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EVALUATING THE EFFECTIVENESS OF PROPRIETARY ADDITIVES IN
IMPROVING THE CAPTURE AND SEQUESTRATION OF OXIDIZED MERCURY
IN SCRUBBER SYSTEMS

by

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A Thesis

Submitted to the Graduate Faculty

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2012

This thesis, submitted by Junior Neguieh Domkam Nasah in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done, and is hereby approved.

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This thesis is being submitted by the appointed advisory committee as having met all of the requirements of the Graduate School at the University of North Dakota and is hereby approved.

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Dean of the Graduate School

Title Evaluating the Effectiveness of Proprietary Additives in Improving
 Capture and Sequestration of Oxidized Mercury in Scrubber Systems

Department Chemical Engineering

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Junior Neguieh Domkam Nasah
February 13, 2012.

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ABSTRACT

Mercury released during thermal processing (induration) of beneficiated taconite ore (referred to as green balls) can be captured by scrubber waters if it is in an oxidized form. Consequently, mercury emissions from Taconite facilities can be reduced by oxidation of the mercury released from the green balls, followed by capture in their scrubbers. Moreover, sequestration of the captured mercury from the scrubber slurry could prevent possible (re-)emission by ensuring that the driving force for oxidized mercury capture by scrubber liquids is at an optimum; and prevent recycling of captured mercury back to previous process steps.

This research investigates the ability of certain proprietary additive-based technologies to achieve oxidation, capture and sequestration of mercury in Taconite facilities. The said additive-based technologies have showed successful mercury control capabilities in coal-fired utilities, but need to be retrofitted for Taconite facilities. The additive-based technologies consist of the injection of powdered activated carbon (PAC) and ESORB-HG-11 (a halogenated PAC) into the waste gas of a selected Taconite facility and dosing of the plant's scrubber slurry with diethyl dithiocarbamate (DEDTC).

Testing of the technologies was done in three steps: bench- , pilot- , and field-scale testing. Bench-scale testing was done to determine sequestering capabilities of the additives used in the technologies investigated, and it involved testing the interaction of

PAC, ESORB-HG-11, diethyldithiocarbamate (DEDTC), and a fourth additive, TMT-15®; with mercuric chloride in a 200 ml scrubber slurry sample obtained from a Taconite facility. Pilot-scale testing was a scale up of the bench-scale tests using a glass scrubber consisting of a 30 L tank and a 6 ft high scrubbing tower for scrubbing mercuric chloride. Flue gas generated from combusting methane (natural) gas was spiked with mercuric chloride generated by permeation tubes from VICI Metronics, and scrubbed using a Taconite plant's scrubber slurry that was dosed with the additives.

The final step involved testing of the three best additives: ESORB-HG-11, PAC and DEDTC; at United States (U.S.) Steel Minnesota Taconite (Minntac) Plant –Line 3. ESORB-HG-11 and PAC were injected in Line 3's waste gas. DEDTC was added to scrubber re-circulating tank. ESORB-HG-11 technology was the most successful with injection resulting in reductions in stack mercury emissions of up to 80% (oxidation and capture of mercury), while scrubber liquids dissolved mercury concentration decreased by greater than 90% (sequestration). However, during ESORB-HG-11 testing, an increase in particulate mercury (Hg^P) was observed, suggesting that the ESORB-HG-11 penetrates the scrubber as a result of its fine particulate size.

ESORB-HG-11 was the only additive-based technology that showed potential of oxidation, capture and sequestration when tested at U.S. Steel Minntac Line 3. Additional testing would however be required to retrofit this technology in other Taconite facilities and/or Lines. Measures also need to be taken to address the increase in Hg^P observed during ESORB-HG-11. Finally, potential separation steps for mercury sequestered in scrubber solids also need to be investigated based on the way each facility handles its scrubber slurry.

CHAPTER I

INTRODUCTION

The Great Lakes – Superior, Michigan, Huron, Erie and Ontario; comprise the largest fresh surface water systems on earth (1); and are bordered by eight states of the United States of America (USA). In 1978, an amendment to the 1972 historic agreement known as the *Great Lakes Water Quality Agreement (GLWQA)* was signed between the USA and Canada to maintain the chemical, physical and biological integrity of the Great Lakes Basin Ecosystem (2). Another amendment to GLWQA in 1987 led to the development and implementation of Lakewide Management Plans (LaMP) for each Great Lake, aimed at identifying the critical pollutants that affect the beneficial uses of the lake and outline strategies necessary to reduce loadings and restore those uses (3). The research covered in this thesis was funded partly due to the desire to achieve the requirements of the LaMP established for Lake Superior.

Lake Superior is the largest of the Great Lakes and is bordered by the states of Minnesota, Wisconsin, Michigan, and the Canadian province of Ontario. Its integrity is protected not just by its LaMP, established through the 1978 GLWQA amendment, but also by the *Lake Superior Binational Program* established in 1991 (4) and the Clean Water Act. The first two programs required establishing a Zero Discharge Demonstration Program aimed at achieving zero discharge and zero emission (or virtual elimination) of

nine toxic, persistent and bio-accumulative chemicals through a four stage approach: 1) defining the problem and identifying critical pollutants; 2) establishing load reduction schedules; 3) selecting remedial measures; 4) confirming, through monitoring, that the contributions of all critical pollutants towards impairment of lake integrity have been eliminated (5). The nine toxins identified were mercury, total polychlorinated biphenyls (PCB), dieldrin/aldrin, chlordane, dichlorodiphenyltrichloroethane (DDT), toxaphene, dioxin, hexachlorobenzene (HCB) and octachlorostyrene (OCS). Load reduction schedules were set for all the nine toxins listed above with specific deadlines. This research focuses on efforts undertaken to eliminate mercury. Meanwhile, the Clean Water Act (CWA) required that every state establish Water Quality Standards for their rivers, streams, lakes and wetlands (6). These standards identified required levels for pollutants, such as mercury, that were required in order to protect human health, fish, and wildlife. Permits were to be issued by the states or the EPA, to persons discharging mercury into waters.

Ongoing mercury discharge/deposition into the Lake Superior basin was identified in stage 2 of its LaMP to come from several different sources ranging from municipal discharge to industrial and mining activities in 1990. Significant reductions in these discharges/deposits were reported in 1999 suggesting that measures taken so far to reduce mercury were effective. However, the mining sector of the state of Minnesota was identified as the one area in which more reduction work needs to be done (7). Looking at Table 1 below, it is observed that the most significant source of mercury to Lake Superior is from mining. The main mining activity around Lake Superior's basin is taconite ore

mining and beneficiation. A sector specific reduction strategy is thus needed to reduce these emissions significantly.

Table 1: Ongoing Release: Mercury to Air and Water from sources in the Lake Superior Basin, 1990 and 1999 (kg/year) (7)

Source	US 1990	Canada 1990	Total 1990	US 1999	Canada 1999	Total Remaining 1999	Percent Reduction
Industrial	11	23	34	11	20	31	8.8%
Mining	912	604	1516	385	0.4	385.4	74.6%
Fuel Combustion	137	126	263	193	122	315	+19.8%
Incineration	85	1	86	14	1	15	82.6%
Products	150	41	191	1	34	35	81.7%
Municipal	61	53	114	40	53	93	18.4%
Re-emission (from 15% potential release of land filled mercury)	146	55	201	34	15	49	75.6%
Total	1502	903	2405	705	244	949	60.5%

In 1999, partly due to the LaMP reduction schedule for mercury and the requirements of the Clean Water Act, the Minnesota legislature tasked the Minnesota Pollution Control Agency (MPCA) to prepare a Total Maximum Daily Load (TMDL) to evaluate mercury sources and quantify reductions needed to meet water quality standards; and to develop an implementation plan for attaining reduction requirements of the TMDL. The proceedings of these two plans require that the Taconite Industry reduce emissions to 210 lbs/yr by the year 2025, a 75% reduction from 1999 levels (8). In order to attain these reduction targets, the Minnesota Department of Natural Resources (DNR) and others have funded research aimed at identifying control technologies capable of achieving the 75% reduction in mercury emissions from the Taconite industry.

CHAPTER II

BACKGROUND

Mercury Cycle and Health Effects

Mercury is an element that exists as a heavy, silvery-white liquid at typical ambient temperatures and atmospheric pressures (9). It exists in three main oxidation states: metallic/elemental (Hg^0), mercurous (Hg_2^{2+}), and mercuric (Hg^{2+}); and its properties and behavior depend on the oxidation state (9). Natural and anthropogenic activities create a mercury 'cycle' in the environment which consists mainly of release of mercury into the atmosphere, transport from point of release, re-deposition (which depends partly on the chemical form of mercury (10)), re-release into atmosphere or chemical transformation. Anthropogenic emissions of mercury are believed to have increased significantly in the last century, with U.S. emissions alone in 1994 to 1995 estimated at 158 tons/year, 3% of the estimated total annual global output of 5,500 tons (9). In the U.S. specifically, the EPA estimated that from 1994 to 1995, anthropogenic emissions deposited within the 48 contiguous states was greater than deposits from the global reservoir (9).

Mercury and its many different forms have been shown to bioaccumulate in aquatic biota and living organisms and are toxic to humans (9,11,12). Toxicity was ascertained following epidemics in Japan and Iraq where infants exposed to different

mercury forms were born with birth defects and/or were mentally retarded (12). The Iraq episode involved acute high dose exposure during fetal development associated with alkylmercury-contaminated grain; meanwhile the Japan episode involved longer high dose exposure from methylmercury contaminated fish (12). Methylmercury is a form of mercury formed through a chemical process known as methylation. It is the main form in which mercury is present in fish, and is believed to bioaccumulate more significantly than other forms of mercury (9). The events in Iraq caused the EPA to establish a reference dose (RfD) for mercury of 0.1 $\mu\text{g}/\text{kg}/\text{day}$, based on benchmark dose modeling of neurological endpoints reported for children exposed in utero (13). More mercury toxicity research work was conducted focusing more on long term, low dose exposure to mercury and/or its other forms. The results showed considerable uncertainty in determining the exact dose-response relationships for mercury toxicity in humans (14,15,16,12). However, in August of 2000, the National Research Council reaffirmed the EPA's mercury exposure RfD following extensive evaluation of scientific evidence of prior and ongoing research (17). Because of its greater ability to bioaccumulate in aquatic biota such as fish, coupled with its higher toxicity, methylmercury is of greater concern when looking at the potential health risks of mercury. Research shows that high methylmercury concentrations present in aquatic environments are due to microbial and chemical methylation of inorganic mercury (18). Consequently, reducing the load of inorganic mercury deposited in aquatic environment is necessary to reduce the concentration of methyl mercury found in fish consumed by humans.

Taconite Industry Profile

Taconite is a low grade iron ore with 20 to 30 percent iron content and is the principal form in which iron ore is mined in the United States (US). US Ore reserves are located in Minnesota (Mesabi Iron Range) and Michigan (Marquette Iron Range) (19). It accounted for 70% of US domestic demand in 2000 with 76% of the total production coming from the State of Minnesota alone (19). The production process as shown in Figure 1 is divided into open pit mining, beneficiation of mined ore, and agglomeration to give pellets. Beneficiation involves crushing and grinding to liberate iron-bearing particles inside the ore and then concentrating the ore by using mainly magnetic separation and/or flotation. Magnetic concentration targets iron existing as magnetite and maghemite which show magnetic properties, meanwhile other forms of iron (hematite) are concentrated mainly through froth flotation (20).

Agglomeration, also known as pelletization, is the final major step in taconite ore processing. Concentrated ore is rolled in balling drums into small pellets either after addition of just a binder to form green balls referred to as 'acid pellets'; or addition of a binder and 1 to 10 percent limestone forming green balls referred to as 'fluxed pellets'. The main binder used is bentonite; however, one plant uses a different proprietary binder. The pellets are then heated up in oxidizing conditions through a process known as induration to temperatures ranging from 1290 °C to 1400 °C for several minutes. Induration is achieved using either a straight grate or grate/kiln (one facility used a vertical shaft furnace, but the facility has been shut down) with natural gas being the most common fuel used. Some facilities also (co-)fire other fuels such as biomass, coal, coke

and heavy oils (20). Mercury release is believed to occur during induration of the pellets (21).

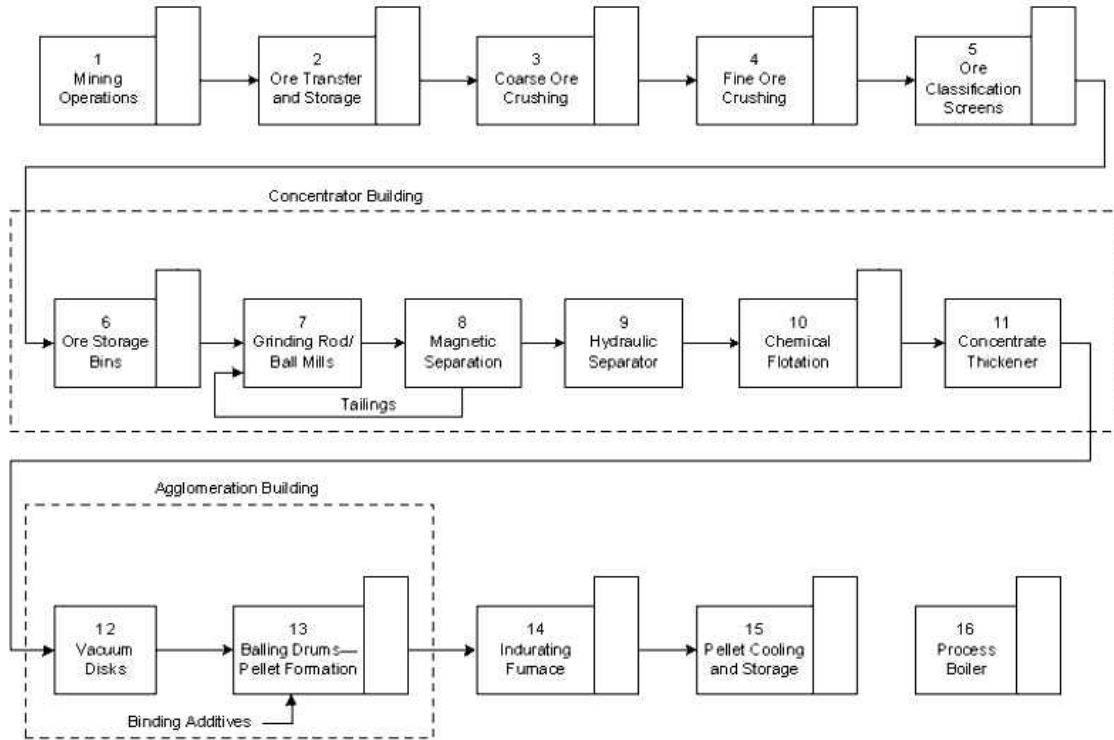


Figure 1: Production process for Taconite pellets (19)

Induration in the Minnesota range involves use of grate-kilns and straight grate furnaces. Straight grates consists of a horizontal travel grate where the pellets are dried, preheated, fired to oxidize the magnetite to hematite, and finally cooled; meanwhile, grate-kilns consist of a straight grate with a drying zone usually called down draft zone 1and/or 2(DD1and/or DD2); and a preheat zone, followed by a kiln for oxidation of the magnetite to hematite. Finally, there is an annular cooler which uses ambient air to cool the pellets. In the grate-kiln, a portion of the air used to cool the fired pellets flows into the kiln in a countercurrent direction to pellet flow. It enters the preheat zone and flows

vertically down through the pellets heating them up and then exits under the grate. It is then transported by preheat fans to the top of the drying zone of the grate where it flows once more in a down draft direction to dry the green balls, hence the name down draft (19). The waste gas fan then transports the waste gas from the drying zone containing dust, moisture and particles from the pellets; released during heating of the green balls in the grate and/or kiln. The waste gas is transported to various pollution control devices (multiclones, wet scrubber or electrostatic precipitator [ESP]). After cleaning by these control devices, it is then emitted from the plant stack. Pollution control devices depend on the plant and operating line, with a wet scrubber being the most common, usually preceded by multiclones in some plant lines. Field testing was done at a grate-kiln facility - United States Steel Minnesota Taconite – Line 3 (USS Minntac), so focus would be on grate-kiln operation. The grate portion is divided into the drying zone (DD1) and the preheat zone, with two fans (the preheat fans) responsible for moving the waste gas through this region. The kiln is inclined and followed by the cooling bins which collect and cool the fired pellets using air from two fans known as cooling fans. A portion of this air exits through the cooler vent stack above the cooling bins, meanwhile the rest flows through the kiln to the preheat and DD1. Waste gas from the grate then flows through multiclones, a waste gas fan, a wet scrubber and finally, the stack. Grate-kilns from the other lines are similar to that of Minntac-Line 3, with differences being the grate size, air flow, fuel burnt, number of fans, design of the drying zone (other lines have two drying zones – DD1 and DD2); and type of pollution control devices.

Mercury in Taconite Plants

The main source of mercury in taconite plant emissions is from the ore with contribution from coal (if used) minimal (22,23). Most of the mercury in the ore is associated with the gangue (80%) and is removed during beneficiation of the ore (21); however, mercury associated with the green balls is still significant as it is the main source of mercury stack emissions (21). Research (24) suggests that mercury is bound predominantly to the magnetite portion of the green balls and is completely released after conversion to hematite. Moreover, at temperatures of 400 °C to 500 °C, magnetite converts to a solid solution of magnetite and maghemite, which reacts with waste gas mercury. The behavior of mercury with the different crystal structures of iron oxides have been shown to be significant because they could influence the oxidation of elemental mercury (Hg^0) to oxidized mercury (Hg^{2+}) especially in the presence of gaseous hydrogen chloride and/or nitrogen oxides (25,26). Mercury released during induration is believed to interact with taconite dust (mainly iron oxides), maghemite and chlorine (from fluxing agents and pore fluids) in the oxidizing conditions of the grate-kiln (25,27). These interactions are believed to result in oxidation of Hg^0 to Hg^{2+} (17,25) and formation of particulate mercury (Hg^{P}) (28), thus explaining the high concentrations of mercury seen in scrubber systems present on the range (28). Any mercury that is not captured by the scrubber systems should then be emitted through the plant stack.

More work was performed on scrubber systems to better evaluate the mercury captured. First, it was observed that the fate of captured mercury depends on adsorption to particles in the scrubber slurry, and plant routing of said slurry (28). Mercury captured by the wet scrubbers was present both in the liquid portion of the slurry as dissolved

mercury (Hg^{D}), and in the solid portion as particulate mercury (Hg^{P}). However, the concentration of Hg^{D} was seen to decrease with time, while the concentration of Hg^{P} increased. This suggested that Hg^{D} was adsorbing unto the solid portion of the slurry with time to become Hg^{P} , and also that the mercury captured by the scrubber was captured both as Hg^{2+} , which is soluble, and as Hg^{P} (28). This behavior is considered significant because it could determine the final fate of the captured mercury. Handling of scrubber slurry varies with different facilities and lines. For the liquids, some plants/lines recycle their scrubber liquids and make up for losses with a fresh stream of water; others discharge their liquids. Meanwhile for the solids, some plants recycle their solids captured by the scrubber back to the front-end of the process (agglomerator or concentrator) after settling in a scrubber thickener; others discharge their solids. For plants which recycle their solids, any Hg^{P} would be re-introduced into the system; meanwhile, high Hg^{D} in scrubbers that recycle their waters might reduce the driving force for Hg^{2+} capture over time. More analyses also suggested that the scrubber Hg^{P} is mainly associated with the non-magnetic portion of the scrubber slurry, thus magnetic separation during ore beneficiation could be used to provide an “exit” point for the Hg^{P} from the process (28).

With this understanding of mercury in taconite processing, the Minnesota Department of Natural Resources (MN DNR), co-funded by the MPCA and Environmental Protection Agency (EPA), was tasked with identifying and testing potential mercury control technologies applicable to the Taconite industry.

Potential Control Technologies for Taconite Industry

A review funded by the MN DNR, identified two potential mercury control technologies for the Taconite industry: Sorbent and Oxidation technologies (22). Sorbent technologies refer mainly to technologies that use powdered activated carbon (PAC) or halogenated PAC for mercury control. The sorbents are delivered either by injection directly into the waste gas ducts or as a fixed bed through which the waste gas flows through. Oxidation technologies refer to the use of chemical additives which would enhance oxidation of Hg^0 in the process.

