-15 by precipitating mercury from the liquor through the formation of fine mercury salts. The full-scale test results using both of these scrubber additives on the jet bubbling reactor (JBR) FGD system on Unit 1 at Plant Yates are the subject of this topical report.

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.

EXPERIMENTAL

Test Overview

Two full-scale scrubber additive tests were conducted at Southern Company's Plant Yates Unit 1, which fires 1% sulfur, Eastern bituminous coal. The coal reportedly 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 $10 \mu\text{g}/\text{Nm}^3$ or less. The host unit has a tangentially fired PC boiler and a turbine-generator with a 123-MW nameplate rating. The unit operating load rarely exceeds 110 MW, though. It uses a relatively small (design SCA of $173 \text{ ft}^2/\text{kacfm}$) 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 SCR installed. Figure 1 illustrates the Plant Yates flue gas configuration.

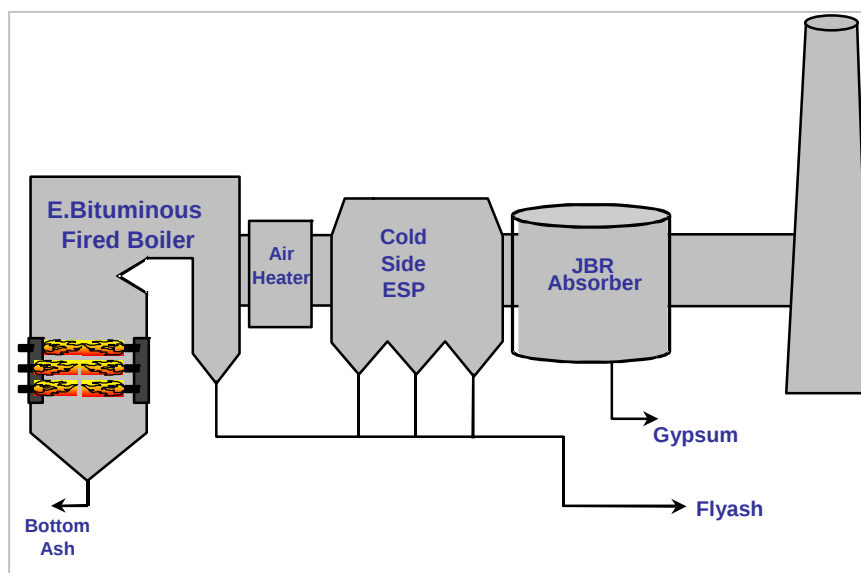


Figure 1. Plant Yates Flue Gas Configuration

Figure 2 shows a simplified schematic of a JBR, which is different than a conventional spray/tray absorber tower in that there is no 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.

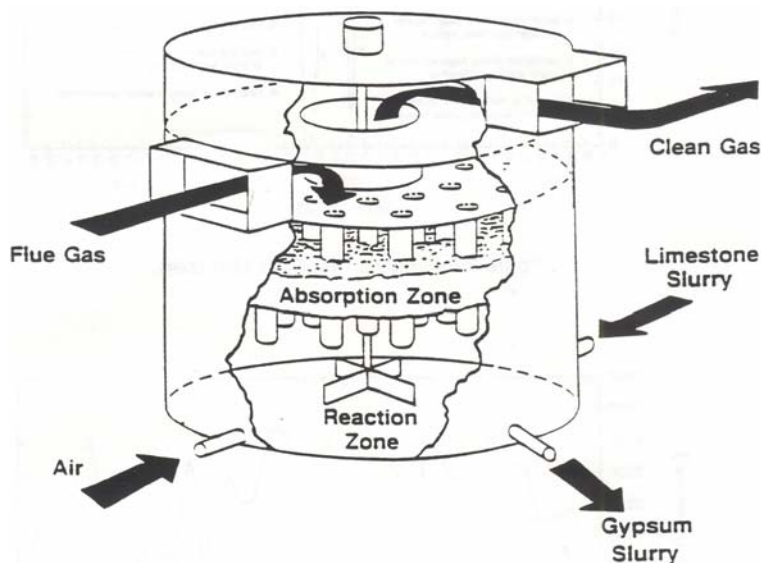


Figure 2. Simplified Schematic of a JBR

Source: Burford et al, "Plant Yates ICCT CT-121 Demonstration Results of Parametric Testing," 1993

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). Both measurement devices are described later in this section. 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 3 illustrates the Plant Yates dewatering scheme.

