

**EVALUATION OF SCRUBBER ADDITIVES
AND CARBON INJECTION TO INCREASE
MERCURY CAPTURE**

August 17, 2012



Institute for Energy Studies / 243 Centennial Drive Stop 8153 / Grand Forks, ND 58202-8153

701-777-2533 / und.instituteforenergystudies@und.edu / engineering.und.edu/institute-for-energy-studies

UNIVERSITY OF NORTH DAKOTA

FINAL REPORT

Project 1

**EVALUATION OF SCRUBBER ADDITIVES AND CARBON INJECTION TO
INCREASE MERCURY CAPTURE**

**Steven A. Benson, Junior Nasah, Charles Thumbi, Shuchita Patwardhan, Lance
Yarbrough, Harry Feilen and Scott F. Korom**

**University of North Dakota
Institute for Energy Studies
Upson II Room 366
243 Centennial Drive, Stop 8153
Grand Forks, ND 58202-8153**

**Srivats Srinivasachar
Envergex, LLC**

August 17, 2012

Contents

SUMMARY	4
BACKGROUND	6
Problem Description	6
Approach.....	6
Screening Tests	7
Minntac Line 3	7
METHODS	9
Testing on Minntac Line 3	9
Stack Sampling	12
Green Ball Sampling.....	12
Scrubber Sampling.....	13
Multiclone Solids Sampling.....	13
Field Testing Matrix	14
RESULTS	17
Green Ball Sampling Data	17
Baseline Stack Measurements.....	18
ESORB-HG-11 Testing at Preheat Injection Location	29
Conclusion – ESORB-HG-11 Testing at Preheat Fan Inlet Location.....	42
ESORB-HG-11 Testing at Preheat Grate Injection Location	42
Conclusion – ESORB-HG-11 Testing at Preheat Zone Injection Location.....	47
PAC testing at Preheat Fan Inlet Location.....	47
Conclusion for PAC injection at preheat fan location	50
DEDTC addition to scrubber slurry	50
Conclusion on testing of DEDTC	53
Mercury Reductions with Average Baseline Mercury Emissions	53
CONCLUSION.....	55
REFERENCES	56
APPENDIX A: BENCH AND PILOT RESULTS	57
Bench Testing Summary.....	57
Pilot Testing Summary	58
APPENDIX B – ADDITIONAL FIELD DATA	64

SUMMARY

The results presented in this report are from Project 1 – “Evaluation of Scrubber Additives and Carbon Injection to Increase Mercury Capture.” This project was part of a larger effort coordinated by the Minnesota DNR to examine technologies that have the potential to achieve 75% reduction in mercury emissions from the taconite industry [Taconite Mercury QAPP, 2010]. Project 1 was being conducted by the University of North Dakota (UND) and Envergen LLC team with support from IAC International and Western Kentucky University. The goals of Project 1 include:

- Increasing the degree of oxidation of elemental mercury that is released during induration through the use of additives
- Maximizing the capture of mercury in the scrubber and preferentially sequestering to the solid non-magnetic portion of the scrubber slurry, providing possible options for further separating and discharging ‘mercury-rich’ non-magnetic solid fraction.

The scope of work involved bench, pilot and full scale testing to examine the efficiency of various additives to oxidize and sequester the mercury. The information included in this report is mainly from field tests performed on Minntac Line 3 with supporting data derived from bench and pilot scale testing.

To attain the first goal of oxidation and capture, the technology employed two additives: ESORB-HG-11, a proprietary brominated powdered activated carbon provided by Envergen LLC; and Powdered Activated Carbon (PAC). These additives have been tested and have proven to control mercury emissions in coal-fired power plants. Meanwhile for the second goal, the ability of ESORB-HG-11, PAC and a third additive- diethyl dithiocarbamate (DEDTC), to maximize the sequestration of dissolved mercury was investigated. Sequestering the mercury captured by the scrubber to the solid portion of the slurry and removal of the solids from the process loop would provide an ‘exit’ for the captured mercury. This can also prevent possible re-emission of the captured mercury in the scrubber.

Field tests of the technology were conducted at U.S. Steel Minntac’s Line 3 grate kiln. In the grate kiln, the green balls are sequentially dried in a drying zone (downdraft), then heated and oxidized (induration) in both a preheat and kiln zone, respectively. It is believed mercury release from the green balls begins in the preheat zone. Consequently, the mercury oxidation technology targeted flue gas exiting the preheat zone. The test was divided into four main areas: stack sampling to determine mercury concentration leaving the stack; sampling of green balls to determine mercury input; multiclone dust and scrubber slurry sampling; and injection of the powdered carbon (technology deployment) in the flue gas exiting the preheat zone.

Baseline total mercury stack emissions from Minntac Line 3 ranged from 3.5 to 8.2 $\mu\text{g}/\text{m}^3$; with most values between 4.0 and 6.2 $\mu\text{g}/\text{m}^3$. Particulate mercury emissions during baseline operation were minimal, with most values below 3% of the total mercury emitted. The

predominant form of mercury in the stack emissions was elemental; values ranged between 83 and 90%, with the exception of one measurement.

Of the additives tested, only ESORB-HG-11 showed the potential to attain the target reduction of 75% mercury emission reduction. Results from the field testing further indicated significant reductions in vapor phase stack Hg emissions from a baseline value of $5.1 \mu\text{g}/\text{m}^3$ to $0.83 \mu\text{g}/\text{m}^3$, an 84% reduction, with injection rates of ESORB-HG-11 of 0.5 pound per long ton (150 lb/h of sorbent) of taconite processed. However, reductions in vapor phase mercury during ESORB-HG-11 injection were coupled with an increase in the particulate mercury emissions. Including the particulate mercury emission increased the emission value to $1.5 \mu\text{g}/\text{m}^3$, still a 71% reduction from the baseline values. While the particulate scrubber is effective for capturing the taconite dust entrained in the flue gas, it is less effective in capturing the powdered carbon additive. Increases in particulate mercury emissions suggest that the tested technology requires higher particulate capture efficiencies, which may be achieved by improved operation of the scrubber. Another key result from the testing indicated a dramatic decrease in dissolved mercury in the scrubber liquid, (from 3000-5000 ng/L to 20 ng/L) during ESORB-HG-11 injection. This suggests that the dissolved mercury in the scrubber slurry preferentially adsorbed to ESORB-HG-11, a non-magnetic phase, establishing the sequestering capabilities of the additive.

The fate of sequestered mercury associated with ESORB-HG-11 and the scrubber solids depends on the process configuration. In Minntac Line 3, the scrubber slurry is transported to a thickener and the solids are subsequently discharged. This provides an exit for all mercury captured by the system. However, not all taconite plants discharge their solids; instead they are recycled to the front end of the process. This creates a recycle loop for the mercury in the entire process that would lead to increases in the green ball mercury concentrations and a subsequent increase in the stack mercury concentrations. Therefore, for this sorbent injection technology to be effective at mercury oxidation and mercury capture at other facilities, a fraction of their solids from the scrubber would have to be discharged to prevent building up of the concentration of mercury in the system.

BACKGROUND

Problem Description

The Lake Superior Lakewide Management Plan (LAMP) identified the taconite industry as a major contributor of atmospheric mercury in the Lake Superior basin [Taconite Mercury QAPP]. Mercury is a leading concern among the air toxic metals addressed in the 1990 Clean Air Act Amendments because of its volatility, persistence and bioaccumulation as methylmercury in the environment, and its neurological health impacts.

Current industry wide mercury emissions are estimated at 440-880 lb/yr [Berndt 2003]. In addressing this issue, the Minnesota taconite industry set a goal of achieving a 75% reduction in its mercury emissions by 2025. Several projects were selected by the Minnesota Taconite Mercury Control Advisory Committee (MTMCAC) to identify different mercury-control technologies that have the potential to help the industry achieve this goal.

Previous research work done at taconite processing plants by the Minnesota Department of Natural Resources (MN DNR) suggested that the main source of mercury during taconite processing originates from induration of the ore (heating, oxidizing and sintering), or during the heating of “green balls” to form hardened taconite pellets [Berndt 2003]. Green balls are rolled from a mixture of moist taconite concentrate and a clay binder. Further research suggested that mercury release from the green balls starts at temperatures of approximately 200°C up to 600°C [Galbreath et al 2005], which corresponds to temperatures seen in the preheat zone of the induration furnaces.

Some of the released mercury is captured by a particulate scrubber system; this scrubber is the predominant pollution control device in taconite plants [Berndt et al 2005]. Analysis of scrubber slurry indicated significant mercury concentrations [Berndt et al, 2003], suggesting that some of the mercury released during induration may be oxidized through a variety of oxidation pathways. Oxidized mercury can be captured in a wet particulate scrubber because it is water-soluble; however, elemental mercury cannot. Additional studies also suggest that the mercury captured by the scrubbers in some of the plants adsorbs preferentially to the non-magnetic portion of the scrubber solids [Berndt and Engesser, 2005b].

The University of North (UND) proposed an innovative way of reducing mercury emissions from taconite plants in response to a Request for Proposals (RFP) issued by the MN DNR. This report discusses results of the technological approach taken by UND.

Approach

The approach taken by the UND team comprised the following objectives:

- Use proven mercury control technologies to increase oxidation of mercury in the flue gas upstream of the scrubber. These technologies consisted of injecting plain

Powdered Activated Carbons (PAC) or a proprietary bromated PAC referred to as ESORB-HG-11 in the flue gas and dosing the scrubber recirculation tank with DEDTC.

- Increase the capture of the oxidized mercury by the scrubber through addition of mercury complexing and/or sequestering agents to the scrubber waters; thus reducing the dissolved mercury scrubber concentration, and increasing the driving force for fresh oxidized mercury capture.
- Promote the tendency of the mercury to associate with the non-magnetic portion of the scrubber slurry (complexing/sequestering additives are non-magnetic) while allowing for separation and rejection of the non-magnetic phase as a possible route to sequestering captured mercury and to promote further reduction of recycled mercury by directing it back to the front end of the processing loop.

The information included in this report is mainly from field tests performed on Minntac Line 3 with supporting data provided by screening tests done using bench and pilot-scale equipment at UND.

Screening Tests

Screening tests were performed using bench and pilot-scale equipment to determine the best complexing agents compatible with scrubber slurry chemistry. Initially a series of five different scrubber additives for oxidized mercury capture and sequestration was proposed. They were PAC and ESORB-HG-11 for sequestration, TMT 15, Ca-EDTA (ethylene diamine tetraacetate), and DEDTC (diethyl dithiocarbamate) for complexing. Based on further research covering taconite scrubber chemistry as well as additive efficacy, the additive Ca-EDTA was eliminated. The additives selected from the bench/pilot tests for field testing were ESORB-HG-11, PAC, and DEDTC. The results used to justify their selection are discussed in Appendix A.

Minntac Line 3

Field testing of the technological approach was performed at Line 3 of the Minntac plant located in Virginia, Minnesota. Line 3 is Minntac's smallest line, and operates a grate-kiln furnace with a downdraft drying zone (DD1), followed by a preheat zone, the kiln, and finally the cooler. Mercury release from the green balls is believed to occur in the preheat zone and further down in the kiln. A clear understanding of the flue gas flow is important as it details the flow of the mercury after release.

Flue gas/air flow through the grate-kiln system is moved using a series of interconnected fans. Fired pellets are cooled using ambient air, drawn in by cooling fans, and a portion of this stream is used to pre-heat combustion air in the kiln, while the rest is exhausted to the atmosphere via a cooling vent stack. In the kiln, fuel (natural gas and biomass) is added to the heated air to initiate combustion and heat the taconite pellets.

Flue gas, resulting from the combustion of the fuel, flows through the kiln in the opposite direction as the flow of the pellets and through the pellet bed in the grate kiln. Gases from the pellet bed (within the preheat grates) are then routed to the front of the furnace section, transported through a series of multiclones, directed through a wet particulate scrubber, and sent to the stack.

As flue gas is transported through the system it entrains some taconite dust; some of which is removed in the multiclones. However a majority of the particulates are removed by the wet particulate scrubbers. The captured solids are then transported to a thickener. Oxidized mercury (Hg^{2+}) and particulate mercury (Hg^{p}) in the flue gas stream is believed to be captured mainly in the scrubber, while elemental mercury (Hg^0) is emitted through the stack. Line 3 uses a recirculating scrubber equipped with a recirculation tank. Fresh water is provided to the scrubber while the recirculation tank blowdown pumps prevent slurry build up. The pH of the scrubber slurry is amended with lime to neutralize acidity and to promote gypsum precipitation.

METHODS

The testing on Minntac Line 3 and sampling methods for the stack flue gas, scrubber slurry, green balls, and multiclone solid discharge are discussed below.

Testing on Minntac Line 3

Testing on Minntac Line 3 was performed over a period of three weeks from October 10, 2011 to October 28, 2011. Monitoring equipment was installed on October 11 and 12 and removed on October 27 and 28. The first stage of testing established pre-test baseline emissions; this took four days. Testing consisted of injecting brominated activated carbon (ESORB-HG-11) and PAC sorbents into the process flue gas using injection equipment supplied by a UND subcontractor (IAC International) and dosing the recirculation tank with the complexing/sequestering agents. Sorbents were supplied by Envergen LLC in 1000-lb bulk bags.

The sorbent injection equipment (Figures 1 and 2) consisted of a bulk bag handling system, a feeder to meter sorbent, a blower and a compressor to supply the conveying air, an eductor to pick up the sorbent discharged from the feeder, hoses to convey the sorbent, and distributors and injection lances to disperse the sorbent into the flue gas duct. The injection test agents, PAC and ESORB-HG-11, were transported through the hoses and distributors to the injection lances and into the flue gas using compressed air. The sorbent feed hopper was placed on a mass scale to determine additive injection rate. All the injection equipment was installed on a trailer; positioning the trailer was a challenge because of space constraints and uneven flooring; the final trailer location was several hundred feet from the target injection location, which was the preheat fans.

The first injection test ports were about 30 feet upstream of the preheat fan inlet. Injection of the sorbents upstream of the fans allowed for improved mixing and distribution of sorbent particles in the flue gas. Four ports were installed by Minntac personnel on each of the two ducts leading to the fans.

Initially, it was planned to inject upstream of the waste gas fan; however, due to the short residence time that would be available for mercury oxidation and capture, coupled with the low flue gas temperatures, it was anticipated that the mercury capture efficiencies would be low. Therefore, changing the injection location to the preheat zone wall was considered because this would provide a higher temperature. However, injection at this location would require redesigned injection lances that had cooling jackets, which could not be procured within the project schedule. Hence, as a compromise, a request was made to the MN DNR that the lances be placed on the edges of the preheat zone wall; the request was approved.



Figure 1. A close-up photo of the sorbent bulk-bag handling system. The bulk bag is placed on the top (upper arrow). The discharge pipe below (lower arrow) comes from the educator and is attached to a hose that connects to the distributors and injection lances.



Figure 2. Sorbent injection trailer with the bulk bag lifter assembled and the bulk bag in place. The IAC box in the foreground houses the blower and compressor that provide the pressurized air to conveying the sorbent into the flue gas duct.

To improve the removal of mercury in the scrubber liquids using DEDTC as a complexing agent during field testing, PAC and ESROB-11-HG were separately injected into the flue gas stream to increase the degree of oxidation of elemental mercury. It was deduced that a higher concentration of oxidized mercury present in the scrubber liquid would increase the effectiveness of DEDTC. Therefore, DEDTC was added to the scrubber by dosing the scrubber recirculation tank to a concentration of 7 mg/L. It was also noted that PAC and ESORB-HG-11 injected into the flue gas ended up in the recirculation tank, so no direct addition into the scrubber was needed. However, this subsequently slowed a return to baseline conditions because, being a recirculating scrubber, it would take almost 4 hours to replace one tank volume or more than 12 hours for the injected ESORB-HG-11/PAC to reduce to insignificant levels in the scrubber tank. Consequently, the sequestering properties of these additives kept the dissolved mercury concentrations lower than normal for most of the test period, except on Mondays (10/10/12, 10/17/12, and 10/24/12) as no injection was performed on weekends.

Stack Sampling

Stack measurements were performed by UND's sub-contractor, Western Kentucky University's (WKU) Institute for Combustion Science and Environmental Technology (ICSET). WKU used a PS Analytical (PSA) continuous mercury monitor (CMM) with a wet conversion system to obtain semi-continuous mercury concentrations in the flue gas and an extractive sampling method - ASTM D 6784 (commonly known as Ontario Hydro Method or OHM) to measure total and speciated mercury concentrations in the stack gases. Measurements were performed on the roof of the facility housing the stack. Several ports are located at the stack and two of these ports were used to set up the probes for the OHM and CMM. The OHM was the preferred measurement technique for evaluating performance of the additive, while the CMM was used to track trends during testing. The OHM method provides an average of all components of the mercury emission over the sampling period: Hg^0 , Hg^{2+} , and Hg^{P} . The sum of these components provides the total mercury concentration (Hg^{T}) in the stack gas. The OHM test was operated for approximately 1-2 hour periods during each run, with a sampled flue gas volume in the range of 0.70 to 0.90 m^3 . During a typical test day, one OHM sample was collected before (baseline) sorbent injection and at least one sample during the sorbent injection phase. This made it possible to obtain a baseline value and average mercury reductions for each test day. The CMM was operated continuously during each testing day; however it was taken offline at the end of the test day. Due to the long duration of each test, coupled with the fact that the CMM was not operated overnight, the stack mercury behavior at the end of each test day was not fully investigated; on some testing days the monitoring equipment was not always deployed immediately after performing the baseline OHM. As a result, the OHM baseline for these days might require a correction based on the CMM baseline just before monitoring began.

Impinger solutions obtained in the OHM test were immediately analyzed at the end of each test by ICSET's mobile laboratory. The quality of OHM data was ensured by using standard quality control procedures for laboratory and field analyses. Leak checks were performed during all runs and duplicate (and sometimes triplicate) samples were analyzed by ICSET mobile laboratory, along with sample spikes, standard samples, and sample blanks, to insure analytical precision and accuracy. The PSA monitor for semi-continuous mercury concentration measurement was calibrated at the beginning of each day and re-calibrated after any troubleshooting during sampling. Measurement accuracy was further checked by comparing OHM and CMM results at local O_2 concentrations (approximately 18%) and on a dry basis; they showed good agreement. Relative differences between OHM and CMM were less than 12%, except for one measurement (24%), which is considered good agreement when compared to data from similar mercury testing using OHM and CMM [Benson 2007].

Green Ball Sampling

Green balls were sampled to determine the daily average mercury concentration in the feed to the taconite furnace. Due to variability observed in green ball mercury concentrations

during previous research [Berndt, 2008], it was decided that the daily average mercury concentration of the green balls would be used for all mass balance calculations of that test day.

Green ball samples were collected by Minntac laboratory personnel and consisted of collecting a 5 minute composite sample in buckets from the roll feeders upstream of the grate. After collection the samples were delivered to the UND sampling team and the samples were transferred into clean plastic bags, labeled, and then stored until they were given to ICSET for mercury analysis. Samples were collected at three different time intervals each day. Composite green ball samples were analyzed using EPA Method D6722.

Scrubber Sampling

Scrubber samples were collected by the UND testing team from the scrubber recirculation tank from a valve located upstream of the scrubber blowdown pump. The slurry in the tank was agitated continuously, thus providing a well-mixed sample from the blowdown pump. For sample collection, the valve was first purged for at least 10 seconds before a sample was collected in a large bucket. The bucket was then transported to the filtration area. Here, the bucket was further agitated and a 500 mL sample was collected and filtered. The filtrate was then transferred into pre-washed containers containing nitric acid to maintain the $\text{pH} < 2$ and stored on ice. Another 500 mL sample was collected and filtered to determine total suspended solids (TSS). Initially, the filtrate samples were sent to ICSET for mercury analysis using EPA Method 7470. However, it was observed that most filtrate samples obtained during carbon injection testing had mercury concentration values below the detection limit for this method. Samples were then sent to Pace Analytical, which used a more sensitive method (EPA Method 1631) for obtaining mercury concentration in the filtrate obtained from the scrubber slurry. For filtrate samples analyzed by ICSET that were below the detection limit of $0.2 \mu\text{g/L}$, a default value of $0.2 \mu\text{g/L}$ was assumed during data analysis.

For quality control, duplicate samples and field blanks were taken. Field blanks were performed by transporting bottles of deionized water to the field site, transferring them into pre-cleaned sample bottles when other scrubber samples were processed, and analyzing them with the other scrubber samples. The analytical results for the field blanks were below the detection limits for both methods used (EPA Method 1631-low mercury analysis, and EPA Method 7470). Duplicate samples also showed good agreement.

Multiclone Solids Sampling

Multiclone solids were collected by the UND testing team from the multiclone blowdown system. Minntac Line 3 is equipped with 8 cyclones, each having its own blowdown port. Sampling from all ports required collecting a composite from each blowdown port consecutively. Multiclone dust samples were taken to provide an estimate of the mercury leaving the system through the multiclones. The blowdown rate (mass loading) was not able to be measured precisely and varied significantly during different sampling periods, with no substantial sample

amounts being collected during certain sampling periods. Additionally, analysis of multiclone dust samples showed large variability in mercury concentrations. An estimate of the blowdown rate was reached using the scrubber TSS and an assumed cyclone efficiency of 90%. The estimated value was calculated to be 390 lb/hr of solids and was combined with the highest multiclone mercury measurement of 450 ng/g to give a maximum possible mercury flux of 0.08 grams/hr through the blowdown, which is less than 3% of the average mercury (3.0 grams/hr) entering the system. This is consistent with measurements done by Berndt (Berndt 2003) that showed very low mercury content in multiclone blowdown.

The multiclones solids sampling technique involved collecting blowdown dust into a clean plastic bag and then transferring into a second plastic bag for storage. The location of the blowdown port required care during sampling to avoid the risk of contamination of collected samples by the water used to wash and transport the blowdown dust to a thickener located downstream of the multiclones. Collected samples were stored on ice for particulate bound mercury conducted by ICSET.

Field Testing Matrix

Table 1 summarizes the testing done at Minntac Line 3 and includes dates, times, test conditions, sorbent types, injection rates, injection locations, sampling locations, sampling types, and samples collected.