Oxidation technologies were the first technologies tested in different plants by the MN DNR. The tests were carried out for just one hour to determine if the oxidants used had the potential to achieve significant reduction in stack mercury emission. Longer testing would be necessary to fully assess effectiveness of the technologies. The tests consisted of: 1) Adding sodium chloride (NaCl) or calcium bromide (CaBr_2) to the green ball feed of both a straight grate and grate-kiln; 2) Halide salt (bromide or chloride) injection into the preheat zone of a straight grate and grate-kiln facility; 3) Using oxidants in the scrubber waters to oxidize Hg^0 . Of the three different tests performed, bromide salt injection into pre-heat or kiln seemed to be the most promising in reducing stack emissions of mercury (29,30). However, during bromide salt injection, an increase in Hg^{2+} at the stack was observed suggesting that either all the Hg^{2+} was not captured by the scrubber, or Br_2 was formed during injection of the salt which was not captured by the scrubber. The uncaptured Br_2 then possibly oxidizes Hg^0 in the stack or the sampling probe, biasing the oxidized mercury reading (30). Moreover, use of halide salts raised the possibility of corrosion of plant equipment (29).

With this preliminary knowledge of how effective oxidation technologies could be in controlling mercury emissions from Taconite facilities, the MN DNR then submitted a *Request for Proposals* (RFP) aimed at funding testing of different mercury control technologies with the potential of achieving significant reductions in the Taconite Industry. This research presents the results of one of the technologies proposed by the University of North Dakota – Department of Chemical Engineering and Envergenx LLC. The objectives of the proposed work were: 1) Investigate the effectiveness of two mercury sorbents: plain activated carbon (PAC), and ESORB-HG-11 (a proprietary halogenated carbon supplied by Envergenx LLC of Sturbridge, MA); to capture mercury in the waste gas stream; 2) Sequester both dissolved and captured mercury onto either the sorbent or a mercury complexing agent (TMT-15® or DEDTC) which can be physically or magnetically differentiated from the scrubber process solids. The benefit of this approach would be threefold: 1) Increase mercury capture, thus reducing total stack mercury emitted; 2) Improve driving force of oxidized mercury capture by scrubber liquids through sequestration to solid phase (also preventing any possibility of mercury re-emission from scrubber slurry); 3) Provide a possible ‘exit’ point for captured mercury by sequestering it to a non-magnetic or physical differentiable sorbent. This research documents the methods used and results obtained from testing the technologies proposed.

Chemistry of Proposed Control Technologies

Powdered Activated Carbon (PAC)

Activated carbon is considered one of the most advanced commercially available mercury control technologies (22). Significant amount of testing has been performed using PAC in the coal industry (31,17,32) establishing PAC as a potential mercury

control technology. Several factors: flue gas composition, sorbent particle size, temperature, and presence of moisture; have been shown to affect the performance of PAC in mercury control during different bench-scale fixed-bed work (17). However, for the case of the Taconite Industry specifically, flue gas composition is probably the most important factor. This is because even though physical adsorption is believed to be one of the methods for mercury capture on PAC (33), capture of Hg^0 by PAC is most effective when acid gases (SO_2 , NO_x , HCl) are present in the flue gas (33,34,17). It is believed that oxidation of elemental mercury followed by chemisorption is a significant component in the mechanism of mercury capture by PAC (34,35,36). So for PAC to show some amount of success in capturing mercury in Taconite facilities, the waste gas constituents should be able to promote oxidation of Hg^0 to the oxidized species followed by chemisorption in the presence on PAC. Measurements of flue gas compositions at a taconite facility suggests lower CO_2 , NO_x , and SO_2 (facilities not burning high sulfur coal as fuel) concentrations (37) as compared to flue gas in coal facilities (38,39,17). The HCl concentration is roughly the same for both systems. On the other hand, Taconite waste gas has a high dust loading comprising largely of reactive iron oxides believed to be responsible for the high degree of oxidation observed in the systems (26,24). So even though the waste gas composition of acidic gases such as SO_2 and NO_x is lower than in coal flue gas, the presence of HCl and iron oxides is expected to enhance Hg^0 oxidation and capture with PAC. The results obtained from testing PAC are discussed in chapters IV and VI.

ESORB-HG-11

It has been shown that chlorine (as HCl) is one of the important factors in mercury control using PAC (17,36). Consequently, effectiveness of PAC may be limited when the amount of chlorine in the flue gas is insufficient (40). Moreover, PAC testing has been most effective for controlling mercury emissions in coal facilities equipped with a fabric filter (FF) over electrostatic precipitators (ESP) as the particulate control device (PCD) (17). To overcome these limitations, PAC sorbents such as ESORB-HG-11 impregnated with compounds containing halogens, have been developed to reduce the dependence of the Hg^0 capture mechanism on chlorine from waste/flue gas. Testing of halogenated PACs has shown that mainly bromine based PACs achieve high mercury control potential even in the absence of FF (41,22). Taconite facilities use multiclones and wet scrubber systems as their main PCDs, so halogenated sorbents might be the best sorbent technology able to overcome the short residence time of the injected sorbent in the waste gas (residence time depends mainly on waste gas flow rates and duct lengths). However, for better results, good distribution of the sorbent in the waste gas and higher injection loadings might be necessary to achieve significant capture of mercury (22).

Other than capture, another important aspect concerning mercury control with Taconite facilities' wet scrubber systems, is the ability of the sorbent used to sequester Hg^{2+} (as Hg^{D}) from liquid to solid portion of scrubber slurry. ESORB-HG-11, supplied Envergenx LLC of Sturbridge, MA, is a proprietary brominated powdered activated carbon sorbent believed to be able to achieve both capture and sequestration of mercury. Testing was carried out to investigate the potential of ESORB-HG-11 to sequester Hg^{D} and capture Hg^{2+} after oxidation of Hg^0 . The results are discussed in chapters IV and VI.

TMT-15® & DEDTC

TMT-15® is a commercially available heavy metal chelator containing the functional group 2,4,6-trimercaptotriazine (TMT) and is used to precipitate heavy metals from solution. Meanwhile, diethyldithiocarbamate (DEDTC) is a chemical compound containing the carbamate functional group capable of forming chelates with heavy metals such as mercury. TMT reacts with mercury in aqueous solutions to form mercaptotriazine (Hg-TMT) which precipitates from solution (42); meanwhile the chemistry of dithiocarbamates reacting with mercury is not well documented. The two additives were tested to determine their efficiency in sequestering Hg^D in a Taconite plant's scrubber slurry. Their effectiveness was also compared with the sequestering capabilities of sorbents – PAC and ESORB-HG-11. Several other concerns would need to be investigated if these metal chelators are to be adopted by scrubber systems, such as their toxicity and stability. The results from using them are discussed in chapters IV and VI.

CHAPTER III

EXPERIMENTAL METHODS (BENCH & PILOT)

Demonstration of the mercury control technologies proposed by UND & Envergenx LLC was done in three phases:

- Bench-scale testing to establish sequestration properties of the additives in Taconite scrubber slurry.
- Pilot-scale tests to establish improved driving force of Hg^{2+} capture by scrubber slurry containing additives.
- Field-scale tests to establish oxidation and capture of Hg^0 by the two sorbents – PAC and ESORB-HG-11; and demonstrate sequestration of Hg^D from the liquid portion of the scrubber slurry.

Each different step is described in detail in the subsequent sections and chapter. However, field testing methods and results are discussed separately in chapters V and VI respectively. Chapter III focuses on the experimental methods used during bench- and pilot-scale tests meanwhile chapter IV looks at their results. Bench- and pilot-scale tests investigated only the sequestering abilities of all four sorbents/chelates proposed. Field tests investigated oxidation, capture and sequestration of mercury from waste gas. US Steel Minntac-Line 3 was selected as the facility and line at which field testing was going

to be conducted, so all calculations, methods and estimates for the bench and pilot work were done based on Line 3 conditions.

Bench-Scale Test

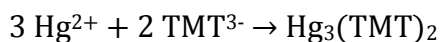
For all bench-scale tests, scrubber slurry obtained from Minntac-Line 3 was used. First, a mercury mass balance was performed on Minntac Line 3 using concentrations reported in work performed in 2005 by Berndt and Engesser (28,27), to obtain an estimate of the mercury concentration captured by the liquid portion of the scrubber slurry from the process waste gas. This gave an estimate of the total mercury (Hg^{T}) in the scrubber slurry of $62.5 \mu\text{g Hg /l}$. The mass balance was performed because Berndt (28) determined that Hg^{D} adsorbs onto the solid particles in the slurry significantly with time, implying that the scrubber slurry obtained from Line 3 would have little Hg^{D} . Mercury analysis of the slurry confirmed this, with results showing less than $1 \mu\text{g Hg/l}$ of slurry. So samples used for bench tests were spiked with mercuric chloride (HgCl_2) to a concentration of $62.5 \mu\text{g Hg/l}$. The mercury residence time in the scrubber of line 3 was also calculated to be approximately 10 min.

Testing apparatus consisted of a 500 ml conical flask, magnetic stirrer, a Buchner funnel, 0.7 micron Whatman glass fiber filters purchased from Millipore, and acidified sample bottles for EPA Method 7470 analysis obtained from Pace Analytical Services. The procedure consisted of measuring 200 ml of Line 3 scrubber slurry and spiking with 50 μl of 0.25 g/l mercury (as mercuric chloride) to obtain a mercury concentration in the slurry of $62.5 \mu\text{g Hg/l}$. The solution was stirred and a fixed volume or mass of the sorbent or chelate was added and stirred for 10 min, followed by filtration into the sample bottles.

The samples were then shipped to Pace Analytical laboratories for analysis of mercury content left.

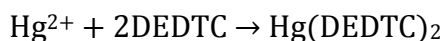
The test matrix for the bench-scale experiments consisted of first testing the sorbents/chelates following a low, mid and high loading; in the scrubber sample spiked with mercury. A different method was used to determine the loadings for each additive and sorbent. For PAC and ESORB-HG-11, PAC testing in coal fired utilities suggest that carbon/Hg ratio is a function of sorbent particle size (17) with the minimum carbon-mercury ratio for effective removal usually around 1000 (17). Consequently, the loadings used in the bench scale tests were 0, 25, 50 and 100 mg/l, which correspond to a carbon/Hg ratio of 400, 800 and 1600 g carbon/g Hg. PAC testing in coal fired utilities consists of injection into flue gas ducts to achieve mercury capture, not sequestration; so using this method as a means to estimate the bench-scale loading of sorbents in the scrubber slurry might seem misleading at first look. However, since during field-scale tests, the sorbents would not be added directly into the scrubber recirculation tank but injected into the waste gas stream and end up in the scrubber slurry, C/Hg ratios from PAC injection is actually a reliable way to estimate minimum concentration of sorbent in the scrubber slurry.

To estimate the loadings of TMT-15®, a ratio of 15 liters TMT-15®/kg of Hg was used. This ratio was obtained from the manufacturer, and is 6 times larger than the ratio from the stoichiometric equation for mercury chelation by TMT-15®:



The final loadings used for TMT-15® were 0.42, 0.56 and 1.12 mg TMT-15®/l of scrubber slurry (TMT-15® was supplied as a 15% solution; the loadings reported are based on the actual mass present in the solution added to the scrubber slurry).

For DEDTC, the loadings used were based on the stoichiometric equation for Hg chelation with DEDTC.



The loadings used were 0.13, 0.43 and 0.69 mg DEDTC/l of scrubber slurry. DEDTC exists as a white crystalline solid, but it was administered as a solution of 860 mg/l. The volume of this solution containing the mass required was measured and delivered to the scrubber slurry using microsyringes. Table 2 summarizes the loadings investigated for the first series of tests.

Table 2: Loading of sorbents and additives during bench-scale testing

Level	ESORB-HG- 11 (mg/l)	PAC (mg/l)	TMT-15® (mg/l)	DEDTC (mg/l)
Low	25	25	0.40	0.13
Mid	50	50	0.60	0.43
High	100	100	1.12	0.69

The next tests involved testing the PAC sorbent impregnated with either TMT-15® or DEDTC. PAC was impregnated with the chelates using a two level, one factor design; with mass being the factor. The impregnation technique used was the *incipient wetness impregnation (IWI)*. The two levels used for PAC were 25 and 100 mg PAC/l of scrubber solution. The levels used for TMT-15® were 0.28 and 2.24 mg TMT/l of scrubber slurry; while that for DEDTC was 0.43 and 0.69 mg DEDTC/l of scrubber

slurry. The impregnation sought to investigate the effectiveness of PAC combined with heavy metal chelators; and if this combination significantly improved the sequestering capabilities of PAC. Table 3 summarizes the impregnation test matrix. Two different IWI methods were used to prepare TMT-15® as it was suspected that the initial method might cause degradation of TMT during impregnation. The loading for each preparation method was kept the same.

Table 3: Loadings used during incipient wetness impregnation testing

PAC (mg/l)	TMT-15®		DEDTC	
	Low (mg/l)	High (mg/l)	Low (mg/l)	High (mg/l)
25	0.28	2.24	0.43	0.69
100	0.28	2.24	0.43	0.69

The last test performed investigated the effect of time on sequestration of Hg^{2+} by PAC. This test was performed to verify that the initial results obtained during the PAC test was a function of PAC loading only and not time. Moreover, determining the effect of time helped determine if the experiment was kinetically or mass transfer limited. In this test, 20 mg of PAC was used and stirred for 1, 2, 4 and 10 minutes. The slurry was then filtered and sent for analyses.

To conclude, bench-scale tests were performed to establish sequestration properties such as minimum loading versus sequestration of Hg^D , effect of time on sequestration experiments, and effectiveness in Taconite scrubber slurry.

Pilot-scale Test

The goal of the pilot-scale tests was to investigate the effectiveness of the sequestration additives when used with a pilot scrubber system. Flue gas spiked with mercuric chloride (HgCl_2) was scrubbed using a glass, counter-current flow scrubber. The post-scrubber flue gas concentration was then sampled and analyzed to determine its Hg^0 and Hg^{2+} concentration. Initially, it was planned to monitor both the pre-scrubber Hg concentration and post-scrubber Hg concentration, but pre-scrubber sampling was not effective. Details concerning testing methodology are further discussed below. During operation, one of the sorbents or chelates from the bench-scale tests was added by dosing to the scrubber recirculation tank to observe the effect it had on Hg^{2+} scrubbing from the flue gas. The testing process could be summarized into five main steps: Flue gas generation, Hg^{2+} (as HgCl_2) generation and injection into the flue gas stream, flue gas scrubbing, sampling and conditioning of scrubbed flue gas, and finally, analysis of conditioned sample gas. Each step, methodology and equipment used is discussed in further detail.

Flue Gas Generation

Flue gas was generated using a modified natural gas home furnace equipped with a Mass Trak 810C Mass Flow Controller (MFC), calibrated for methane gas and provided by Sierra instruments. The flue gas flowed from the furnace to the scrubber and was then vented through the roof of the building housing the equipment. Flue gas flow rate was controlled using an eductor located downstream of the scrubber. The eductor uses compressed air and is controlled by a rotameter located on the furnace. Several operating factors were monitored during each experimental run. First the flue gas, which was

sampled before the scrubber, was conditioned and analyzed for the O₂ concentration using a Model 3000M series O₂ analyzer supplied by Teledyne Analytical Instruments. This measurement was used to calculate the excess air and flow rate of the flue gas produced. To determine the flue gas flow rate, first the molar flow of natural gas burnt (as methane-CH₄) was calculated from the flow rate reading of the MFC (in liters per minute). The molar flow is then combined with the O₂ concentration and stoichiometric combustion equation for CH₄ to estimate the volumetric flow of the flue gas. The average flue gas flow during testing was 50±10 lpm, with an average oxygen concentration of 17.0±1.5%. The second factor monitored was the temperature of the flue gas before injection of the oxidized mercury, using type K thermocouples inserted in the flue gas sample lines. A temperature range of 150°C ± 20°C was the target to prevent condensation from occurring in the lines and ensure the Hg²⁺ is not reduced to Hg⁰. The furnace and rotameter are depicted in Figure 2 below. The MFC is not shown in the picture.



Figure 2: Modified furnace and rotameter controlling eductor

HgCl₂ Generation

Mercuric chloride (HgCl₂) was generated using two certified Dynacal mercuric chloride permeation tubes obtained from VICI Metronics. The tubes were certified traceable to NIST standards for permeation rates of 10,470.60 ng/min and 12,963.90 ng/min, when maintained at a constant temperature of 80⁰C. The permeation tubes were inserted into a constant temperature chamber known as Dynacalibrator, obtained from VICI Metronics. The Dynacalibrator maintained the tubes at the 80⁰C temperature. The permeation chamber was then swept out at a constant rate of 1 liter per minute using nitrogen as carrier gas with flow rate controlled by a Brooks Instrument Mass Flow Controller - Series 4850, certified for N₂ gas flow. High purity N₂ from a gas tank was used. With the temperature of the calibrator at 80⁰C, and using both permeation tubes, a

nitrogen stream containing approximately 23 $\mu\text{g}/\text{min}$ of HgCl_2 flowing at a rate of 1 lpm, was expected. Adding this to a flue gas flow rate of approximately 50 (± 10) lpm, meant that final Hg^{2+} concentration in the flue gas would be less than 1 $\mu\text{g}/\text{m}^3$, a lot less than what was required. Surprisingly though during preliminary testing of the equipment set-up mercury concentrations higher than 18 $\mu\text{g Hg}/\text{m}^3$ were detected in the flue gas stream. This suggested that the permeation rate of the tubes was either higher than the certified rates or better yet, that there was a significant build up of HgCl_2 concentration in the Dynacalibrator during temperature ramp-up and steady-state, producing a nitrogen stream with very high mercury concentrations. To verify this, the HgCl_2 -containing N_2 stream was diluted with air using a dilution chamber and then analyzed. High Hg readings of $> 20 \mu\text{g Hg}/\text{m}^3$ confirmed that the 1 lpm stream coming from the dynacalibrator had high concentrations of mercury. Figure 3 below shows a picture of the Dynacalibrator and Brooks MFC.



Figure 3: Brooks MFC and Dynacalibrator

Scrubber Operation

The scrubber consists of a 30 L slurry tank with a 6 ft high, 3 inch internal diameter scrubbing tower as shown in Figure 4 and 5. The tank is connected to a diaphragm pump which circulates the slurry through the scrubber. The slurry is pumped through perfluoralkoxy (PFA) tubing from the slurry tank to the spray nozzles. The flue gas flows into the scrubber at the base of the scrubbing tower, and exits the scrubber at the top. The spray nozzles provide a 90° spray pattern, are clog resistant, spray slurry counter-current to the flue gas flow, and scrub Hg^{2+} in the process. However, because of the small 3 inch internal diameter, most of the slurry sprayed in the 90° cone-shape hits and flows down the walls of the scrubbing tower, reducing the effective liquid-gas contacting. An atomizing nozzle was used to try and circumvent this problem, and even though it worked effectively producing a fine mist, significant clogging was observed

when used with scrubber slurry. As a result, the 90° spray nozzles were maintained for the test. The diaphragm pump was operated using compressed air at 80 psig giving slurry flow rates of 2.0 to 3.0 lpm (depending on number of spray nozzles used), measured using a Seametrics Low Flow Magnetic Flowmeter. Sampling of the flue gas for analyses was done from the top of the scrubber through PFA lines heated to 150 ± 20 °C with silicone heat tapes. It was initially planned to sample before and after scrubbing so as to get a ‘mercury in - mercury out’ measurement; but the only possible pre-scrubber sampling point was from a U-shaped, 2 ft long Teflon-coated stainless steel pipe used for injecting the HgCl₂ - carrying nitrogen gas into the flue gas. Sampling from this pipe produced abnormal results attributed to poor mixing of the HgCl₂ in the flue gas before entering the glass scrubber. Flue gas flow in the scrubber was believed to be better mixed thanks to the longer residence time and contacting with the scrubber liquids. As a result, sampling was done from the top of the scrubber only.

