

# **Field Testing of a Wet FGD Additive for Enhanced Mercury Control – Task 3 Full-scale Test Results**

## **Topical Report**

Prepared by:

Gary M. Blythe

**May 2007**

**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 Cochran's Mill Road  
Pittsburgh, Pennsylvania 15236



## **DISCLAIMER**

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

## ABSTRACT

This 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 a flue gas desulfurization (FGD) additive, Degussa Corporation’s TMT-15, to prevent the re-emission of elemental mercury ( $\text{Hg}^0$ ) 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 TMT 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 TMT-15 additive in wet FGD absorbers. The tests are intended to determine required additive dosages to prevent  $\text{Hg}^0$  re-emissions and to separate mercury from the normal FGD byproducts for three coal types: Texas lignite/Power 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, TXU Generation Company LP, Southern Company, and Degussa Corporation. TXU Generation has provided the Texas lignite/PRB co-fired test site for pilot FGD tests, Monticello Steam Electric Station Unit 3. Southern Company is providing 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 to be tested. IPL, an AES company, provided the high-sulfur Eastern bituminous coal full-scale FGD test site and cost sharing. Degussa Corporation is providing the TMT-15 additive and technical support to the test program as 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 were completed in 2005 and have been previously reported. This topical report presents the results from the Task 3 full-scale additive tests, conducted at IPL’s Petersburg Station Unit 2. The Task 5 full-scale additive tests will be conducted later in calendar year 2007.

# TABLE OF CONTENTS

	Page
<b>Disclaimer</b> .....	<b>iii</b>
<b>Abstract</b> .....	<b>iv</b>
<b>Introduction</b> .....	<b>1</b>
Background .....	1
Report Organization.....	3
<b>Experimental</b> .....	<b>4</b>
Test Description.....	4
Mercury SCEM .....	6
Test Plan .....	7
<b>Results and Discussion</b> .....	<b>11</b>
Flue Gas Data .....	11
Mercury SCEM Results .....	11
Ontario Hydro Flue Gas Measurement Results .....	12
FGD Liquor and Solid Byproduct Analysis Data .....	14
FGD Liquor Mercury Concentrations.....	14
FGD Byproduct Solids Mercury Concentrations.....	15
FGD Byproduct Solids Particle Size Analyses.....	18
FGD Absorber Blow Down Slurry Chemistry.....	19
SPLP Analyses of Byproduct Solids.....	19
Follow-up Measurements at Petersburg Unit 2.....	21
<b>Conclusion</b> .....	<b>23</b>
<b>References</b> .....	<b>25</b>

## LIST OF FIGURES

Figure 1. Schematic of Byproduct Slurry Dewatering Scheme for Petersburg Unit 2.....	5
Figure 2. Schematic of Mercury SCEM .....	6
Figure 3. SCEM Results for the Petersburg Unit 2 Stack Flue Gas .....	11

## LIST OF TABLES

Table 1. Test Sequence for Petersburg Full-scale TMT-15 Additive Tests .....	8
Table 2. Sampling and Analysis Plan for Petersburg Full-scale TMT-15 Additive Tests ..	8
Table 3. TMT-15 Dosing Event Log.....	10
Table 4. Results of Ontario Hydro Measurements During TMT-15 Test at Petersburg Unit 2 (mean values for three Ontario Hydro runs $\pm$ 95% confidence interval about mean) .....	12
Table 5. Results of Daily Absorber Blow Down and Primary Hydrocyclone Overflow Liquor Mercury Concentrations During Baseline and TMT Addition Periods.....	14
Table 6. Results of Liquor Mercury Concentrations in Unit 2 FGD Slurry Dewatering Train.....	15
Table 7. Results of Daily Absorber Blow Down and Primary Hydrocyclone Overflow Solids Mercury Concentrations During Baseline and TMT Addition Periods .....	16
Table 8. Results of FGD System Solids Mercury Concentration Data for Baseline and Steady-state TMT Addition Ontario Hydro Test Periods .....	16
Table 9. Unit 2 Coal Sample Data.....	17
Table 10. Daily Absorber Blow Down Slurry Mercury Concentrations During Baseline and TMT Addition Periods.....	18
Table 11. Results of Particle Size Analyses on Byproduct Solid Samples .....	18
Table 12. FGD Absorber Slurry Analysis Results.....	20
Table 13. FGD System Solids Divalent Transition Metal Concentration Data for Baseline and Steady-state TMT Addition Ontario Hydro Test Periods .....	21
Table 14. Results of TMT Addition Beaker Tests at Petersburg Unit 2, January 2007..	22