Table 1. Field Test Matrix

Date	Time	Test Condition	Sorbent Type	Injection Rate	Injection Location	Sampling Location	Sampling Type	Samples Collected
10/10/2011	7am -7 pm	Orientation by Minntac						
10/11/2011	7am -7 pm	Equipment Setup				Scrubber Stack		
	7am -7pm	Equipment Setup				Scrubber Stack		
10/12/2011	7am-7pm	Pre-Test				Scrubber Stack		
10/13/2011	7am -10am	Baseline				Scrubber Stack	CMM & OHM	Green Pellets, Scrubber Slurry
	10am - 1pm	Baseline				Scrubber Stack	CMM & OHM	
	1pm - 4pm	Baseline				Scrubber Stack		
	4pm - 7pm	Baseline				Scrubber Stack		
10/14/2011	7am – 4pm	Baseline				Scrubber Stack	CMM & OHM	Green Pellets, Scrubber Slurry, Multiclone solids
	4 pm - 5 pm	Condition 1	ESORB-HG-11	25 lb/hr	Preheat Fans	Scrubber Stack	CMM	
	5pm - 7pm	Condition 2		50 lb/hr		Scrubber Stack	CMM	
	7pm - 9pm	Condition 3		100 lb/hr		Scrubber Stack	CMM & OHM	
10/17/2011	7am - 10am	Baseline			Preheat Fans	Scrubber Stack	CMM & OHM	Green Pellets, Multiclone Solids, Scrubber Slurry
	10am - 2pm	Condition 2	ESORB-HG-11	50 lb/hr		Scrubber Stack		
	2pm - 4pm	Condition 3	ESORB-HG-11	100 lb/hr		Scrubber Stack	CMM	
	4pm - 7pm	Condition 4	ESORB-HG-11	150 lb/hr		Scrubber Stack	CMM & OHM	
10/18/2011	7am - 10am	Baseline	ESORB-HG-11		Preheat Fans	Scrubber Stack	CMM & OHM	Green Pellets, Multiclone Solids, Scrubber Slurry
	10am - 7pm	Condition 3	ESORB-HG-11	100 lb/hr		Scrubber Stack	CMM & OHM	
10/19/2011	7am -11am	Baseline			Preheat Fans	Scrubber Stack	CMM & OHM	Multiclone Solids, Scrubber Slurry
	11am - 2pm	Condition 1	DEDTC	0.7 mg/L		Scrubber Stack	CMM	
	2pm - 3pm	Condition 2	DEDTC	1.4 mg/L		Scrubber Stack	CMM	
	3pm -5pm	Condition 3	DEDTC	7.0 mg/L		Scrubber Stack	CMM	
	5pm – 9pm	Condition 4	DEDTC and ESORB-HG-11	BC = 50 lb/hr DEDTC = 7.0 mg/L		Preheat Fans	Scrubber Stack	CMM & OHM

Table 1. (Continued)

Date	Time	Test Condition	Sorbent Type	Injection Rate	Injection Location	Sampling Location	Sampling Type	Samples Collected
10/20/2011	7am - 11am	Baseline				Scrubber Stack	CMM & OHM	Multiclone Solids, Scrubber Slurry, Green Pellets
	11am - 12pm	Condition 1	PAC	50 lb/hr	Preheat Fans	Scrubber Stack	CMM	
	12pm - 3pm	Condition 2	PAC	100 lb/hr		Scrubber Stack	CMM & OHM	
	3pm -5pm	Condition 3	PAC	150 lb/hr		Scrubber Stack	CMM & OHM	
10/21/2011	7am -12pm	Baseline				Scrubber Stack	CMM & OHM	Green Pellets, Multiclone Solids, Scrubber Slurry
	12am - 5pm	Condition 4	ESORB-HG-11	150 lb/hr	Preheat Fans	Scrubber Stack		
10/24/2011	7am - 10am	Baseline				Scrubber Stack	CMM & OHM	Green Pellets, Multiclone Solids, Scrubber Slurry
	10am - 1 pm	Condition 5	ESORB-HG-11	75 lb/hr	Preheat Fans	Scrubber Stack	CMM & OHM	
10/25/2011	7pm – 10am	Baseline				Scrubber Stack	CMM & OHM	Green Pellets, Multiclone Solids, Scrubber Slurry
	10am - 12pm	Condition 1	ESORB-HG-11	50 lb/hr	preheat fans (4 inj. Lances) + Preheat zone (8 inj. Lances)	Scrubber Stack	CMM	
	12pm - 4pm	Condition 2	ESORB-HG-11	75 lb/hr		Scrubber Stack	CMM & OHM	
	4pm - 5pm	Condition 3	ESORB-HG-11	75 lb/hr	preheat fans (4 inj. Lances) + Preheat zone (4 inj. Lances)	Scrubber Stack	CMM	
10/26/2011	7pm – 10am	Baseline				Scrubber Stack	CMM & OHM	Green Pellets, Multiclone Solids, Scrubber Slurry
	10am -12pm	Condition 4	ESORB-HG-11	100 lb/hr	preheat fans (4 inj. Lances) + Preheat zone (4 inj. Lances)	Scrubber Stack	CMM	
	2pm -6pm	Condition 5	ESORB-HG-11	100 lb/hr	preheat fans (4 inj. Lances) + Preheat zone (4 inj. Lances)	Scrubber Stack	CMM & OHM	
10/27/2011	7am -7pm	Equipment Tear-Down				Scrubber Stack		
10/28/2011	7am -7 pm	Equipment Tear-Down				Scrubber Stack		

RESULTS

Results from the UND research team follow and include data and discussion pertaining to the sampling of green balls and baseline stack measurements, as well how the addition of ESORB-HG-11, PAC, and DEDTC reduced mercury emissions during taconite production.

Green Ball Sampling Data

Table 2 lists the green-ball mercury concentrations during the testing. Composite green-ball samples had mercury levels varying from 4 ng/g to 18 ng/g. The results for October 13 and 21 appear to be anomalously low. The analytical results on Table 2 were done at two separate times and there was variation in the results between the two testing periods. The low values obtained for samples collected on October 13th and 21st have been flagged on Table 2 as being outside the acceptable range of values and were not considered further.

The average mercury concentration in the green balls for the entire test period was 12.4 (± 2.9) ng/g (± 1 standard deviation). The average value showed good agreement with previous work conducted on Minntac Line 3 [Berndt 2008]. Additionally, it has also been reported that there could be a large daily variability in the green-ball mercury concentrations [Berndt 2003, 2005a &b, 2008]. The daily average green-ball concentrations were assumed to provide a sufficiently reliable estimate of the mercury entering the system; as such, they were used by the UND research team to calculate mercury reductions in the taconite production system by the addition of mercury-sorbing agents.

Table 2. Total Hg in green ball feed during testing period. Note: Only samples collected on days where additive testing showed promising results per the OHM were submitted for mercury analysis.

Date	Sample ID	Collection time	Mercury concentration ng/g	Daily Average, ng/g (Std Dev)
10/13/2011*	GB1	7:20 AM	6	
	GB2	10:50 AM	7	6.3
	GB3	2:55 PM	6	(0.6)
10/14/2011	GB4	7:10 AM	15	
	GB5	11:00 AM	13	14.3
	GB6	2:00 PM	15	(1.2)
10/17/2011	GB10	7:15 AM	12	
	GB11	10:45 AM	12	10.7
	GB12	1:40 PM	8	(2.3)
10/18/2011	GB13	7:15 AM	18	
	GB14	10:45 AM	15	16.3
	GB15	1:55 PM	16	(1.5)
10/19/2011	GB16	7:10 AM	12	
	GB17	10:50 AM	13	12.0
	GB18	1:25 PM	11	(1.0)
10/20/2011	GB19	7:15 AM	11	
	GB20	10:45 AM	15	11.0
	GB21	1:40 PM	7	(4.0)
10/21/2011*	GB22	7:23 AM	5	
	GB23	11:06 AM	5	4.7
	GB24	1:55 PM	4	(0.6)
10/24/2011	GB25	7:00 AM	11	
	GB26	11:00 AM	11	10.3
	GB27	2:00 PM	9	(1.2)

* Values flagged as out of range.

Baseline Stack Measurements

As a result of the fluctuations in mercury concentrations in the green ball metered to the grate kiln inlet, baseline emissions were considered crucial for the success of the project. Further, following recommendations and directions stipulated by the *Data Quality Assessment Worksheet* [Taconite Mercury QAPP, 2010], estimates of the annual mercury emissions with and without the sorption agents tested were required. Consequently, an entire day, October 13, was used to calculate baseline mercury emissions. These measurements were coupled with a baseline measurement performed every day before sorbent injection, to estimate the average plant baseline emission. The main technique used for measuring mercury concentrations was the Ontario Hydro Method (OHM), with the PS Analytical semi-continuous mercury monitor (CMM); both were used to track mercury trends during the test day so the effects of sorbent injection could be monitored.

The baseline emission data for the stack gases from the three-week testing period is summarized in Table 3. OHM provides information on mercury speciation, which is inclusive of particulate-bound mercury (Hg^P), and vapor phase mercury measured as the oxidized species (Hg^{2+}) and as elemental mercury (Hg^0). In this work, the sum of the oxidized and elemental

vapor mercury components is represented as total vapor mercury (Hg^{VT}). The sum of all the mercury components, including the particulate bound mercury, is the total mercury (Hg^{T}). Table 3 also lists the vapor phase mercury species concentrations, as measured using CMM. Hg^0 , Hg^{2+} and their sum Hg^{VT} , are calculated as an average of the CMM data during the period the OHM sampling was performed. The standard deviations of the CMM data are also calculated and presented.

Several observations can be made from the data shown in Table 3. Baseline Hg^{T} from the OHM data for stack emissions at Minntac Line 3 ranged from 3.5 to 8.2 $\mu\text{g}/\text{m}^3$, with most values between 4.0 and 6.2 $\mu\text{g}/\text{m}^3$ (dry basis). Hg^{P} emissions during baseline operation were minimal, with most values below 3% of the total mercury emitted. This indicates that the taconite dust has a low propensity to adsorb mercury during the time it is in contact with the flue gas in the ductwork leading to the scrubber and the stack. The predominant form of mercury in the stack emissions was Hg^0 with values ranging between 83 and 90 % of Hg^{T} , with the exception of one measurement. The high fraction of elemental mercury species in the stack gases validates the strategy taken in this study to oxidize the mercury for capture in the scrubber.

The CMM data only provides the vapor phase mercury concentrations. There was a reasonable correspondence between the CMM and the OHM measurements for the vapor phase mercury components. A specific example of the comparison between OHM and CMM data is for October 13, the full day of baseline measurements. During this test period, the three OHM measurements showed consecutive values of 4.45, 4.93 and 5.19 $\mu\text{g}/\text{m}^3$ for Hg^{VT} . For comparison, average CMM measurements during the same test periods were 4.24 (± 0.41), 3.88 (± 0.30) and 4.10 (± 0.32) $\mu\text{g}/\text{m}^3$, respectively. The average relative difference (Equation 1) between the OHM and CMM values was 8.7%. This trend was also seen during other test days.

$$\text{Average Relative Difference} = \frac{[\text{OHM} - \text{CMM}]}{[\text{OHM} + \text{CMM}]} * 100 \quad \dots (1)$$

On October 18 the CMM was undergoing troubleshooting during OHM baseline measurements. Troubleshooting also occurred on October 14 and 18, where the injection of ESORB-HG-11 did not begin immediately after baseline measurement.

Table 3. Baseline mercury concentrations in the stack gas (OHM and CMM averages) over the time OHM measurements were performed.

Date	OHM				CMM			
	Hg ⁰ µg/m ³	Hg ^{VT} µg/m ³	Hg ^P µg/m ³	Hg ^T µg/m ³	Hg ⁰ µg/m ³	Std Dev	Hg ^{VT} µg/m ³	Std Dev
13th	3.70	4.45	-	-	2.32	0.26	4.24	0.41
	3.98	4.93	-	-	2.58	0.13	3.88	0.30
	4.64	5.19	-	-	2.78	0.08	4.1	0.32
14th	5.86	6.69	-	-	4.20	0.19	5.51	0.27
17th	5.82	8.22	0.02	8.24	5.12	0.30	7.08	0.88
*18th	5.35	6.17	0.03	6.20	n/a	n/a	n/a	n/a
19th	4.63	4.86	0.07	4.93	4.08	0.13	5.19	0.15
20th	3.14	3.44	0.03	3.47	1.56	0.14	2.11	0.17
21st	4.50	5.04	0.02	5.06	3.12	0.50	3.96	0.13
24th	4.38	4.98	0.08	5.06	3.56	0.16	5.11	0.41
25th	3.35	3.81	0.20	4.01	3.11	0.29	4.39	0.39
26th	3.84	4.09	0.10	4.19	4.03	0.37	4.55	0.30

*CMM not running during OHM due to troubleshooting.

The baseline values as measured by the CMM showed larger-than-normal variations with standard deviations of around 10% of the mean value. These baseline results were taken on October 13 (Figure 3) and on October 17, 24, and 25 (Figure 4). The average Hg^{VT} during baseline test periods for the latter were 7.08 (± 0.88), 5.11 (± 0.41), and 4.39 (± 0.39) $\mu\text{g}/\text{m}^3$ respectively. These days had the highest standard deviations during the testing campaign.

More detailed, time-resolved CMM data are presented in Figures 5 through 8. The CMM baseline data for the period covering OHM baseline testing is represented by the vertical lines in each figure. Baseline CMM data for Oct 19 and 21 (Figure 5) indicated low and high mercury concentrations, respectively, at the start of the measurement period, while data for Oct 14, 20, and 26 (Figure 6) showed steady Hg concentrations.

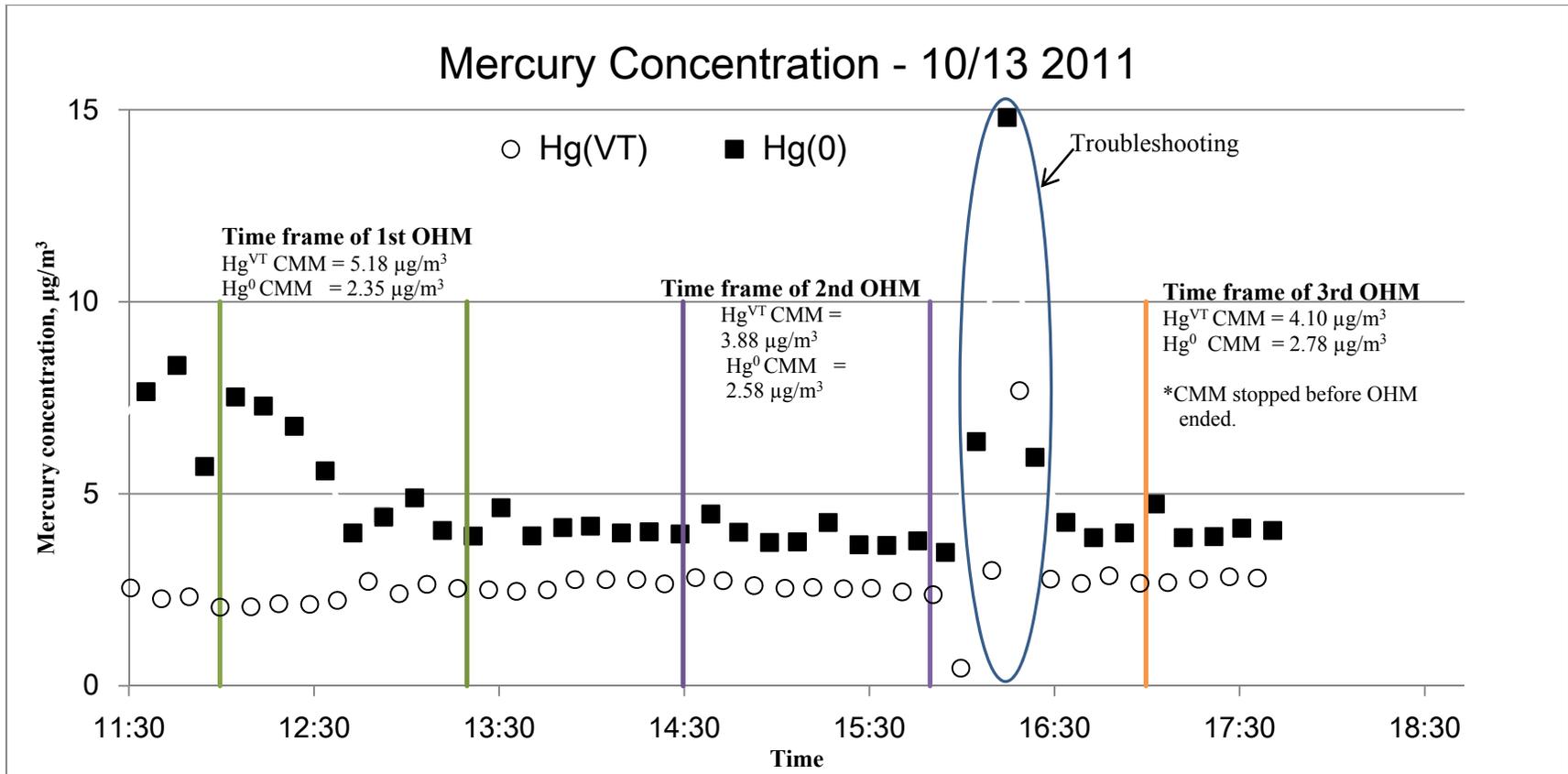


Figure 3. Average CMM measurements to determine baseline concentrations the day before testing.

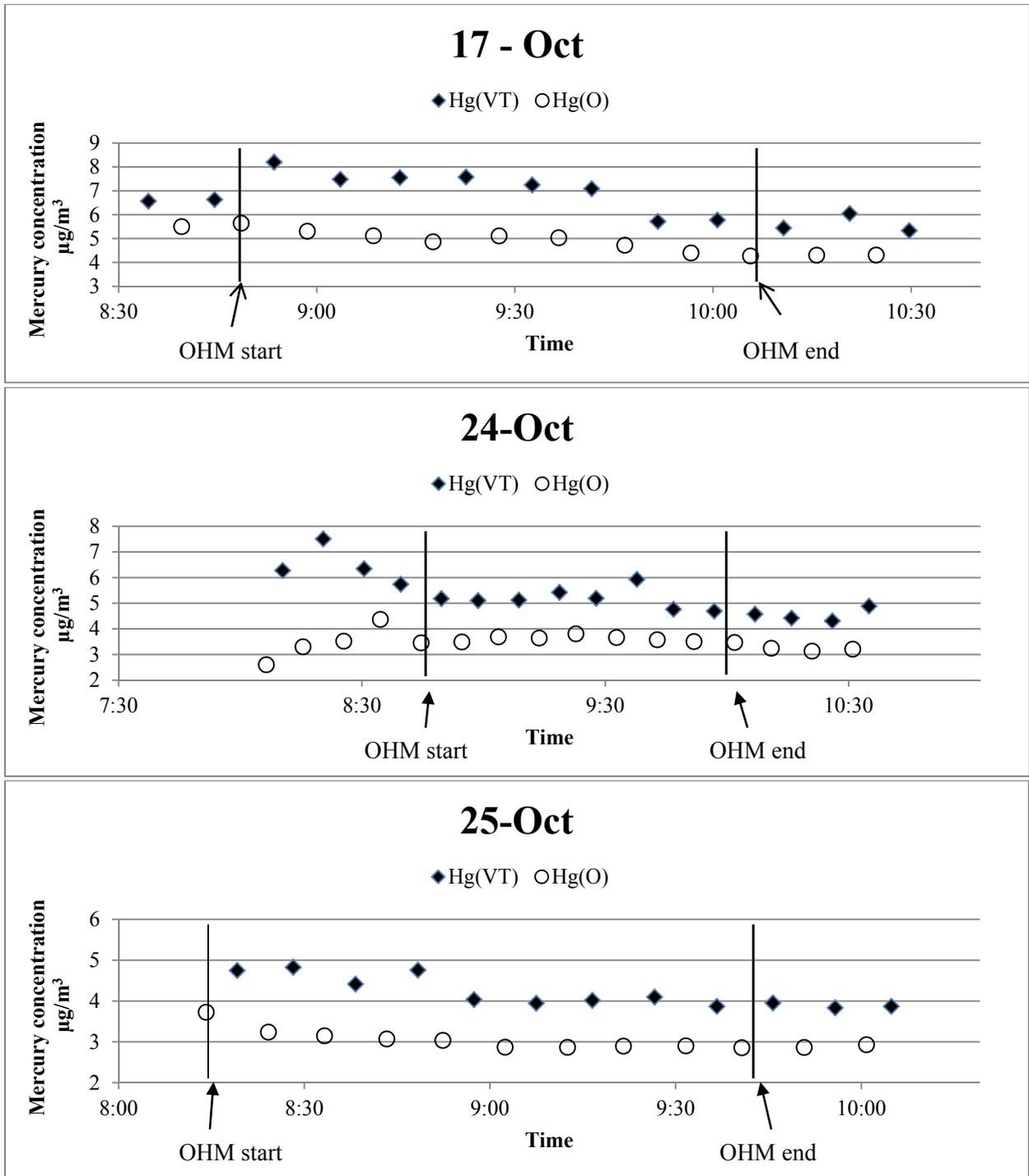


Figure 4. CMM baseline for Oct 17, 24, and 25. As can be observed the mercury concentrations was not steady especially for Oct 17 were the oxidized mercury (difference between Hg^{VT} and Hg^0) can be seen to increase. For Oct 24, the baseline shows a spike followed by a slight decrease slightly accounts for the high standard deviation of $0.41 \mu\text{g}/\text{m}^3$.

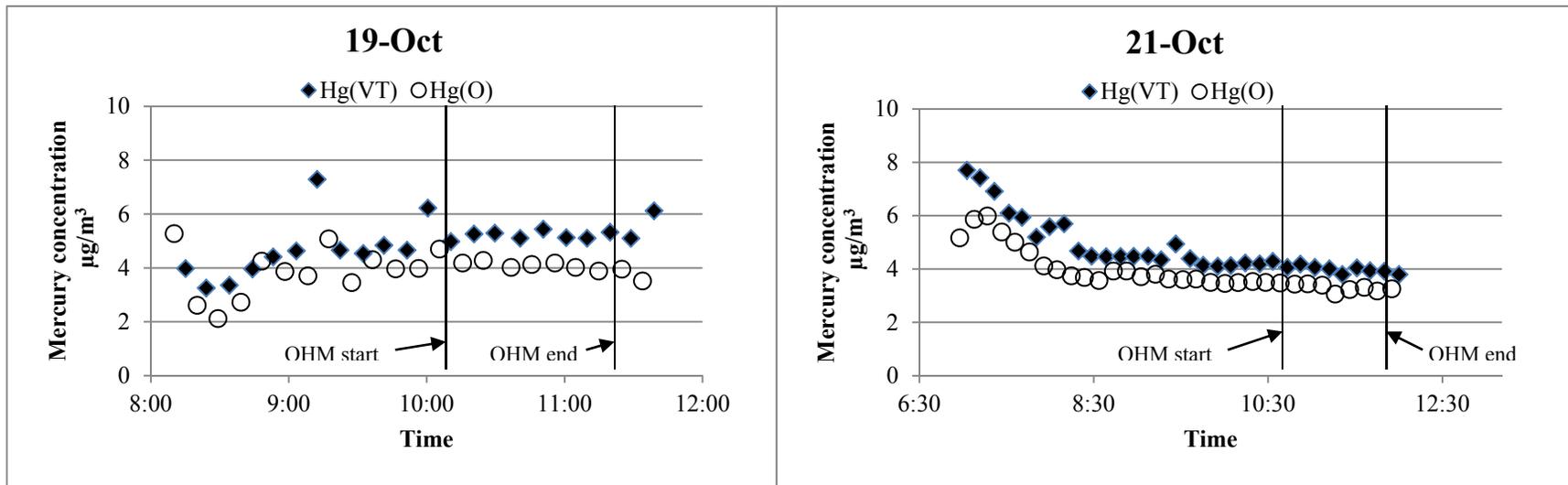


Figure 5. CMM baseline Hg concentrations for Oct 19 and 21, with low and high mercury concentrations at the start of measurements, respectively. In general, the baseline OHM mercury concentrations are steady for both days.