The planned 30-day test was begun in May 2007. TMT-15 was introduced to the JBR via the hydrocyclone return, 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

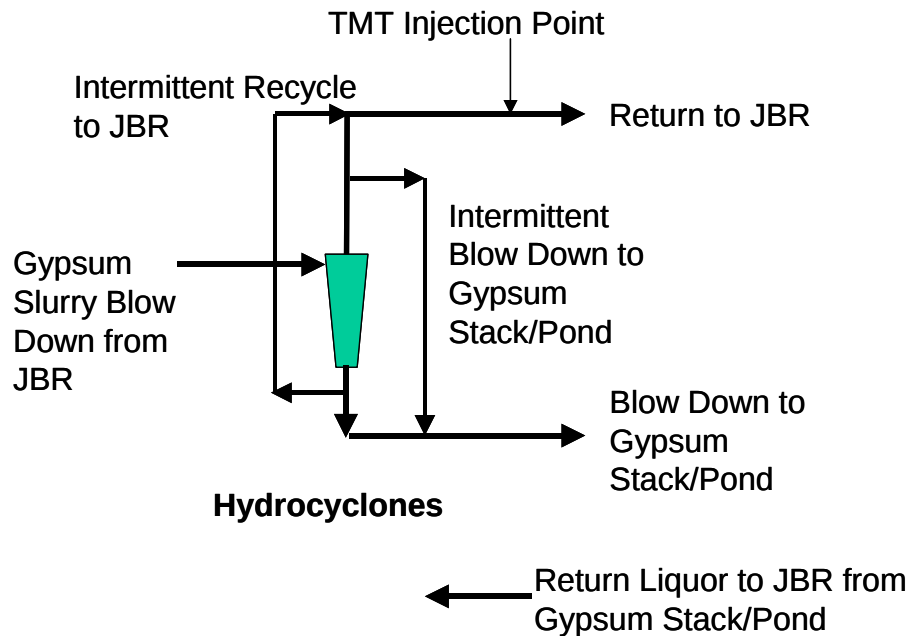


Figure 3. Illustration of Plant Yates JBR Slurry Dewatering Scheme

analyses. Samples of limestone reagent, makeup water and gypsum stack return liquor were also taken. The flue gas and FGD liquor and solids mercury concentration data were subsequently analyzed to determine TMT-15 effects on mercury re-emissions, and on mercury concentrations in the FGD liquor and solids.

The only on-site, real-time indication of the effectiveness of TMT-15 at preventing mercury re-emissions during the test was 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 during the Nalco 8034 test were the same as during the TMT-15 test as described above.

Mercury SCEM

A mercury SCEM developed for EPRI was used to measure JBR inlet mercury concentrations and speciation, to quantify net oxidized mercury (Hg^{+2}) removal and mercury re-emissions under baseline and additive conditions. The SCEM is illustrated in Figure 4.

Flue gas was pulled from an inertial gas separator (IGS) filter installed at a JBR inlet flue gas sampling 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 sample 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 a downstream analytical gold surface.