## 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 a flue gas desulfurization (FGD) additive, Degussa Corporation’s TMT-15, to prevent the re-emission of elemental mercury ( $\text{Hg}^0$ ) 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 TMT 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 TMT-15 additive in wet FGD absorbers. The tests are intended to determine required additive dosage requirements to prevent  $\text{Hg}^0$  re-emissions and to separate mercury from the normal FGD byproducts for three coal types: Texas lignite/Power 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, TXU Generation Company LP, Southern Company, and Degussa Corporation. EPRI is providing technical input and co-funding. TXU Generation 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 is providing 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 to be 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, Degussa Corporation is providing the TMT-15 additive and technical support to the test program as 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.<sup>1</sup>

This report presents the results from the Task 3 full-scale, high-sulfur Eastern bituminous FGD additive tests. The Task 5 full-scale additive test will be conducted later in calendar year 2007.

### 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 ( $\text{Hg}^{+2}$ ) is absorbed from the flue gas into the FGD liquor, while water insoluble elemental mercury ( $\text{Hg}^0$ ) 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 potentially becoming a regulatory compliance issue in FGD blow down liquor; or 3) Being retained in the FGD byproduct solids. This project is investigating the use of an FGD additive to rapidly precipitate mercury in FGD liquor as a solid salt, to minimize pathways 1 and 2. Pathway 3 may be the most desirable for FGD systems that landfill their FGD solid byproducts, but could become an issue if the byproducts are reused such as for wallboard production. A second objective of the project is to determine whether this same additive can be used to minimize mercury concentrations in reused FGD solid byproducts, through separation of the fine mercury-containing salts formed from the remainder of the byproduct.

The wet FGD additive being tested is a 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 not seen widespread use in U.S. plants. 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 in Europe, using hydroxide precipitation followed by precipitation of the complexed metals with trimercapto-s-triazine, tri-sodium salt (TMT). TMT is commercially available from Degussa Corporation as a 15-wt% aqueous solution, TMT 15. TMT is also used directly in wet FGD systems to reduce mercury re-emissions. Mercury re-emissions occur when soluble  $\text{Hg}^{+2}$  reacts with sulfite ion (absorbed  $\text{SO}_2$ ) in wet FGD liquors and is reduced to the insoluble  $\text{Hg}^0$  form, which is released back into the FGD outlet flue gas. Conversion of  $\text{Hg}^{+2}$  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 worldwide 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.<sup>2</sup>

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  $\text{H}_2\text{S}$ .

In the FGD blow down slurry, fine particles of mercury-TMT compound are transferred to the wastewater/fines blow down, absorber recycle and/or partly to the byproduct gypsum. TMT-metal compounds are reportedly quite stable. Degussa reports that temperatures in excess of  $210^\circ\text{C}$  (which is well above the gypsum calcining temperature) are needed to begin to

decompose the mercury-TMT salt, and TMT-metal compounds easily meet the leachability limits of the TCLP. It is anticipated that 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 is 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 is conducting two sets of pilot-scale TMT-15 additive tests and two full-scale TMT-15 additive trials. To date, the pilot-scale tests and one of the full-scale tests have been conducted. The full-scale test results are the subjects 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 Description