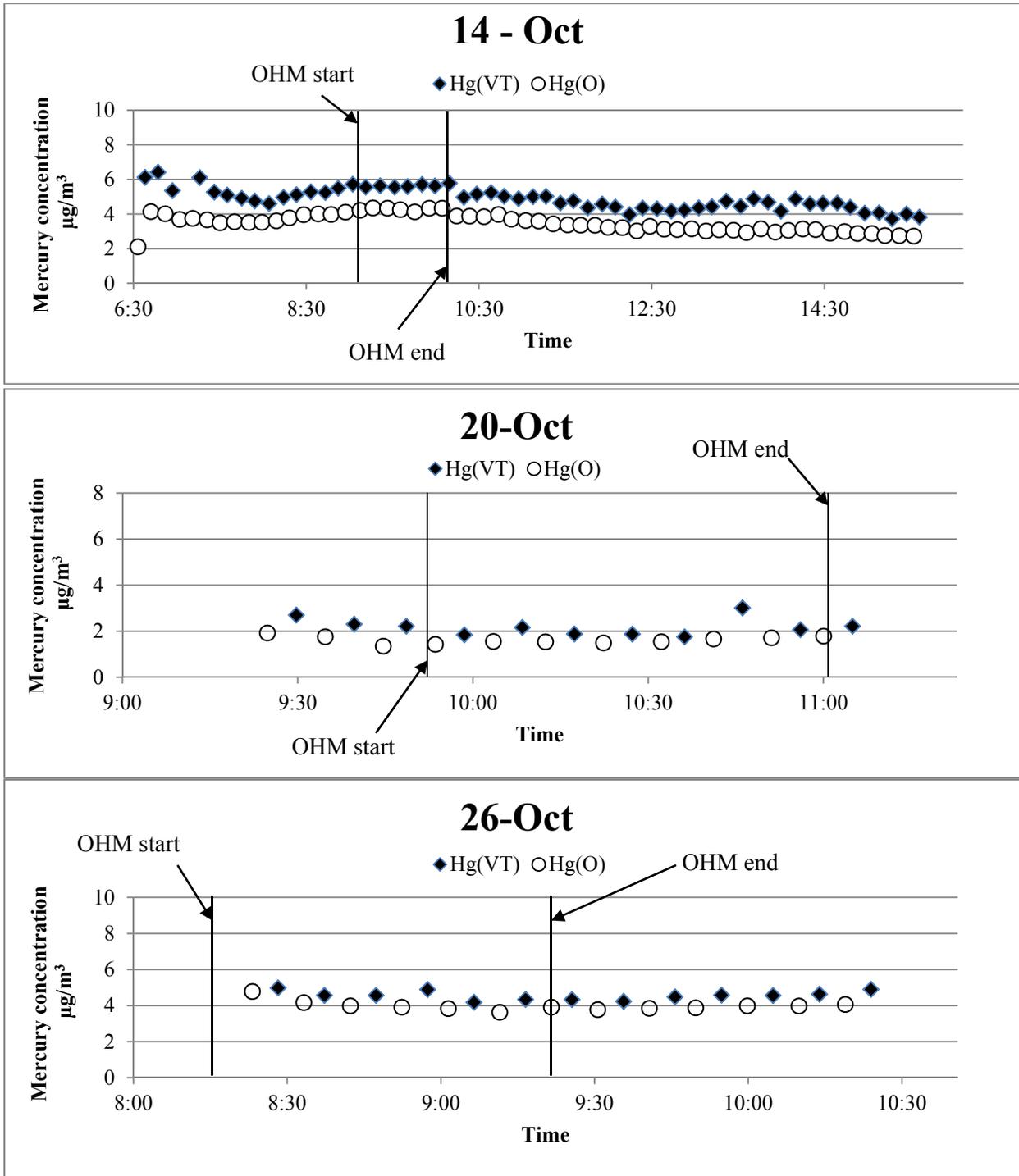


Figure 6. Data for Oct 14, 20, and 26. After the OHM on Oct 14, a problem with the injection equipment delayed testing by 5 hours after OHM. This is why the baseline period is a lot longer than other days. For Oct 26, OHM was started before the CMM started measuring stack mercury concentration. All three graphs show the steady values obtained during baseline OHM.

Figure 7 shows the total vapor phase mercury concentration values measured using the OHM method and tracked using the CMM. As can be seen, the OHM and CMM measurements showed close agreement, with OHM measurements slightly higher than CMM values in most cases. This difference, as mentioned earlier, has also been observed during mercury emission testing at coal-fired plant stack gases, [Benson 2007] and is believed to be due to differences in measurement techniques. On Oct 17, the total vapor mercury concentration showed a high baseline value; however, closer inspection of the OHM and CMM data on Figure 7 indicates that high oxidized mercury is the probable cause. This disparity can be attributed to some process abnormality. The variability in mercury emissions during the three-week testing period, from a low of 3.44 $\mu\text{g}/\text{m}^3$ (OHM data for Oct. 20) to a high of 8.22 $\mu\text{g}/\text{m}^3$ (OHM for Oct. 17), makes it difficult to estimate the baseline value that should to be used to determine reduction potentials of the sorption technologies tested. For individual test days, the respective OHM measurements were used to provide an estimate of actual reduction during testing as shown by Equation (2)

$$\% \text{ Hg Removal} = \frac{[\text{Hg}(1) - \text{Hg}(2)]}{\text{Hg}(1)} * 100 \quad \dots (2)$$

Where, Hg(1) is the OHM baseline total Hg concentration in $\mu\text{g}/\text{m}^3$ and Hg(2) is the OHM total mercury concentration, in $\mu\text{g}/\text{m}^3$ during additive injection and when stack mercury emissions are at steady state. The steady-state point was determined from the CMM charts..

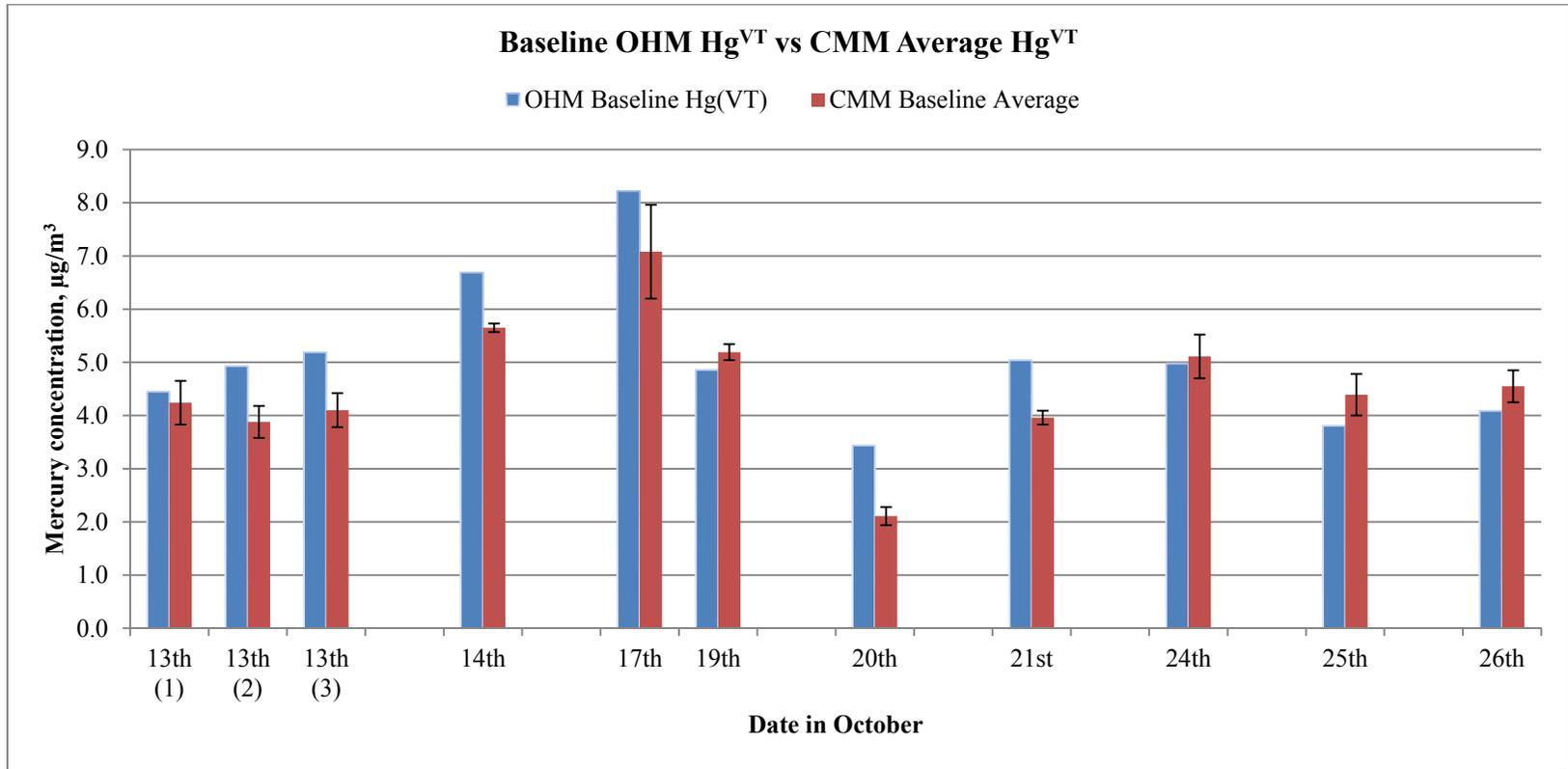


Figure 7. Summary of OHM and CMM baseline data. Error bars represent standard deviation of CMM averages.

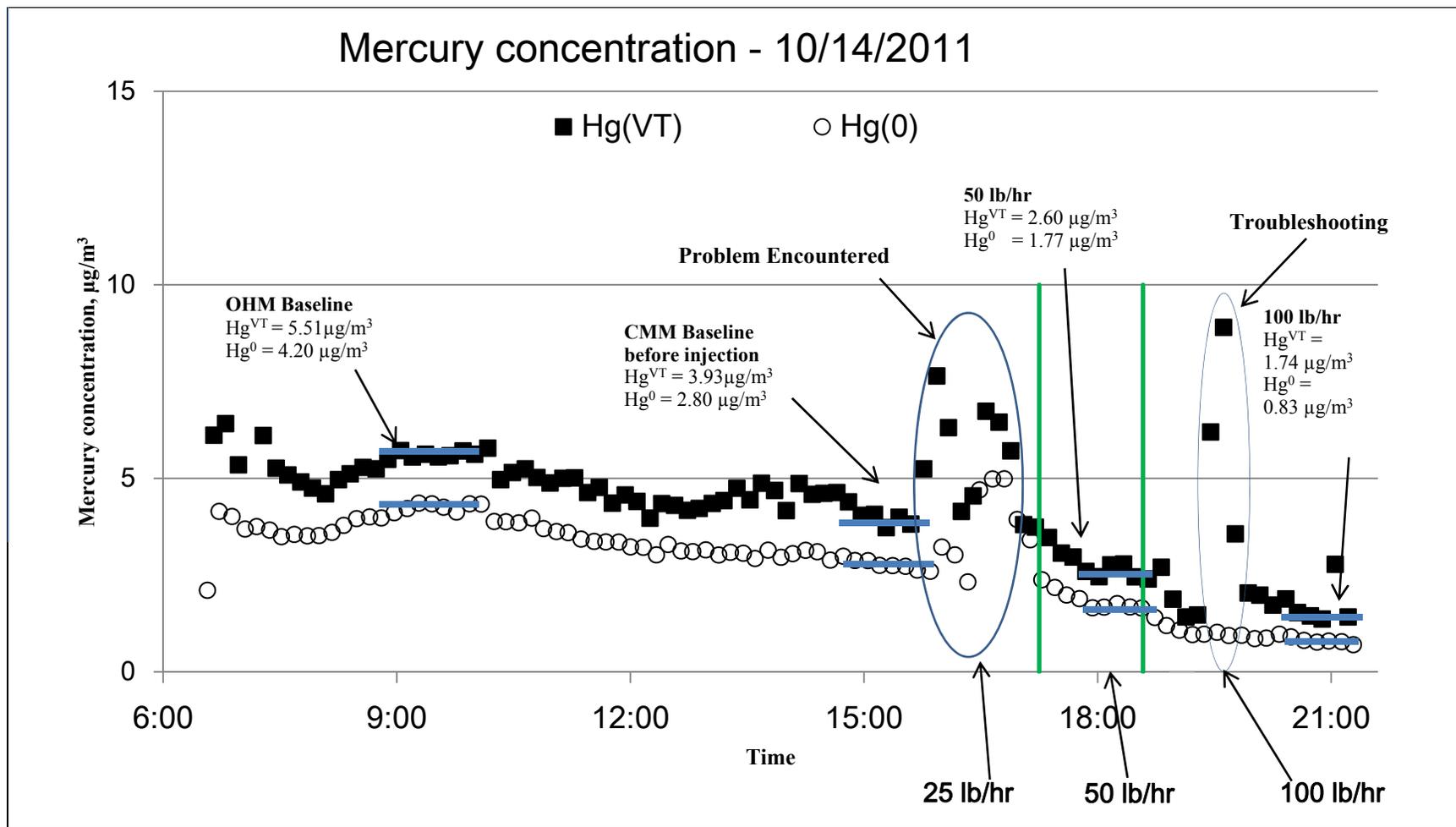


Figure 8. CMM data for Day 1 of ESORB-HG-11 injection. The average CMM mercury concentrations during OHM sampling are shown. It can be observed that the baseline decreased by approximately $1.50 \mu\text{g}/\text{m}^3$ during the time from baseline OHM to start of injection at 16:10. However, when injection started, a problem occurred on the CMM. As soon as the problem was corrected, injection was increased to 50 lb/hr.

ESORB-HG-11 Testing at Preheat Injection Location

As indicated earlier, the UND research team wanted to increase the oxidation and capture of mercury in the flue gas through injection of powdered activated carbon and brominated activated carbon. The proprietary halogenated PAC tested was ESORB-HG-11, provided by Enverge LLC.

A key aspect of the proposed technology was the identification and choice of a suitable injection location. While most sorbent injection approaches in the power industry have targeted the flue gas at low flue gas temperatures (around 120-150°C), the approach used in this study used injection of the sorbents at higher flue gas temperatures. The first injection test locations were located approximately 30 feet upstream of the preheat fan inlets. This was after the process gases have exited the preheater section of the grate kiln. Four ports were installed by Minntac personnel on each of the two ducts leading to the fans. This allowed the placement of a total of eight injection lances for sorbent introduction. Injection of the sorbent upstream of the fans provided the added benefit of enhanced mixing and improved distribution of the sorbent particles in the flue gas.

Filtrate from the slurry samples taken during the first four sampling days were analyzed using EPA Method 7470 which has a detection limit of 0.2 µg/L or 200 ng/L. Consequently, a 200 ng/L value was assigned as the default value for non-detect samples.

The first test day, Oct 14, involved injecting ESORB-HG-11. Baseline values from the OHM measurements showed Hg^{VT} of 6.69 µg/m³. The CMM trend and the OHM results are shown in Figure 8. As a result of a malfunction in the injection equipment, injection started five hours after the OHM baseline measurements were taken. During this time the CMM data decreased from Hg^{VT} of 5.51 µg/m³ (same time frame as OHM baseline) to 3.93 (± 0.10) µg/m³ just before the additive was injected. Because this was the first test run, the priority was to determine which injection rate showed greatest promise, so the drop in the CMM baseline was not considered critical during data evaluation.

The first injection rate investigated was 25 lb/hr of ESORB-HG-11. During this injection period, a problem occurred, as seen on the CMM chart, so no actual reduction was seen. After the effects of the problem on the CMM subsided, the injection rate was increased to 50 lb/hr, and Hg^{VT} , per the CMM, dropped to a steady value of approximately 2.60 µg/m³. The injection rate was then increased to 100 lb/hr and the OHM results showed Hg^{VT} of 2.85 (± 0.57) µg/m³, as shown on Figure 9.

Scrubber slurry samples were taken when the OHM measurements were done for the baseline condition and for the 100 lb/hr sorbent injection rate condition. The filtrate from the baseline sample showed the dissolved mercury concentration (Hg^{D}) to be = 1100 ng/L; however, the slurry sample corresponding to when the sorbent was injected at a rate of 100 lb/hr showed a non-detect ($\text{Hg}^{\text{D}} < 0.2$ µg/L). This suggests there was a large decrease in dissolved mercury after injection of ESORB-HG-11. These results are summarized in Figure 10.

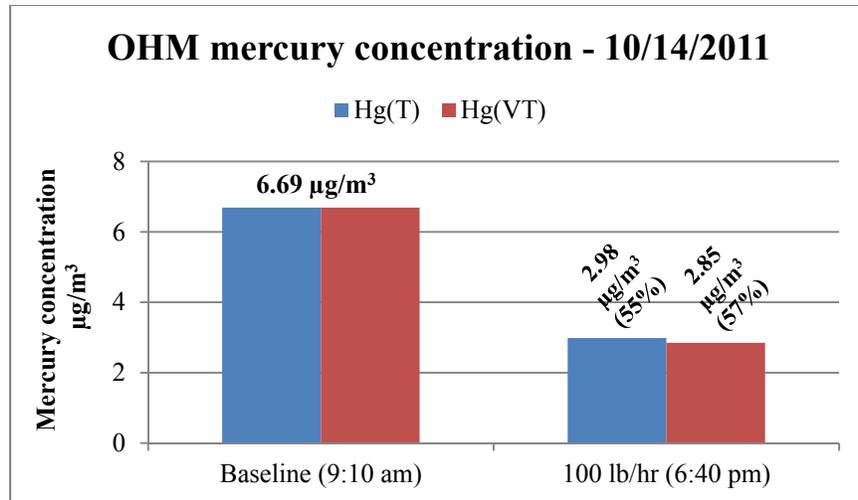


Figure 9. Step 1 testing of ESORB-HG-11 showing OHM results for baseline and 100 lb/hr injection on the 14th. Hg^T is total Hg in stack gas and Hg^{VT} is Hg^T minus particulate mercury, Hg^P, from probe filters. The time listed in brackets is the approximate start time of the OHM. Percent reduction for OHM shown in brackets by the final concentration is estimated from the baseline OHM. However, as will be seen in the CMM graph below, these reductions were calculated before the system came to steady state.

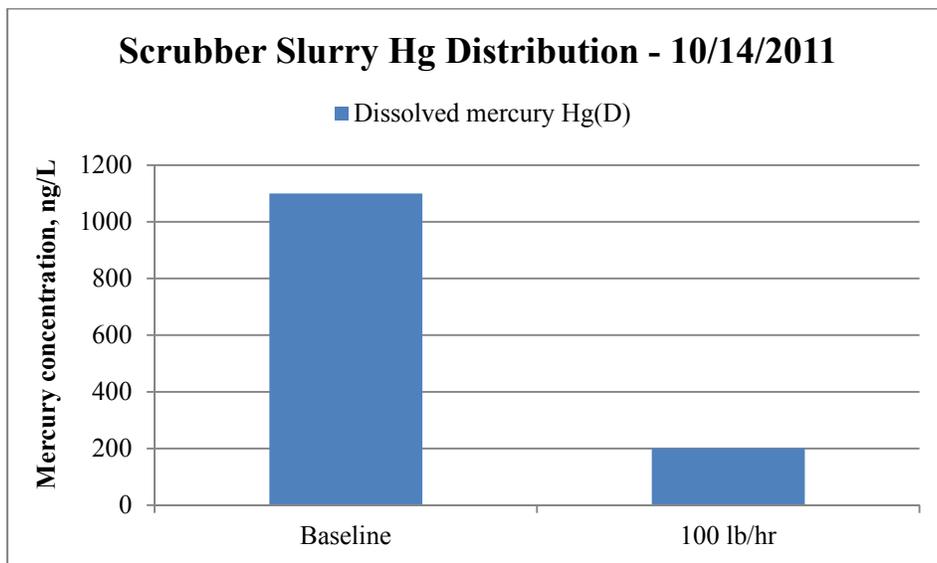


Figure 10. Bar chart showing behavior of mercury in scrubber slurry before and during testing. Dissolved mercury - Hg^D can be seen to decrease significantly with injection of ESORB-HG-11; ESORB-HG-11 is very efficient in sequestering mercury from solution and confirms results obtained in bench scale tests.

Day 2 of ESORB-HG-11 injection testing was Oct 17. The injection rates tested were 50, 100, and 150 lb/hr. OHM measurements were conducted for baseline conditions as well as for sorbent injection rates of 50 and 150 lb/hr. Figure 11 is a summary of the results, while Figure 12 summarizes the data for the 150-lb/hr injection rate. The OHM baseline Hg^{VT} was $8.22 \mu\text{g}/\text{m}^3$. The CMM average during the same period was $7.08 (\pm 0.88) \mu\text{g}/\text{m}^3$. However, looking more closely at the CMM trend depicted in Figure 13, a spike can be observed for the oxidized mercury from 8:50 am to 9:40 am, consistent with OHM data, which also shows an abnormally high oxidized mercury concentration of $2.40 \mu\text{g}/\text{m}^3$. OHM measurements for the 50 and 150 lb/hr injection rates yielded values for Hg^{VT} of 2.16 and $1.22 \mu\text{g}/\text{m}^3$, respectively. The total vapor mercury concentration does not include the particulate mercury component [Hg^{P}]. Hg^{T} from the OHM measurements for the 50 and 150 lb/hr injection rates were 2.22 and $1.81 \mu\text{g}/\text{m}^3$ (Figure 11). The disparity in results suggests that at the higher injection rates, some of the injected carbon (with the captured mercury) escapes the scrubber and contributes to the stack emissions as particulate mercury.

The CMM average Hg^{VT} concentration during the same time as the OHM sampling gave values of $2.93 (\pm 0.21) \mu\text{g}/\text{m}^3$ and $1.07 (\pm 0.29) \mu\text{g}/\text{m}^3$ for 50 and 150 lb/hr injection rates respectively. The relatively close agreement between OHM and CMM data validate the significant reduction in mercury emissions at each of the injection rates investigated. Based on the reductions in mercury emissions as a result of ESORB-HG-11 injection rates of 50 and 150 lb/hr, the Minntac line 3 test matrix was updated to include long term testing at these specified injection rates.

With regard to mercury distribution in the scrubber slurry samples, the results mirrored those obtained on Day 1 with a high Hg^{D} of 4000 ng/L during baseline operation. This value decreased significantly with injection of ESORB-HG-11, suggesting sequestration of the mercury captured in the scrubber to the scrubber solids. Figure 12 summarizes these results.

The first step of ESOR-HG-11 testing was conducted on Oct 14 and 17 and was aimed at determining the performance of each injection rate over a short term (≤ 3 hours). From the results above, the rates of 75, 100, and 150 lb/hr were selected for long-term testing (> 3 hours).

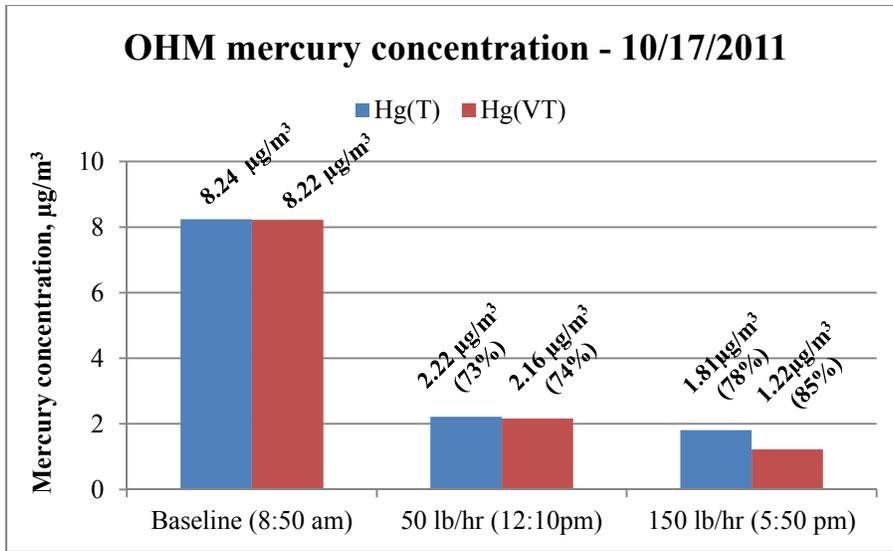


Figure 11. OHM results for Day 2 ESORB-HG-11 testing. OHM performed for baseline, 50 and 150 lb/hr injection rates. Baseline concentrations are believed to be higher than actual due to an unexplained increase observed in oxidized mercury during the measurement period. Results for 150 lb/hr suggest Hg^P emissions increase with increase in injection rate, suggesting ESORB-HG-11 has a higher penetration through the scrubber than taconite dust. As is the case with Oct 14, percent reduction for OHM shown in brackets by the final concentration is estimated from the baseline OHM and is calculated before the system came to steady state.