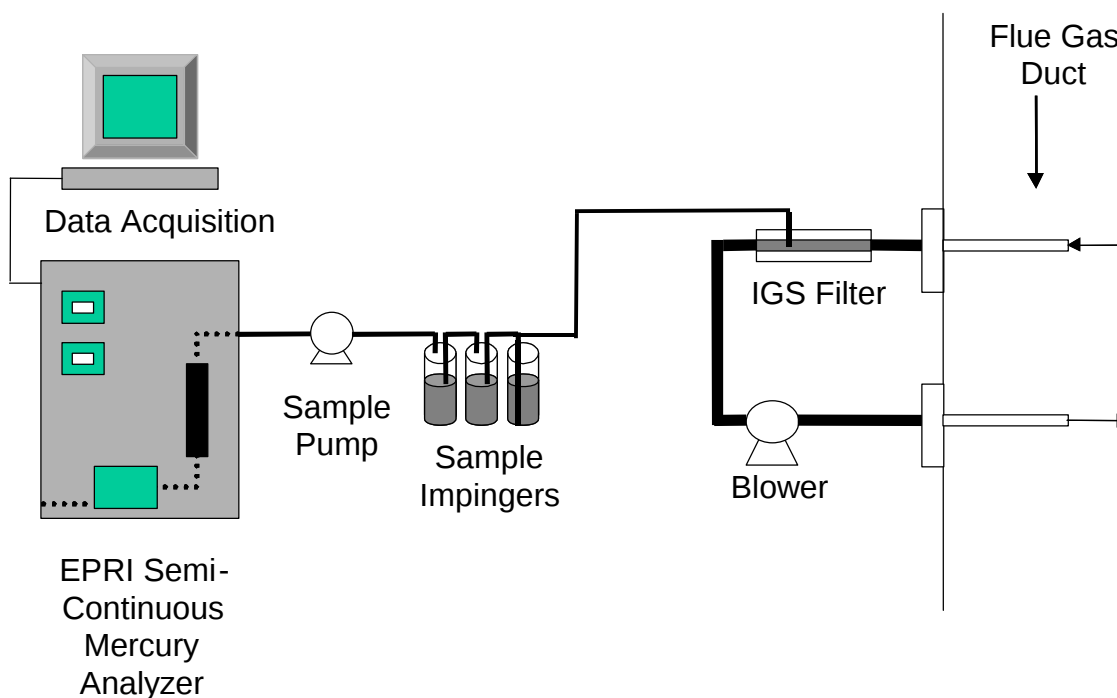


Figure 4. Schematic of Mercury SCEM

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 ($>700^{\circ}\text{C}$) 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.

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. 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 (stack) gas mercury concentrations. The analyzers are switched intermittently between sampling for elemental versus total mercury concentrations. For this testing, the plant CEM was used instead of the SCEM analyzer for obtaining flue gas mercury concentrations from the stack location. During the TMT-15 testing in May 2007, the plant CEM measured only total mercury concentration. It was assumed that virtually all of the mercury present in the flue gas after the JBR was in elemental form. The Ontario Hydro results presented later in this report confirm that this was a reasonable assumption. For the Nalco 8034 testing in August/September 2007, software modifications made it possible for the plant CEM to provide speciated mercury measurements as well as total. A second SCEM analyzer was occasionally used at the stack outlet location during the baseline and Ontario Hydro sampling periods as an additional measurement.

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 5 shows the Thermo MFS instrumentation and probe.

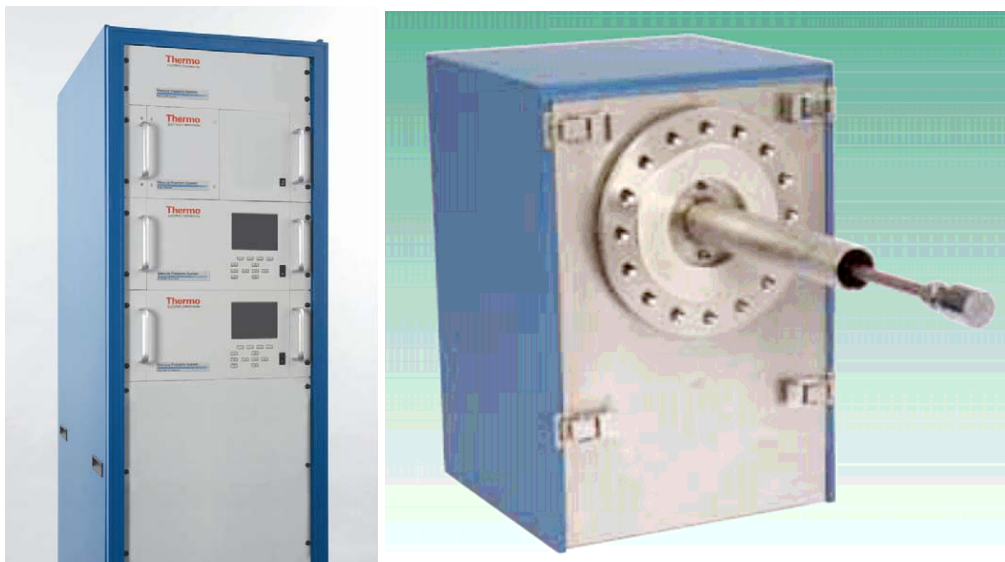


Figure 5. Thermo Mercury Freedom CEM instrumentation and probe

Test Plan

Table 1 shows the test sequence for the TMT-15 testing. The units of mL of TMT-15 injected per ton of coal fired is an Evonik Degussa dosing convention.

Table 1. 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

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.

Periodically during the baseline and injection test periods, a set of JBR reaction tank/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, 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 2 summarizes sampling and analysis events for this testing.

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.