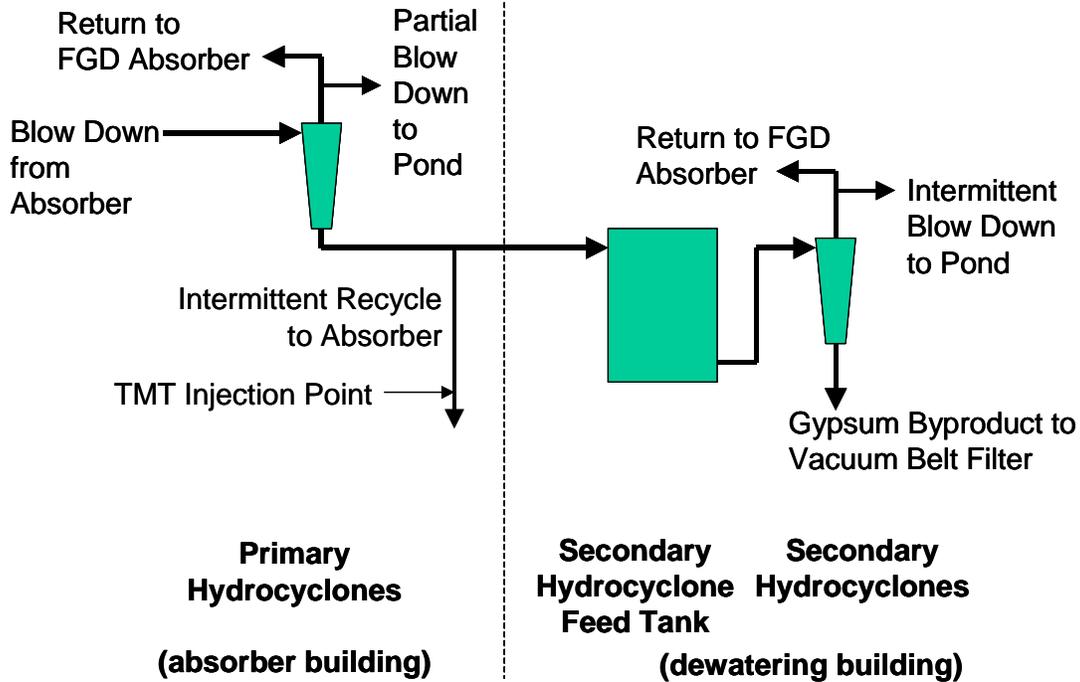
In July 2006, a full-scale TMT-15 test was conducted at IPL's (an AES company) Petersburg Station, Unit 2. Unit 2 is rated at 455-MW of gross generating capacity, and has a tangential-fired boiler that fires Indiana high-sulfur coal. Air pollution control equipment includes selective catalytic reduction (SCR) for NO<sub>x</sub> control, a cold-side ESP, and a wet FGD system. The wet FGD system operates in limestone forced oxidation (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 at 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. 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 semi-continuous emissions monitors (SCEMs), as described later 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. During baseline operation and after one week of operation with TMT injection, a full complement of FGD system slurry samples were collected, including samples throughout the slurry dewatering system and of the dewatered byproduct gypsum. The flue gas mercury data and the FGD liquor and solids mercury data were subsequently analyzed to determine TMT-15 effects on mercury re-emissions, and on mercury concentrations in the FGD liquor and solids.

Degussa recommends that TMT-15 be spiked into the FGD absorber slurry on a continuous basis, and that the ideal injection location is 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 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 Degussa, an alternate injection location was agreed upon.

Before describing the injection location, it would be helpful to describe the blow down slurry dewatering scheme at Petersburg Unit 2. The dewatering scheme is illustrated in Figure 1. Because of space limitations near the FGD system, the dewatering scheme 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 which is 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 1. 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.

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 out as they were emptied. A total of 27 drums were used over the course of the test.

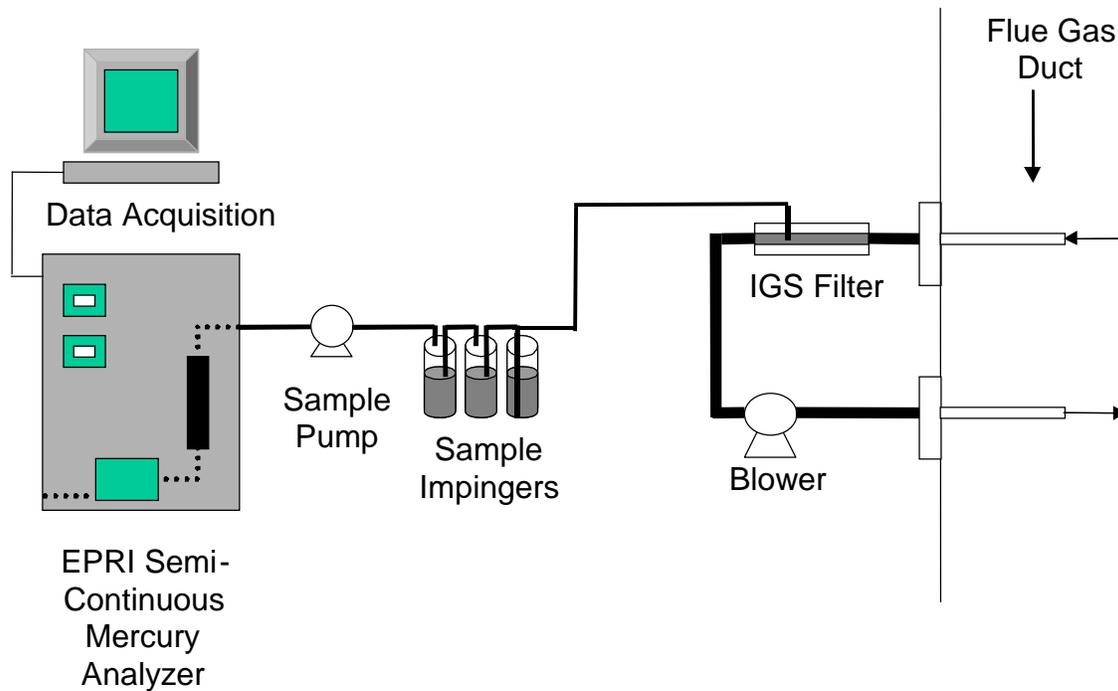
One of the planned measurements during the test, mercury SCEM measurements of absorber inlet total mercury and oxidized mercury concentrations, was not made successfully during the test program. The analyzer showed poor recovery of mercury spikes during the baseline test, which was speculated to be due to an interferent present in the flue gas, possible ammonia slip from the SCR. After several days of trying to troubleshoot and correct this problem, the atomic absorption spectrophotometer on the analyzer 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.