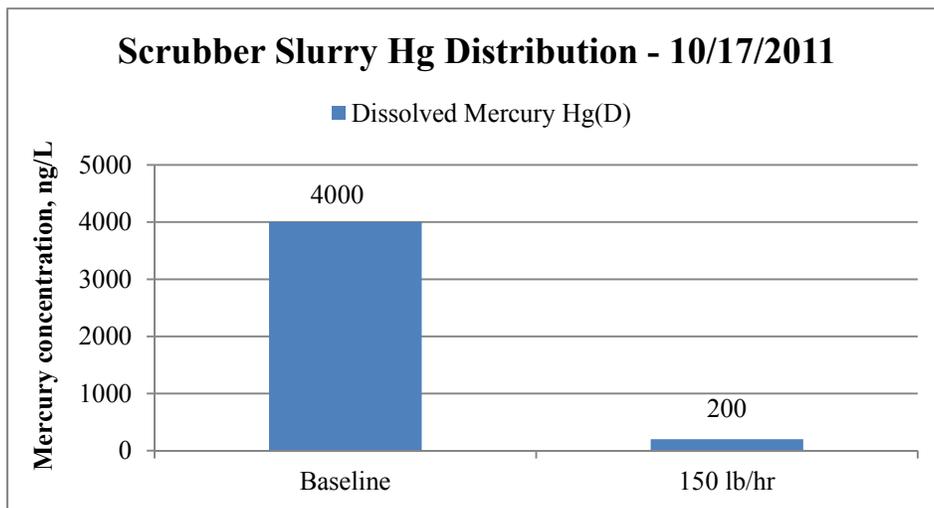


Figure 12. Bar chart showing behavior of mercury in scrubber slurry during ESORB-HG-11 injection. Hg^D concentrations decreased significantly from 4000 ng/L to < detection (200 ng/L) during 150 lb/hr.

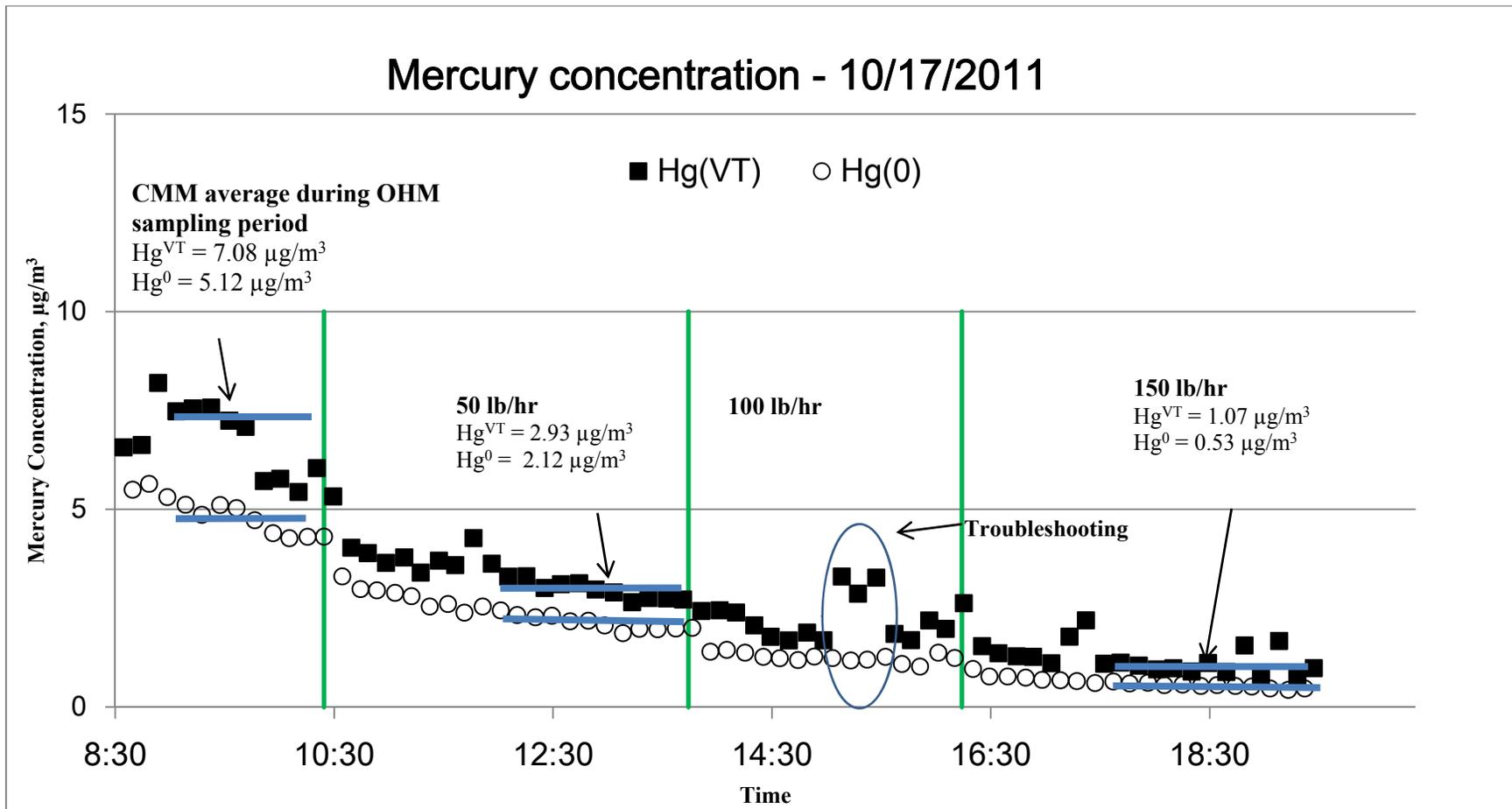


Figure 13. CMM data for Day 2. Injection rates of ESORB-HG-11 of 50, 100, and 150 lb/hr were investigated. Baseline measurements show increase in oxidized mercury as observed in OHM data; the reason for this increase is not known. Significant reductions in Hg emissions observed during testing suggested that these injection rates should be investigated further during long-term sorbent injection testing during Step 2.

On Day 3 (Oct18), a longer-term test that included injection of ESORB-HG-11 at a rate of 100 lb/hr was performed. The test duration was 5 hours and three OHM measurements were performed. These OHM measurements included the baseline as well as 3 and 5 hours after injection was started. The baseline value for the total vapor mercury concentration, before injection was started, was $6.17 \mu\text{g}/\text{m}^3$. Hg^{T} for the baseline condition was $6.20 \mu\text{g}/\text{m}^3$, as shown on Figure 14. Figure 15 shows the dissolved mercury decreased with the addition of 100 lb/hr of ESORB-HG-11.

Injection did not start immediately following the baseline OHM measurement because of troubleshooting of the CMM analyzer. The analyzer was subsequently brought back online for two hours before sorbent injection was started. The mercury concentration as measured by the CMM during this hour of baseline testing was stable at an average of $5.06 (\pm 0.22) \mu\text{g}/\text{m}^3$ (Figure 16). A reasonable agreement between this average and the OHM baseline value suggests that the baseline mercury emissions did not change significantly. The OHM baseline value was thus used to compute the percent mercury reduction.

OHM data showed that the stack values for mercury concentration decreased over time (Figure 16), suggesting that steady-state performance took time to achieve. This is likely because the system comprising the gas ducts and other surfaces continue to accumulate a portion of the injected sorbent and provide additional reduction in the mercury concentrations with time. The stack gas Hg^{VT} at the end of about 5 hours of injection as determined by OHM measurements was $1.4 \mu\text{g}/\text{m}^3$, representing a 77% reduction from baseline values. The corresponding value for Hg^{VT} determined from the CMM data was $1.15 \mu\text{g}/\text{m}^3$.

The contribution from particulate bound mercury changed Hg^{T} to $1.95 \mu\text{g}/\text{m}^3$, as shown on Figure 14. When compared to baseline values, this resulted in a 69% overall reduction for total mercury emissions. These results suggest that the brominated carbon sorbent, ESORB-HG-11, penetrates the scrubber in this unit, carrying with it a portion of the captured mercury. Therefore, greater mercury emission reductions may be obtained with improved scrubber operation.

With regard to the scrubber slurry taken during the long-term sorbent injection at 100 lb/hr, it was observed that the baseline filtrate sample was 600 ng/L, lower than baseline values obtained during previous short-term injection tests (Figure 15). The lower baseline filtrate result suggests that ESORB-HG-11 was still present in the system. Even with the lower levels of ESORB-HG-11, there was some sequestration still taking place in the recirculation tank. When long-term sorbent injection was started, the dissolved mercury concentration in the scrubber filtrate decreased to very low values ($\sim 50 \text{ ng}/\text{L}$), confirming the sequestration ability of ESORB-HG-11. Mass balance calculations suggest it would take several hours for ESORB-HG-11 present in the scrubber tank to be reduced to insignificant levels. This was further confirmed by the fact that the baseline Hg^{D} for Oct 17, a Monday, was significantly higher (4000 ng/L) as the ESORB-HG-11 previously injected into the system on the previous Friday most likely reduced to insignificant levels in the recirculation tank.

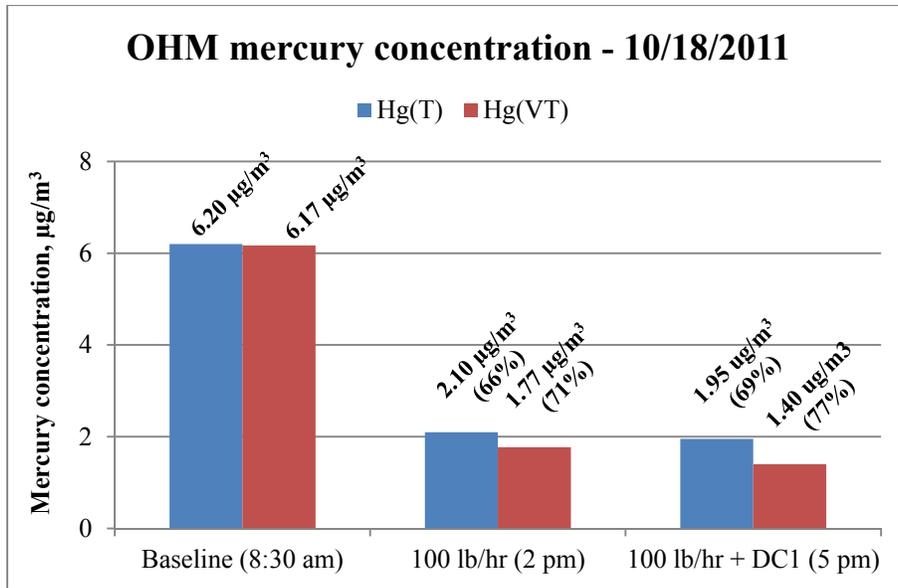


Figure 14. OHM results for Day 3 testing. OHM measurements were performed for baseline, and 3 hrs and 5 hrs into injection. Assuming OHM baseline is still valid at the start of injection, significant reductions can be observed for both Hg^T and Hg^{VT} . Results are also consistent with observation that Hg^P increased during technology testing; suggesting that ESORB-HG-11 penetrated the scrubber.

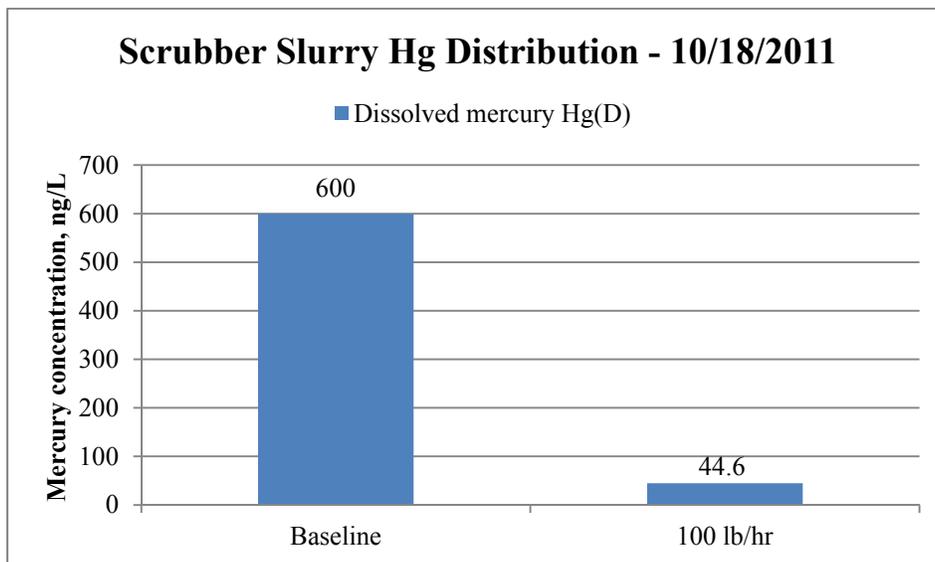


Figure 15. Scrubber mercury distribution during long term testing of ESORB-HG-11 with an injection rate of 100 lb/hr. Hg^D decreases with additive injection.

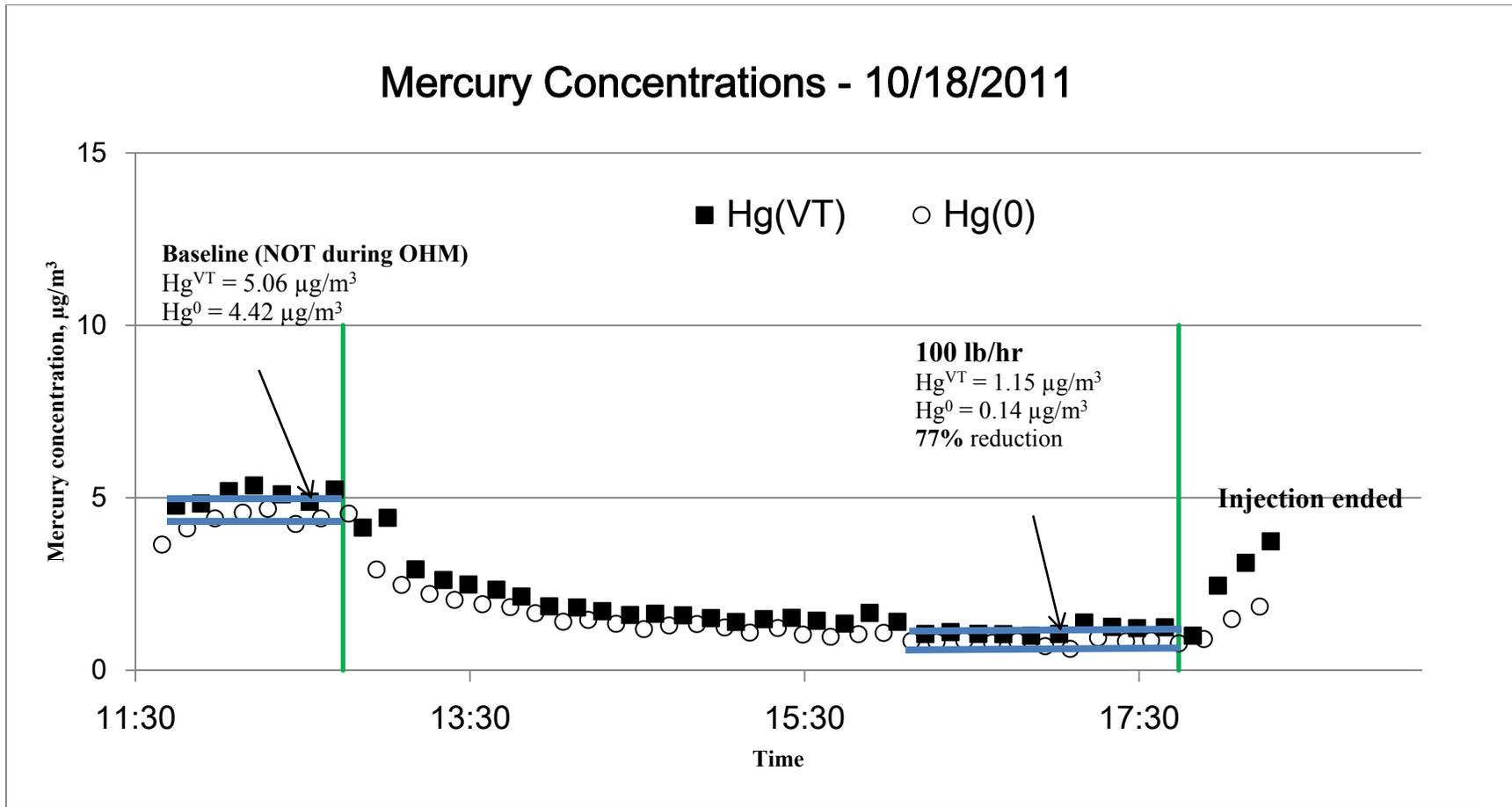


Figure 16. CMM data for Day 3. The CMM average baseline depicted is 3 hours after OHM baseline. Hg^{VT} average during 100 lb/hr injection was calculated over the same time the third OHM measurement was performed this day. OHM average, $1.40 \mu\text{g}/\text{m}^3$, and CMM average, $1.15 (\pm 0.14) \mu\text{g}/\text{m}^3$, agree closely.

Testing performed on Day 4 and 5 involved the injection of the scrubber additive, diethyl dithiocarbamate (DEDTC), and plain powdered activated carbon (PAC). These results are discussed later.

ESORB-HG-11 testing was resumed on day 6, October 21st with an injection rate of 150 lb/hr. Two OHM measurements were performed; one for the baseline, and the other started 4 hours into the injection schedule. The baseline OHM measurement showed a value for Hg^{VT} of $5.04 \mu g/m^3$ as shown on Figure 17. After 5 hours of injection, the OHM value was $0.83 \mu g/m^3$ corresponding to a reduction of 84% for Hg^{VT} . Figure 18 shows that the dissolved mercury decreased with the addition of 150 lb/hr of ESORB-HG-11. The CMM values for the stack Hg^{VT} was steady and near $0.61 \mu g/m^3$, as shown on Figure 19. Hg^T in the stack gas at this test condition, as measured by the OHM method was $1.50 \mu g/m^3$, corresponding to a 70% reduction from the baseline value. When compared to previous tests where sorbent injection rates were lower, Hg^P increased at this higher injection rate. Filters for both the CMM and OHM showed evidence of carbon penetration through the scrubber potentially contributing to Hg^P emission in the stack gas. This further corroborates the possibility that a portion of the sorbent laden with mercury penetrates the scrubber, and thereby increases the mercury emission rates.

Hg^D in the scrubber slurry decreased as a result of ESORB-HG-11 injection (Figure 18), which is consistent with previous tests. However, the baseline value was very low to start with, probably as a result of PAC still present in system from the run on the previous day. The dissolved mercury concentration in the scrubber liquids during ESORB-HG-11 injection at a rate of 150 lb/hr was 20 ng/L.

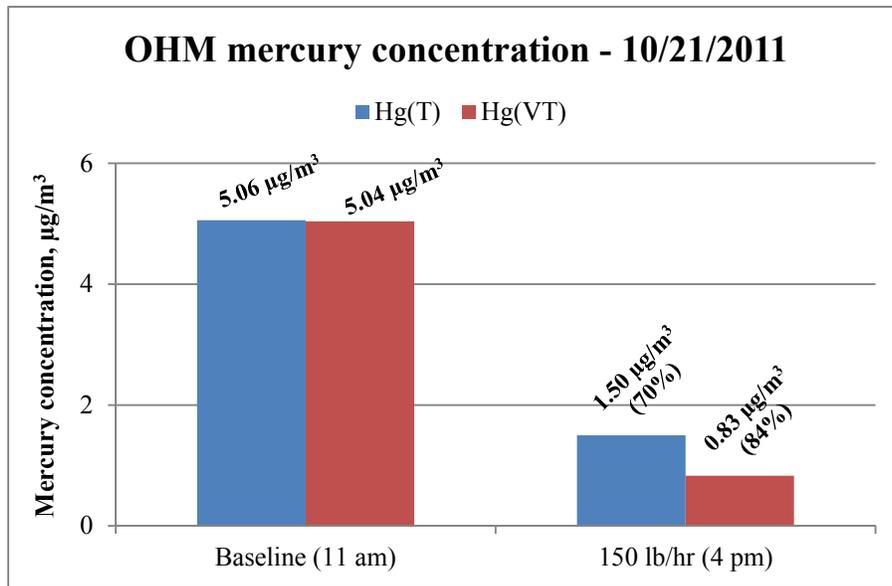


Figure 17. OHM results for Day 6 testing. OHM performed for baseline and 5 hrs into injection. Time listed in brackets is for OHM start. Hg^P increased significantly with higher injection rate as compared to Day 3, with 100 lb/hr injection rate.

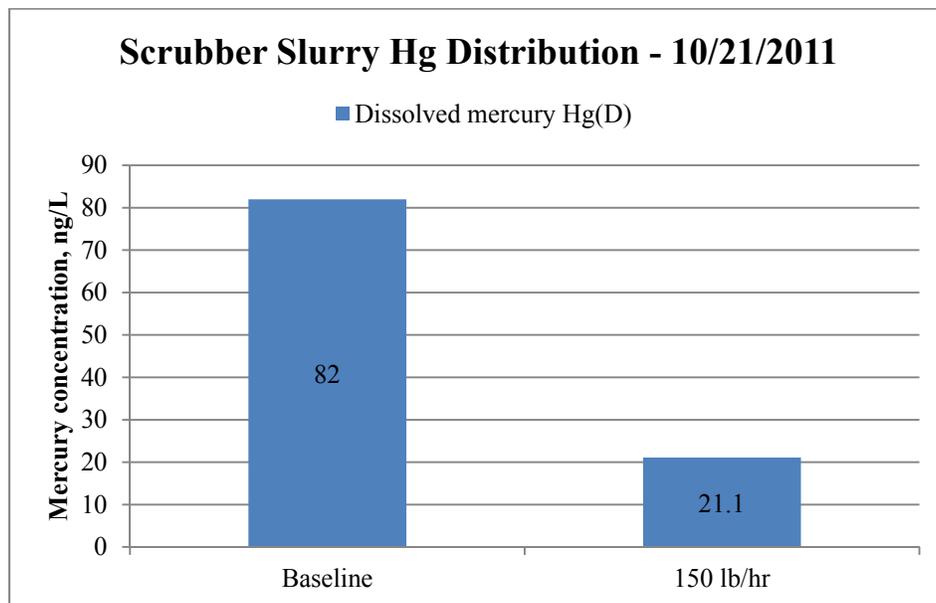


Figure 18. Slurry mercury distribution during injection of 150 lb/hr ESORB-HG-11. Hg^D is low but still decreased from 82 ng/L to 21 ng/L. The low baseline is probably because of residual PAC in the recirculation tank from testing on the previous day.

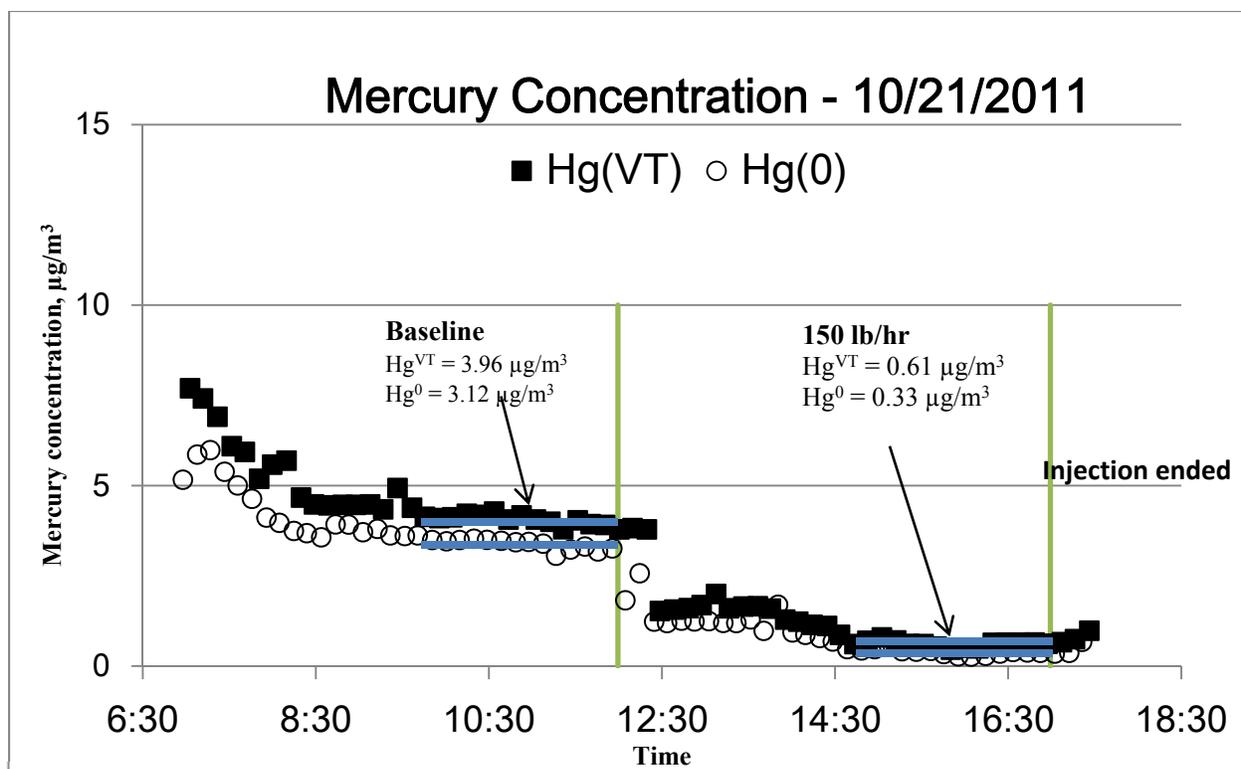


Figure 19. CMM data for Day 6. Injecting 150 lb/hr for 5 hrs shows Hg^{VT} decreased significantly to < 1 µg/m³. Average values showed in graph were computed during the same period the OHM measurement was performed.