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 2. 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 injection	Hg concentration and speciation by Hg SCEM; Hg concentration by Plant CEM
		Triplicate runs, Baseline and during scrubber 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 slurry	Filtered and preserved liquor, whole slurry	Baseline and 2 -3 times per week during injection	FGD chemistry
JBR blow down slurry	Filtered and preserved slurry liquor, solids	Baseline and 2 -3 times per week during injection	Hg concentration, metals
JBR blow down slurry hydrocyclone overflow	Filtered and preserved slurry liquor, solids	Baseline and 2 -3 times per week during injection	Hg concentration, metals
JBR blow down slurry hydrocyclone underflow	Filtered and preserved slurry liquor, solids	Baseline and 2 -3 times per week during injection	Hg concentration, metals
Gypsum stack return liquor	Liquor	Baseline and once per week of injection	Hg concentration
JBR blow down slurry	Whole slurry, five 5-gallon buckets	Baseline and last week of injection	Ship to DOE contractor

Table 3 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 Nalco 8034 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. Note that 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 3 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 active ingredient (TMT) per gram of oxidized mercury in the JBR inlet gas.

Table 3. 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 around noon to empty additive container
9/27/2007		Stopped injection ~ 6:00

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 µg/Nm³ 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 with a large surplus of Nalco 8034 in the JBR liquor it may actually act as a reductant, 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 reduction in re-emissions.

Near the end of the end of the 30-day injection period, plant personnel altered the FGD chemistry in the JBR 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. Unit 1 was removed from service as planned on 9/28/07 at 21:00.

RESULTS AND DISCUSSION

This section provides details of technical results for TMT-15 and Nalco 8034 additive tests conducted on the Yates Unit 1 full-scale wet FGD system described in the previous section. 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 in a third subsection below.

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 4, 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). The re-emissions percentage shown in this report 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.

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.

The available inlet elemental mercury concentration data from the SCEM are compared to the mercury concentrations from the plant CEM in Figure 6, for the TMT-15 addition period in May 2007. These data illustrate the apparent increase in elemental mercury concentration in the flue gas across the JBR.

Table 4. 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, $\mu\text{g}/\text{Nm}^3$ @ 3% O_2		JBR Outlet Total Hg, $\mu\text{g}/\text{Nm}^3$ @ 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

Flue gas mercury concentration data measured by the Ontario Hydro method⁴ 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 5. Note that 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 $11.9 \mu\text{g}/\text{Nm}^3$, whereas the other two runs (other five runs considering the earlier baseline measurements) measured $7.9 \mu\text{g}/\text{Nm}^3$ 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 $6.0 \mu\text{g}/\text{Nm}^3$ with a single maximum value of $7.8 \mu\text{g}/\text{Nm}^3$, significantly less than the $11.9 \mu\text{g}/\text{Nm}^3$ elemental mercury concentration value measured for that Ontario Hydro run. Although the data are presented both ways in Table 5, the remainder of the discussions of the Ontario Hydro results considers only the two stack runs for May 24.