While the stack 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.

### Mercury SCEM

As described above, flue gas mercury measurements were made at the stack using a mercury SCEM developed for EPRI. The SCEM is illustrated in Figure 2.



**Figure 2. Schematic of Mercury SCEM**

Flue gas was pulled from an inertial gas separator (IGS) filter installed at the stack (FGD absorber 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 sample pump.

To measure total mercury in the flue gas, the impinger solutions consist of stannous chloride ( $\text{SnCl}_2$ ) followed by a sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) buffer and sodium hydroxide ( $\text{NaOH}$ ). The  $\text{SnCl}_2$  solution reduces all flue gas mercury species to elemental mercury. After passing through the  $\text{SnCl}_2$  impinger, the gas flows through the  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  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  $100^\circ\text{C}$ . 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. As mentioned above, though, the SCEM at the FGD inlet never operated successfully during this test.

## **Test Plan**

Table 1 shows the test sequence and Table 2 summarizes sampling and analysis plan for this testing. The units of mL of TMT-15 injected per ton of coal fired, as shown in Table 1, is a Degussa dosing convention.

**Table 1. 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 2. 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 liquor	Filtered and preserved liquor	Daily	Hg concentration
		Baseline and end of steady-state TMT injection period	FGD chemistry
FGD reaction tank/ blow down 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
	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

<b>Location</b>	<b>Sample Type</b>	<b>Frequency</b>	<b>Planned Analyses</b>
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

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.

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 3 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 SCSEM 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/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, 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.

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

**Table 3. TMT-15 Dosing Event Log**

<b>Date/Time</b>	<b>Event</b>
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

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.

## RESULTS AND DISCUSSION

This section provides details of technical results for TMT additive tests conducted on the Petersburg Unit 2 full-scale wet FGD system described in the previous section.