Oct 24 was the last test day of ESORB-HG-11 performance at the preheat fan inlet injection location. A new injection rate (75 lb/hr) was investigated for a time of 5 hours. The goal was to investigate if a lower feed rate would still produce significant reductions in mercury emissions. As shown in Figure 20, the OHM baseline value for Hg^{VT} was 4.98 µg/m³. ESORB-HG-11 injection started 20 minutes after the OHM baseline measurement was completed. Reductions of 56% and 66% for Hg^{VT} were observed for OHM measurements performed 2 hours and 4 hours after injection. After the initial drop in the mercury concentration over a 30-minute ESORB-HG-11 injection period, the values remained nearly steady at an average of 2.70 µg/m³ for the rest of the injection period. A gradual increase was observed in Hg^{VT}, which corresponded to the process recovering after injection stopped. However, measurement using the CMM was stopped well before the stack mercury emissions returned to baseline values. Hg^P was significantly higher during this test condition than previously observed, even though the injection rate investigated here was lower than for previous tests.

Hg^D for the scrubber slurry during the baseline run was 4370 ng/L, suggesting the scrubber system had returned to baseline values over the weekend (Figure 21). The levels of Hg^D decreased once ESORB-HG-11 injection at a rate of 75 lb/hr was started. Hg^D did not drop as significantly as it did on previous days when sorbent injection started. This was an unexpected trend similar with the stack mercury concentration that showed a lower decrease than that observed for the 50 lb/hr injection test.

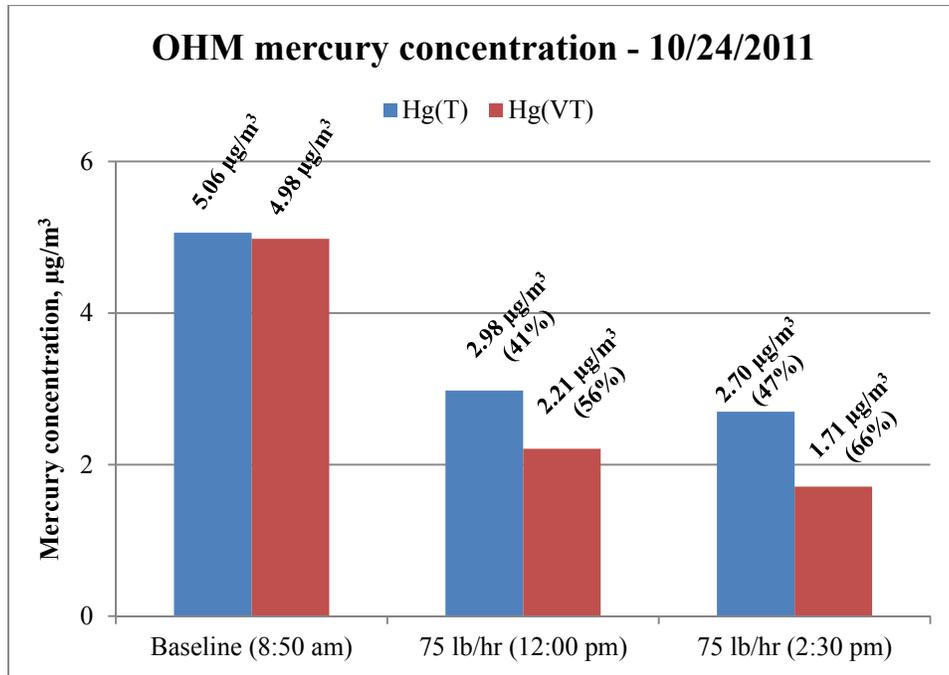


Figure 20. OHM results for testing on the 24th. OHM performed for baseline, 2 hrs and 4 hrs into injection. Time listed in brackets is for OHM start. Hg^P increased by 15% and 19%.

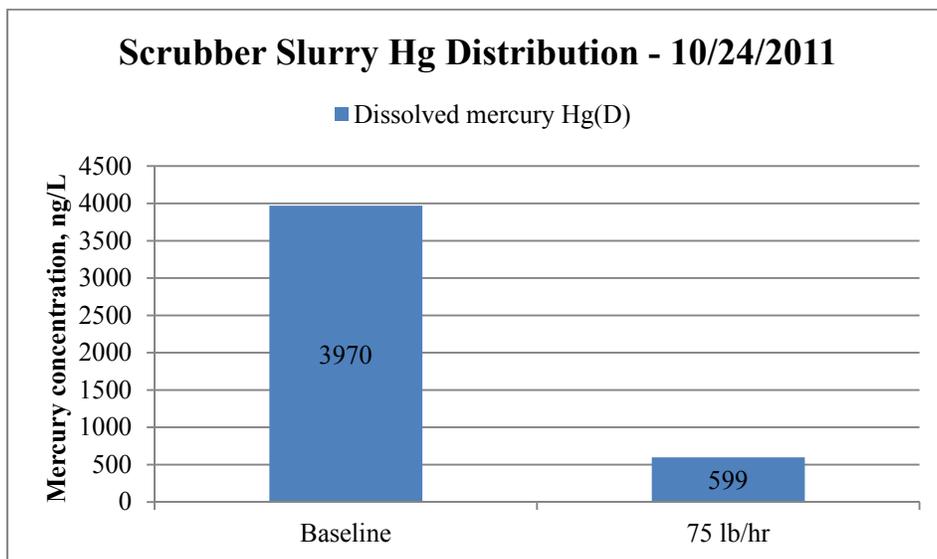


Figure 21. Scrubber mercury distribution during the injection of 75 lb/hr. Hg^D is seen to decrease but the final value after 6 hours of injection was higher than expected. Correspondingly high Hg^P stack emissions may suggest less ESORB-HG-11 was captured.

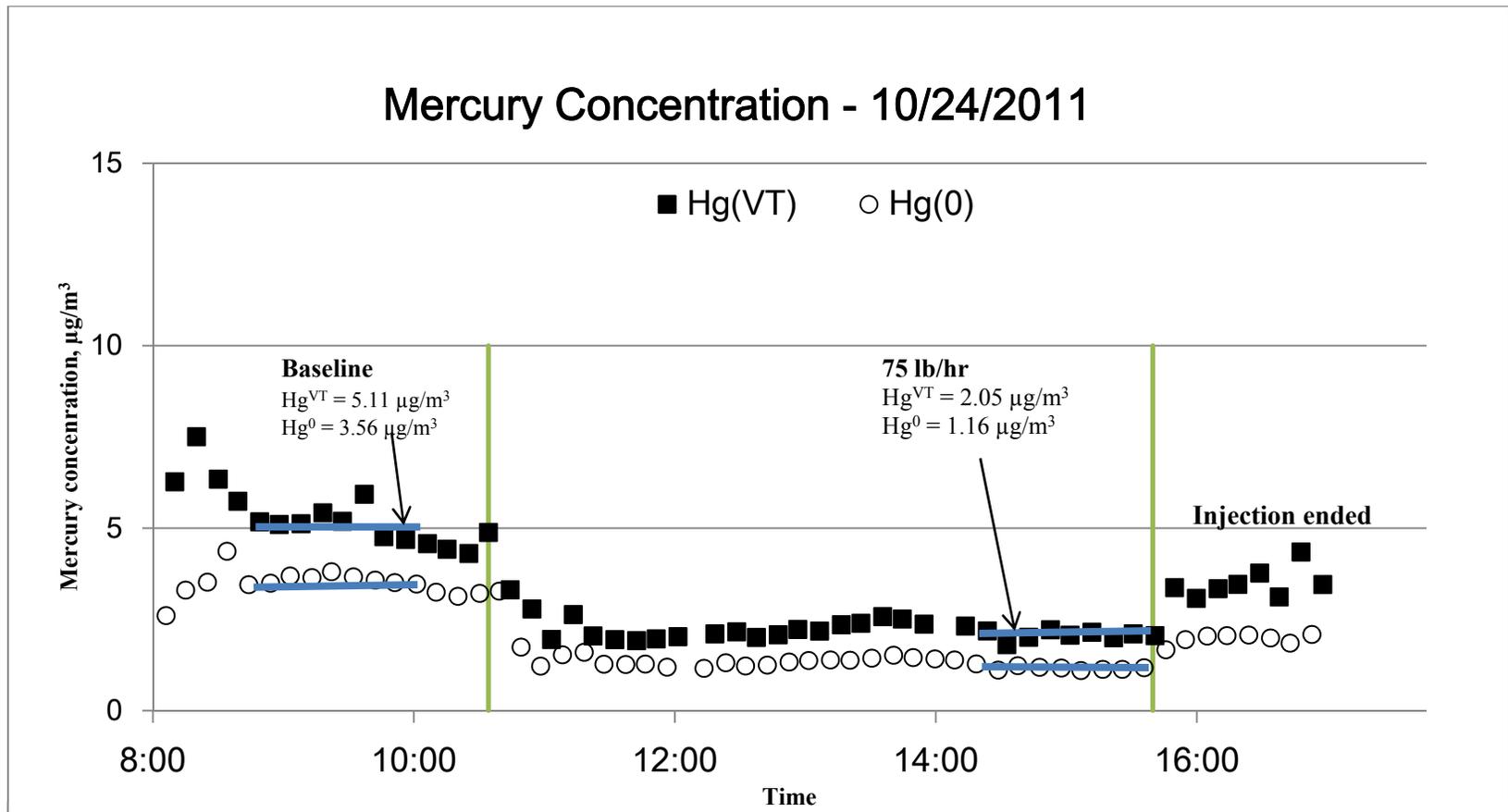


Figure 22. CMM for tests on the 24th at an injection rate of 75 lb/hr for 5 hrs. A sharp decrease can be observed followed by a stable value throughout the injection period.

Conclusion – ESORB-HG-11 Testing at Preheat Fan Inlet Location

ESORB-HG-11 testing at the preheat fan inlet injection location showed significant reductions in Hg^{VT} . At ESORB-HG-11 injection rates of 100 and 150 lb/hr, there were 77% and 84% reduction in stack mercury emissions from baseline, respectively. While there were significant reductions in stack vapor phase mercury emissions, Hg^{P} in the stack gases were seen to increase as a result of the penetration of ESORB-HG-11 through the plant scrubber. This was confirmed by visual inspection of the probe filters for both the OHM and CMM. The Hg^{P} emissions increased the Hg^{T} in the stack gas for the 100 and 150 lb/hr injection rates to 1.95 and 1.50 $\mu\text{g}/\text{m}^3$, respectively. The corresponding total stack mercury emission reductions for the 100 and 150 lb/hr injection rates compared to the baseline emissions were 69% and 71%, respectively. Baseline emission values on the day these tests were performed were 6.2 and 5.06 $\mu\text{g}/\text{m}^3$, respectively. At an injection rate of 75 lb/hr, Hg^{VT} reported a reduction of 66%, with its Hg^{P} emissions being the most significant during the entire testing period. While there are significant reductions in stack mercury emissions as a result of ESORB-HG-11 injection, the contribution from particulate bound mercury to the sorbent cannot be ruled out. It is suggested that identifying ways of improving the particulate capture efficiency of the scrubber may result in further reductions of stack mercury emissions, especially during ESORB-HG-11 injection.

Scrubber slurry analysis showed reductions in the levels of Hg^{D} as a result of ESORB-HG-11 injection. The captured mercury was associated with the non-magnetic portion of the scrubber slurry, in this case ESORB-HG-11. This confirms the sequestering ability of ESORB-HG-11. Minntac Line 3 slurry solids are discharged and not recycled, so captured mercury has been removed from the process permanently.

The reductions mentioned above were determined based on the baseline OHM concentrations of the respective test days and OHM concentrations taken during sorbent injection. The differences in the baseline average values as outlined earlier may require that another reduction calculation method be considered for overall additive performance that takes into consideration an average baseline emission, rather than a value determined for a particular period.

ESORB-HG-11 Testing at Preheat Grate Injection Location

The second sorbent injection location investigated at Minntac Line 3 was injection at the preheat zone. The goal was to test whether changing to an upstream location and using low injection rates could achieve reductions comparable or greater than those seen during injection at the preheat fan inlet zone. These tests were conducted on October 25 and 26. Injection into the preheat zone was also chosen with the idea that longer residence times would provide longer contact times between the sorbent and the mercury, with the expectation of improving the performance of ESORB-HG-11. Ports located at the base of the preheat zone wall were used, which enabled injection of ESORB-HG-11 directly into the preheat section upstream of the grate. However, the location of the ports on the walls of the zone coupled with the lack of suitable high temperature injection lances that could be inserted into the grate and withstand the high temperatures did not allow for effective distribution of the injected material into the flue gas above the pellet bed. At this location, injection rates of 50, 75, and 100 lb/hr were investigated, as shown

in Figures 23 – 26; however, no CMM measurements were done for the 50 lb/hr rate. For the other two rates, OHM and CMM baseline measurements showed good agreement during testing; however, reductions from baseline values were lower than 50%. As summarized in Figures 23 and 24, for 75 lb/hr and 100 lb/hr, respectively, stack mercury emission reductions ranged from 43 to 50% for Hg^{VT} and 25 to 31% for Hg^{T} . Results from these test runs suggest that injected carbon is transported in the flue gas and is not fully combusted in preheat zone. However, lower reductions than previous test results conducted at 75 lb/hr of ESORB-HG-11 injection suggest that the poor distribution of the sorbent in the preheat zone could be responsible for the diminished effectiveness.

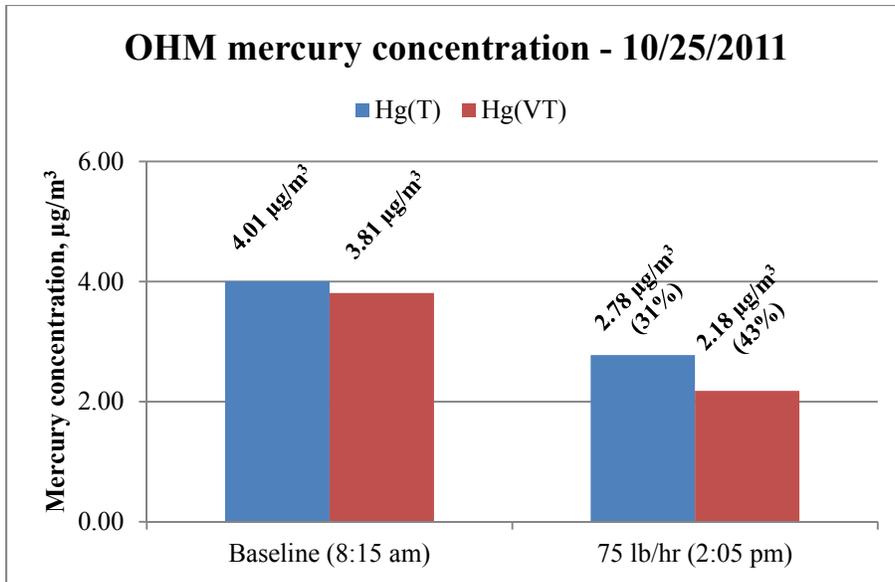


Figure 23. OHM results during preheat zone injection testing of 75 lb/hr of ESORB-HG-11. Reduction was < 50% for both Hg^T and Hg^{VT}. Significant Hg^P emissions during testing were also observed. This suggests that injected carbon is transported by flue gas and not combusted in the preheat zone. However, lower reductions than previous testing suggest distribution of ESORB-HG-11 into preheat zone is poor.

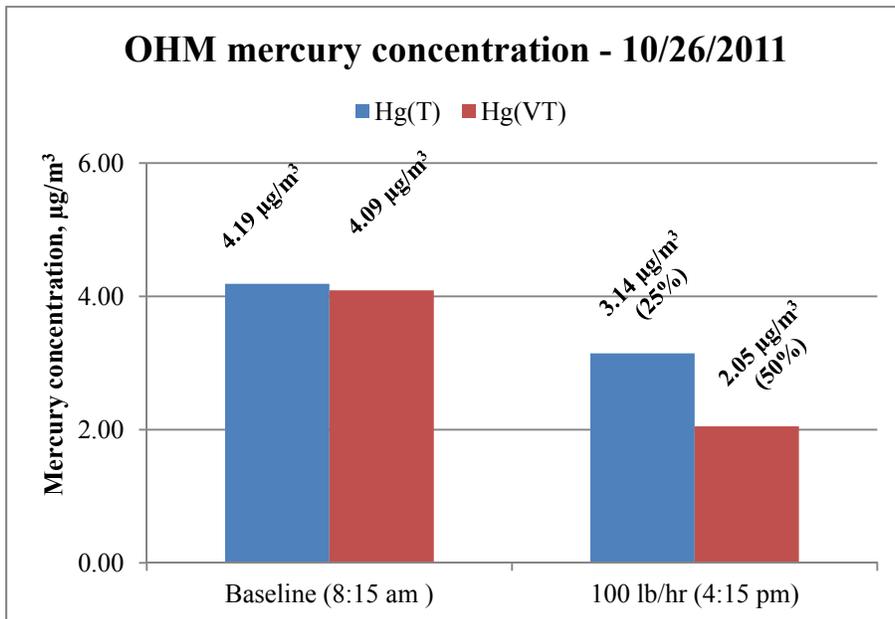


Figure 24. OHM results during preheat zone injection at 100 lb/hr of ESORB-HG-11. Hg^P was significant after injection began for close to 7 hrs.

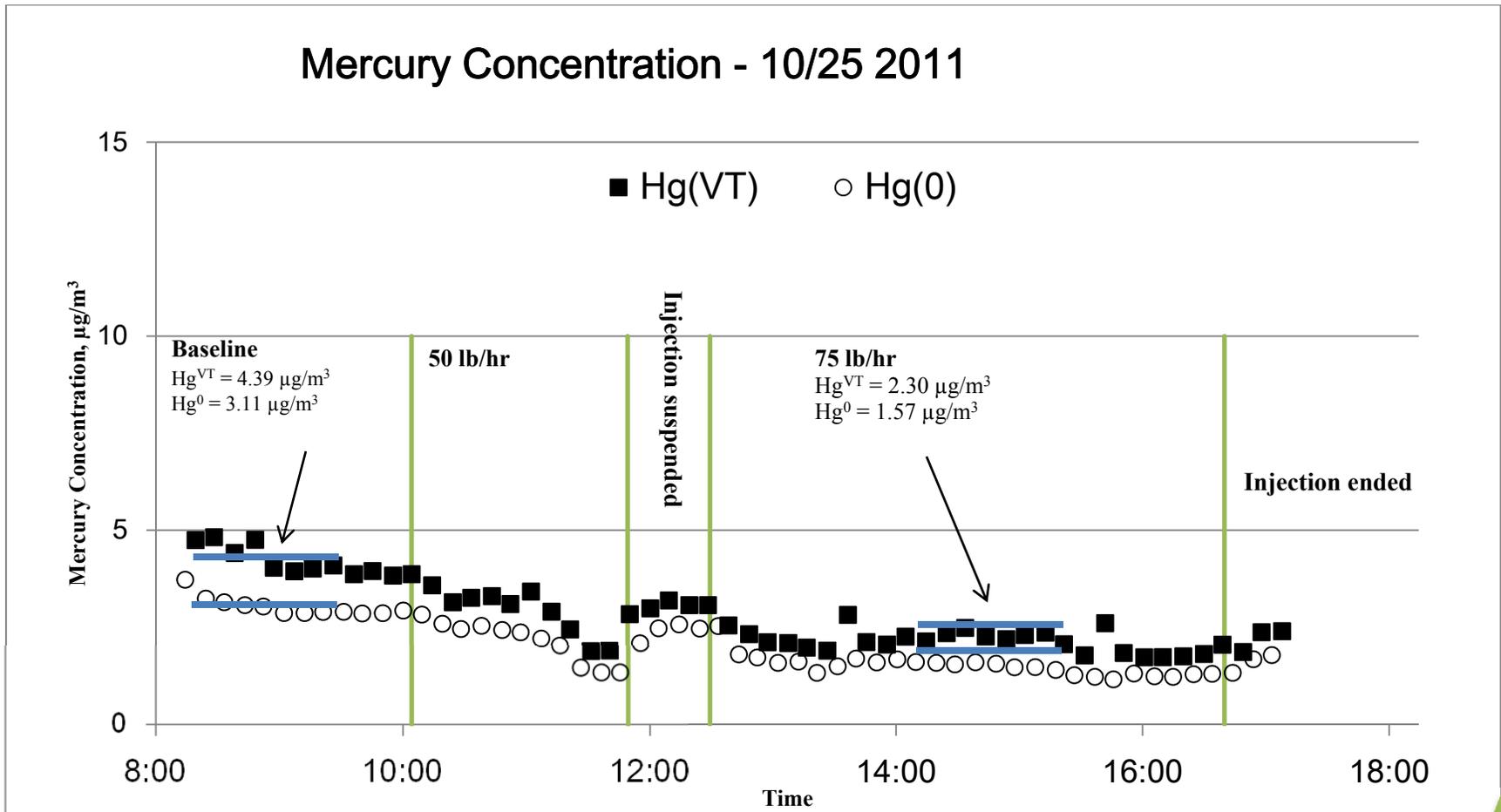


Figure 25. CMM data during preheat zone testing of 50 lb/hr and 75 lb/hr of ESORB-HG-11. Average values calculated during period OHM measurements were carried out.