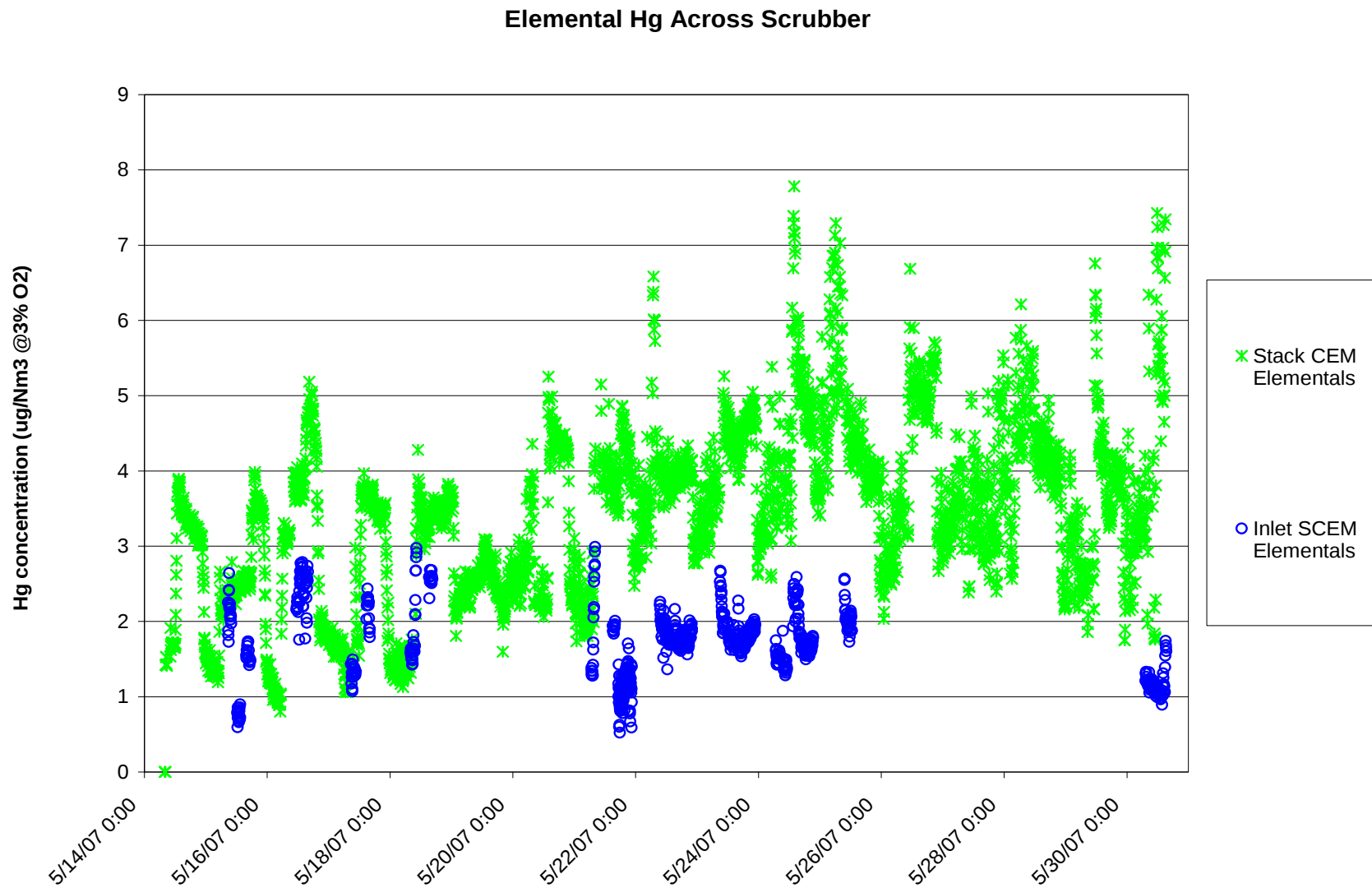


Figure 6. SCEM and CEM Results from the TMT-15 testing at Plant Yates Unit 1

Table 5. Results of Ontario Hydro Measurements During TMT-15 Test at Yates Unit 1 (mean values for three Ontario Hydro runs $\pm$ 95% confidence interval about mean)

Condition	Baseline		With TMT-15 @ 40 mL/ton coal		
	5/15/07		5/24/07		
	JBR Inlet	Stack	JBR Inlet	Stack*	Stack**
Hg ⁰ , $\mu\text{g}/\text{Nm}^3$	3.6 ± 0.6	4.6 ± 0.2	4.7 ± 0.7	8.9 ± 2.9	7.5 ± 0.9
Hg ⁺² , $\mu\text{g}/\text{Nm}^3$	3.4 ± 0.7	0.18 ± 0.05	4.8 ± 0.2	0.65 ± 0.22	0.54 ± 0.08
Total Hg, $\mu\text{g}/\text{Nm}^3$	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, %	-	$95\% \pm 2\%$	-	$87\% \pm 5$	$89\% \pm 0.9$
Hg ⁰ Re-emissions across Absorber, $\mu\text{g}/\text{Nm}^3$	-	1.0 ± 0.7	-	4.2 ± 2.7	3.0 ± 1.9
Hg ⁰ Re-emissions, % of JBR inlet Hg ⁺²	-	$29\% \pm 17\%$	-	$88\% \pm 59\%$	$60\% \pm 34\%$
Overall Hg Removal across Absorber, %	-	$31\% \pm 6\%$	-	$-0.53\% \pm 31\%$	$15\% \pm 16\%$

*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 4 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 4 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 4 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 pilot-scale TMT test results¹, 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 6 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. 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.¹

Table 6. 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 pilot-scale TMT test results¹, 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 7. 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.

The JBR liquor and solids mercury concentration data from Tables 6 and 7 are repeated in Table 8 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. As shown in the table, the 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 supports the flue gas data, which show that TMT-15 was not effective at controlling mercury re-emissions from the JBR.

Table 7. 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., $\mu\text{g/g}$	Hydrocyclone Overflow Solids Hg Conc., $\mu\text{g/g}$	Hydrocyclone Underflow Solids Hg Conc., $\mu\text{g/g}$
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

Table 8. Absorber Blow Down Slurry Mercury Concentrations During Baseline and TMT Addition Periods

Date	TMT-15 Dosage	JBR Liquor Mercury Concentration, $\mu\text{g/L}$	JBR Solids Mercury Concentration, $\mu\text{g/g}$	Slurry wt% Solids	% of 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

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 9. 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.

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 in this subsection.