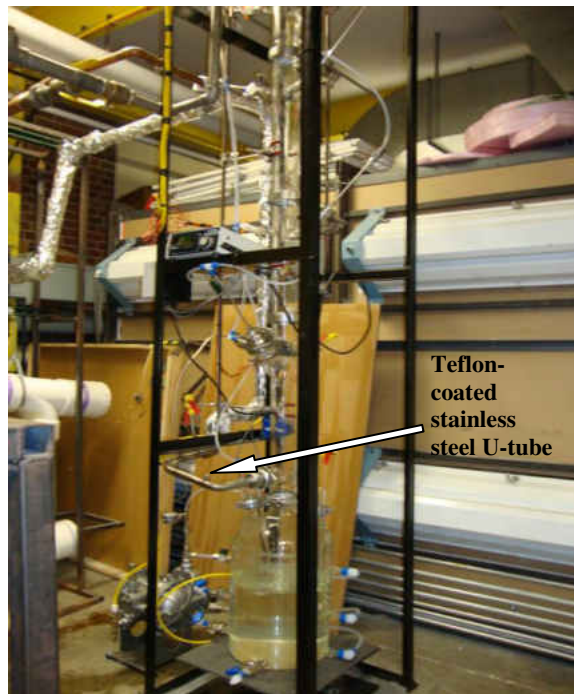


Figure 4: Glass scrubber and Teflon-coated U-tube for injecting HgCl₂



Figure 5: Diaphragm pump and scrubber 30 L tank

Wet-Chemistry Pre-Treatment Unit

A wet chemistry pre-treatment was used to condition the sample gases before mercury analysis. It consisted of two parallel sets of impingers: one for determining Hg^0 concentration in sample gas, while the other for determining Hg^T concentration in the sample gas. The set-up was designed based on a modified wet chemistry PS Analytical pre-treatment conversion system (43) and ASTM D6784-02 (also known as the Ontario Hydro [OH] method). In this design, the first impinger train is for conditioning the elemental mercury stream. It consists of two impingers in series: The first impinger contains a 200 ml of 1N potassium chloride (KCl) solution that captures the oxidized mercury in order to obtain only elemental mercury concentration, while the second impinger sits in an ice bath and traps all moisture present in the gas sample before analysis by the mercury analyzer. The second impinger train is for conditioning the total

mercury stream. Here, the first impinger contains 200 ml of 10% (w/v) stannous chloride (SnCl_2) solution. The SnCl_2 reduces the oxidized mercury in order to obtain a total mercury measurement of the flue gas. The second impinger sits in an ice bath and traps all moisture present in the gas sample before analysis. The trains were modified from a continuous flow to a batch system. Previous work done using a wet chemistry method involved a continuous or semi-continuous system in which the chemicals used for conditioning the mercury were continuously replaced (43,44,45). Also, NaOH was added in the Hg^{T} line to scrub out acid gases (43,45,44); and in some cases, sodium thiosulfate was either added to KCl in the Hg^0 impinger to prevent oxidation of Hg^0 (44), or replaced KCl completely (45). Most of these modifications were done to prevent flue gas constituents such as Cl_2 , Br_2 , particulates and SO_2 from interfering with Hg pre-treatment or accumulating in the impingers. However, the flue gas used for pilot-scale tests was obtained from burning natural gas, and was considered free of all the interferents listed above, so solutions were prepared based on the OH method. Figure 6 presents a schematic of the impingers used.

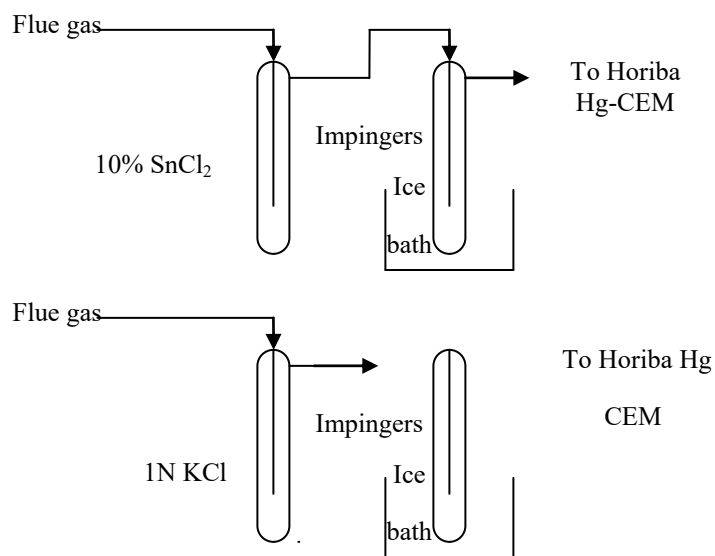


Figure 6: Schematic of wet-chemistry set-up

Mercury Analysis of Sample Gas

Conditioned gas from the wet pre-treatment step was analyzed using a Horiba DM-6B continuous mercury monitor (CMM) with dual channel analyzers belonging to the department of Chemical Engineering - University of North Dakota. It consists of a detector which uses cold vapor atomic absorption spectroscopy (CVAAS), and reports mercury concentration every 10 seconds. It also has a mercury generator (MG1), used to calibrate the Horiba DM-6B detector by producing a stream of gas of known Hg^0 concentration. A dry speciation unit was also supplied with the CMM, but researchers who worked previously with the analyzer recommended that the dry speciation unit be replaced with a wet-chemistry pre-treatment unit (43). The detector is equipped with a vacuum pump on each channel, controlled using a rotameter and pressure indicators. The flow rate for each channel was set at the manufacturer's recommended setting of 0.5 lpm, and pulled the sample gas from the scrubber through the pre-treatment units. Figure 7 is a picture showing the Horiba and mercury generator.

A typical pilot-scale run consisted of first turning on the furnace and heat tapes to bake out any residual mercury left in the sampling lines or scrubber tower after cleaning. The next step was calibrating the Horiba DM-6B and O_2 analyzer. Calibration of the O_2 analyzer was done with high purity oxygen (99.6%); meanwhile the Horiba DM-6B was calibrated with the mercury generator set at a flow rate of 1.75 lpm producing a concentration of 9.1 ug Hg/m^3 . During calibration of the analyzers the chemicals for the pre-treatment were prepared and the impinger train assembled and a leak check performed. To perform the leak check, the assembled impinger train is connected to the calibrated Horiba DM-6B and the impinger inlet is sealed using parafilm.

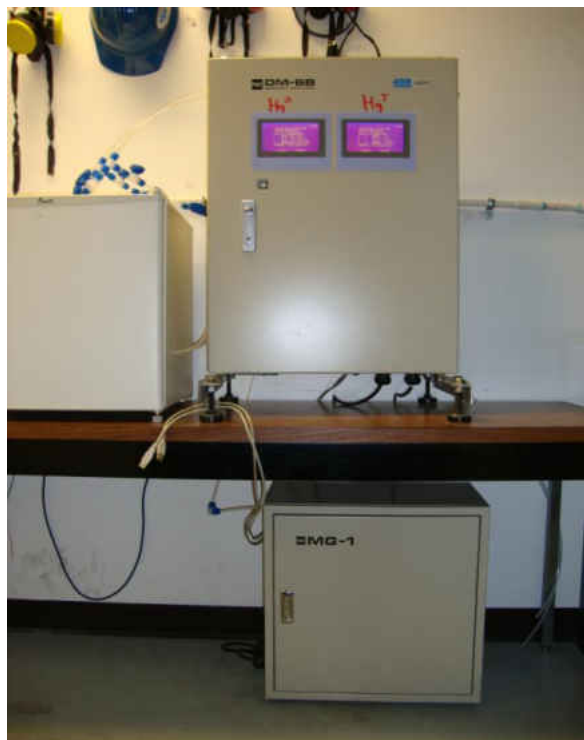


Figure 7: Horiba DM-6B and MG-1 mercury generator

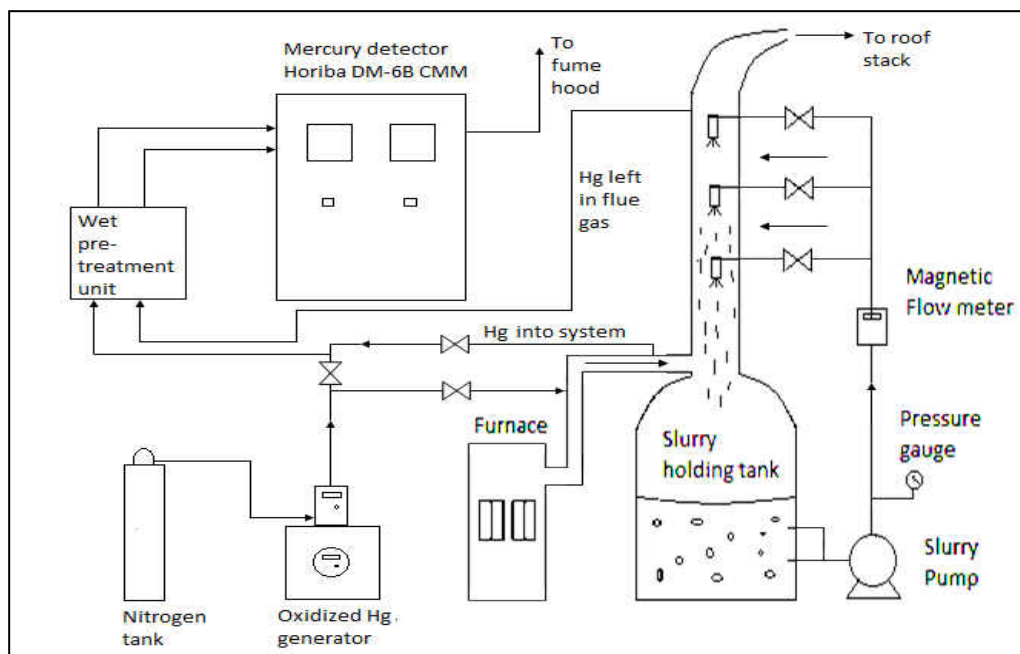


Figure 8: Schematic summarizing pilot-scale test equipment set-up

The pumps of the Horiba DM-6B then pull a vacuum through the trains, and the leak test is successful if a vacuum of at least 20 psi is pulled within one minute. If the leak test is successful, a calibration verification is then performed by connecting the calibration gas to the impinger train inlet. Once the calibration verification is completed, the heated sampling lines are connected to the impinger train IF the temperature of the heat tapes is steady at approximately 150⁰C; and IF there is no more condensation on the scrubber walls. The Dynacalibrator is then turned on with the permeation tubes loaded, and allowed to come to steady-state. These steps took a minimum of 2 hrs. During heating up, the flow of N₂ through the Dynacalibrator was turned on, but diverted from the flue gas stream to a carbon trap bed with the discharge end leading to a fume hood. While the Dynacalibrator was getting to a steady temperature (80⁰C), the Horiba DM-6B was measuring the scrubber baseline Hg concentration. Once steady, the N₂ stream containing HgCl₂ was then diverted back to the flue gas flow entering the scrubber. The mercury concentration of the flue gas leaving the scrubber was then allowed to reach a new steady-state value. This usually took 1 to 2 hours. Once the new steady-state was attained, the pump was turned on and slurry spray began to scrub the flue gas of Hg²⁺. After scrubbing for 1 hour, the sorbent/chelate to be investigated was added by dosing to the scrubber slurry and the effect recorded. After the effect of the additives on the scrubbing efficiency was steady once more, the set-up was then shut-down. Shut down consisted of first disconnecting the pre-treatment unit, then turning off the HgCl₂ stream, the scrubber, furnace and finally heat tapes. Post-run calibration verification of the Horiba DM-6B and O₂ analyzer was then performed and the data obtained saved. The scrubber was then washed by rinsing three times with tap water, followed by baking out

with flue gas and then a final rinse. A complete mercury wash of glassware requires soaking in nitric acid for at least 12 hours, but because of the size of the scrubber this was not feasible so only the bake out and rinse method was used.

CHAPTER IV

RESULTS (BENCH & PILOT)

Bench-Scale Test Results and Discussions

The bench-scale test investigated three different goals: performance of each respective sorbent/chelate; the effect of combining PAC with the chelates; finally, the effect of time on sequestration of additives. For the first goal, the results obtained from analysis of the filtered scrubber slurry for all the additives are shown in Figure 9.

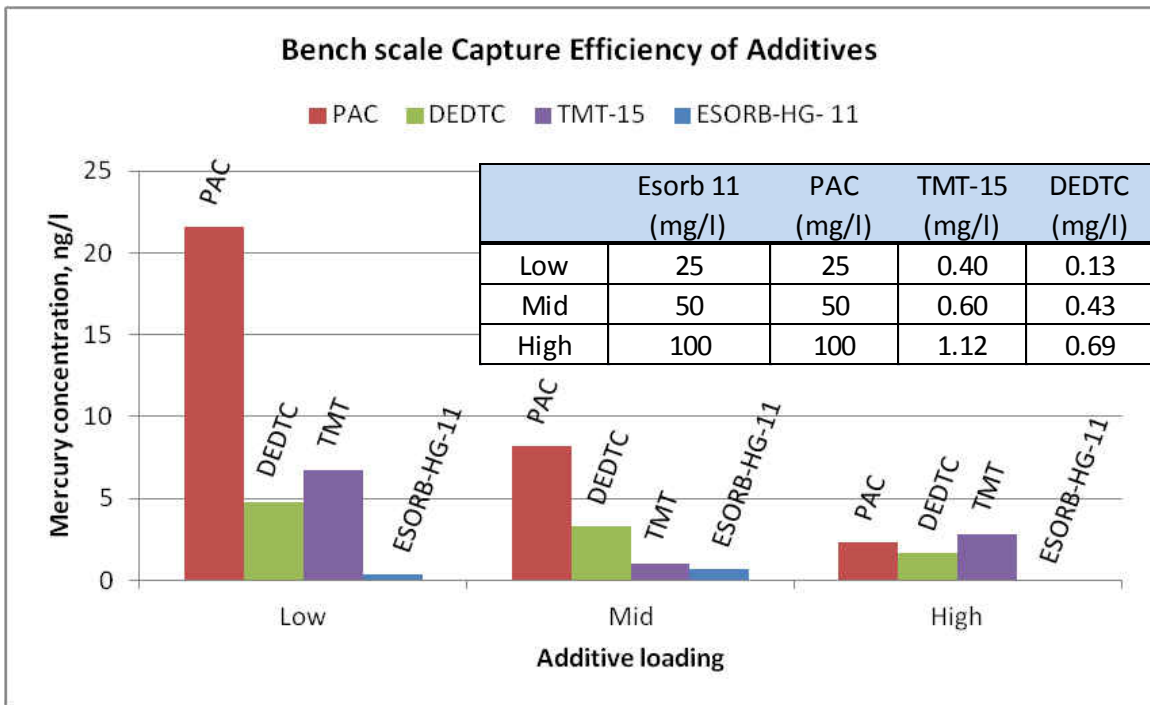


Figure 9: Sequestration results of each additive during bench-scale tests

From the results, it can be seen that ESORB-HG-11 was the most effective additive for all the three loadings investigated. All ESORB-HG-11 gave final slurry concentration of mercury to be less than $1 \mu\text{g}/\text{m}^3$ with the 200 mg/l loading giving a non-detect sample. These results suggest that ESORB-HG-11 is very effective in sequestering Hg^{2+} from solution.

The second sorbent tested was PAC. After testing, PAC showed the lowest Hg^{D} sequestration observed in the analyzed samples for the loadings investigated. The Hg^{D} concentration in the scrubber slurry after filtration decreased from 21.6 to $2.3 \mu\text{g Hg}/\text{m}^3$ for an increased loading of 25 to 100 mg/l. Looking at the clear decrease in slurry Hg^{D} suggests that even though PAC seems to be less effective, at higher loadings it should be more effective. So its effectiveness as a sequestering agent should be investigated further at higher loadings.

DEDTC also showed an increase in performance with increase in loading as observed with PAC. Also final slurry Hg^{D} concentrations with DEDTC were lower than those observed for PAC at all the levels investigated. The low (0.13 mg/l), mid (0.43 mg/l) and high (0.69 mg/l) loadings gave final Hg^{D} concentrations of 4.8, 3.3 and 1.7 $\mu\text{g Hg}/\text{l}$ respectively.

The results obtained from TMT-15® testing did not show a decrease in Hg^{D} with increase in loading. The low (0.40 mg/l), mid (0.60 mg/l) and high (1.12 mg/l) loadings gave final Hg^{D} concentrations of 6.7, 1.0 and 2.8 $\mu\text{g Hg}/\text{l}$ respectively. The differing behavior observed was attributed to possible experimental error. Final TMT-15® concentrations were also comparable to the final concentrations of DEDTC. To fully

compare effectiveness between TMT-15® and DEDTC, it is important to recall that DEDTC loading was based on the stoichiometric mass required to form a complex with Hg^{2+} ; meanwhile TMT-15® loading was based on the vendor's suggested dose which is 6 times more than the stoichiometric requirement for chelation of Hg^{2+} by TMT. This therefore suggests that DEDTC is more effective than TMT-15® on a stoichiometric basis.

Compared to ESORB-HG-11, none of the additives were as effective, so PAC was combined with TMT-15® and DEDTC by incipient wetness impregnation (IWI), to verify if this would produce a more effective sequestration agent. One important step of IWI is drying of the PAC at a temperature of 103 °C to drive off water. However, TMT-15® has a lower boiling point of 101 °C. So to ensure that the PAC was effectively impregnated with TMT-15®, two different drying temperatures were used: 103 °C and approximately 90 °C. Two TMT-impregnated PACs were thus produced and tested. The results for the impregnated PAC are shown in Figures 10 and 11 below, as well as the result obtained for testing PAC with no impregnation. A two level design was used with mass loading as the level.

For DEDTC, the main observable difference was the 25 mg PAC/l and 0.45 mg DEDTC/l combination. The value for Hg^{D} was 8.6 µg/l which was half the value for 25 mg PAC/l only and 25 mg PAC/l + 0.75mg DEDTC/l. However, when looking at the higher PAC dosing, no significant difference was observed except that sequestration seemed to decrease with increase in DEDTC loading on PAC. This trend was also observed for 25 mg PAC/l, and suggesting that impregnation with DEDTC is counter-productive with increase in DEDTC loading. However, PAC-alone testing already

established that higher concentrations of PAC (> 100 mg/l) would be needed for the sequestration to be significant ($Hg^D < 1 \mu g/l$). So the similar reductions between DEDTC impregnated on PAC and PAC alone, suggests DEDTC impregnation is not an effective option worth investigating further.

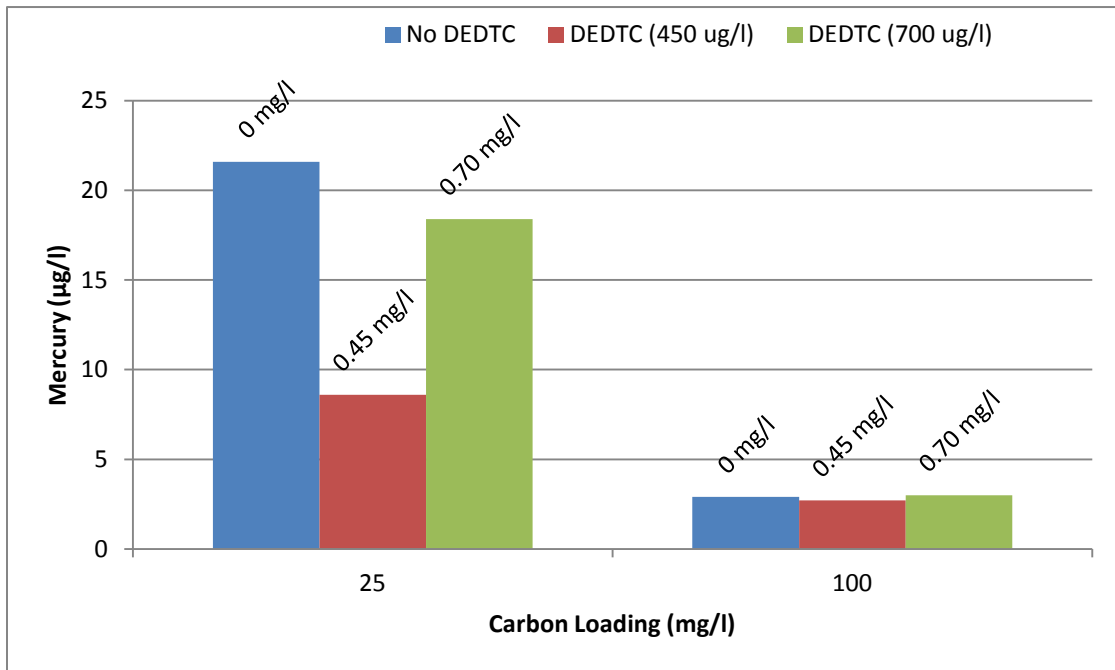


Figure 10: Results for dissolved Hg concentration with PAC and PAC impregnated with DEDTC

As mentioned earlier, PAC impregnated with TMT-15® was prepared using two different temperatures, so the samples were labeled A and B - where B referred to the lower temperature preparation. Looking at the results in Figure 11, the first point noticed was a similar trend as with DEDTC impregnation. Increase in the amount of TMT-15® with respect to PAC led to a decrease in mercury capture. However, combining TMT-15B at the low or high level with carbon led to sequestration values as good as those seen for ESORB-HG-11, except for the TMT-15B (2240 µg/l) which gave an abnormally high

value and was treated as an outlier attributed to experimental error. The results also suggested that the lower temperature preparation was more effective, and that most of the sequestration ability of the sorbent was more dependent on TMT-15® than on PAC. This final point is backed by the fact that the TMT-15® concentration used for the high level (2240 µg/l) is twice that used during TMT-15® alone tests.