Mercury Concentration - 10/26/2011

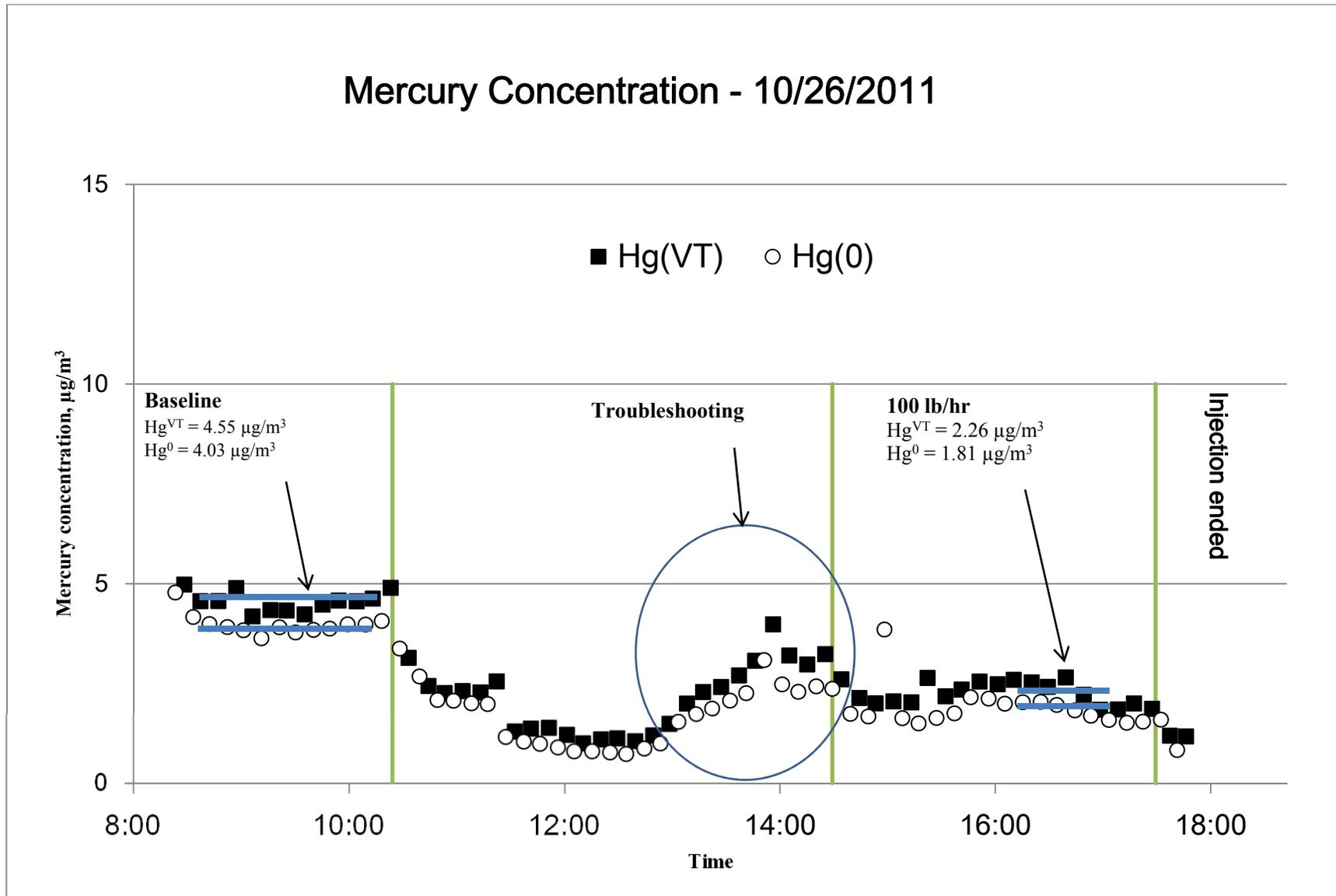


Figure 26. CMM data during preheat zone injection testing at 100 lb/hr. Some reduction observed but reduction was not significant.

Conclusion – ESORB-HG-11 Testing at Preheat Zone Injection Location

Injection of the brominated sorbent into the preheat zone showed less effectiveness in mercury emission reduction when compared to the preheat fan inlet injection for similar injection rates. This is believed to be largely due to the poor distribution of ESORB-HG-11 at this injection location, given that injection was at the preheat zone wall and not over the entire bed cross-section. In order to deliver a more uniform coverage of the sorbent into the flue gas at the high temperatures in the preheat zone, cooled lances that can be inserted further into the grate area will be required.

As a result of the lower stack mercury emission reduction from injection testing at this location, further analyses of other samples collected were not performed. It is believed that improving the injection distribution in the preheat zone using high temperature-tolerant lances and better port locations should lead to better reduction percentages.

PAC testing at Preheat Fan Inlet Location

On October 20, short-term tests using plain powdered activated carbon (PAC) were performed. The injection rates investigated were 50, 100 and 150 lb/hr. Baseline OHM results showed a low stack Hg^{VT} value of $3.44 \mu\text{g}/\text{m}^3$, which was the lowest baseline for the entire testing period. These results are summarized in Figures 27 - 29. CMM baseline results were also lower, averaging $2.11 \mu\text{g}/\text{m}^3$. The CMM trend for this test period is shown in Figure 29. Injection with PAC showed very little reduction in stack mercury emissions measured using the OHM method and reported on Figure 27. The CMM trend as shown in Figure 29 shows nearly no reductions in stack mercury emissions. PAC is effective in oxidizing mercury and capturing it if oxidizing components (like halogens) are present in the flue gas. Presumably, the flue gas from taconite processing at this plant did not contain sufficient concentrations of such oxidizing components. In as much, the Hg^{P} did not increase during PAC injection as was observed when injecting ESORB-HG-11. This could be explained either by the fact that the PAC did not capture any mercury species or by the fact that the PAC was more easily captured by the scrubber as compared to ESORB-HG-11.

PAC also exhibits mercury sequestering capabilities; hence even though stack mercury emissions did not decrease, its presence in the system affected mercury speciation in the slurry. Analysis of scrubber samples collected during testing confirmed this trend as shown on Figure 28. Baseline dissolved Hg^{D} was reported as a non-detect value; hence, a default of $0.2 \mu\text{g}/\text{L}$ was reported, which corresponds to the method detection limit. Other samples were analyzed using low-level mercury analysis (EPA Method 1631). Results indicated that Hg^{D} decreased during injection of PAC, confirming bench and pilot testing that showed that PAC also has the capacity to effectively capture and sequester mercury from the scrubber liquids.

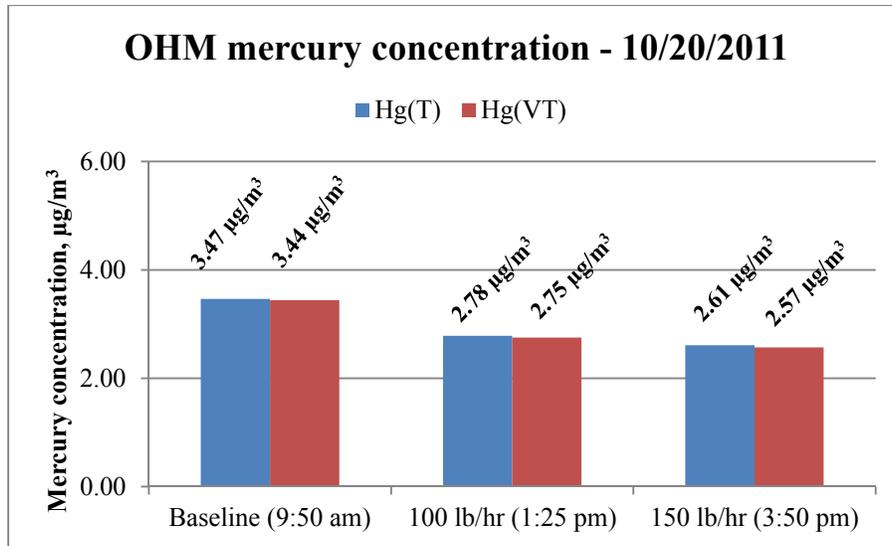


Figure 27. OHM concentrations during PAC testing. Decreases in Hg^T and Hg^{VT} shown on this figure are not believed to be due to injection of PAC, but rather due to baseline fluctuations during the test period. No significant increase in Hg^P observed during injection.

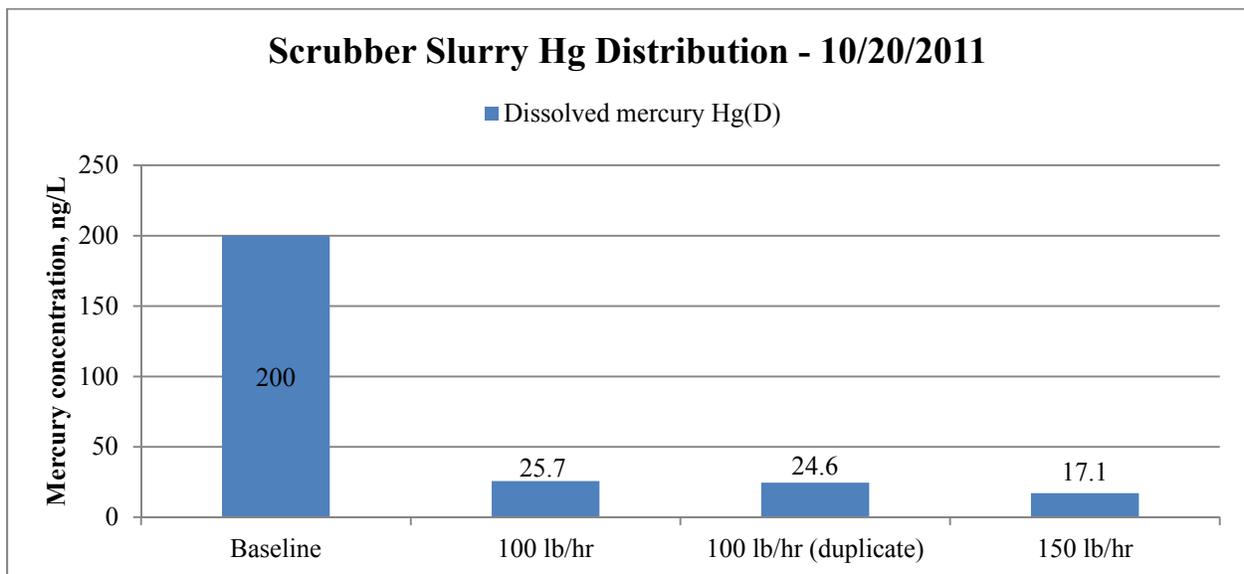


Figure 28. Hg^D values in the scrubber slurry during PAC injection. Hg^D is seen to decrease with injection of PAC. The 100 lb/hr samples were analyzed in duplicate. Hg^D sample for baseline was estimated at 200 ng/L. Meanwhile, Hg^D for 100 lb/hr and 150 lb/hr were 25.2 ng/L (average of 25.7 and 24.6) and 17.1 ng/L. The low Hg^D baseline is believed to be caused by ESORB-HG-11 that was added to the system on the Oct 19 during DEDTC testing.

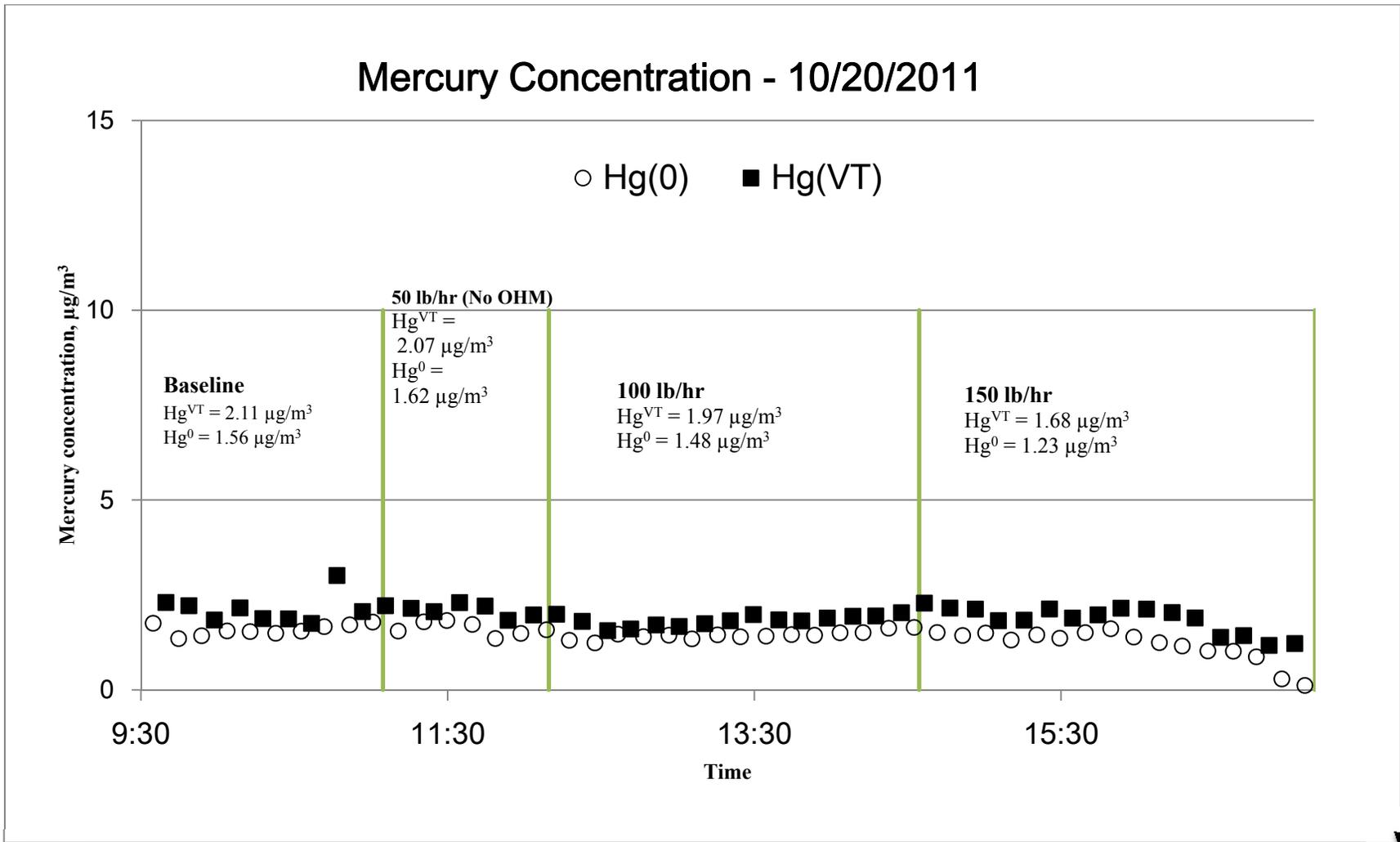


Figure 29. CMM data during PAC testing. The trend suggests that PAC did not increase oxidation of mercury in the system.

Conclusion for PAC injection at preheat fan location

Test results for short-term injection of plain powdered activated carbon (PAC) indicated that PAC did not significantly reduce stack mercury emissions. Even though PAC showed sequestering capabilities in the scrubber slurry, it would not be sufficient to attain the goal of 75% reduction in stack mercury emissions. Consequently, PAC was not investigated further in the test program.

DEDTC addition to scrubber slurry

The last technology tested was the addition of a scrubber additive diethyl dithiocarbamate (DEDTC); the test was performed on Oct 19. DEDTC is a mercury complexing agent used to improve oxidized mercury capture in the scrubber by reducing Hg^D concentrations. Testing of DEDTC was performed in two steps. The first step involved testing DEDTC without any other additive or sorbent. This test was conducted to determine whether DEDTC could improve the capture of oxidized mercury not already captured by scrubber liquids. The second step of testing involved DEDTC as well as ESORB-HG-11 to aid in mercury oxidation in the flue gas. The idea behind the second step was that injection of ESORB-HG-11 at 50lb/hr would increase oxidation of mercury species upstream of the scrubber while DEDTC would capture the oxidized mercury in the scrubber liquids. The results from these two steps would also be compared to test results from Oct 17 during which ESORB-HG-11 was injected at a rate of 50 lb/hr .injection.

In the first step, DEDTC was added to the scrubber recirculation tank by dosing to maintain a concentration of 1.4 mg/L, which was later increased to 7.0 mg/L. Scrubber slurry samples were collected at least one hour after dosing the recirculation tank. Stack mercury concentrations and slurry analysis during this test period showed no impact on mercury emissions after dosing of scrubber slurry with DEDTC. The results are shown in Figures 30 - 32. On the contrary, the Hg^D increased from low baseline values. This was attributed to left over ESORB-HG-11 from the previous test conducted on Oct 18 and not the chelating effects of DEDTC.

In the second stage of testing, which involved both the addition of the DEDTC to the scrubber recirculation tank and the injection of ESORB-HG-11 at the preheat fan inlet location, the mercury concentration in the stack gases decreased as expected. This is shown in Figure 31. However, the reduction in mercury emissions was similar with and without the addition of DEDTC to the scrubber slurry. This indicates that the entire impact on the mercury concentrations was from the injection of the brominated sorbent. Injection of ESORB-HG-11 also decreased Hg^D in the scrubber slurry filtrate after just two hours of injection (Figure 30). In summary, injection of the scrubber additive DEDTC did not improve mercury capture or mercury sequestration.

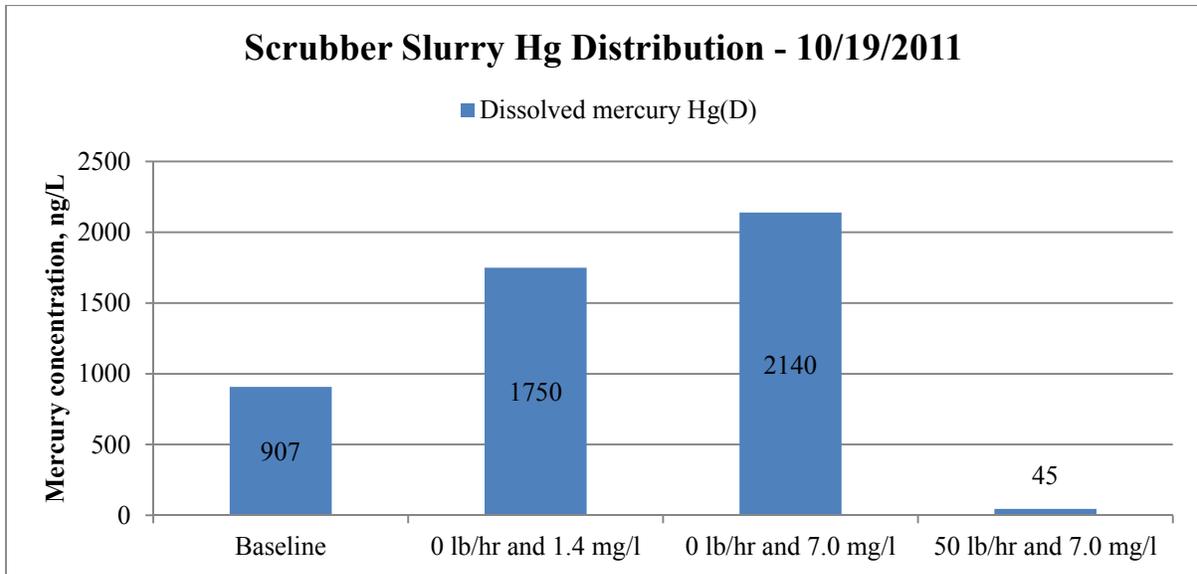


Figure 30. Hg^D is seen to increase even after addition of DEDTC up to 7.0 mg/L. The scrubber slurry two hours into injection of ESORB-HG-11 at 150 lb/hr saw Hg^D drop from 2140 to 45 ng/L.

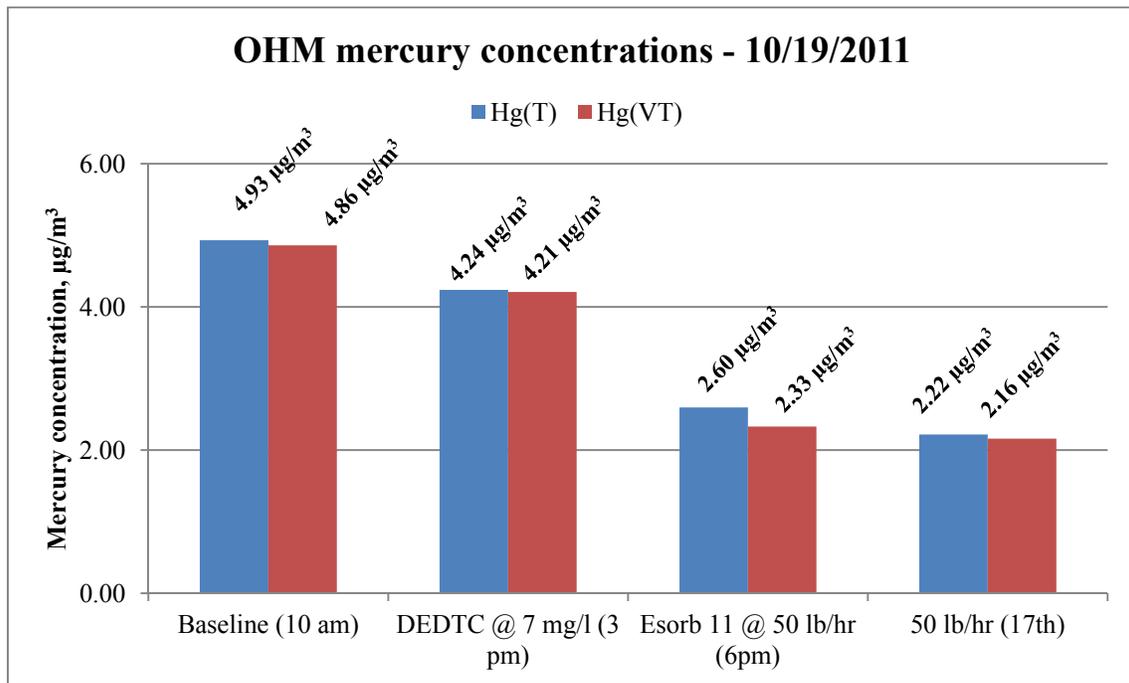


Figure 31. OHM during DEDTC testing and comparing 50 lb/hr injection with that of Oct 17th. Decrease in OHM measurements for DEDTC at 7 mg/L is assumed to be based on fluctuations in the system as confirmed by the CMM chart below. Comparing both 50-lb/hr tests suggests that DEDTC + ESORB-HG-11 shows similar reduction as for ESORB-HG-11 only.

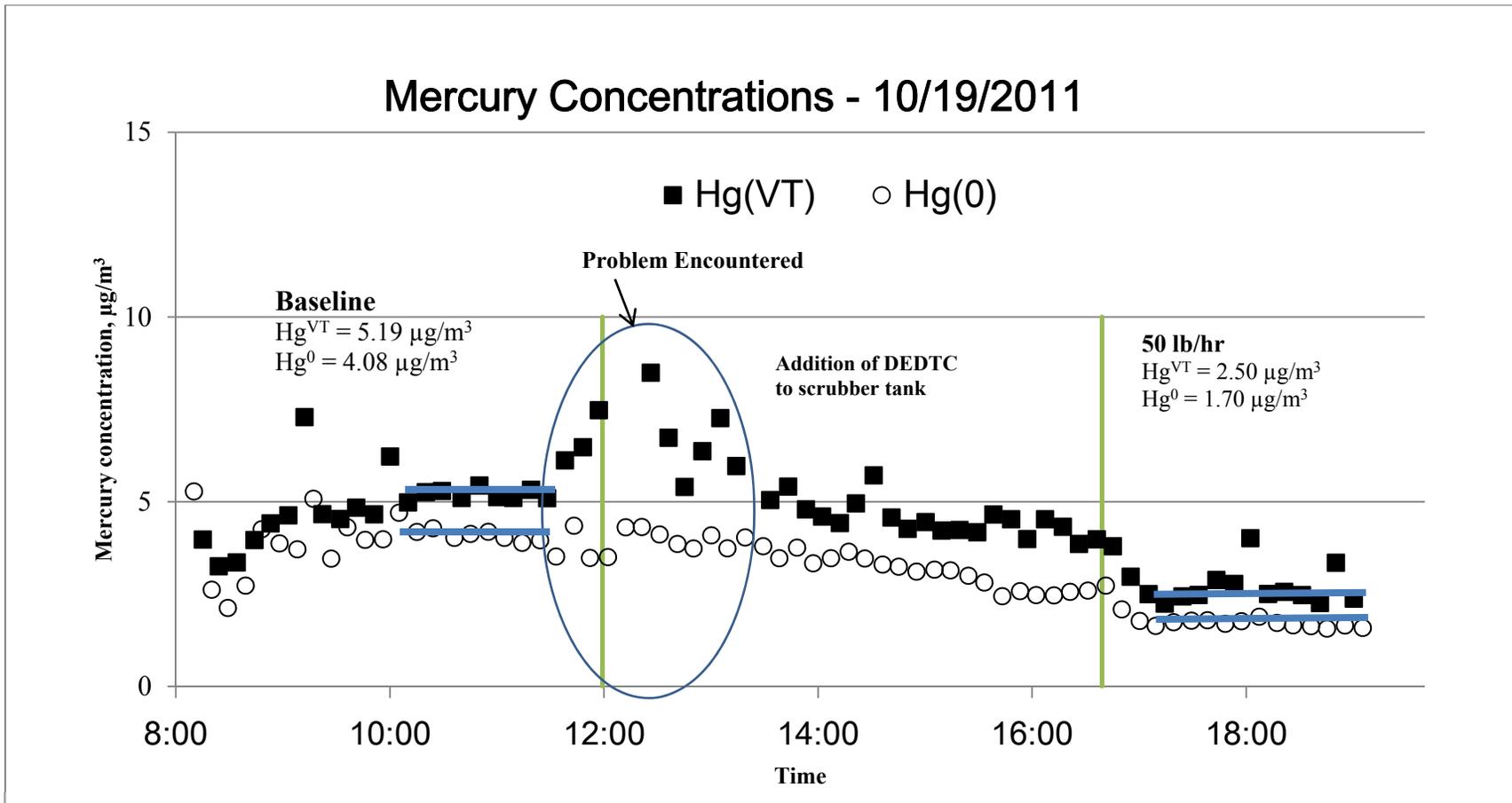


Figure 32. Showing CMM data during addition of DEDTC to scrubber followed by injection of 50 lb/hr of ESORB-HG-11 to the preheat fan inlet. After the problem with the CMM analyzer, the Hg^{VT} values decreased only slightly, if at all. However, once ESORB-HG-11 injection is started, mercury concentrations are seen to decrease sharply.