### 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 3. 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.

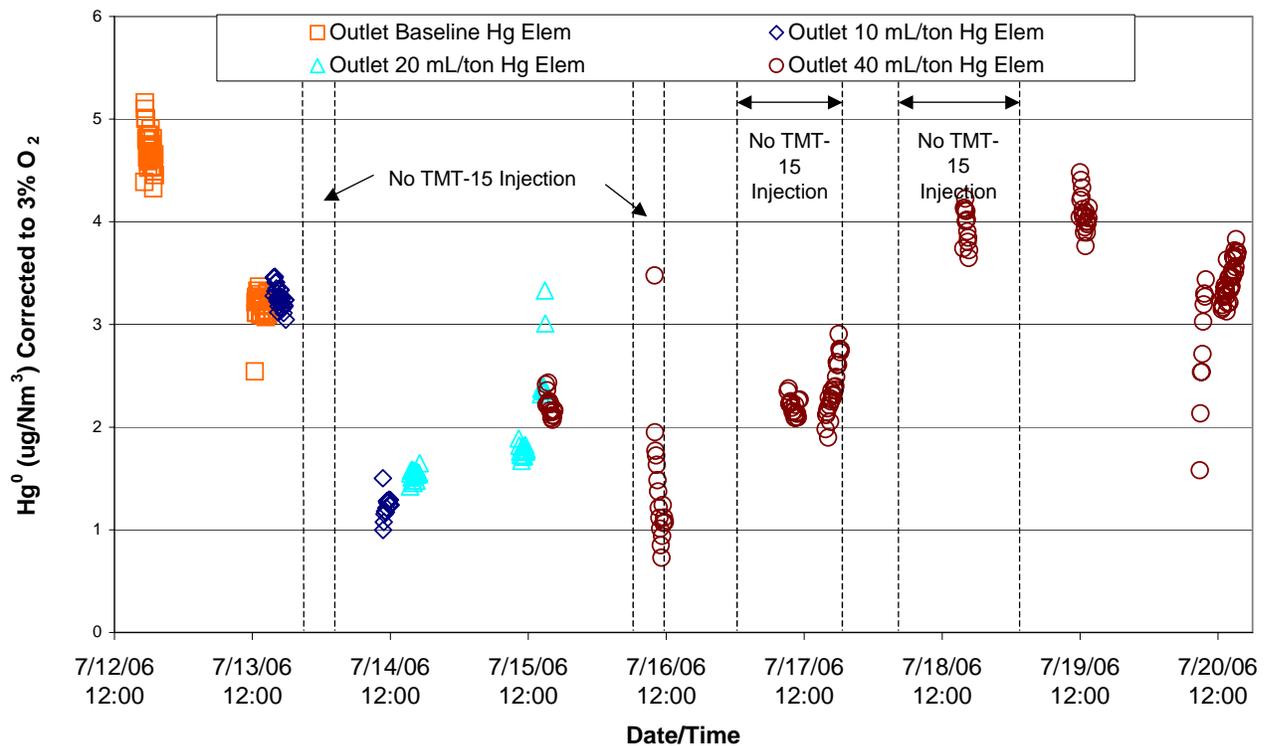


Figure 3. SCEM Results for the Petersburg Unit 2 Stack Flue Gas

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  $\mu\text{g}/\text{Nm}^3$  (corrected to 3%  $\text{O}_2$ ) on July 14, from earlier values in the range of 3 to 5  $\mu\text{g}/\text{Nm}^3$  on July 12 and 13. However, as the week went on, the stack elemental mercury concentrations increased back into the range of about 4  $\mu\text{g}/\text{Nm}^3$  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, it is unlikely that TMT-15 effectiveness would become reduced at higher dosage rates. Furthermore, the FGD liquor mercury concentration data, 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,<sup>3</sup> and FGD system liquor and solids mercury concentration data which are discussed later in this section. These results did not become available until some time 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 4.

**Table 4. Results of Ontario Hydro Measurements During TMT-15 Test at Petersburg Unit 2 (mean values for three Ontario Hydro runs  $\pm$  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**
$\text{Hg}^0$ , $\mu\text{g}/\text{Nm}^3$	2.3 $\pm$ 0.3	5.7 $\pm$ 0.4	2.0 $\pm$ 0.7	4.8 $\pm$ 0.6	4.6 $\pm$ 0.8
$\text{Hg}^{+2}$ , $\mu\text{g}/\text{Nm}^3$	6.9 $\pm$ 0.7	0.38 $\pm$ 0.10	7.6 $\pm$ 1.0	1.0 $\pm$ 1.1	0.49 $\pm$ 0.29
Total Hg, $\mu\text{g}/\text{Nm}^3$	9.2 $\pm$ 1.0	6.1 $\pm$ 0.3	9.6 $\pm$ 1.3	5.8 $\pm$ 1.4	5.1 $\pm$ 0.5
Mercury Oxidation at FGD Inlet, %	75 $\pm$ 1	-	80 $\pm$ 6	-	-
$\text{Hg}^{+2}$ Removal across Absorber, %	-	95% $\pm$ 2%	-	86% $\pm$ 18	94% $\pm$ 4
$\text{Hg}^0$ Re-emissions across Absorber, $\mu\text{g}/\text{Nm}^3$	-	3.4 $\pm$ 0.4	-	2.8 $\pm$ 0.5	2.6 $\pm$ 0.4
$\text{Hg}^0$ Re-emissions, % of FGD inlet $\text{Hg}^{+2}$	-	<b>49% <math>\pm</math> 6%</b>	-	<b>37% <math>\pm</math> 12%</b>	<b>35% <math>\pm</math> 5%</b>
Overall Hg Removal across Absorber, %	-	<b>34% <math>\pm</math> 5%</b>	-	<b>39% <math>\pm</math> 23%</b>	<b>47% <math>\pm</math> 1%</b>