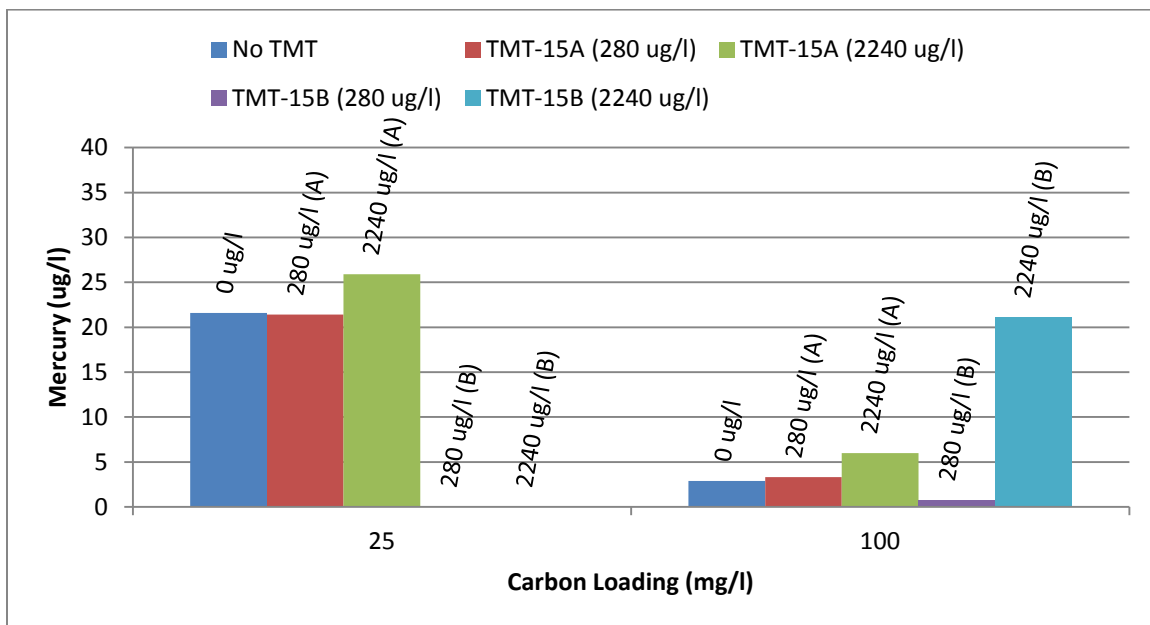


Figure 11: Results for dissolved Hg concentration with PAC and PAC impregnated with DEDTC

The last test investigated was the effect of time on the capture efficiency. As seen in Figure 13, PAC was chosen for this test due to its low sequestering ability at the temperatures investigated. A very slight decrease in Hg^D concentration was observed with increase in time suggesting that the effect of time on sequestration could be considered negligible. So time is not significant factor in sequestration.

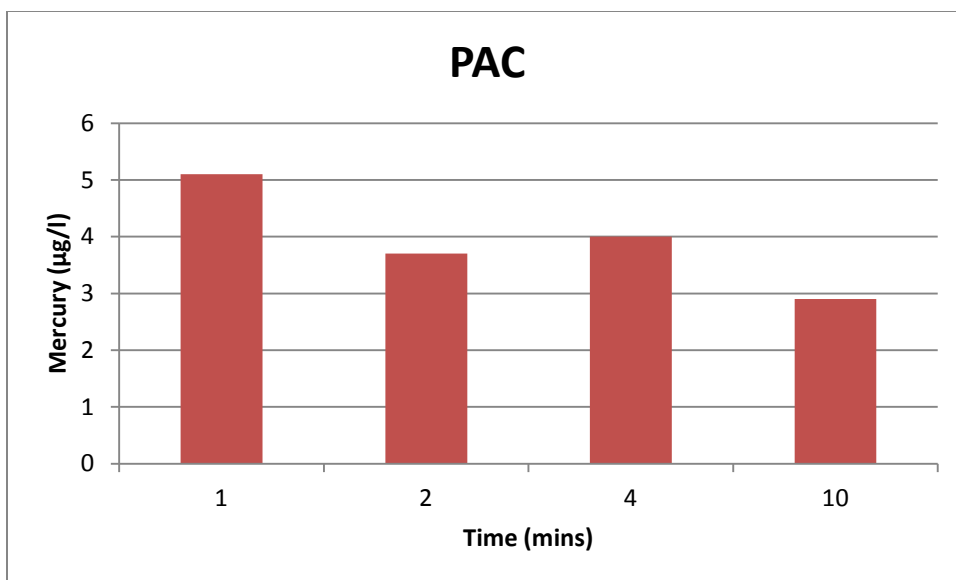


Figure 12: Effect of time on sequestration of Hg^D by PAC

Bench-Scale Testing Conclusion

To conclude, ESORB-HG-11 was the most effective additive capable of achieving sequestration significantly ($< 1 \mu\text{g}/\text{m}^3$) for all loadings used. Other additives showed promise as sequestration agents except for PAC whose results suggested higher loadings would be required for better results. Impregnating PAC with TMT-15® at temperatures lower than 100°C showed the best possible results, with reductions of Hg^D in the slurry to less than $1 \mu\text{g}/\text{m}^3$. However, producing impregnated PAC at temperatures lower than 100°C led to long drying times (> 24 hrs), making this preparation method not very plausible for future applications such as large scale production. So for the scope of this work, the impregnated sorbents were not investigated further.

One other important thing obtained from the bench-scale tests was it provided loading rates to be used during pilot-scale tests. For ESORB-HG-11, a minimum loading of 100 mg/l was chosen as the desired concentration of the slurry waters during testing.

For PAC, a minimum concentration of 100 mg/l was chosen; DEDTC was 1.1 mg/l; and TMT-15® was 10 mg/l. For the chelates, the concentrations chosen for the pilot-scale tests were increased from the bench-scale high values to account for scale-up issues.

Pilot-Scale Test Results and Discussion

The first results obtained for the pilot-scale tests were for preliminary testing of the scrubber using water as scrubbing liquid. For the tests, 200 ml of both pre-treatment solutions (1N KCl and 10% w/v SnCl₂) were prepared and loaded into the impingers. The sampling lines were all heated to 150 ± 20 °C, the volume of natural gas burnt was 0.9 ± 0.1 lpm, the oxygen concentration was 16.40 ± 0.30%, for an estimated average flue gas flow rate of 45 ± 10 lpm; the volume of water in the scrubber was approximately 2 gallons.

The first test was done using TMT-15®. The run lasted a total of approximately 6.5 hrs and Figure 13 summarizes the results obtained from the Horiba DM-6B. Region A represents the baseline of the mercury concentration for total and elemental mercury. The average for the values was 3.2 µg/m³ (σ = 0.4 µg/m³) and 1.0 µg/m³ (σ = 0.1 µg/m³) respectively. Region B is the start of oxidized mercury injection into the system. Sampling for regions A and B was from the pre-scrubber sample lines. Very little speciation of the mercury, Hg^T = 17.6 µg/m³ (σ = 4.8 µg/m³), Hg⁰ = 16.7 µg/m³ (σ = 2.4 µg/m³); was observed in this region. This was attributed to possible degradation of mercury in pre-scrubber sample lines. So sampling was switched to the post-scrubber outlet lines (region C), which was the sampling location for the rest of the pilot tests.

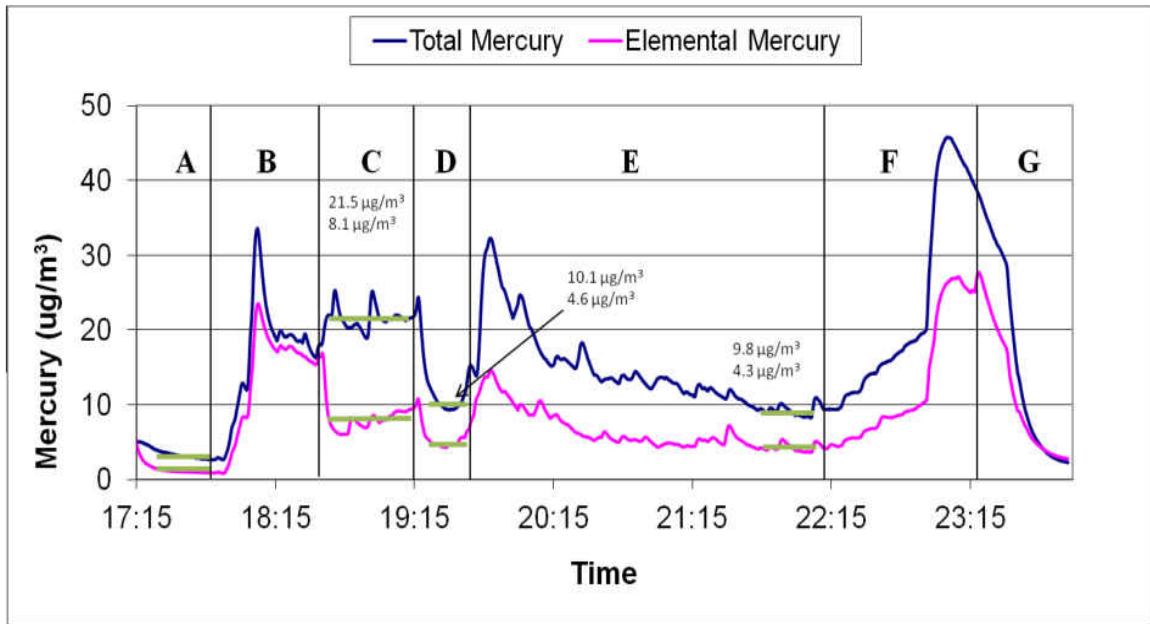


Figure 13: Preliminary pilot-scale test using water as scrubber liquid and dosed with TMT-15®

In region D, the scrubber waters were turned on, and a drop of approximately 53% was seen for the total mercury (18.3 to 8.5 $\mu\text{g}/\text{m}^3$); and 43% for the elemental mercury (7.1 to 3.6 $\mu\text{g}/\text{m}^3$). However, after 20 min of scrubbing, the mercury concentration in the flue gas started increasing again. TMT-15® was added 25 min after scrubbing started (Region E) to give a concentration of 11.2 mg TMT/l of scrubber water. The result was a peak that went as high as 32 $\mu\text{g}/\text{m}^3$ and then gradually decreased to previous levels averaging 9.8 $\mu\text{g}/\text{m}^3$ ($\sigma = 1.0 \mu\text{g}/\text{m}^3$) for total mercury and 4.3 $\mu\text{g}/\text{m}^3$ ($\sigma = 0.5 \mu\text{g}/\text{m}^3$) for elemental mercury. Addition of the TMT-15® was by dosing. The flow of scrubber slurry through the nozzles was interrupted during dosing, thus explaining the peak observed when the additives were added to the slurry tank (Region E). In region F, scrubber waters were turned off and the mercury concentration steadily increased. Region G corresponds to shut down. The huge spike seen between region F and G occurred as

the waters on the walls of the scrubber dried off, which possibly resulted in re-emission of the Hg^D .

The second preliminary test was done using DEDTC. The operating parameters were kept the same as with the TMT-15® test and run time was also 6.5 hrs. The result is shown in Figure 14. During this test, after switching on the scrubber waters, mercury was allowed to reach a steady value before DEDTC was added to the scrubber water.

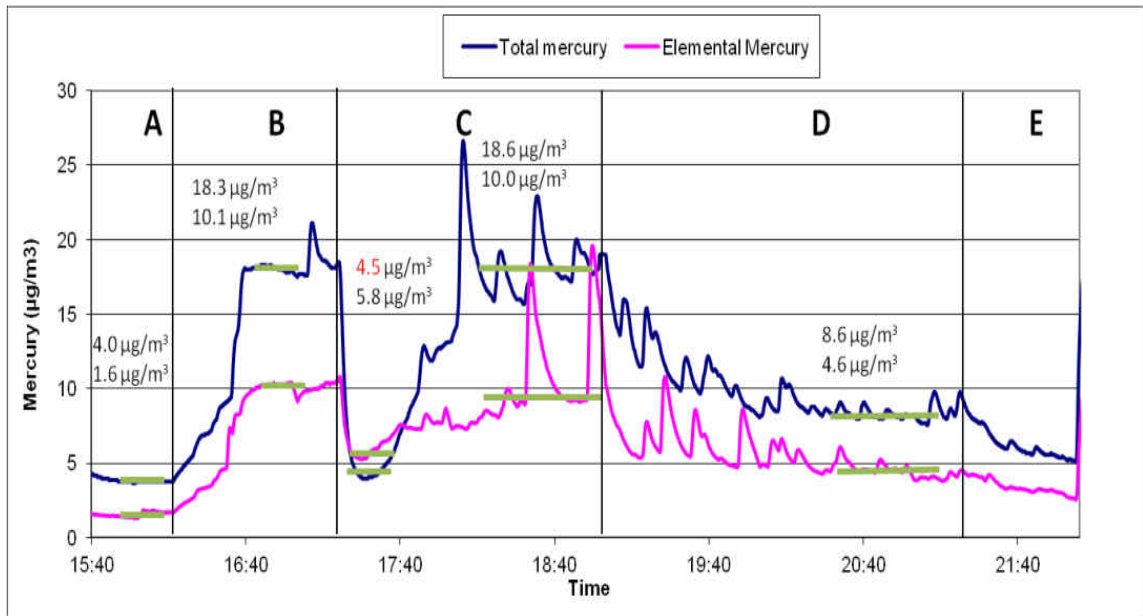


Figure 14: Preliminary pilot-scale test using water as scrubber liquid dosed with DEDTC

Region A represents the baseline mercury concentrations which averaged $4.0 \mu\text{g}/\text{m}^3$ ($\sigma = 0.2 \mu\text{g}/\text{m}^3$) and $1.6 \mu\text{g}/\text{m}^3$ ($\sigma = 0.2 \mu\text{g}/\text{m}^3$) for total and elemental mercury respectively. Region B represents the start of injection of mercury. The average concentrations here were different from those obtained during the TMT-15® test: Hg^T was $14.3 \mu\text{g}/\text{m}^3$ ($\sigma = 0.8 \mu\text{g}/\text{m}^3$) and Hg^0 was $8.5 \mu\text{g}/\text{m}^3$ ($\sigma = 0.3 \mu\text{g}/\text{m}^3$), compared to previous test values $18.3 \mu\text{g}/\text{m}^3$ and $7.1 \mu\text{g}/\text{m}^3$ respectively. In region C, the scrubber

waters were turned on, producing a drop of $13.9 \mu\text{g}/\text{m}^3$ to an average Hg^{T} value of $4.5 \mu\text{g}/\text{m}^3$ which was lower than that for Hg^0 of $5.8 \mu\text{g}/\text{m}^3$. This unusual occurrence was attributed to possible upset in the pre-treatment unit. The upset didn't last and during the reemission phase, Hg^{T} became higher than Hg^0 once more. This time, the scrubber was allowed to reach a steady re-emission level (period from 6:03 pm to 6:55 pm). The average concentration at these levels was $14.6 \mu\text{g}/\text{m}^3$ ($\sigma = 2.5 \mu\text{g}/\text{m}^3$) for Hg^{T} ; and $8.4 \mu\text{g}/\text{m}^3$ ($\sigma = 2.9 \mu\text{g}/\text{m}^3$) for Hg^0 . 10 ml of 860 mg/l DEDTC was added to the scrubber to obtain a concentration of 1.1 mg/l in the scrubber waters. This produced a drop of approximately 50% ($14.3 \mu\text{g}/\text{m}^3$ to $4.6 \mu\text{g}/\text{m}^3$) for Hg^{T} and 46% ($9.1 \mu\text{g}/\text{m}^3$ to $3.6 \mu\text{g}/\text{m}^3$) for Hg^0 .

From the preliminary results obtained using water in the scrubber, it can be seen clearly that adding a sequestration agent to the water helps improve the driving force for Hg capture by the scrubber waters. The decrease in Hg once the additives was added was not as immediate as when the scrubber slurry was turned on suggesting that some other factors are in play and time might be one of them. It is possible that because the scrubber tank was not agitated, sequestration of Hg^{D} might be limited by mass transfer. However, because the actual kinetics of the complexing equation was not studied, it is also possible that sequestration was kinetically limited. Whatever the reason, it is clear that it takes at least an hour for the full effect of adding chelates to be seen (full effect defined as new steady Hg concentration in post scrubber flue gas).

The next set of runs done were runs using scrubber slurry obtained from Minntac-Line 3. Line 3 slurry has a TSS of approximately 0.7%. Each additive was tested twice. During the first test of each additive, 2 spray nozzles were used to deliver a flow rate of

approximately 2.5 ± 0.50 lpm. Meanwhile during the second test, one spray nozzle was used to improve the spray pattern of the nozzle even though flow rates now averaged 1.5 ± 0.50 lpm. All other operating parameters were kept the same during all the tests as mentioned in Chapter III. The results on all the graphs are divided into these regions:

- Region A: Scrubber baseline with only flue gas flowing.
- Region B: Steady-state concentration of Hg^{2+} injected into flue gas.
- Region C: Scrubber waters with NO additive turned on.
- Region D: Additive added to scrubber recirculation tank by dosing.
- Region D': More additive added to increase slurry concentration (not done in all experiments).
- Region E: Shut down of experiment.

ESORB-HG-11 Results and Discussion

For the first test in Figure 15 below, 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. ESORB-HG-11 was added to the slurry (region D) to give a concentration of 100 mg/l and a drop to $7.6 \mu\text{g}/\text{m}^3$ ($\sigma = 0.5 \mu\text{g}/\text{m}^3$). More ESORB-HG-11 was added to increase the concentration to 200 mg/l further decreasing the final concentration to $5.1 \mu\text{g}/\text{m}^3$ ($\sigma = 0.4 \mu\text{g}/\text{m}^3$). This suggested a 75% decrease from baseline concentrations (region C) to additive concentration (region D'). Meanwhile, during test 2 the data was less smooth as shown in Figure 16. An increase in the Hg^{T} value was observed from region B to C, followed by a third increase in region C only. Addition of ESORB-HG-11 led to a final decrease of 68%, from Hg^{T} of $12.0 \mu\text{g}/\text{m}^3$ ($\sigma = 1.1 \mu\text{g}/\text{m}^3$) to $3.8 \mu\text{g}/\text{m}^3$ ($\sigma = 0.8 \mu\text{g}/\text{m}^3$). The noise in the data was due to fluctuations of the air flow

controlling the educator. Pulsing of the educator flow due to moisture in the rotameter caused pulsing of the flue gas flow rate and hence the spikes observed.