Flue Gas Data

Mercury speciation and removal data as measured by SCЕМ at the JBR inlet and by CЕМ at the stack (JBR outlet) are shown in Table 10. As discussed previously, during the Nalco additive test the CЕМ at the stack was set up to speciate whereas it measured only total mercury during the TMT-15 test.

Table 9. JBR 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, °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

As summarized in Table 10, 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 for the TMT-15 results, 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.

Table 10. 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, $\mu\text{g}/\text{Nm}^3$ @ 3% O ₂		JBR Outlet Hg, $\mu\text{g}/\text{Nm}^3$ @ 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

The available inlet elemental mercury concentration data by SCEM are compared to the stack elemental mercury concentrations from the plant CEM in Figure 7 for the Nalco 8034 test period. Also included in this plot are measurements by SCEM at the stack outlet location, which confirm the stack concentration data showing no significant reduction in re-emissions with the Nalco additive.

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 11. 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 SO₃ 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 $<0.53 \mu\text{g}/\text{Nm}^3$. The other two runs that day averaged $3.4 \mu\text{g}/\text{Nm}^3$. This data point qualifies as an outlier based on a “Q test” for three data points, with a 98+% degree of confidence.⁵ 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.

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.

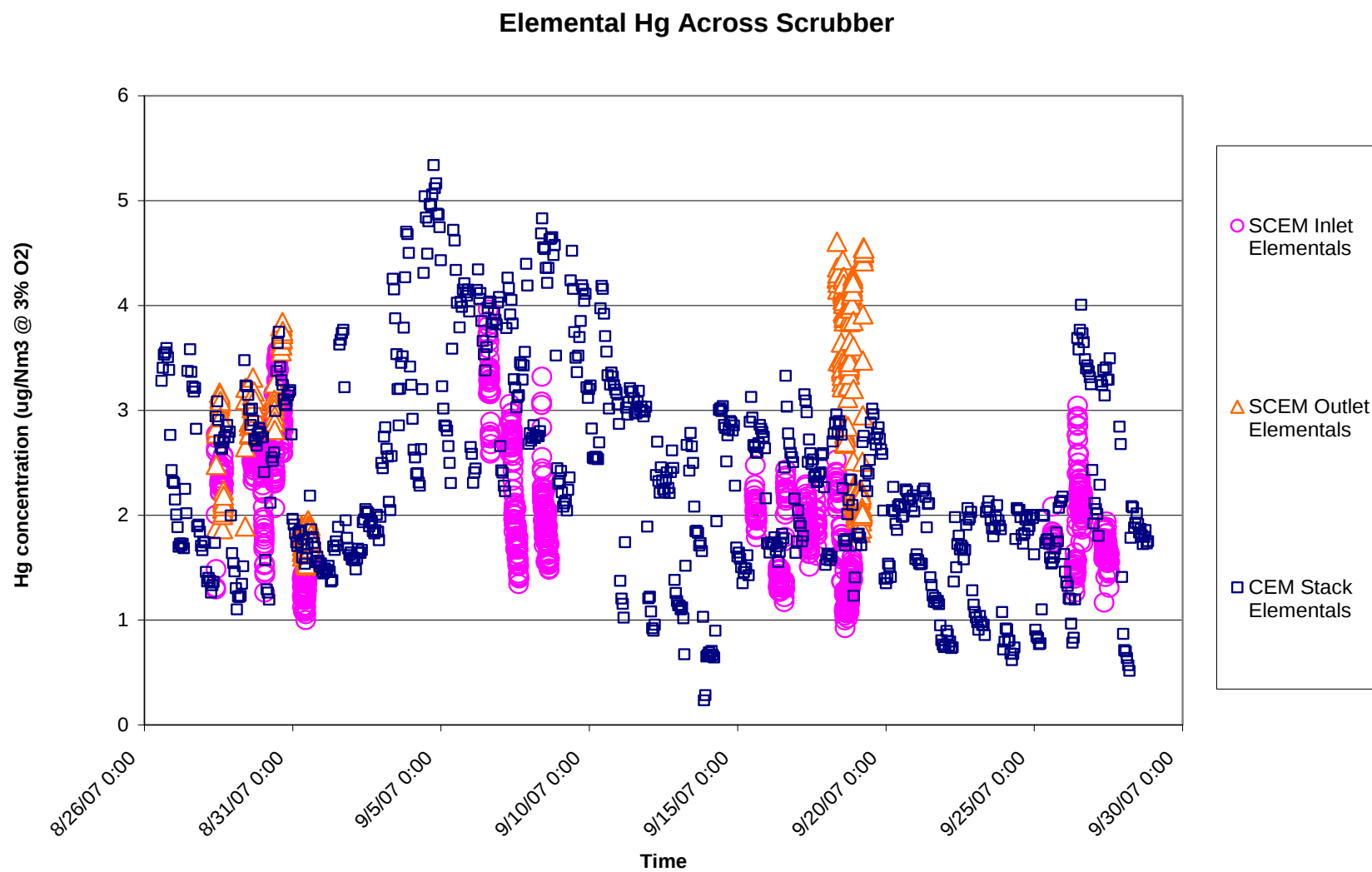


Figure 7. SCEM and CEM Results from the Nalco 8034 testing at Plant Yates Unit 1

Table 11. Results of Ontario Hydro Measurements During Nalco 8034 Test at Yates Unit 1 (mean values for three Ontario Hydro runs $\pm$ 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 , $\mu\text{g}/\text{Nm}^3$	3.7 $\pm$ 0.9	4.2 $\pm$ 1.1	4.5 $\pm$ 0.3	5.0 $\pm$ 0.3
Hg ⁺² , $\mu\text{g}/\text{Nm}^3$	2.9 $\pm$ 0.3	<0.3 $\pm$ 0.1	3.4 $\pm$ 0.3	<0.5 $\pm$ 0.0
Total Hg, $\mu\text{g}/\text{Nm}^3$	6.6 $\pm$ 1.2	4.2 $\pm$ 1.1	8.0 $\pm$ 0.1	5.0 $\pm$ 0.3
Mercury Oxidation at JBR Inlet, %	56 $\pm$ 4	-	56 $\pm$ 5	-
Hg ⁺² Removal across Absorber, %	-	>90%	-	>86%
Hg ⁰ Re-emissions across Absorber, $\mu\text{g}/\text{Nm}^3$	-	0.5 $\pm$ 0.9	-	0.5 $\pm$ 0.1
Hg ⁰ Re-emissions, % of JBR inlet Hg ⁺²	-	18% $\pm$ 32%	-	15% $\pm$ 1%
Overall Hg Removal across Absorber, %	-	36% $\pm$ 13%	-	38% $\pm$ 4%

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

However, note that when expressed on an absolute concentration basis, the re-emissions levels averaged 0.5 $\mu\text{g}/\text{Nm}^3$ (corrected to 3% O₂) 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 (0.3 to 1.1 $\mu\text{g}/\text{Nm}^3$ corrected to 3% O₂). 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 over the test period. The JBR slurry liquor was sampled more frequently than were the hydrocyclone overflow and underflow.