\*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 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. This is a very relevant criterion for expressing mercury re-emission levels, since it is the FGD inlet oxidized mercury that gets absorbed and reduced by sulfite in the FGD liquor to produce re-emissions. At baseline, the re-emissions represented 49% of the FGD inlet oxidized mercury. With TMT addition, the re-emissions 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  $2.2 \mu\text{g}/\text{Nm}^3$ , whereas the other two runs (other five runs considering the baseline measurements a week earlier) measured  $0.6 \mu\text{g}/\text{Nm}^3$  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.<sup>4</sup> 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  $0.5 \mu\text{g}/\text{Nm}^3$  during the second Ontario Hydro run period on July 20, and nowhere near the indicated value of  $2.2 \mu\text{g}/\text{Nm}^3$  for that Ontario Hydro run.

Although the data are presented both ways in Table 4, 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 previously in pilot-scale TMT test results<sup>1</sup>, 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 5 summarizes the mercury concentration results.

**Table 5. 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 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.

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 6. Review Figure 1 for a better understanding of 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 6. Results of Liquor Mercury Concentrations in Unit 2 FGD Slurry Dewatering Train**

<b>Sample</b>	<b>7/12/2006 (Baseline), µg/L</b>	<b>7/20/2006 (after five days of TMT-15 Injection at 40 mL/ton), µg/L</b>
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 previously in pilot-scale TMT test results<sup>1</sup>, 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 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 for the daily absorber blow down and primary hydrocyclone overflow samples. Table 8 summarizes results for solids from throughout the Unit 2 byproduct dewatering system for the baseline and steady-state TMT addition Ontario Hydro test periods. Refer to Figure 1 for a review of these sample locations relative to the Unit 2 FGD dewatering scheme.

Comparing the data from July 12-13 with those for July 20, the results show 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 would suggest an overall lowering in the mercury mass removal rate by the FGD system compared to the SO<sub>2</sub> mass removal rate, rather than indicating the expected TMT effect.

**Table 7. 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, $\mu\text{g/g}$	Primary Hydrocyclone Overflow Solids Mercury Concentration, $\mu\text{g/g}$
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 8. Results of FGD System Solids Mercury Concentration Data for Baseline and Steady-state TMT Addition Ontario Hydro Test Periods**

Sample	7/12/2006 (Baseline), $\mu\text{g/g}$	7/20/2006 (after five days TMT-15 Injection at 40 mL/ton), $\mu\text{g/g}$
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

Coal sample analysis data from July 12 through July 20 are shown in Table 9 (coal moisture and mercury content only for July 13-19), and actually show a slightly higher rather than lower coal mercury concentration on the 20<sup>th</sup> compared to the 12<sup>th</sup>. 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 9. Unit 2 Coal Sample Data**

<b>Task Number, Power Plant</b>	<b>Heating Value (Btu/lb as received)</b>	<b>Total Moisture, wt %</b>	<b>Ash (Wt % as received)</b>	<b>Sulfur (Wt % as received)</b>	<b>Sulfur (lb SO<sub>2</sub>/MM Btu)</b>	<b>Hg (Dry ppm)</b>	<b>Chlorine (Dry ppm)</b>
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 7 show that the absorber blow down and primary hydrocyclone overflow solids mercury concentrations varied up and down over the test period, probably 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 – and that was 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 5 where the absorber liquor and primary hydrocyclone mercury concentrations were reduced on July 19. The stack mercury SCEM data plotted in Figure 3 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 10. 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.

**Table 10. Daily Absorber Blow Down Slurry Mercury Concentrations During Baseline and TMT Addition Periods**

Date	Time	TMT-15 Dosage	Absorber Liquor Mercury Concentration, $\mu\text{g/L}$	Absorber Solids Mercury Concentration, $\mu\text{g/g}$	Slurry wt% Solids	% of Mercury in Slurry 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 11.

**Table 11. Results of Particle Size Analyses on Byproduct Solid Samples**

Sample Location	D <sub>10</sub> , $\mu\text{m}^*$	D <sub>50</sub> , $\mu\text{m}^*$	D <sub>90</sub> , $\mu\text{m}^*$	Mean, $\mu\text{m}$
Baseline (no TMT injection) Samples, 7/12/2006:				
Absorber	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	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 observed. These data further support the observation that TMT addition did not have many 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 12. 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 13. 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.