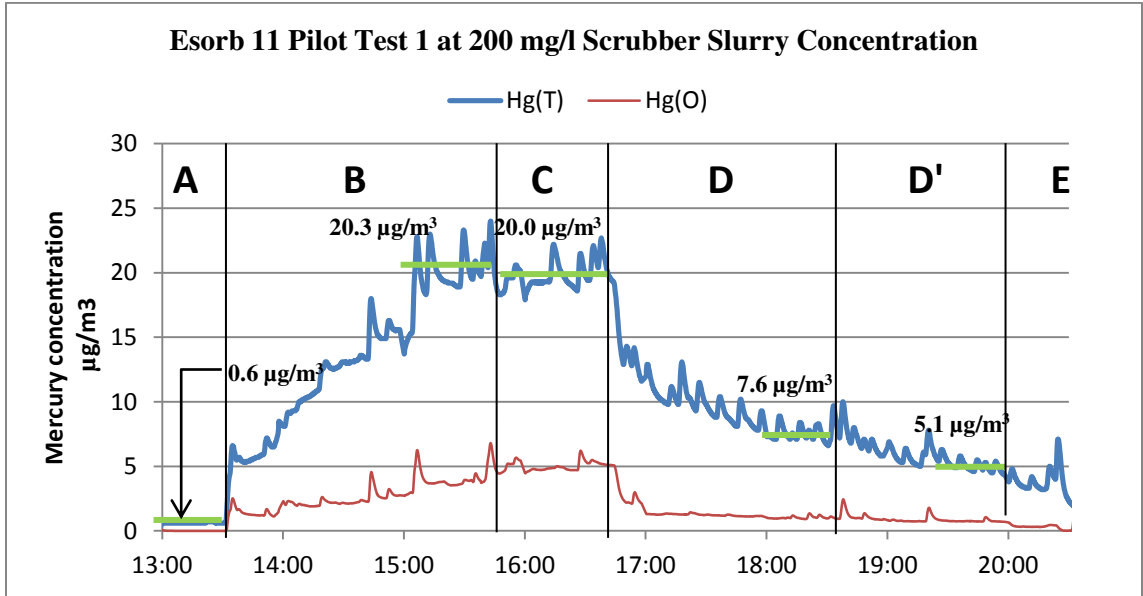


Figure 15: Pilot-scale test result for slurry ESORB-HG-11 concentration of 100 and 200 mg/l

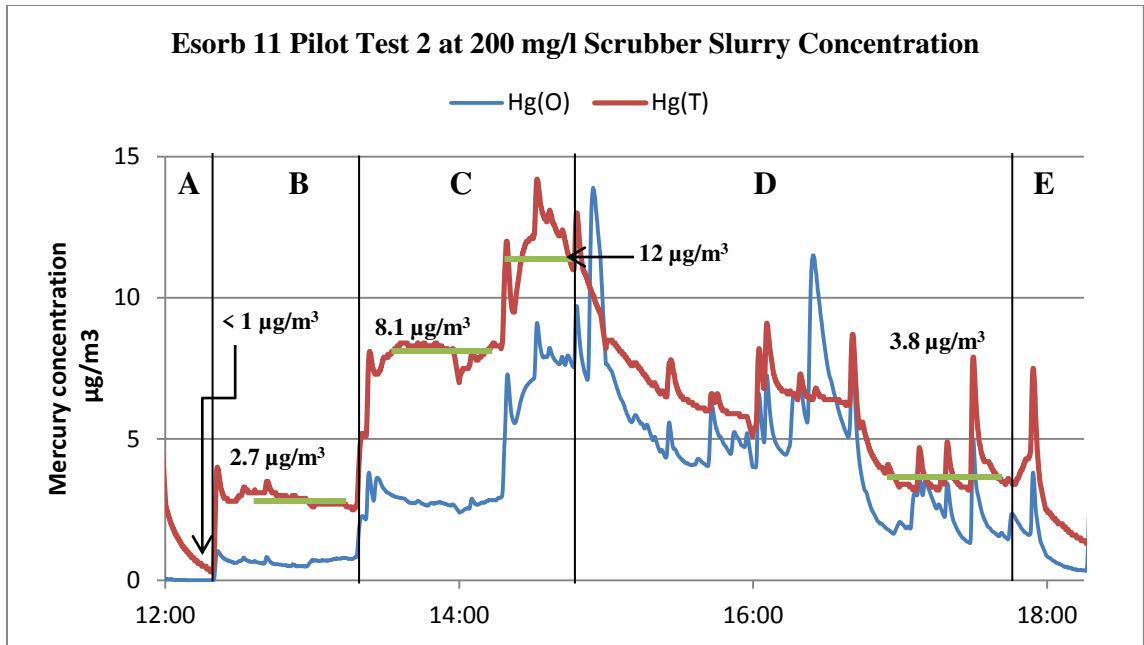


Figure 16: Pilot-scale test results for slurry ESORB-HG-11 concentration of 200 mg/l

The fluctuations in the flue gas flow explain the bump observed during test 2 just after 16:00 hour. As soon as the fluctuations were controlled, the bump dropped to a final value. ESORB-HG-11 was the additive which showed the best reductions in flue gas Hg^{T} concentrations: 75% and 68%.

PAC Results and Discussions

During PAC testing, a lot of noise was observed especially in the Hg^{O} concentration. It was not determined if any additional factors other than flue gas flow were responsible for the fluctuations, but some of the large spikes observed in data occurred once the scrubber waters were turned on, suggesting the cause might be related to the flow in the scrubber. Now for the first PAC test, the slurry PAC concentration was first set at 100 mg/l, which had a very small effect, see Figure 17, so the concentration

was then increased to 200 mg/l. This resulted in a decrease of 39%, from Hg^T of $14.4 \mu\text{g}/\text{m}^3$ ($\sigma = 0.8 \mu\text{g}/\text{m}^3$) to $8.6 \mu\text{g}/\text{m}^3$ ($\sigma = 1.6 \mu\text{g}/\text{m}^3$). For the second test, a 200 mg/l slurry concentration was used and the decrease was 53% for Hg^T , $21.2 \mu\text{g}/\text{m}^3$ ($\sigma = 2.2 \mu\text{g}/\text{m}^3$) to $9.9 \mu\text{g}/\text{m}^3$ ($\sigma = 0.9 \mu\text{g}/\text{m}^3$), as shown in Figure 18 below. The second test for PAC had a higher average baseline Hg^T concentration of $21.2 \mu\text{g}/\text{m}^3$ as compared to that of the first test which was $14.4 \mu\text{g}/\text{m}^3$. These different baseline averages are the main reasons for the difference in reduction of 39% and 53% for PAC for the two tests because the final mercury concentrations for both tests were within $1.5 \mu\text{g}/\text{m}^3$.

Clearly PAC does achieve some degree of sequestration, and even though the results are not as good as the results seen with ESORB-HG-11, it is worth investigating the effect PAC would have on Hg^D sequestration during field testing at Minntac Line 3 scrubber.

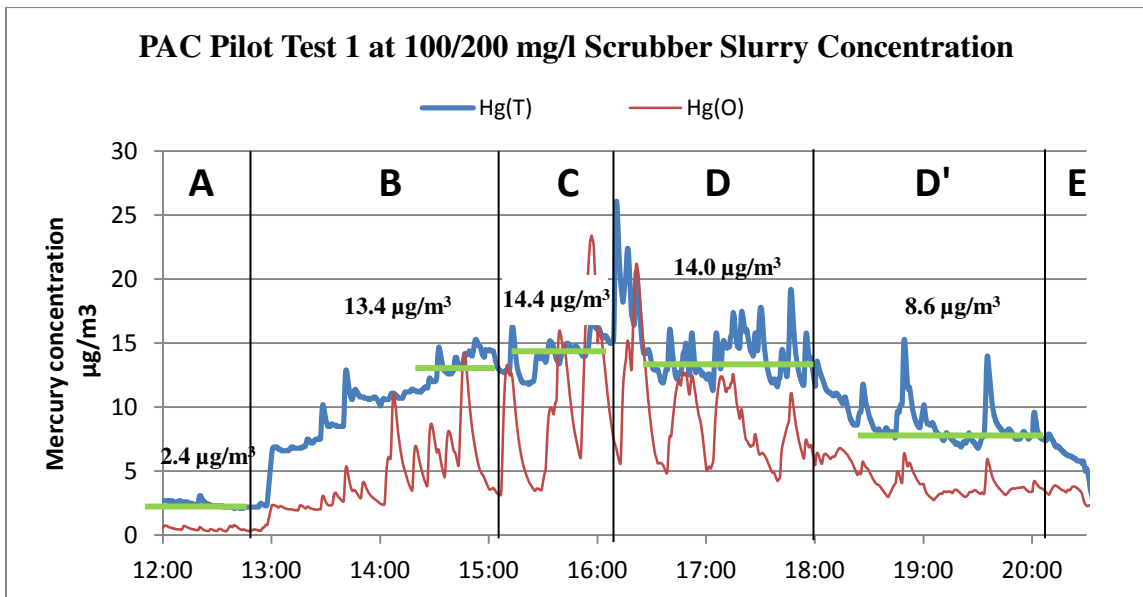


Figure 17: Pilot-scale test result for slurry PAC concentration of 100 mg/l and 200 mg/l

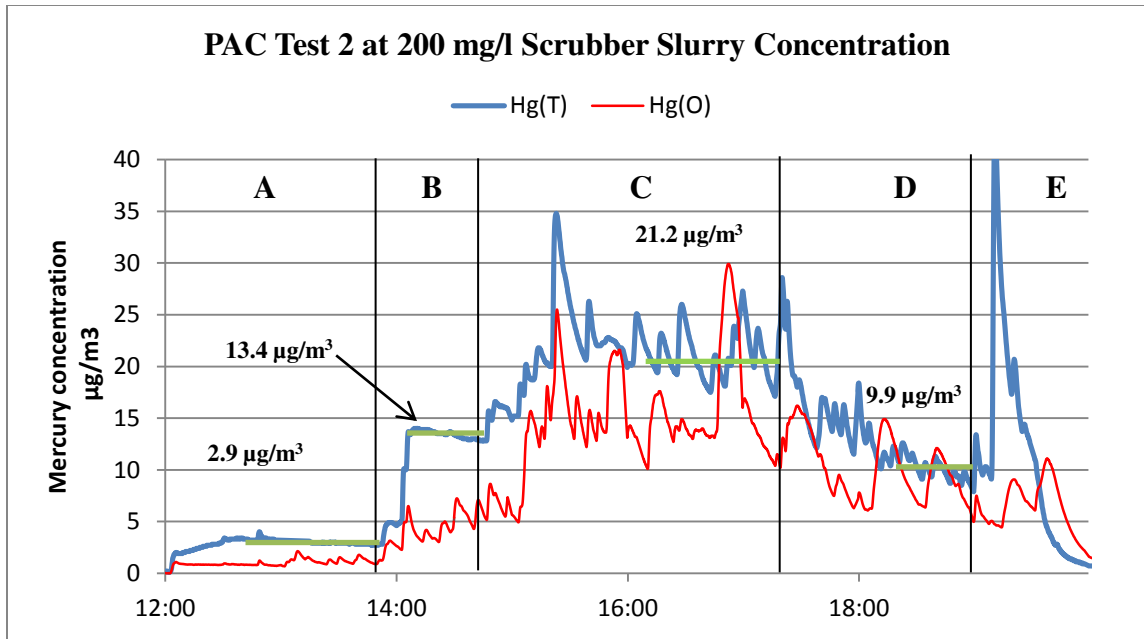


Figure 18: Pilot-scale test result for slurry PAC concentration of 200 mg/l

DEDTC Results and Discussions

The first test using DEDTC as additive, see Figure 19, showed an increase in mercury average when scrubbing started (region C). This increase was attributed to better mixing of the flue gas showed by a higher Hg^{T} average value for the period the scrubber waters were turned on. During this test, a DEDTC concentration of 1.1 mg/l was used to match the value used during the preliminary test. A reduction of 46% for Hg^{T} occurred after this, $27.0 \mu\text{g}/\text{m}^3$ ($\sigma = 4.2 \mu\text{g}/\text{m}^3$) to $14.5 \mu\text{g}/\text{m}^3$ ($\sigma = 1.5 \mu\text{g}/\text{m}^3$). Test 2 however, had a significant amount of noise, as shown in Figure 20, and was characterized by constant spikes that had to be formatted out of the graph. The spiking was seen mainly with the Hg^{T} concentration while the Hg^{O} concentration showed very little spiking. Resolving the data showed a possible concentration of $16.3 \mu\text{g}/\text{m}^3$ in region C, and a drop to $11.3 \mu\text{g}/\text{m}^3$

after DEDTC concentration was increased to 2.2 mg/l (standard deviations were not calculated due to the spiking).

TMT-15® Results and Discussions

Test 1 of TMT-15® was very smooth, however, it was the only test which showed a drop in average Hg^T value when the scrubber waters were turned on, see Figure 21 region C. A drop of $2.4 \mu g/m^3$ was observed, and no other reason can be given for this except that there was possible channeling of injected Hg^{2+} before scrubber waters were turned on, causing a higher value of Hg^T to be measured in region B. A decrease of 58%, $9.6 \mu g/m^3$ ($\sigma = 0.8 \mu g/m^3$) to $4.0 \mu g/m^3$ ($\sigma = 0.3 \mu g/m^3$), was observed after adding TMT-15® to a concentration of 10 mg/l in the slurry. Test 2 didn't show the drop in average Hg^T for region C as was the case in test 1, instead and increase of $3.9 \mu g/m^3$ was observed, see Figure 22.