Table 12 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 12. 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 13. The JBR slurry solids were analyzed a number of times during the test period, but 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 12 and 13 are repeated in Table 14, 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.

The results of these analyses for the Nalco 8034 test are shown in Table 15, and show no significant scrubber additive effect on FGD chemistry. Sulfite oxidation, limestone utilization, and gypsum purity did not appear to be affected.

Table 13. 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 14. Daily Absorber 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

Table 15. 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, °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

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
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

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 if 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.

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 16. 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 10. 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 16. 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 analysis

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 are summarized in Tables 17 and 18. 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 identified. Significant was defined in this exercise 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 19. 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.

Table 17. Results of Slurry Solids Metals Analyses (all values in µg/g)

Sample Type	JBR Solids		Limestone Solids		Hydrocyclone Overflow Solids		Hydrocyclone Underflow Solids	
Date Collected	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	<0.08	<0.08	<0.08	<0.08	0.82	0.76	<0.08	<0.08
Al	1,680	804	1,099	976	48,780	36,970	1,041	606
As	8.06	2.9	1.56	1.52	158	117	5.69	2.54
Ba	23.8	13.3	9.01	13.1	740	731	17.9	10.7
Be	0.15	0.095	0.05	0.05	4.49	3.26	0.12	0.07
Cd	0.04	<0.03	0.61	1.08	0.83	1.24	<0.03	<0.03
Co	2.29	1.9	6.14	5.45	30.7	23.3	2.02	1.82
Cr	6.81	10.47	10.7	28.1	144	269	3.92	6.2
Cu	2.55	1.3	2.87	1.72	82.4	74.7	1.54	1.08
Fe	1,036	516	709	852	27,760	22,820	655	371
Mn	8.45	1.32	39.1	50.1	122	83.5	2.36	1.06
Mo	2.81	1.7	0.5	0.71	73.2	60.7	2.37	1.3
Ni	15.9	17.4	28.5	31.8	77.6	57.5	15.7	16.8
Pb	2.42	1.09	1.46	1.38	61.2	55.1	1.56	0.94
Sb	0.61	0.34	0.22	0.42	12.8	7.27	0.45	0.29
Se	10.1	9.96	<0.81	1.7	20.7	222	9.79	9.03
Sn	<0.080	<0.080	<0.080	<0.080	7.49	8.63	<0.080	<0.080
Sr	311	336	462	524	640	756	301	304
Ti	102	43	53	51	3,108	2,259	62	31
Tl	<0.01	<0.01	<0.01	<0.01	3.4	1.81	<0.01	<0.01
V	10.1	6.54	7.88	10.2	206	171	8.46	6.59
Zn	18.5	15.2	42.2	52.5	455	542	15.4	15.9