### *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.<sup>5</sup> 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.

**Table 12. FGD Absorber Slurry Analysis Results**

Date	7/12/2006	7/13/2006	7/20/2006	7/20/2006
Time	13:15	8:56	8:03	1600
TMT-15 Injection Rate, mL/ton of coal	0 (Baseline)	0 (Baseline)	40	40
pH	6.41	6.15	6.01	5.93
Temperature, °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 <sub>3</sub> , mg/g	<0.8	<0.8	<0.8	<0.8
SO <sub>4</sub> , mg/g	511	531	525	524
CO <sub>3</sub> , 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 <sup>++</sup> , mg/L	1019	1133	1069	1034
Mg <sup>++</sup> , mg/L	1166	1322	1550	1429
Na <sup>+</sup> , mg/L	115	122	365	132
Cl <sup>-</sup> , mg/L	481	431	463	425
CO <sub>3</sub> <sup>-</sup> , mg/L	91	464	698	656
SO <sub>3</sub> <sup>-</sup> , mg/L	<10	<10	<8	<8
SO <sub>4</sub> <sup>-</sup> , mg/L	3773	3297	3921	2016

**Table 13. FGD System Solids Divalent Transition Metal Concentration Data for Baseline and Steady-state TMT Addition Ontario Hydro Test Periods**

	Baseline	With TMT @ 40 mL/ton coal	Observed % Reduction (% Increase)
Sample Date	7/12/2006	7/20/2006	-
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 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. 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, 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. 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, a 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 14.

**Table 14. Results of TMT Addition Beaker Tests at Petersburg Unit 2, January 2007**

<b>TMT-15 Dosage, mL/ton of coal</b>	<b>Absorber Liquor Mercury, µg/L</b>	<b>Hydrocyclone Overflow Slurry Mercury, µg/L</b>	<b>Hydrocyclone Overflow Liquor Mercury, µg/L</b>	<b>Hydrocyclone Overflow Liquor Mercury, µg/L (Nitric acid added to pH 2.89)</b>
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

One result was quite surprising, in 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 5). 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 7]). After considering the weight percent solids in the absorber slurry (15-16% in both cases), the January sample actually has more mercury in the slurry than the July sample, but almost all of the mercury is in the solids (>99%).

Looking at the TMT beaker test results, the baseline 0 mL/ton TMT-15 dosage value for the filtered hydrocyclone overflow liquor mercury for the middle data set appears to be biased low. Otherwise, the data for all three test conditions show that continued increases in TMT-15 dosage lowered the liquor mercury concentrations. However, again, these data are for a much lower initial mercury concentration than was encountered in July.

The biggest known difference between July 2006 and January 2007 is that the SCR was operating in July and not 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 is an SCR-related effect. It is clear that a return to Petersburg is warranted in May 2007, when the SCR goes back in service (ozone season), to conduct another set of beaker tests and to measure the baseline (no TMT) absorber mercury concentration.

## CONCLUSION

Testing of the Degussa TMT-15 additive for controlling mercury re-emissions has been completed at both planned pilot-scale wet FGD sites and one of two planned full-scale sites. 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. TMT-15 is believed to control re-emissions by precipitating mercury from the FGD liquor before it can undergo chemical reduction to produce re-emissions. The FGD liquor samples from the TMT test showed little or no reduction in mercury concentrations due to TMT addition.

It is speculated that a component in the FGD liquor is interfering with the effectiveness of TMT in precipitating mercury from this liquor. However, more work is needed to try to identify what this component might be and how to counteract it. This additional work cannot be conducted until the SCR on Unit 2 goes back into service at the beginning of the ozone season in May, so that FGD conditions will be similar to those during the TMT-15 test in July of 2006.

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 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 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 is not known whether it was the SCR operating status that so greatly impacted the liquid phase mercury concentrations. It is also not known whether or not there were any mercury re-emissions from the Unit 2 wet FGD system during the January 2007 operation when the liquor mercury concentrations were much lower.

## 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. 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.
3. 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.
4. 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.
5. Method 1312, Synthetic Precipitation Leaching Procedure, U.S. EPA, [www.epa.gov/sw-846/pdfs/1312.pdf](http://www.epa.gov/sw-846/pdfs/1312.pdf)