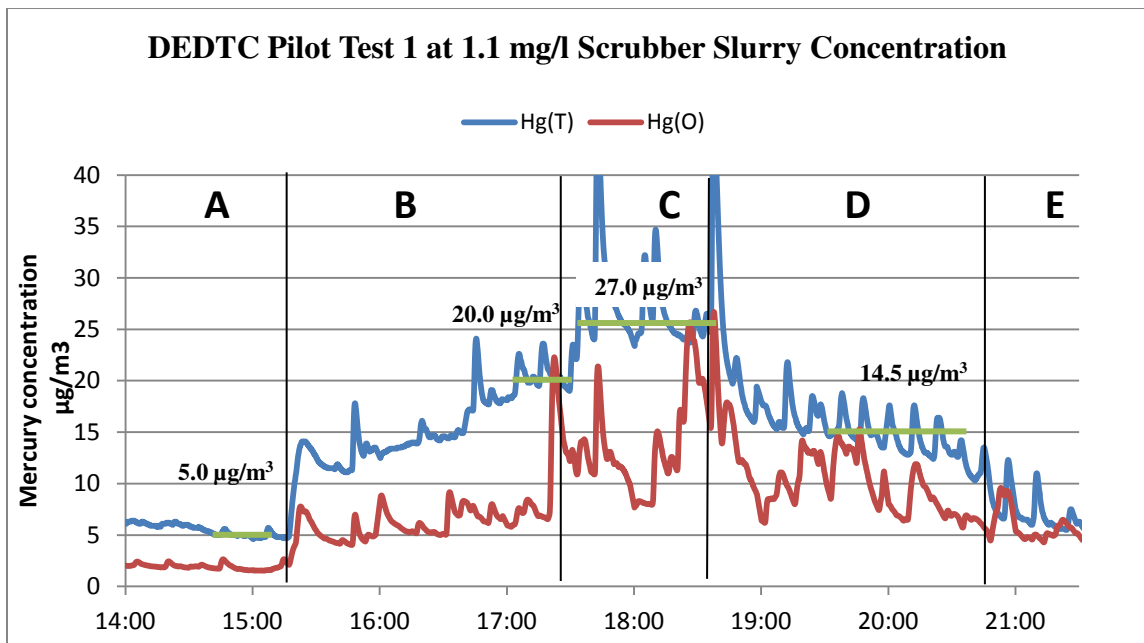


Figure 19: Pilot-scale test result for scrubber DEDTC concentration of 1.1 mg/l

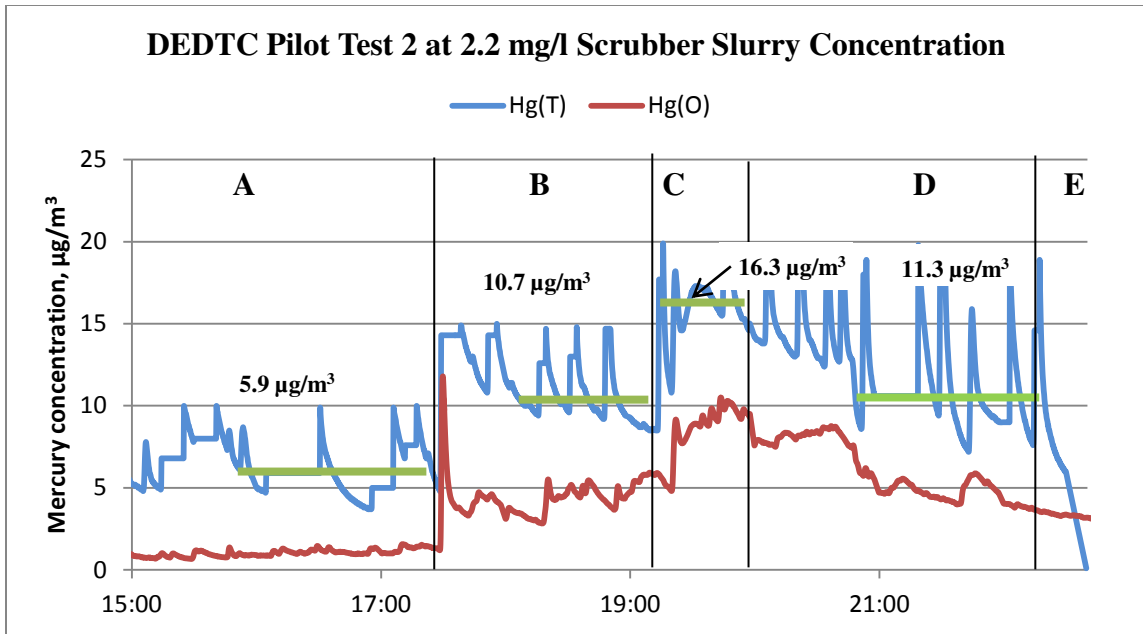


Figure 20: Pilot-scale test result for scrubber DEDTC concentration of 2.2 mg/l

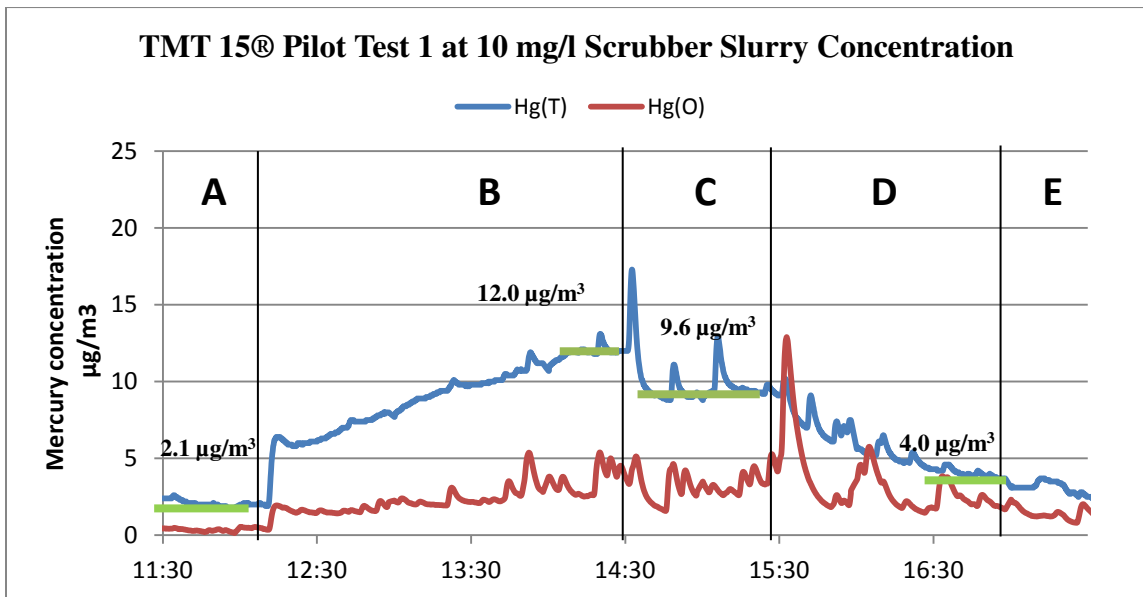


Figure 21: Pilot-scale test result for scrubber TMT-15® concentration of 10 mg/l

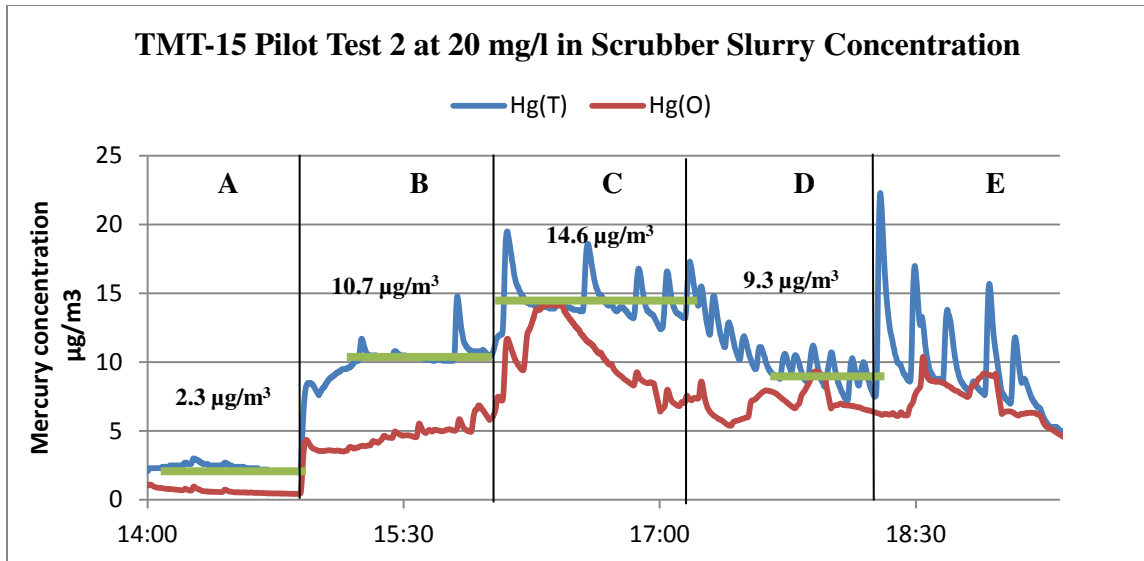


Figure 22: Pilot-scale test result for scrubber TMT-15® concentration of 20 mg/l

Pilot-Scale Testing Conclusion

It has been clearly demonstrated that addition of a sequestering agent into the slurry of a scrubber would improve the driving force for capture of Hg^{2+} , and in the particular case of this example, even though the slurry waters were recirculating at a rate of 2.0 to 3.0 lpm for a slurry volume of 2 gallons; the sequestering agents added were at increasing the capture of Hg^{2+} with time. ESORB-HG-11 was the most effective of the sequestering agents, confirming the results of the bench-scale test. During ESORB-HG-11 addition, average concentrations dropped by $14.9 \mu\text{g}/\text{m}^3$ and $8.9 \mu\text{g}/\text{m}^3$ after at least two hours of adding the sorbent to the scrubber recirculation. Other additives also showed sequestration, but none as significant as with ESORB-HG-11.

Also Line 3 slurry showed no capacity of capturing mercury even though analysis of its waters showed Hg^{D} concentrations less than $1 \mu\text{g}/\text{m}^3$. This was unexpected because all the mercury in solution was believed to be adsorbed unto the solid particles, so it was

expected that the slurry might still be able to capture HgCl_2 . Preliminary testing also showed that fresh water gets saturated pretty fast when used to scrub Hg^{2+} , and once that occurs Hg^{2+} concentration in the flue gas increases again. Re-emission of the Hg^D captured with tap water was not investigated, so it wasn't determined if that might be a contributing factor to the flue gas Hg concentrations increase during scrubbing with water.

During the repeat tests for all the additives, a lot of noise was observed in the data. This was due to a couple of problems encountered with the test equipment. The first of these problems was the flow rate of the flue gas. Flue gas flow was controlled using air obtained from a compressor and an eductor. Fluctuations in the compressed air pressure and significant presence of moisture in compressed air lines, as observed during repeat tests, caused intermittent surges in the flue gas flow rate that resulted in significant spikes (noise) observed in the CMM mercury reading. This phenomenon largely affected the smoothness of the data reported, and even required resolving the data for DEDTC repeat test. Steps required to mitigate this occurrence are constant monitoring of the flow rate coupled with purging of the compressed air lines to eliminate moisture. Optimizing test equipment performance (spray pattern of nozzles, stable flue gas flow and stable Hg^{2+} stream) also would improve the quality of the results.

CHAPTER V

FIELD TESTING METHODOLOGY

Testing Plan

Field testing was performed at Minntac-Line 3 plant located in Mountain Iron, Minnesota. Testing on Minntac-Line 3 was performed over a period of three weeks starting on October 10, 2011 and lasting until October 28, 2011. Equipment set-up occurred on October 11 and 12; meanwhile, tear down was on October 27 and 28. The first stage of testing involved equipment set-up and establishing pre-test baseline emissions. This took a total of four days. Testing consisted of injecting halogenated activated carbon (ESORB-HG-11) and PAC sorbents into the process waste gas using injection equipment supplied by a UND sub-contractor (IAC International, Mission, KS); and dosing the recirculation tank with the mercury chelate - DEDTC.

Sorbents were supplied by Envergex LLC of Sturbridge, MA in 1000-lb bulk bags. The sorbent injection equipment (Figures 23 and 24) consisted of a bulk bag handling system, feeder to meter sorbent, blower and compressor for supplying the conveying air, an eductor to pick up the sorbent discharged from feeder, hoses to convey the sorbent, distributors, and injection lances to disperse the sorbent into the flue gas duct. The injection testing agents - PAC and ESORB-HG-11; were transported through the hoses and distributors to the injection lances and into the flue gas, using air as

transport media. The sorbent feed hopper was placed on a mass scale to determine additive injection rate.



Figure 23: Sorbent injection trailer with blower and compressor housing; bulk bag lifter assembled, and the bulk bag in place.



Figure 24: Close-up view of bulk/sorbent bag handling system and discharge hose

The first injection test ports were about 30 feet upstream of the pre-heat fans. The pre-heat fans are the fans located under the pre-heat section of the grate, and they handle

waste gas flow from the pre-heat to the drying zone of the grate (see chapter II for description). Four ports were installed by Minntac personnel on each of the ducts leading to the fans. This allowed the installation of eight lances for sorbent injection. Injection of the sorbent upstream the fans provided an additional benefit of improved distribution of the sorbent particles in the flue gas.

The second injection location were ports located on the wall of the preheat zone. 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 capture at this location and the low temperatures of the flue gas after the drying zone, it was anticipated that the mercury capture efficiencies would be low. It was decided to have this injection location changed to the preheat zone wall. A request regarding this change was presented to the plant and Minnesota DNR and approval was obtained.

For the dosing of the scrubber, DEDTC was added to the scrubber by dosing the scrubber recirculation tank to concentrations of 0.7, 1.4 and 7 mg/l; meanwhile, PAC and ESORB-HG-11 injected into the flue gas ended up in the recirculation tank so no direct addition into scrubber was needed. The fact that the scrubber of Line 3 is a recirculation had the unfortunate effect of affecting a return to baseline speciation of mercury in the scrubber slurry. It would take approximately 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 as no injection was performed on weekends). Table 1 summarizes the testing matrix at Minntac Line 3.

Table 4: 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	CMM		
	7am -7pm	Equipment Setup				Scrubber Stack	OH		
10/12/2011	7am-7pm	Pre-Test				Scrubber Stack	CMM		
10/13/2011	7am -10am	Baseline				Scrubber Stack	CMM	Green Pellets, Scrubber Slurry	
	10am - 1pm	Baseline				Scrubber Stack	CMM & OH		
	1pm - 4pm	Baseline				Scrubber Stack			
	4pm - 7pm	Baseline				Scrubber Stack			
10/14/2011	7am – 4pm	Baseline				Scrubber Stack	CMM & OH	Green Pellets, Scrubber Slurry	
	4 pm - 5 pm	Condition 1	ESORB-HG-11	25 lb/hr	1A & 1B Pre-Heat Fans	Scrubber Stack	CMM	Multi-clone solids, Scrubber Slurry	
	5pm - 7pm	Condition 2		50 lb/hr		Scrubber Stack	CMM		
	7pm - 9pm	Condition 3		100 lb/hr	Scrubber Stack	CMM & OH			
10/17/2011	7am - 10am	Baseline				1A & 1B Pre-Heat Fans	Scrubber Stack	CMM & OH	Green Pellets, Multi-Clone 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 & OH	Scrubber Slurry		

Table 4. Cont.

Date	Time	Test Condition	Sorbent Type	Injection Rate	Injection Location	Sampling Location	Sampling Type	Samples Collected				
10/18/2011	7am - 10am	Baseline	ESORB-HG-11		1A & 1B Pre-Heat Fans	Scrubber Stack	CMM & OH	Green Pellets, Multi-Clone Solids, Scrubber Slurry				
	10am - 7pm	Condition 3	ESORB-HG-11	100 lb/hr								
10/19/2011	7am -11am	Baseline			1A & 1B Pre-Heat Fans	Scrubber Stack	CMM & OH	Multi-Clone Solids, Scrubber Slurry				
	11am - 2pm	Condition 1	DEDTC	0.7 mg/l								
	2pm - 3pm	Condition 2	DEDTC	1.4 mg/l								
	3pm -5pm	Condition 3	DEDTC	7.0 mg/l								
	5pm - 9am	Condition 4	DEDTC and ESORB-HG-11	BC = 50 lb/hr DEDTC = 7.0 mg/l					1A & 1B Pre-Heat Fans	Scrubber Stack	CMM & OH	Scrubber slurry & Multi-clone
	10am -1 pm	Condition 3										
10/20/2011	7am - 11am	Baseline			1A & 1B Pre-Heat Fans	Scrubber Stack	CMM & OH	Multi-Clone Solids, Scrubber Slurry, Green Pellets				
	11am - 12pm	Condition 1	PAC	50 lb/hr								
	12pm - 3pm	Condition 2	PAC	100 lb/hr								
	3pm -5pm	Condition 3	PAC	150 lb/hr								
10/21/2011	7am -12pm	Baseline			1A & 1B Pre-Heat Fans	Scrubber Stack	CMM and OH	Green Pellets, Multi-Clone Solids, Scrubber Slurry				
	12am - 5pm	Condition 4	ESORB-HG-11	150 lb/hr								
10/24/2011	7am - 10am	Baseline				Scrubber Stack	CMM and OH	Green Pellets, Multi-Clone Solids, Scrubber Slurry				

Table 4. Cont.

Date	Time	Test Condition	Sorbent Type	Injection Rate	Injection Location	Date	Time	Test Condition
	10am - 1 pm	Condition 5	ESORB-HG-11	75 lb/hr	1A & 1B Pre-Heat Fans	Scrubber Stack	CMM & OH	
10/25/2011	7pm – 10am	Baseline				Scrubber Stack		Green Pellets, Multi-Clone Solids, Scrubber Slurry
	10am - 12pm	Condition 1	ESORB-HG-11	50 lb/hr	1A & 1B pre-heat fans (4 inj. Lances) + Pre-Heat zone (8 inj. Lances)	Scrubber Stack	CMM	
	12pm - 4pm	Condition 2	ESORB-HG-11	75 lb/hr		Scrubber Stack	CMM and OH	
	4pm - 5pm	Condition 3	ESORB-HG-11	75 lb/hr	1A & 1B pre-heat fans (4 inj. Lances) + Pre-Heat zone (4 inj. Lances)	Scrubber Stack	CMM	
10/26/2011	7pm – 10am	Baseline				Scrubber Stack	CMM & OH	Green Pellets, Multi-Clone Solids, Scrubber Slurry
	10am -12pm	Condition 4	ESORB-HG-11	100 lb/hr	1A & 1B pre-heat fans (4 inj. Lances) + Pre-Heat zone (4 inj. Lances)	Scrubber Stack	CMM	
	2pm -6pm	Condition 5	ESORB-HG-11	100 lb/hr	1A & 1B pre-heat fans (4 inj. Lances) + Pre-Heat zone (4 inj. Lances)	Scrubber Stack	CMM & OH	
10/27/2011	7am -7pm	Equipment Tear-Down				Scrubber Stack		
10/28/2011	7am -7 pm	Equipment Tear-Down				Scrubber Stack		

Sampling Plan

Sampling during mercury control testing was aimed at understanding the fate of mercury during technology deployment. Sampling focused on three areas: Amount of mercury entering induration system, mercury captured by particulate control devices, and mercury emitted through stack (not captured). The mercury entering the system was determined by sampling the green balls; meanwhile, the mercury captured by particulate control devices was determined by sampling multiclones dust and scrubber slurry. Mercury emitted was determined by sampling the stack.

Stack Sampling

Stack measurements were performed by UND's sub-contractor, Western Kentucky University's Institute for Combustion Science and Environmental Technology in Bowling Green, KY (WKU - ICSET). WKU - ICSET used a PS Analytical (PSA) continuous mercury monitor (CMM) with a wet conversion system to obtain semi-continuous mercury concentrations in the stack gas, and an extractive sampling method - ASTM D 6784 (commonly known as Ontario Hydro Method- 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; meanwhile, the CMM was used to observe trends during testing. The OHM method typically provides an average of all components of the mercury emission over the sampling period: Hg^0 , Hg^{2+} , and particulate mercury (Hg^P). The sum of these components provides the total mercury (Hg^T) concentration in the stack gas. The OHM was run for approximately 1

hour during each run, with a gas sampled volume in the range of 0.70 to 0.90 m³. During a typical test day, one OHM sample was collected before testing to obtain a baseline, and at least one during testing. This made it possible to obtain a baseline and average mercury reductions for each test day. The CMM was operated continuously during each testing day but not overnight. Because of the long duration of the tests, coupled with the fact that the CMM was not operated overnight, the stack mercury behavior at the end of each testing was not fully investigated. It is also important to note that on some testing days, the technology investigated was not always deployed immediately after performing the baseline OHM.

Impinger solutions used in the OHM test were immediately analyzed at the end of each test by WKU - ICSET's mobile laboratory. The quality of OHM data was ensured through use of QA/QC procedures as required for laboratory and field analyses. Leak checks were performed during runs, and samples obtained were analyzed by ICSET mobile laboratory following the QA/QC procedures: Sampling analyses as duplicates/triplicates, spiking, use of standards and blanks to ensure 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 upset/troubleshoot during sampling. Accuracy of measurements was further assured by comparing OHM and CMM results at local O₂ concentrations (approximately 18%) on a dry basis. Relative difference between OHM and CMM was less than 12%, except for one measurement (24%). This relative difference is considered good agreement when compared to data from similar mercury testing work using OHM and CMMs (31).

Green Ball Sampling

Green ball samples were collected by Minntac laboratory personnel and delivered to the UND testing team. Sampling of the green balls consisted of collecting a 5 minute composite sample in buckets from roll feeders upstream of the grate. The buckets were then delivered to the UND sampling team that proceeded to transfer the samples into clean, labeled plastic bags and then stored them for submission later to ICSET for mercury analysis. Samples were collected at three different time intervals each day.

The objective of the green ball sampling was 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 work, it was decided that the daily average mercury concentration of the green balls would be considered as the mercury concentration input for all mass balance calculations of that day. The daily average mercury concentration was determined by averaging the results from the samples obtained on each test day. The mercury concentrations obtained for the green ball samples show close agreement with concentrations obtained during previous work performed on Minntac Line 3 (30).

Scrubber Slurry Sampling

Scrubber samples were collected by UND testing team from the scrubber recirculation tank from a valve located upstream of the scrubber blow down pump. The slurry in the tank is agitated continuously, thus providing a high degree of confidence on the representativeness of sampling from the blow down pump. For sample collection, the valve was first purged for at least 10 seconds, and then a sample was collected in a large bucket. The bucket was then transported to the filtration area. Here, using clean

hands/dirty hands, the bucket was further agitated, and then a 500 ml sample was collected and filtered entirely using 0.7 micron Whatman glass fiber filters obtained from Millipore. The filtrate was then transferred into pre-washed containers containing nitric acid (filtrate containers only) 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. ICSET used EPA Method 7470 to determine mercury concentration in the filtrate samples. However, it was observed that most filtrate samples obtained during sorbent injection testing had mercury concentration values below the detection limit for this method. Later, samples were 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 returned a non-detect value, a default value of 0.2 µg/L was assumed during data reduction. This number was selected because it is the detection limit of the method used.

To ensure QA/QC during sampling, duplicates and blanks were also collected to assess sampling accuracy and precision. A field blank was processed which involved transporting a bottle containing clean water, and transferring it into a pre-cleaned sample bottle. The result was below the MDL for EPA Method 1631-low mercury analysis. Duplicates showed good agreement. Blanks initially processed using EPA Method 7470 also showed values below the minimum detection limit.

Multi-clone Solids Sampling

Multi-clone solids were collected by the UND testing team from the multi-clone blow down. Minntac Line 3 is equipped with 8 cyclones each having its own blow down port. Sampling from all ports required collecting a composite from each blow down port

consecutively. Multi-clone dust samples are required to provide an estimate of the mercury leaving the system through the multi-clones. The blow down rate (mass loading) is not measured and varied significantly during different sampling periods, with no sample collected during certain sampling periods. Additionally, analysis of collected samples showed a large variability in mercury concentration. We therefore estimated the blow down rate 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 multi-clone mercury measurement of 450 ng/g to give a maximum possible mercury flux of 0.08 grams/hr through the blow down, which is less than 3% of the average mercury (3.0 grams/hr) entering the system. This is consistent with measurements done by Berndt (23), that showed very low mercury content in multi-clone blow down.

Sampling involved collecting blow down dust into a clean plastic bag and then transferring into a second plastic bag for storage. The location of the blow down port required extra caution during sampling to avoid the risk of contamination of samples by the water used to wash and transport the blow down to the thickener. Collected samples were stored on ice for analysis later by WKU - ICSET.

Samples from the multi-clones and scrubber were collected 30 min after the start of the OHM. This way the samples collected were representative of the testing taking place. Consequently, samples were collected during baseline and technology deployment, providing results obtained during the same time frame.

CHAPTER VI

FIELD TEST RESULTS

Results obtained during field testing are divided into different sections to facilitate interpretation of the data obtained. Three different control technologies were tested: PAC, ESORB-HG-11 and DEDTC. Testing of ESORB-HG-11 was done at two different locations, while testing of PAC and DEDTC was done at one location each. Moreover, three main objectives were sought: Oxidation, capture and sequestration. Only ESORB-HG-11 and PAC were tested for oxidation and capture potential, while all three were tested for sequestration potential. In order to present the results coherently, the following objectives were set when interpreting the data: First, establishing average daily concentration of mercury entering the induration step of the process and corresponding baseline mercury emissions for Minntac-Line 3. The second objective is presenting the results obtained for tests aimed at improving oxidation and capture of mercury, and the third is presenting the results obtained for sequestration tests.

Green Ball and Baseline Sampling Results

Green ball samples were analyzed using EPA Method D6722 and showed mercury levels varying from a low 4 ng/g to a high 18 ng/g for samples collected and analyzed over the three week testing period. The lowest values were obtained for samples collected on October 13 and 21, which were not submitted for analyses to WKU-ICSET

with the rest of the samples collected, so were flagged as possibly not accurate. Table 5 lists the green ball mercury concentrations for the test duration. The average mercury concentration in the green balls for the entire test period was 12.4 ng/g, ($\sigma = 2.9$ ng/g). The average value showed good agreement with previous work (30). The daily results obtained for green ball samples submitted for analyses were averaged. The average value was then used for any mercury reduction calculations. This method of determining green ball concentration was chosen because previous work suggested that concentrations could show large variability even when sampled on the same day (27,28). So it was assumed that this average would provide a sufficiently reliable estimate of the mercury concentration entering the system.