Conclusion on testing of DEDTC

Addition of the scrubber additive, DEDTC to the scrubber waters resulted in no observable effects on the mercury concentration/speciation in either the taconite process flue gases or the dissolved mercury concentration in the scrubber slurry.

Mercury Reductions with Average Baseline Mercury Emissions

From the tests conducted, ESORB-HG-11 was the only additive that showed the potential to attain the objective of 75% reduction in mercury emissions. However, to fully estimate the actual reduction potential of ESORB-HG-11 as a function of injection loading, it is first necessary to estimate a baseline Hg emission rate for the plant. This is calculated by taking the average of all baseline Hg^T measurements obtained during the test period (Oct 13 - 26). The result of averaging out the baseline measurements was $\text{Hg}^T = 5.20 (\pm 1.30) \mu\text{g}/\text{m}^3$. The percent reduction as a function of additive injection rate was then estimated using Equation (3):

$$\% \text{ Hg Reduction} = \frac{\text{HgB}_{\text{ave}} - \text{HgS}_{\text{ave}}}{\text{HgB}_{\text{ave}}} * 100 \quad \dots (3)$$

Where HgB_{ave} is the average baseline Hg^T and HgS_{ave} is the final stack Hg^T concentration during long-term injection.

Long-term testing at 150 lb/hr of ESORB HG-11 gave a final stack concentration of Hg^T of $1.50 \mu\text{g}/\text{m}^3$, which corresponds to a 71% reduction. ESORB-HG-11 injection at 100 lb/hr gave Hg^T of $1.95 \mu\text{g}/\text{m}^3$, which corresponds to a 63% reduction.

In addition, there was a significant increase in Hg^P during injection of ESORB-HG-11. The increase was attributed to poor capture of ESORB-HG-11 by the scrubber. Improving the capture of Hg^P in the scrubber should provide a further decrease in the stack mercury emissions. From the total vapor phase mercury (Hg^{VT}) concentrations taken at ESORB-HG-11 injection rates of 150 lb/hr and 100 lb/hr, the respective stack concentrations were $0.83 \mu\text{g}/\text{m}^3$ and $1.40 \mu\text{g}/\text{m}^3$, which correspond to stack emissions reductions of 82% and 73%, respectively. This suggests that improving particulate capture in the scrubber would further improve the reduction of mercury emissions. Figure 33 summarizes the reductions discussed as well as the significant contributions from Hg^P .

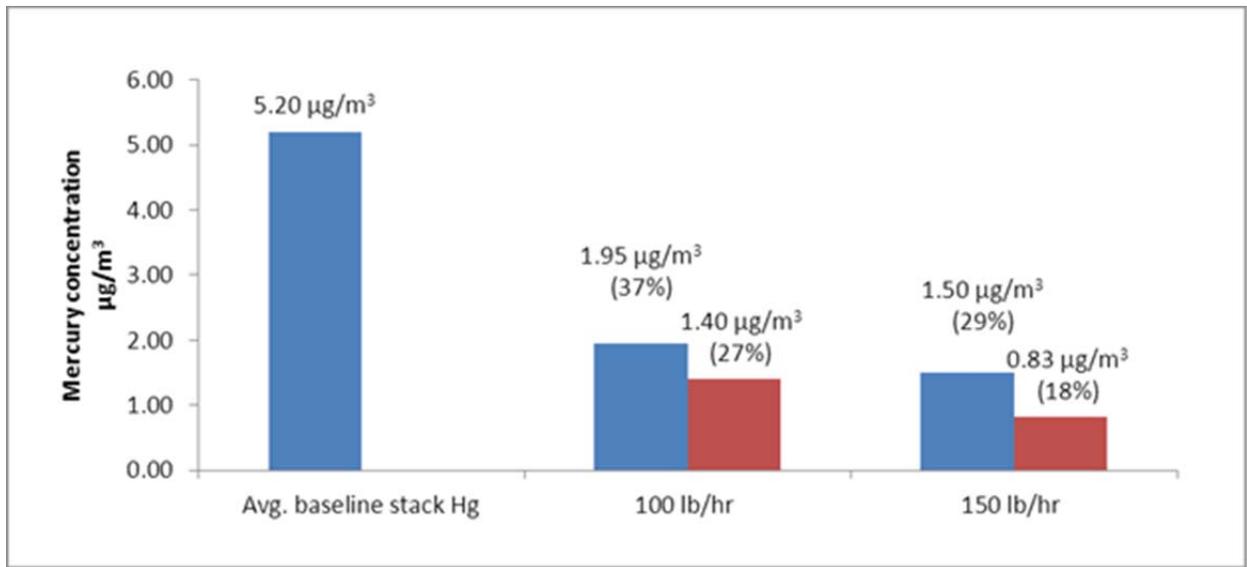


Figure 33. Potential reductions from ESORB-HG-11 as a function of long-term testing with injection rates of 100 lb/hr and 150 lb/hr.

CONCLUSION

Of all the additives tested, ESORB-HG-11 showed the greatest potential to attain target mercury reductions of 75% at injection rates of 100 to 150 lb/hr. The Hg^{VT} concentrations in the stack gases were $1.40 \mu\text{g}/\text{m}^3$ and $0.83 \mu\text{g}/\text{m}^3$ for 100 lb/hr and 150 lb/hr injection rates, respectively; compared to average baseline values of $5.20 \mu\text{g}/\text{m}^3$. However, Hg^{P} increased with injection of ESORB-HG-11, indicating that ESORB-HG-11 penetrates the scrubber. This resulted in Hg^{T} of $1.50 \mu\text{g}/\text{m}^3$ and $1.95 \mu\text{g}/\text{m}^3$ for 150 lb/hr and 100 lb/hr injection rates, respectively. Hg^{P} consists of mercury bound to ESORB-HG-11, a form which could be considered environmentally benign; however, additional research needs to be conducted for confirmation. The higher particulate mercury concentrations with sorbent injection decrease the potential mercury emission control effectiveness of the proposed technology. At an ESORB-HG-11 injection rate of 150 lb/hr, the emission reduction decreased from 84% to 70% and for the 100 lb/hr injection rate, the emission reduction decreased from 72% to 63%. Improved sorbent performance will require improved scrubber operation to increase particulate capture efficiencies.

Analysis of the scrubber slurry during testing showed significant decreases in dissolved mercury [Hg^{D}] during ESORB-HG-11 injection. These results point out the Hg^{D} sequestration capability of ESORB-HG-11. A majority of the injected ESORB-HG-11 that does not burn or coat the flue gas ducts gets captured by the scrubber waters and serves as an adsorbent for the dissolved mercury. This can be corroborated by the fact that ESORB-HG-11 was still present in the recirculation tank on days that were preceded by ESORB-HG-11 injection. As a result, Hg^{D} concentrations remained low for almost all test days except for days when the system had fully recovered (mainly occurring after a two-day weekend) and in the first week of testing. Consequently, use of ESORB-HG-11 for mercury capture ensures that recycling of scrubber waters does not increase the mercury released in the furnace and keeps stack emissions low by avoiding mercury build up in the system and through re-emission from the scrubber liquid.

REFERENCES

- Benson, S.A. *Controlling Mercury Emissions for Utilities Firing Lignites From North America*, Summary Report, 2007.
- Berndt, M. *Mercury and Mining in Minnesota*, Minerals Coordinating Committee, Department of Natural Resources (DNR), Minnesota, 2003.
- Berndt, M.; Engesser J.; Berquo, T.S. *Mercury Chemistry and Mossbauer Spectroscopy of Iron Oxides During Taconite Processing on Minnesota's Iron Range*, Department of Natural Resources (DNR), Minnesota, 2005.
- Berndt, M.; Engesser, J.; Johnson, A. *On the Distribution of Mercury in Taconite Plant Scrubber Systems*, Department of Natural Resources (DNR), Minnesota, 2003.
- Berndt, M.; Engesser, J. *Mercury Transport in Taconite Processing Facilities: (II) Fate of Mercury Captured by Wet Scrubbers*, Department of Natural Resources (DNR), Minnesota, 2005a.
- Berndt, M.; Engesser, J. *Mercury Transport in Taconite Processing Facilities: (II) Fate of Mercury Captured by Wet Scrubbers*, Department of Natural Resources (DNR), Minnesota, 2005b.
- Berndt, M.; Engesser, J. *Mercury Transport in Taconite Processing Facilities: (I) Release and Capture During Induration*, Department of Natural Resources (DNR), Minnesota, 2005a.
- Berndt, M. *On the Measurement of Stack Emissions at Taconite Processing Plants*, Department of Natural Resources (DNR), Minnesota, 2008.
- Galbreath, K.C. *Mercury Vaporization Characteristics of Taconite Pellets*, Final Report for the Minnesota Department of Natural Resources (Mn. DNR), 2005.
- Quality Assurance Project Plan*, prepared by the Minnesota Department of Natural Sources (Mn. DNR) August 2010

APPENDIX A: BENCH AND PILOT RESULTS

Bench Testing Summary

The bench scale tests consisted of dosing several 200 mL scrubber slurries, obtained from U.S. Steel Minntac Line 3, to a mercury concentration of 62.5 µg/L using mercuric chloride. A concentration of 62.5 µg/L was chosen based on mercury mass balance estimates from literature [Berndt and Engesser, 2005a and 2005b]. To each of these solutions, the additives were added on a mass basis following a low, mid and high level. Once added, the solutions were stirred for 10 minutes, an estimate of mercury residence time in the scrubber; filtered, and the filtrates submitted for mercury analyses. The resulting mercury concentrations provided an initial estimate for best loadings to be used in the pilot tests. See Figure A-1. From the bench tests, ESORB-HG-11 showed the best removal efficiencies for all the loadings tested. The other additives showed appreciable removal, too.

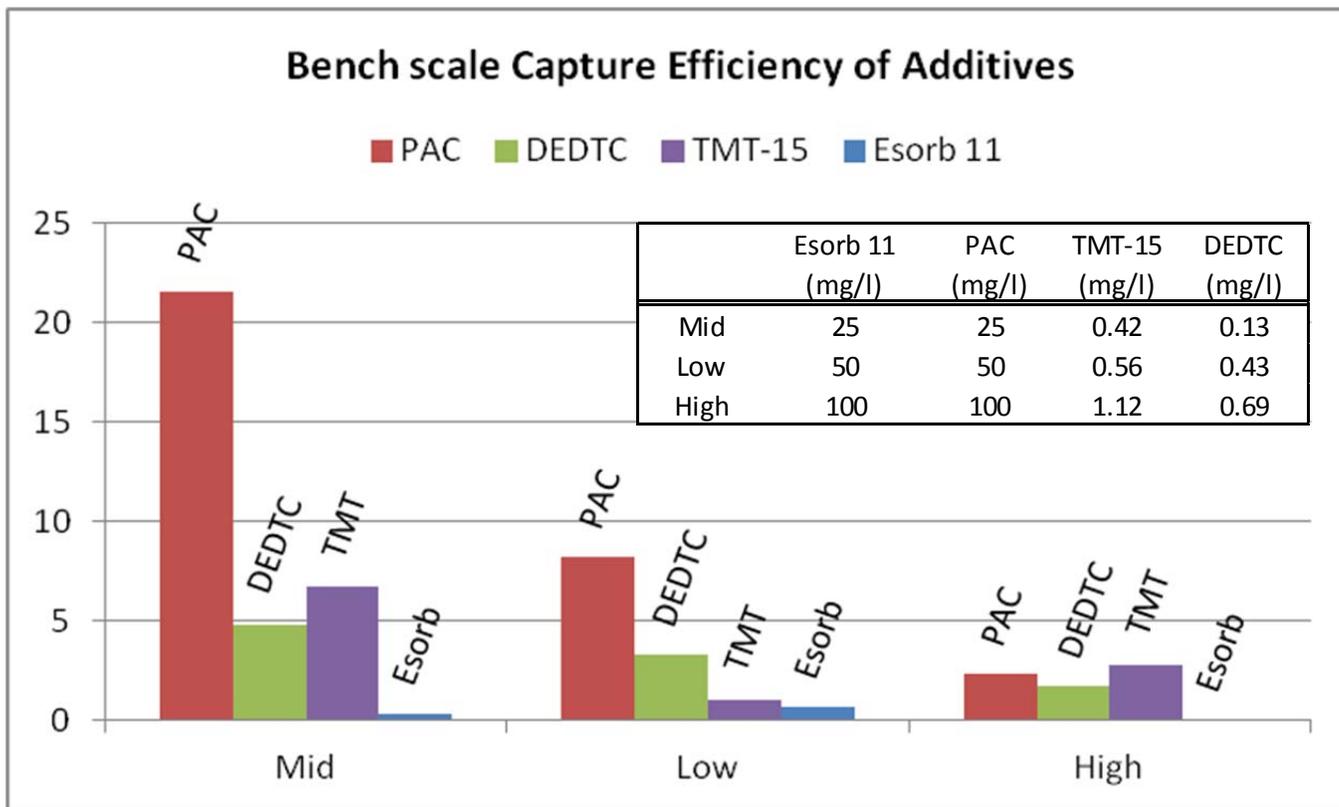


Figure A-1. Bench scale mercury test results for three levels of additive testing. Test involved spiking 200 mL of scrubber slurry with HgCl_2 to obtain a mercury concentration of $62.5 \mu\text{g/L}$. The four additives above were then added to solution and stirred for 10 minutes, filtered, and filtrate analyzed for Hg^{D} . Table in graph provides additive loading for the three levels analyzed. For ESORB-HG-11, 100 mg/L loading reduced mercury to non-detect levels. PAC, DEDTC and ESORB-HG-11 show increasing mercury capture with increase in loading, however, TMT-15 does not show any trend in mercury capture at loadings used.

Pilot Testing Summary

The pilot test consisted of a glass counter current scrubber with of a 30 L tank at the bottom and a 6 ft high scrubbing tower. The tank was connected to a diaphragm pump which circulated slurry from Minntac Line 3 through the scrubber when turned on. Flue gas generated from burning natural gas with a flow rate of approximately 40 L/min was used to simulate plant waste gas. The flue gas flowed through the scrubber from bottom to top with a sample obtained from sample ports at the top of the tower through two heated PFA (a substitute for Teflon™) tubes to a dual channel wet chemistry pre-treatment unit used to condition the sample gases before analysis by Cold Vapor Atomic Absorption Spectroscopy (CVAAS) in a dual channel Horiba DM-6B Continuous Mercury Monitor (CMM). Once the baseline mercury concentration was steady (region A in Figures A-2 to A-5), the flue gas was then spiked continuously with mercuric chloride generated using certified Dynacal permeation tubes and a constant temperature chamber called a Dynacalibrator, both manufactured by VICI Metronics; until a new steady state concentration was obtained (region B). The pump was then turned on with scrubber slurry from U.S.

Steel Minntac line 3 in the scrubber tank to obtain a new steady mercury concentration in the flue gas (region C). Once steady, the additive to be tested was added to the scrubber tank by dosing up to a concentration based on the bench tests. The mercury concentration in the scrubbed flue gas was then monitored. Each additive was tested twice. From the results obtained from testing all four additives, Figures B-2 to B-5, ESORB-HG-11 tested at a scrubber slurry concentration of 200 mg/L, was seen to be the most effective additive in the capture and sequestration of mercury for both tests carried out (Figure A-2). For the first test, a steady mercury concentration of approximately $20 \mu\text{g}/\text{m}^3$ was attained during mercury injection and slurry operation for both regions B and C, meanwhile, test 2 showed an increase in the Hg^{T} steady state value from region B to C, followed by a third increase in region C only. However, addition of ESORB-HG-11 led to a gradual decrease of 75% and 68% for tests 1 and 2 respectively. ESORB-HG-11 also showed lowest final Hg^{T} concentration for both tests, confirming it is the most effective additive for sequestration.

For the PAC test, Figure A-3, both tests showed an increase in mercury baseline when scrubbing started (region C). In the first test, PAC concentration in the scrubber slurry was initially 100 mg/L but very little reduction was observed (D'). It was then increased to 200mg/L and a 39% drop was observed. For the second test, a drop of 53% was observed.

Diethyl dithiocarbamate (DEDTC) also showed an increase in mercury baseline when scrubbing started (region C of Figure A-4). DEDTC concentration for the first test was 1.1 mg/L, had a higher steady state concentration of mercury and a final reduction of 46% when DEDTC. Test 2 showed a reduction of just 31% after using a higher DEDTC concentration of 2.2 mg/L.

Tests using TMT-15 used concentrations 10 and 20 mg/L, Figure A-5. During the first test (10 mg/L), a decrease in steady state mercury concentration was observed (region C). This was the only test that showed this behavior and the possible cause is unknown. However, Test 1 showed decreases in mercury concentration of 58%. Test 2 did show a lower reduction potential for TMT-15 of 36%, even though the concentration of TMT-15 was increased from 10 to 20 mg/L.

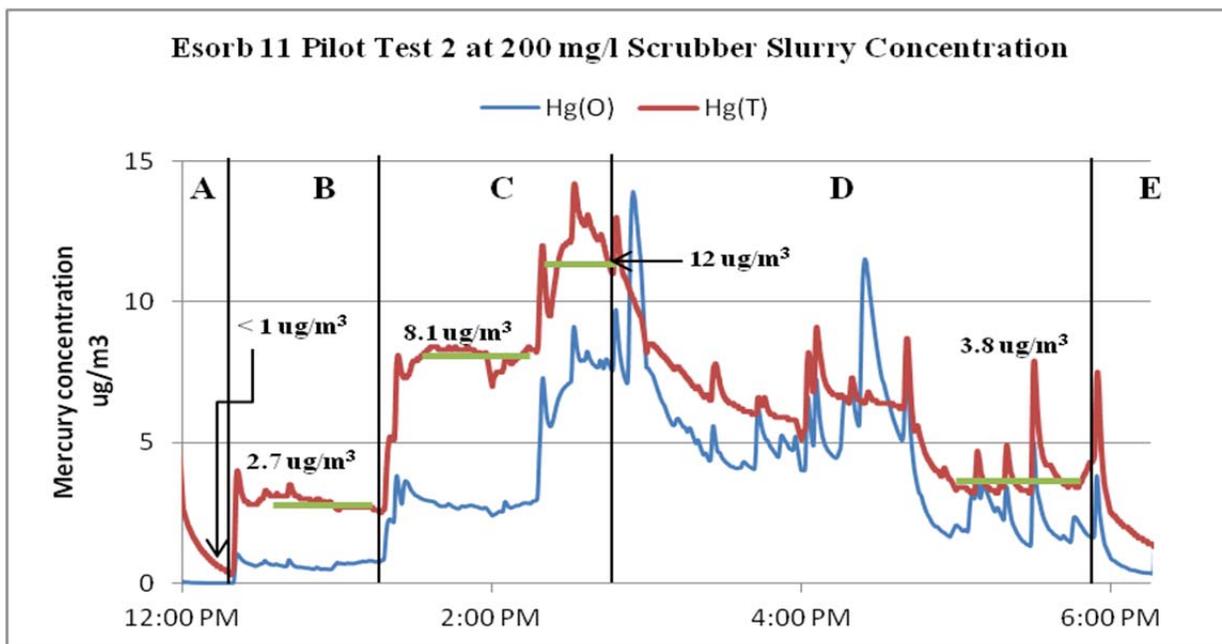
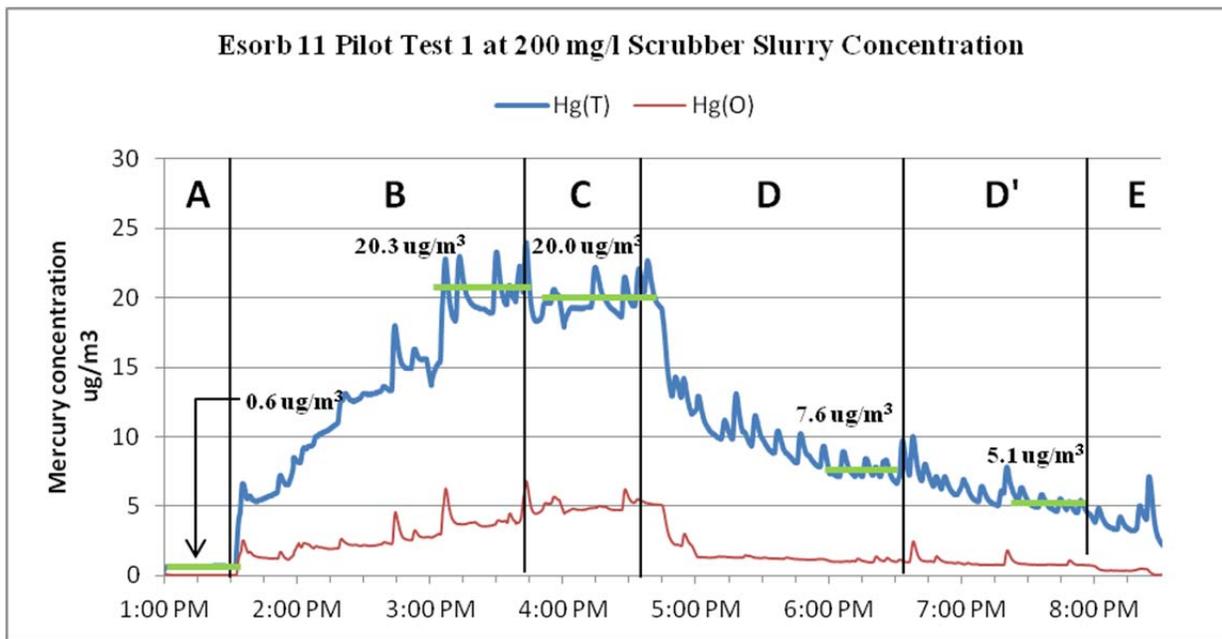


Figure A-2. Pilot scale test results when testing ESORB-HG-11 at 200 mg/L in scrubber slurry. Region A is scrubber baseline mercury concentration; B injection of mercuric chloride into scrubber flue gas until steady state; region C, scrubbing using line 3 slurry; D addition of ESORB-HG-11 by dosing the slurry to a concentration of 100 mg/L for test 1 and 200 mg/L for test 2; D' for test 1 only, increased ESORB-HG-11 concentration in slurry from 100mg/L to 200 mg/L; E Injection of mercury stopped.