Table 18. Results of Slurry Liquor Metals Analyses (all values in µg/L)

Sample Location	JBR Liquor		Limestone Liquor		Field Blank	
Date Collected	5/15/07	8/29/07	5/15/07	8/29/07	5/18/07	8/28/07
Ag	2.28	<0.17	0.43	<0.17	<0.17	<0.17
Al	210,500*	8,050	860	450	136	114
As	65.1	66.7	35.8	45.6	4.3	3.9
Ba	133	229	77.1	73.6	5.1	1.9
Be	23.2	2.84	0.252	0.194	<0.06	<0.06
Cd	257	169	1.67	2.2	<0.06	<0.06
Co	354	78.3	26	16.5	<0.04	<0.04
Cr	57.0	0.48	2.07	<0.48	7.04	4.02
Cu	756	108	11.7	9.4	6.7	4.0
Fe	608	158	655	389	102	122
Mo	89	488	363	618	0.54	1.1
Ni	1,220	736	72.3	229	<0.53	<0.53
Pb	27.3	0.72	<0.56	0.67	8.89	<0.56
Sb	56.2	51.1	31.3	30.7	0.80	<0.13
Se	6,895	3,380	2,750	2,920	12.9	13.1
Sr	7,010	8,290	13,000	13,900	8.0	5.2
Ti	86.2	15.2	26.5	10.4	<3.89	<3.89
Tl	31.4	25.2	7.9	12.8	<0.02	<0.02
V	17	17	17	17	17	17
Zn	12,200	4,610	118	101	19.3	15.3

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

Table 19. 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

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 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. These solid samples were analyzed using a Leco “Lecotrac” particle size analyzer on solids dispersed in methanol.

The results of these particle size analyses are summarized in Table 20. 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 20. 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-15 injection) Samples, 5/15/07:				
JBR 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 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 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 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 21, and results of the mercury balance calculations are shown in Table 22. 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 21. Summary of Hydrocyclone (HC) Overall Mass Balance Estimates

Date	Scrubber Additive	% of FGD Blow Down Slurry Liquor		% of FGD 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 22. Summary of Hydrocyclone (HC) Mercury Balance Calculations

Date	Scrubber Additive	% 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
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 23. 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 23. Results of Overall Mercury Balance Across JBR.

Date	5/15/2007	5/25/2007	8/28/2007	9/18/2007
Coal Heat Content, Btu/lb (dry basis)	13201	*	13072	13308
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 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 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 seen in the bottom rows of the table, the apparent mercury removal across the JBR varies considerably depending on the assumption of 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 23 is that these mass balance calculations 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 1312.⁶ 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 24 identifies the sample collection dates and shows results for the six samples analyzed.

Table 24. 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. With the use of either TMT-15 or Nalco 8034 the leachate mercury concentrations will be near zero.

CONCLUSION

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. Neither test conclusively demonstrated the ability of the additive to control mercury re-emissions across the JBR.

In the first test with TMT-15, 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 $>100 \mu\text{g/L}$. This suggests that TMT-15 was ineffective in the JBR at the dosages tested, which were within the range recommended by the manufacturer. 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: it is possible that part of what was measured as liquor with the URS sampling and analytical protocol was actually present as extremely fine particles. Slurry samples were filtered on site with filter media that have a $0.7\text{-}\mu\text{m}$ pore size, so particles smaller than approximately $0.7 \mu\text{m}$ 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,⁷ and the trace metals analyses presented in Table 18 of this report show about four times greater iron concentration in the JBR liquor in May than in August. 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. 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 $1 \mu\text{g/L}$), and mercury re-emission levels were also low ($0.5 \mu\text{g/Nm}^3 @ 3\% \text{O}_2$). 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 $1.0 \mu\text{g/Nm}^3 @ 3\% \text{O}_2$ instead of the measured value of $0.5 \mu\text{g/Nm}^3 @ 3\% \text{O}_2$. 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. The results 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.

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