Table 5: Showing green ball mercury concentrations

Date	Sample ID	Collection time	Mercury concentration ng/g	Daily Average (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 too low and possibly inaccurate

Due to the fluctuations in taconite feed mercury concentrations in the green ball material metered to the grate kiln inlet, baseline emissions were considered important for estimating oxidation and capture. The first testing day, October 13, was used for baseline mercury emissions. Also a baseline measurement was performed every day before testing, to account for daily variations in mercury concentrations. The main technique used for measuring mercury concentrations was the OHM. The CMM was used to provide trends and observe the effects of sorbent injection.

Baseline emission data for the stack gases from the three week testing period is summarized in Table 6 and Figure 25 below. The OHM provides mercury speciation: Hg^{2+} , Hg^0 and Hg^{P} . Summing Hg^{2+} and Hg^0 give the total vapor mercury (Hg^{VT}). In Table 3, the sum of the different mercury forms, Hg^{VT} and Hg^{P} , gives the total mercury (Hg^{T}) in the waste gas. Table 6 also lists Hg^{VT} concentrations, as measured using the CMM. CMM Hg^0 and Hg^{VT} are also calculated by averaging CMM data obtained during the time period of OHM sampling. The standard deviation of these averages is also listed. Several observations can be made from the baseline data shown in Table 3. Baseline Hg^{T} from the OHM data for stack emissions at Minntac Line 3 ranged from 3.5 - 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 in the time scale that 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 ; and the values ranged from 83 to 90 % of Hg^{T} , with the exception of one measurement.

Table 6: Baseline CMM and OHM concentrations for Hg^{VT}, Hg⁰, Hg^P and Hg^T

Date	CMM		CMM		OHM Hg ⁰ μg/m ³	OHM Hg ^{VT} μg/m ³	OHM Hg ^P μg/m ³	OHM Hg ^T μg/m ³
	Hg ⁰ μg/m ³	Std Dev	Hg ^{VT} μg/m ³	Std Dev				
13th (1)	2.32	0.26	4.24	0.41	3.70	4.45	-	-
13th (2)	2.58	0.13	3.88	0.30	3.98	4.93	-	-
13th (3)	2.78	0.08	4.1	0.32	4.64	5.19	-	-
14th	4.20	0.19	5.51	0.27	5.86	6.69	-	-
17th	5.12	0.30	7.08	0.88	5.82	8.22	0.02	8.24
*18th	n/a	n/a	n/a	n/a	5.35	6.17	0.03	6.20
19th	4.08	0.13	5.19	0.15	4.63	4.86	0.07	4.93
20th	1.56	0.14	2.11	0.17	3.14	3.44	0.03	3.47
21st	3.12	0.50	3.96	0.13	4.50	5.04	0.02	5.06
24th	3.56	0.16	5.11	0.41	4.38	4.98	0.08	5.06
25th	3.11	0.29	4.39	0.39	3.35	3.81	0.20	4.01
26th	4.03	0.37	4.55	0.30	3.84	4.09	0.10	4.19

* CMM not running during OHM due to troubleshooting

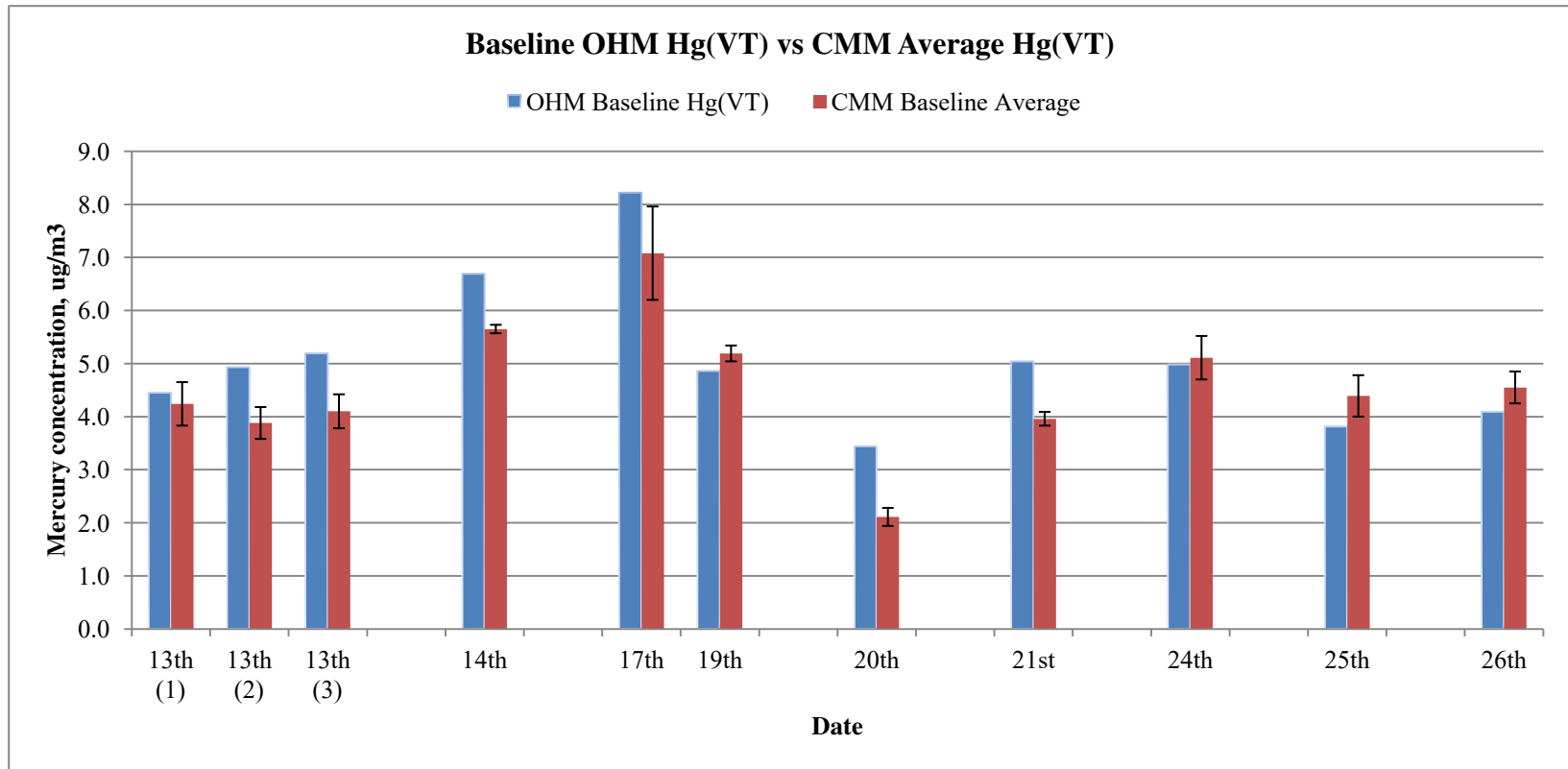


Figure 25: Bar graph summarizing baseline data obtained during entire field test program and showing standard deviation of CMM data

There was a reasonable agreement between the CMM and the OHM measurements for the vapor phase mercury components. The standard deviation of the mercury concentration values as measured by the CMM were typically 10 percent or lower of the average CMM values. A specific example of the comparison of OHM and CMM data is for October 13, a full day of baseline measurements. On this day, three OHM measurements were performed along with data collection on the CMM. The three OHM measurements showed consecutive values of 4.45, 4.93 and 5.19 $\mu\text{g}/\text{m}^3$ for Hg^{VT} . Meanwhile, average CMM measurements during the same period during which each OHM measurement was performed showed concentrations of 4.24 (0.41), 3.88 (0.30) and 4.10 (0.32) $\mu\text{g}/\text{m}^3$ respectively (standard deviations shown in brackets). The relative difference between the OHM and CMM values are less than 12%. This trend was also seen during other test days. Figure 26 shows the CMM baseline data for the 13th.

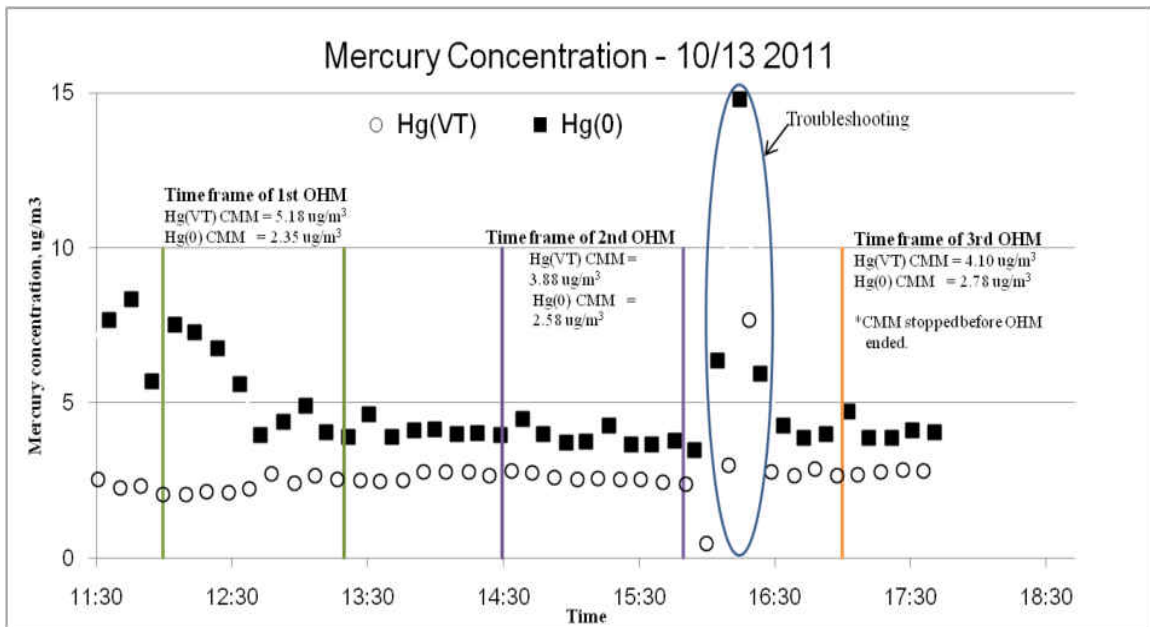


Figure 26: Baseline CMM data for October 13th

Oxidation and Capture Results

ESORB-HG-11 Testing

Pre-heat Fan Injection Location

The objective of injecting ESORB-HG-11 upstream of the preheat fans was to increase oxidation and capture of mercury in the flue gas. ESORB-HG-11 is a proprietary halogenated PAC provided by Envergenx LLC. A key aspect of this proposed technology was the identified choice of the injection location. The first injection test locations were about 30 feet upstream of the preheat fan inlets, after the process gases have exited the preheat section of the grate-kiln. Injection of the sorbent upstream of the fans provided another benefit – the improved distribution of the sorbent particles in the flue gas.

The objective of the first injection tests performed during the first two test days - 14th and 17th; aimed at identifying the most promising sorbent injection rates for mercury reduction in stack waste gas. Injection rates of 25, 50, 100 and 150 lb/hr; were tested for at least an hour. During testing, the CMM was monitored for any observable change. On the 14th, electrical issues were encountered with the injection equipment, delaying the start of testing by 5 hours from the time the OHM baseline was performed. The OHM baseline gave an Hg^{VT} of $6.69 \mu\text{g}/\text{m}^3$ (table 7). The first injection rate investigated was 25 lb/hr of ESORB-HG-11. During this injection period, an upset occurred, as seen on the CMM chart (Figure 27), so no actual reduction was seen. After the effects of the upset on the CMM subsided, the injection rate was then increased to 50 lb/hr and Hg^{VT} , per the CMM, dropped from approximately $3.93 \mu\text{g}/\text{m}^3$ to $2.60 \mu\text{g}/\text{m}^3$. The injection rate was then increased to 100 lb/hr and an OHM performed. The OHM after analysis gave an

Hg^{VT} of 2.85 µg/m³ (table 7). The CMM's average Hg^{VT} during the time the OHM was performed was 1.98 µg/m³.

On the 17th, the injection rates tested were 50, 100, and 150 lb/hr. OHM measurements were done for baseline conditions and for sorbent injection rates of 50 and 150 lb/hr. The OHM baseline Hg^{VT} was 8.22 µg/m³ (table 7). The CMM average during this same period was 7.08 µg/m³ (Figure 28). OHM measurements for the 50 and 150 lb/hr injection rates yielded values for Hg^{VT} of 2.16 and 1.22 µg/m³ respectively. The CMM average Hg^{VT} concentration during the same time as the OHM sampling gave values of 2.93 µg/m³ and 1.07 µg/m³ for 50 and 150 lb/hr injection rates respectively.

Table 7: OHM and CMM Hg concentrations during short term testing on the 14th and 17th

Date		OHM	OHM	OHM	OHM	CMM		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)	S.D.	Hg ^{VT} (µg/m ³)	S.D.
17 th	Baseline	5.82	8.22	0.02	8.24	5.12	0.30	7.08	0.88
	50 lb/hr	1.71	2.16	0.06	2.22	2.12	0.16	2.93	0.21
	150 lb/hr	1.14	1.22	0.59	1.81	0.53	0.06	1.07	0.29
14 th	Baseline	5.86	6.69	n/a	6.69	4.26	0.10	5.65	0.08
	100 lb/hr	2.36	2.85	0.13	2.98	1.16	0.25	1.98	0.57

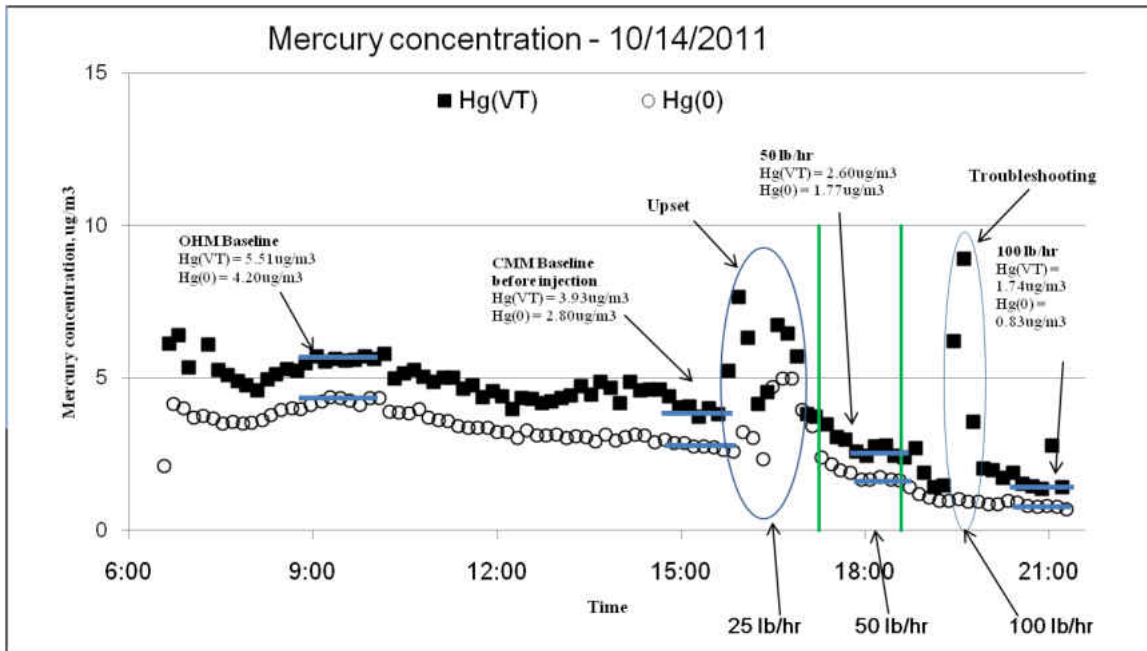


Figure 27: CMM chart for short term testing on 14th

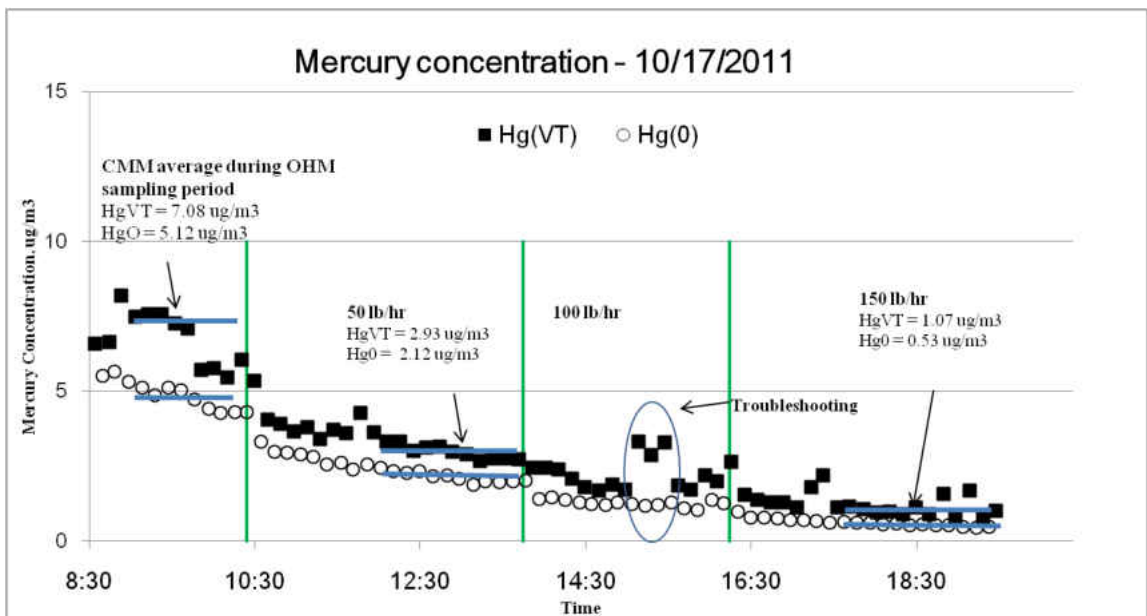


Figure 28: CMM chart for short term testing on the 17th

A couple of observations arose during data reduction. First of all, closer observation of the CMM graph for the 17th (Figure 28), showed a spike for the oxidized mercury from 8:50 to 9:40. This spike was consistent with OHM data, which also showed an abnormally high oxidized mercury concentration of 2.40 $\mu\text{g}/\text{m}^3$ (Table 7). The CMM and OHM used separate probes; meaning whatever caused this spike occurred either before or in the stack. The second observation made was with the Hg^{P} during injection. The total mercury concentrations Hg^{T} from the OHM measurements for the 50 and 150 lb/hr injection rates are 2.22 and 1.81 $\mu\text{g}/\text{m}^3$, compared to Hg^{VT} concentrations of 2.16 and 1.22 $\mu\text{g}/\text{m}^3$ respectively (table 7). This suggests that at the higher injection rates, some of the ESORB-HG-11 penetrates the scrubber and contributes to the stack emission as particulate mercury. Visual inspection of the probe filter confirmed this.

Testing results for 150 lb/hr for the 17th suggested a decrease of 78% from the baseline Hg^{T} value 8.24 $\mu\text{g}/\text{m}^3$. This was actually a very good result, so it was decided that the injection rates of 100 lb/hr and 150 lb/hr be investigated further for longer periods of approximately 5 hrs. An additional injection rate of 75 lb/hr was also investigated to see if a lower injection rate could still provide promising results.

The objective of the second test series was to investigate the effect of injecting ESORB-HG-11 for approximately 5 hrs. The first of these tests was done on the 18th, where injection of 100 lb/hr was performed for a duration of 5 hours. There were three OHM measurements: baseline, 3 hours, and 5 hours after start of injection was started. The baseline values for Hg^{VT} before injection was 6.17 $\mu\text{g}/\text{m}^3$; meanwhile, the Hg^{T} was 6.20 $\mu\text{g}/\text{m}^3$ (Table 8).