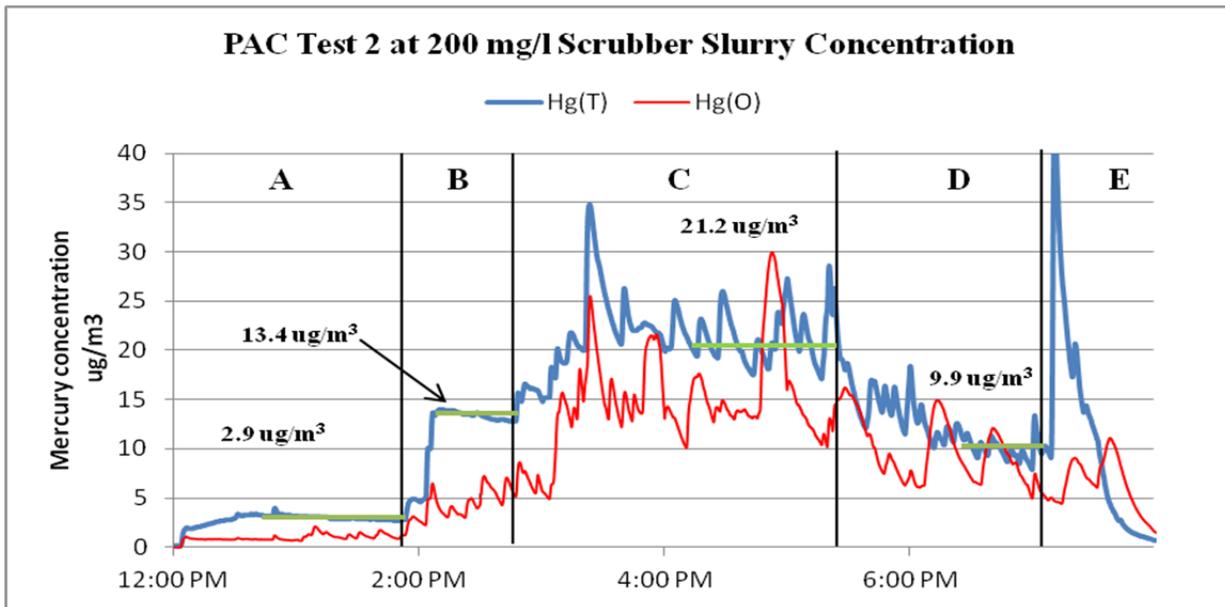
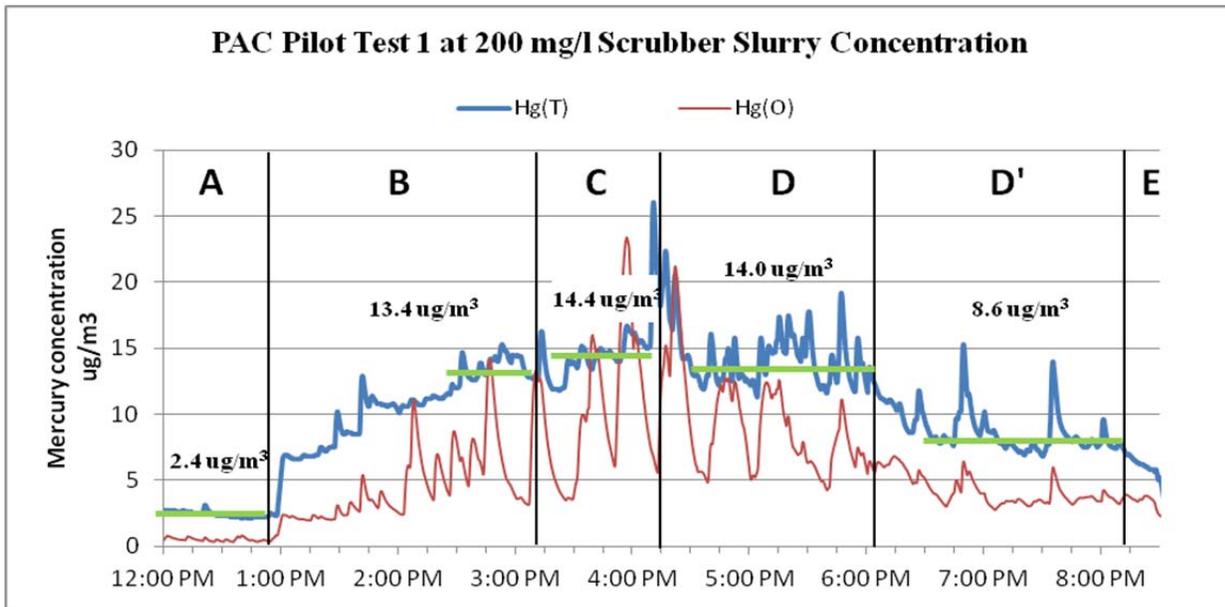


Figure A-3. showing two pilot scale test results when testing PAC at 200 mg/L in scrubber slurry. Region A is scrubber baseline mercury concentration; B injection of mercuric chloride into scrubber flue gas until steady state; region C, scrubbing using line 3 slurry; D addition of PAC by dosing the slurry to a concentration of 100 mg/L for test 1 and 200 mg/L for test 2; D' for test 1 only, increased PAC concentration in slurry from 100mg/L to 200 mg/L; E Injection of mercury stopped.

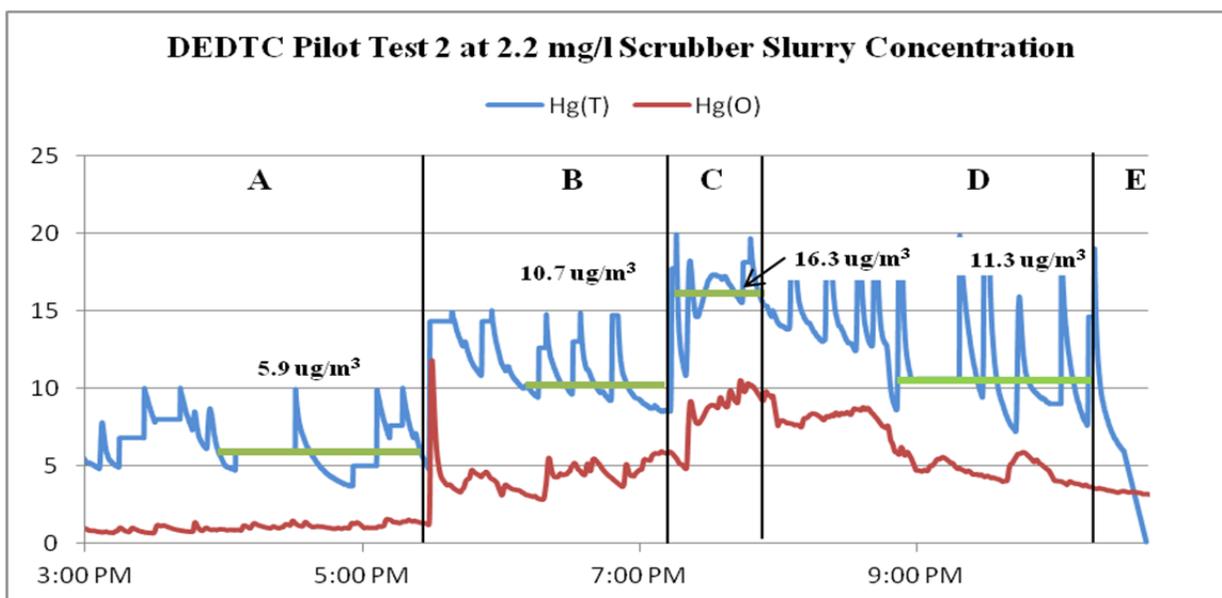
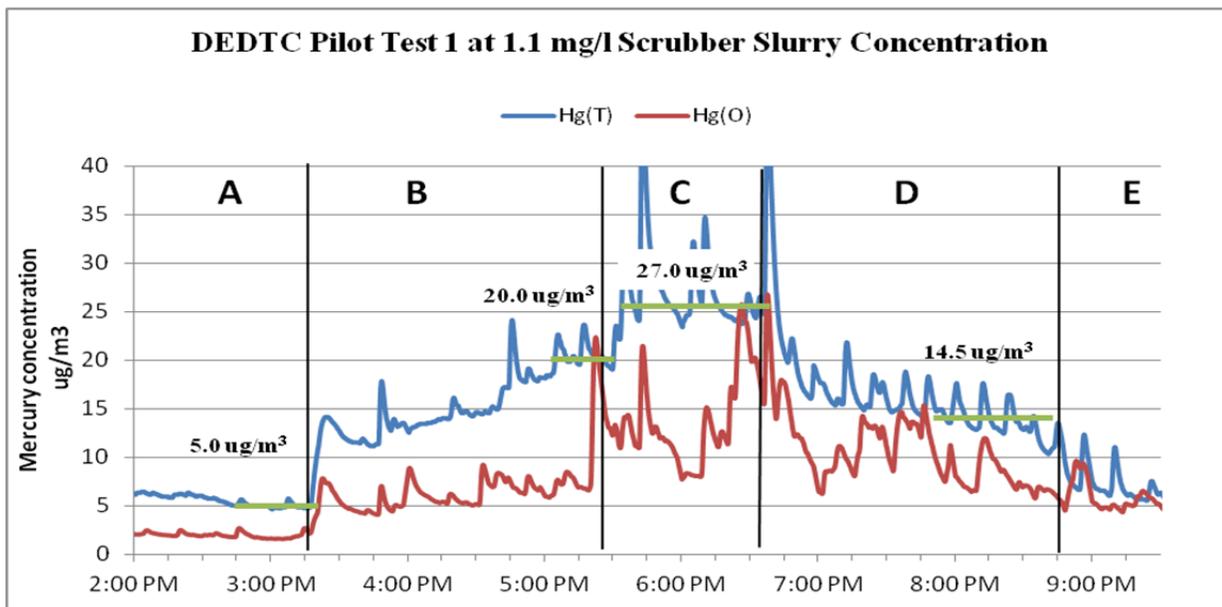


Figure A-4. Pilot scale test results when testing DEDTC at 1.1 and 2.2 mg/L in scrubber slurry. Region A is scrubber baseline mercury concentration; B injection of mercuric chloride into scrubber flue gas until steady state; region C, scrubbing using line 3 slurry started; D addition of DEDTC by dosing the slurry to a concentration of 1.1 or 2.2 mg/L; E Injection of mercury stopped.

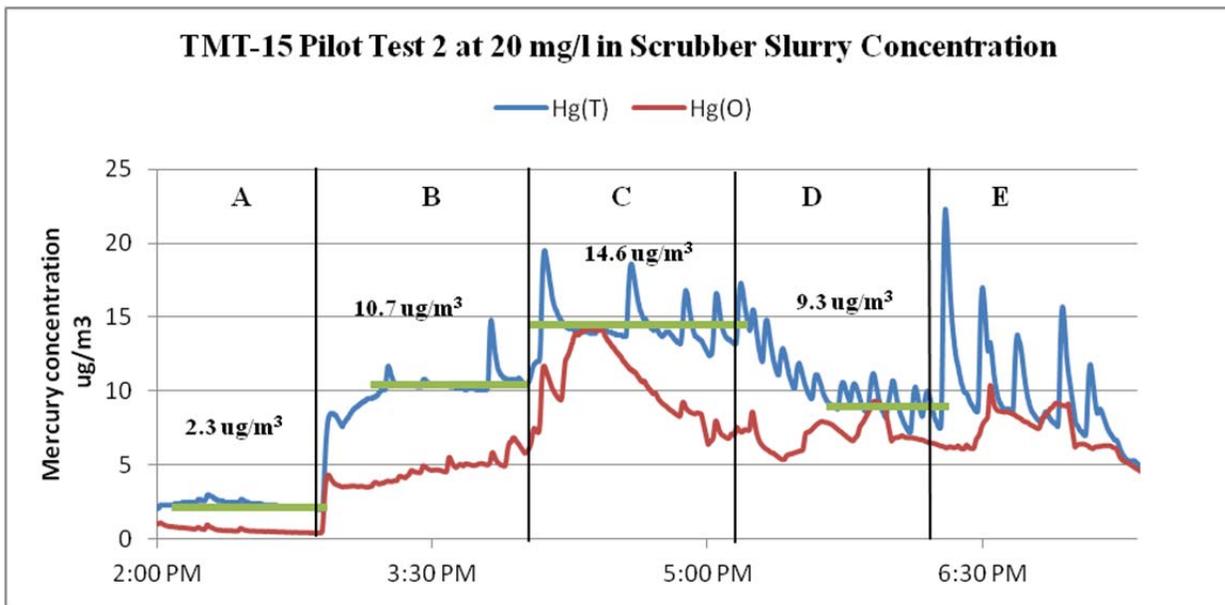
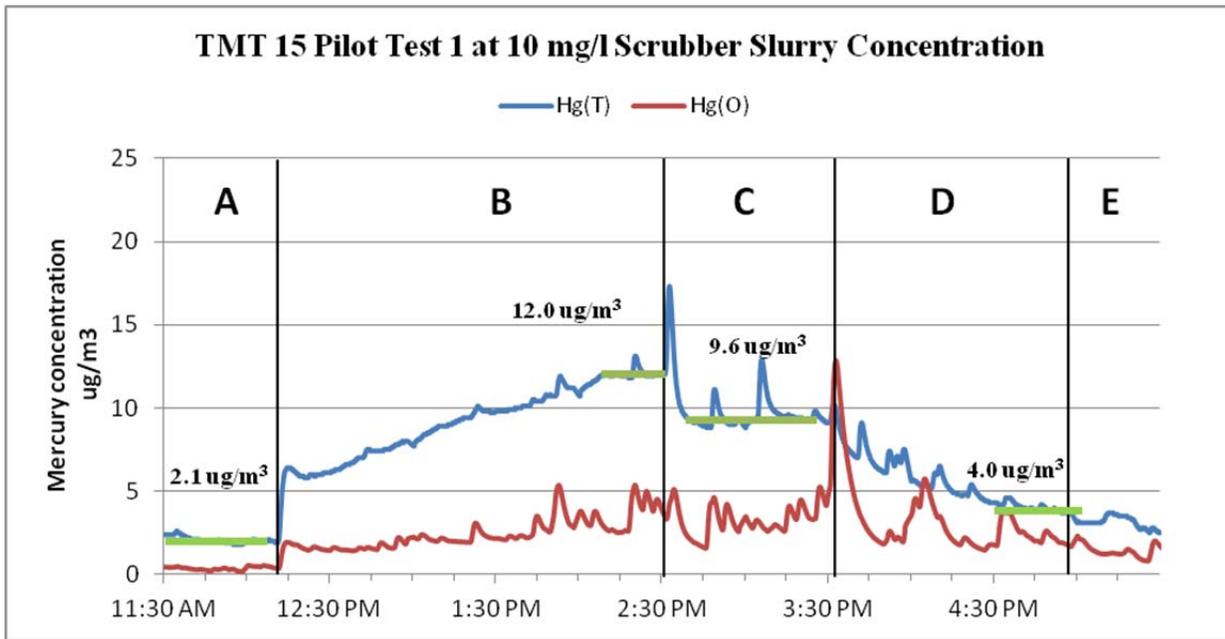


Figure A-5. Pilot scale test results when testing TMT 15 at 10 and 20 mg/L in scrubber slurry. Region A is scrubber baseline mercury concentration; B injection of mercuric chloride into scrubber flue gas until steady state; region C, scrubbing using line 3 slurry started; D addition of TMT-15 by dosing the slurry to a concentration of 10 or 20 mg/L; E Injection of mercury stopped.

APPENDIX B – ADDITIONAL FIELD DATA

Table B-1. OHM raw data for all test days.

DATE	Run	Hg ²⁺ (µg/m ³)	Hg ⁰ (µg/m ³)	Hg ^{VT} (µg/m ³)	Hg ^P (µg/m ³)	Hg ^T (µg/m ³)
20111013**	Baseline 1	0.75	3.70	4.45	n/a	4.45
	Baseline 2	0.95	3.98	4.93	n/a	4.93
	Baseline 3	0.55	4.64	5.19	0.00	5.19
20111014**	Baseline	0.83	5.86	6.69	n/a	6.69
	100lb/hr ESORB-HG-11	0.49	2.36	2.85	0.13	2.98
20111017	Baseline***	2.40	5.82	8.22	0.02	8.24
	50 lb/hr ESORB-HG-11	0.45	1.71	2.16	0.06	2.22
	150 lb/hr ESORB-HG-11	0.08	1.14	1.22	0.59	1.81
20111018	Baseline	0.82	5.35	6.17	0.03	6.20
	100 lb/hr ESORB-HG-11	0.37	1.40	1.77	0.33	2.10
	100 lb/hr ESORB-HG-11	0.33	1.07	1.4	0.55	1.95
20111019	Baseline	0.23	4.63	4.86	0.07	4.93
	DEDTC at 7 mg/l	0.31	3.90	4.21	0.03	4.24
	50 lb/hr ESORB-HG-11	0.24	2.09	2.33	0.27	2.60
20111020	Baseline	0.30	3.14	3.44	0.03	3.47
	100 lb/hr PAC	0.24	2.51	2.75	0.03	2.78
	150 lb/hr PAC	0.26	2.31	2.57	0.04	2.61
20111021	Baseline	0.54	4.5	5.04	0.02	5.06
	150 lb/hr ESORB-HG-11	0.22	0.61	0.83	0.67	1.50
20111024	Baseline	0.60	4.38	4.98	0.08	5.06
	75 lb/hr ESORB-HG-11	0.30	1.91	2.21	0.77	2.98
	75 lb/hr ESORB-HG-11	0.21	1.5	1.71	0.99	2.70
20111025	Baseline	0.46	3.35	3.81	0.20	4.01
	75 lb/hr ESORB-HG-11	0.27	1.91	2.18	0.60	2.78
20111026	Baseline	0.25	3.84	4.09	0.10	4.19
	75 lb/hr ESORB-HG-11	0.40	1.65	2.05	1.09	3.14

* Under local O2 concentration, dry basis.

** Hg(P) is for entire test period.

*** Hg(2+) is unusually high.

Table B-2. Multiclone Hg(P) concentration. No samples were collected on the 14th because sampling location inaccessible. NA refers to sample collection periods where no significant samples were collected from scrubber blowdown dust.

Date collected	Time collected	Hg(P) ng/g
10/14/2011	No Samples Collected	
	1:00 PM	139
10/17/2011	4:00 PM	82
	6:00 PM	42
	9:50 AM	NA
10/18/2011	2:40 PM	212
	5:30 PM	NA
	10:30 AM	45
10/19/2011	2:30 PM	15
	4:10 PM	26
	5:55 PM	90
	8:50 AM	90
10/20/2011	12:20 PM	NA
	2:00 PM	182
	4:20 PM	451
10/21/2011	11:15 AM	65
	4:05 PM	86
	10:00 AM	47
10/24/2011	12:45 PM	NA
	3:30 PM	40

Table B-3. OHM results and CMM concentrations during the same time period.

Date	Time	Loading	OHM	CMM		OHM	CMM	
			Hg ⁰ (µg/m ³)	Hg ⁰ (µg/m ³)	Std Dev	Hg ^{VT} (µg/m ³)	Hg ^{VT} (µg/m ³)	Std Dev
20111026	8:15am to 9:20am	Baseline	3.84	4.03	0.37	4.09	4.55	0.30
	4:15pm to 5:15pm	100 lb/hr-ESORB-HG-11	1.65	1.81	0.21	2.05	2.3	0.3
20111025	8:15am to 9:15am	Baseline	3.35	3.11	0.29	3.81	4.39	0.39
	2:05pm to 3:10pm	75 lb/hr-ESORB-HG-11	1.91	1.57	0.07	2.18	2.30	0.11
20111024	8:50am to 10:08am	Baseline	4.38	3.56	0.16	4.98	5.11	0.41
	12:00pm to 1:00pm	75 lb/hr-ESORB-HG-11	1.91	1.26	0.08	2.21	2.11	0.08
	2:30pm to 3:35pm	75 lb/hr-ESORB-HG-11	1.5	1.16	0.04	1.71	2.05	0.13
20111021	10:55am to 11:58am	Baseline	4.50	3.12	0.50	5.04	3.96	0.13
	4:00pm to 5:08pm	150 lb/hr-ESORB-HG-11	0.61	0.33	0.05	0.83	0.61	0.07
20111020	9:50am to 11:00am	Baseline	3.14	1.56	0.14	3.44	2.11	0.38
	1:25pm to 2:25pm	100 lb/hr-PAC	2.51	1.48	0.07	2.75	1.97	0.15
	3:50pm to 5:10pm	150 lb/hr-PAC	2.31	1.23	0.26	2.57	1.68	0.42
20111019	10:15am to 11:20am	Baseline	4.63	4.08	0.13	4.86	5.19	0.15
	3:20pm to 4:20pm	7 mg/l-DEDTC	3.9	2.68	0.27	4.21	4.29	0.28
	6:00pm to 7:20pm	50 lb/hr-ESORB-HG-11	2.09	1.68	0.11	2.33	2.43	0.12
20111018	8:30am to 9:50am	Baseline	5.35	n/a	n/a	6.17	n/a	n/a
	2:15pm to 3:40pm	100 lb/hr-ESORB-HG-11	1.4	1.22	0.15	1.77	1.53	0.11
	4:40pm to 5:45pm	100 lb/hr-ESORB-HG-11	1.07	0.80	0.10	1.4	1.15	0.14
20111017	8:50am to 10:10am	Baseline	5.82	5.12	0.30	8.22	7.08	0.88
	12:10pm to 1:40pm	50 lb/hr-ESORB-HG-11	1.71	2.12	0.16	2.16	2.93	0.21
	5:50pm to 7:20pm	150 lb/hr-ESORB-HG-11	1.14	0.53	0.06	1.22	1.07	0.29
20111014	9:10am to 10:25am	Baseline	5.86	4.26	0.10	6.69	5.65	0.08
	6:40pm to 7:50pm	100 lb/hr-ESORB-HG-11	2.36	1.16	0.25	2.85	1.98	0.57
20111013	12:00am to 1:20pm	Baseline 1	3.70	2.32	0.26	4.45	4.24	0.41
	2:30pm to 3:50pm	Baseline 2	3.98	2.58	0.13	4.93	3.88	0.30
	5:00pm to 6:20pm	Baseline 3	4.64	2.78	0.08	5.19	4.1	0.32

Table B-4. Scrubber slurry sample analysis results.

Date	Time collected	Hg ^D ng/L	TSS (%)	Comments	
10/13/2011	6:00 PM	5000	NA*	Replicate	
	6:00 PM	5000	NA*		
10/14/2011	10:05 AM	1100	0.68	Hg ^D below MDL	
	8:20 PM	< 200	0.68		
10/17/2011	9:35 AM	< 200	ND**	Blank, Hg ^D below MDL	
	9:45 AM	600	0.67		
	12:45 PM	NA	0.58		
	3:55 PM	NA	0.64		
	6:20 PM	< 200	0.59		
10/18/2011	10:00 AM	< 200	ND**	Blank, Hg ^D below MDL	
	10:00 AM	600	0.88		
	2:40 PM	45	0.65		
	5:10 PM	NA*	0.75		
10/19/2011	11:05 AM	907	0.39		
	2:00 PM	1750	0.78		
	3:55 PM	2140	0.99		
	6:20 PM	45	1.04		
10/20/2011	9:05 AM	< 200	0.76	Hg ^D below MDL	
	12:10 PM	NA*	0.65		
	2:05 AM	25.7	0.69		
	2:15 PM	24.6	ND**		Duplicate
	4:30 PM	17.1	0.67		
10/21/2011	11:10 AM	NA*	ND**	Blank	
	11:10 AM	82	0.59		
	4:15 PM	21.1	0.36		
10/24/2011	9:30 AM	3970	0.77	Blank	
	12:25 PM	NA*	0.64		
	3:15 PM	NA*	ND**		
	3:15 PM	599	0.80		

*Not analyzed. For 10/13/2011, TSS was not determined. For all other days, due to large volume of samples collected, only samples deemed necessary submitted for analysis. Necessity determined by collection period, steady state of CMM measurements, and injection condition.

**Not determined because either not applicable (blanks) or required samples not analyzed.