Table 8: OHM and CMM concentrations during long term testing on the 18th, 21st and 24th

Date		OHM	OHM	OHM	OHM	CMM		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)	S.D.	Hg ^{VT} (µg/m ³)	S.D.
18 th	Baseline	5.35	6.17	0.03	6.20	n/a*	n/a*	n/a*	n/a*
(100 lb/hr)	3 hr	1.40	1.77	0.33	2.10	1.22	0.15	1.53	0.11
	5 hr	1.07	1.40	0.55	1.95	0.80	0.10	1.15	0.14
21 st	Baseline	4.50	5.04	0.02	5.06	3.12	0.50	3.96	0.13
(150 lb/hr)	4 - 5 hr	0.61	0.83	0.67	1.50	0.33	0.05	0.61	0.07
24 th	Baseline	4.38	4.98	0.08	5.06	3.56	0.16	5.11	0.41
(75 lb/hr)	2 hr	1.91	2.21	0.77	2.98	1.26	0.08	2.11	0.08
	5 hr	1.50	1.71	0.99	2.70	1.16	0.04	2.05	0.13

* CMM undergoing troubleshooting during OHM baseline

Injection did not start immediately following the baseline OHM measurement because of troubleshooting of the CMM analyzer. The analyzer was brought back online subsequently and run for two hours before injection was started. The mercury concentration as measured by the CMM during the hour before injection was stable at an average of 5.06 µg/m³; and was close to the OHM baseline value (relative difference of 10% consistent with other OHM and CMM data comparisons), see Figure 29. This suggests that the baseline mercury emissions did not change significantly during troubleshooting.

Looking at the OHM results, it is clear that Hg^T decreases with time at the injection rate. We believe that the reduction profile occurs because the induration process comprises gas ducts and other surfaces which accumulate a portion of the injected sorbent, providing additional reduction in the mercury concentrations with time. The stack gas Hg^{VT} after 5 hours of injection was 1.40 µg/m³, while Hg^T was 1.95 µg/m³, per OHM. This corresponds to 77% and 69% respectively, meaning the Hg^P emissions were

significant with time. The corresponding values for Hg^{VT} determined from the CMM data was $1.15 \mu\text{g}/\text{m}^3$, see Figure 29.

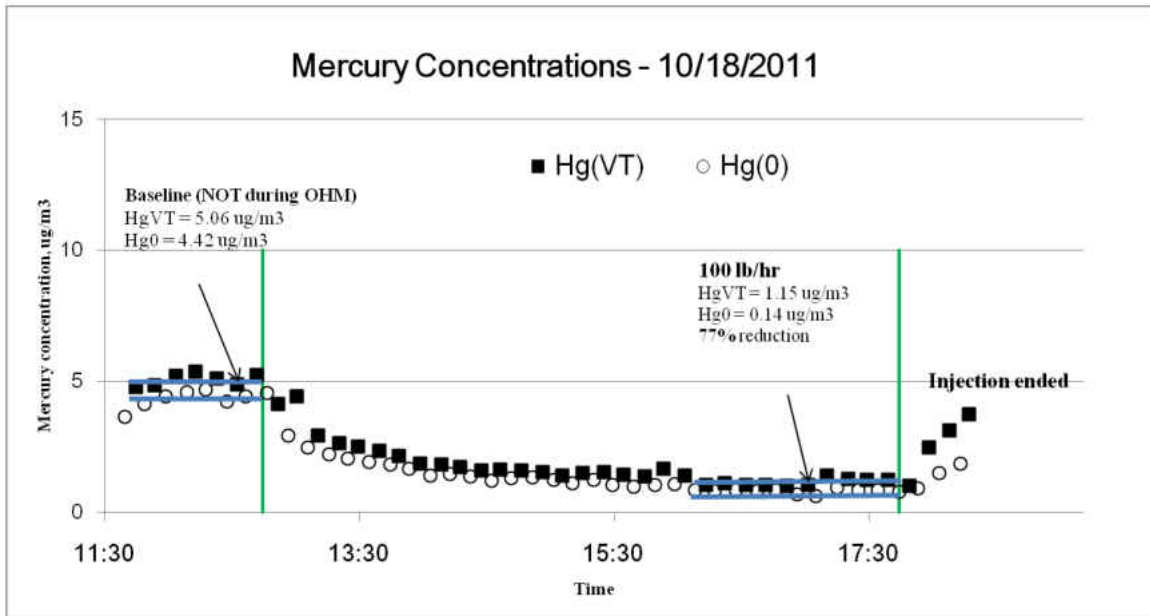


Figure 29: CMM data for the 18th showing results of 100 lb/hr injection

The increase in Hg^P with sorbent injection increased the Hg^T to $1.95 \mu\text{g}/\text{m}^3$, diminishing the overall reduction to 69% for total mercury emissions from the baseline values. These confirmed the previous observation that ESORB-HG-11 penetrates the scrubber in this unit, carrying with it a portion of the captured mercury. So improving the capture of ESORB-HG-11 would definitely increase mercury emission reductions.

The next long term testing investigated was for 150 lb/hr. On the 21st, ESORB-HG-11 testing was performed at 150 lb/hr. Two OHM measurements were performed, one for the baseline, and the other started after 4 hours into the injection schedule. The baseline OHM measurement showed an Hg^{VT} of $5.04 \mu\text{g}/\text{m}^3$ Hg^{VT} (table 7); and Hg^T of $5.06 \mu\text{g}/\text{m}^3$. After 4 to 5 hours of injection, the OHM data showed a value of $0.83 \mu\text{g}/\text{m}^3$, a reduction of 84% for Hg^{VT} ; meanwhile, the Hg^T showed a value of $1.50 \mu\text{g}/\text{m}^3$, a 71%

reduction from the baseline value. Hg^P also increased for this higher injection test condition as compared to previous tests, where the sorbent injection rates were lower. Injection was started immediately after the OHM baseline was completed, and the CMM data showed steady values (Figure 30). Average Hg^{VT} as measured by the CMM was $0.61 \mu\text{g}/\text{m}^3$ (table 7). Filters for both the CMM and OHM showed evidence of carbon penetration through the scrubber contributing.

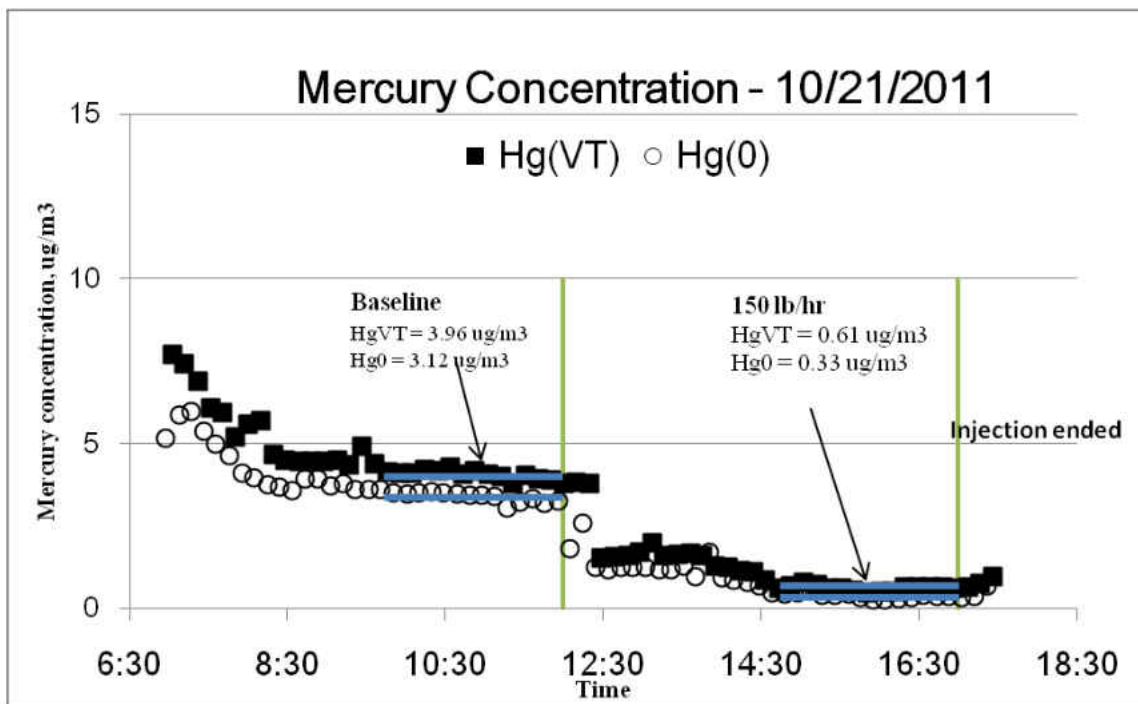


Figure 30: CMM data for the 21st showing results for 150 lb/hr injection

The last long term test involving ESORB-HG-11 at the preheat fans was 75 lb/hr, investigated for a total time of 5 hours. The goal was to determine if a lower feed rate would still produce reductions considered significant. OHM baseline value was $4.98 \mu\text{g}/\text{m}^3$ for Hg^{VT} (table 7), and injection started 20 minutes after the OHM baseline measurement was completed. Reductions of 56% and 66% Hg^{VT} were observed for OHM

measurements performed 2 hours and 5 hours into injection (table 7). Meanwhile in the CMM data (Figure 31), after the initial drop in the mercury concentration over a 30 minute period, the values remained reasonably steady at the lower value for the rest of the injection period. A gradual increase was observed at the end of the injection, but 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 (table 7), than observed previously. The baseline Hg^P was also higher ($0.08 \mu\text{g}/\text{m}^3$) than usual. The possible cause of this was attributed in a drop in performance of the scrubber during that week. This conclusion was drawn based on the fact that the 24th was a Monday, and the baseline values obtained for the rest of that week (see preheat zone injection testing below) were higher than $0.08 \mu\text{g}/\text{m}^3$. Moreover, the slurry mercury concentrations also suggested poor capture by the scrubber (see sequestration results).

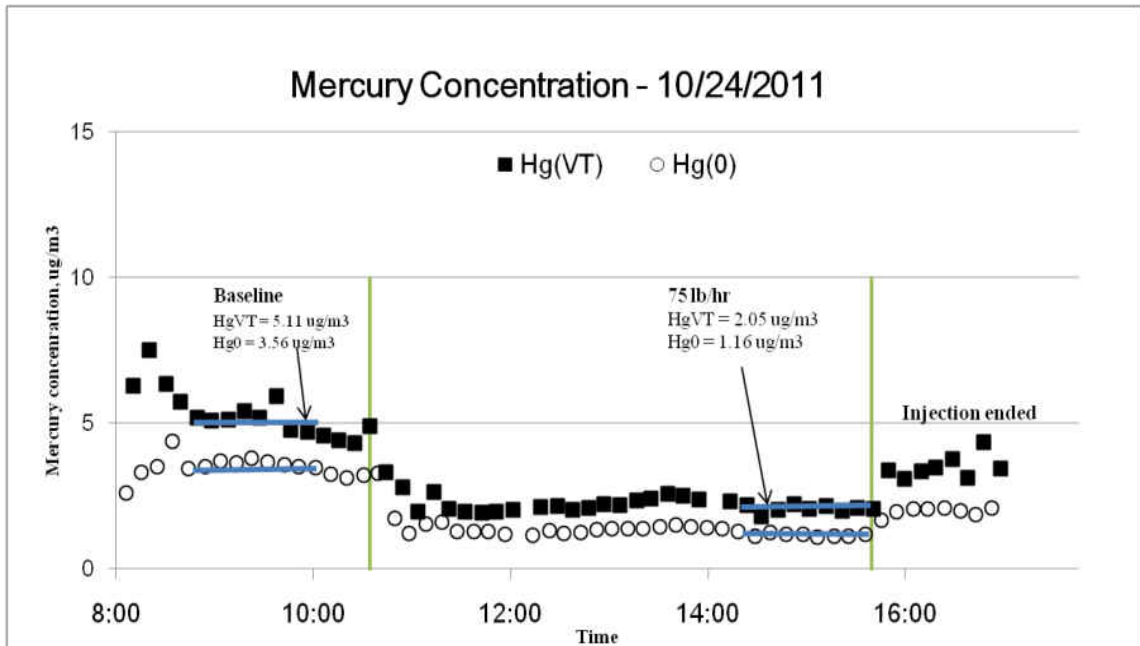


Figure 31: CMM data for the 24th showing injection result for 75 lb/hr

To conclude, long term injections for the rates of 100 lb/hr and 150 lb/hr showed the potential of attaining 75% reduction on Minntac-Line 3, especially if measures are taken to improve capture of fine particulates, as ESORB-HG-11 is a powdered activated carbon with fine particle sizes.. The results from the 75 lb/hr were well below the desired target, however, it is possible that during this period, the scrubber operation was not as optimal as during the previous test week. Unfortunately, it was not possible to verify this.

Pre-heat Zone Injection Location

The second sorbent injection location investigated at Minntac Line 3 was injection into the pre-heat zone. These tests were conducted on the 25th and 26th. Injection into the pre-heat zone was believed to provide a longer contact time between the sorbent and the mercury, and also higher temperatures. Ports located at the base of the preheat zone wall were used, enabling injection of ESORB-HG-11 directly into preheat section. However, the location of the ports on the walls of the zone did not allow for effective distribution of the injected material into the flue gas above the pellet bed. Injection rates of 50 lb/hr, 75 lb/hr and 100 lb/hr were investigated. The goal was to see if changing to an upstream location and using low injection rates could achieve reductions comparable or greater than those seen during injection in the preheat fans.

OHM and CMM baseline measurements (table 8) showed good agreement during testing; however, Hg^P was significantly higher than during the previous week. The high Hg^P was also observed during 75 lb/hr injection in the pre-heat fans, further supporting the suggestion that scrubber performance during the last week of testing was not as effective as previously.

Table 9: OHM and CMM concentrations during injection testing at preheat zone location

Date		OHM	OHM	OHM	OHM	CMM		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)	S.D.	Hg ^{VT} (µg/m ³)	S.D.
25 th	Baseline	3.35	3.81	0.20	8.24	3.11	0.29	4.39	0.39
	75 lb/hr	1.91	2.18	0.60	2.22	1.57	0.07	2.30	0.11
26 th	Baseline	3.84	4.09	0.10	6.69	4.03	0.37	4.55	0.30
	100 lb/hr	1.65	2.05	1.09	2.98	1.81	0.21	2.30	0.30

The injection rates investigated were 50 lb/hr, 75 lb/hr, and 100 lb/hr. However, OHMs were performed during 75 lb/hr and 100 lb/hr injection only. The reductions seen at these rates ranged from 43 to 50% for Hg^{VT} and 25 to 31% for Hg^T respectively. The high Hg^P observed during injection in pre-heat zone suggests that the injected carbon is transported in the waste gas and not burnt in the preheat zone. Lower reductions than testing in pre-heat fans suggest that the poor distribution of ESORB-HG-11 is a lot significant with respect to mercury oxidation and capture. No more testing was performed at the preheat zone due to the low reductions observed as seen on the CMM graphs (Figure 32 and 33).

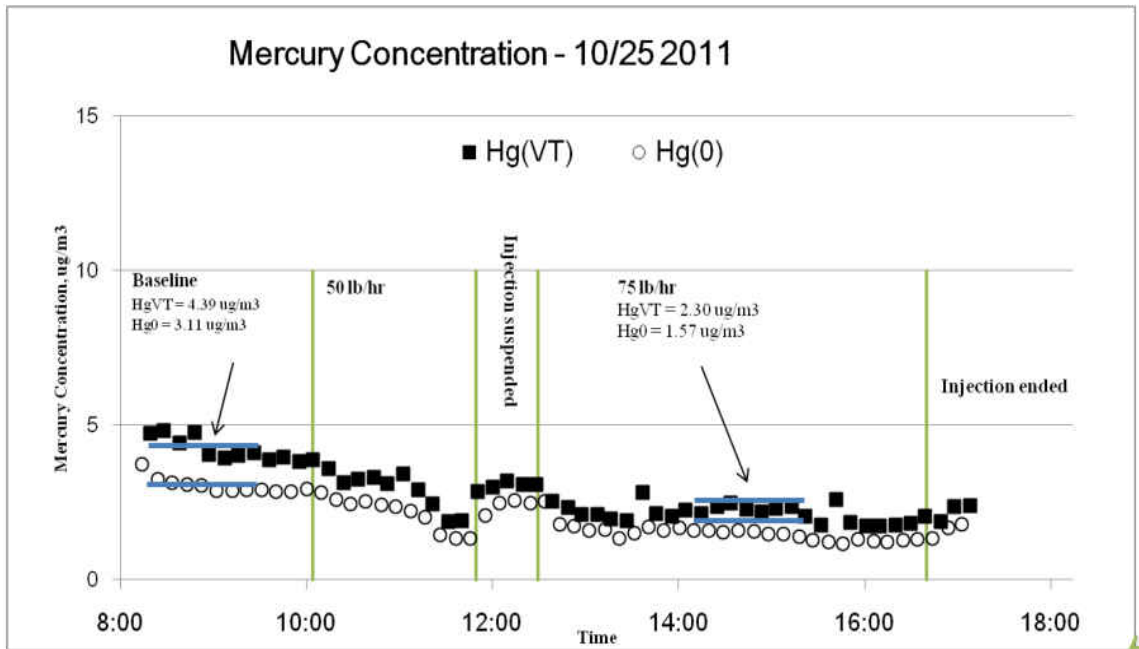


Figure 32: CMM data for the 25th showing injection results for 75 lb/hr in pre-heat zone

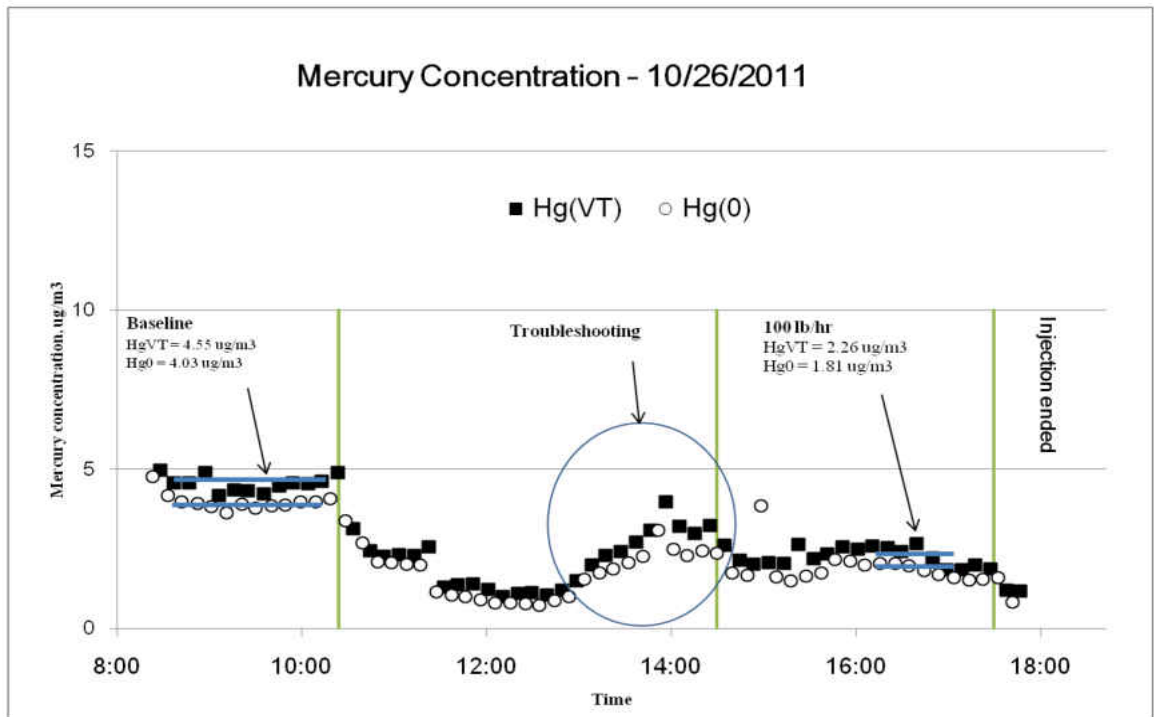


Figure 33: CMM data for the 26th showing injection results for 100 lb/hr in pre-heat zone

PAC Testing

The PAC testing objective was the same with the first two ESORB-HG-11 tests: perform short term tests to determine the PAC injection rate with the most promising mercury reduction. The testing was performed on the 20th and the injection rates investigated were 50, 100 and 150 lb/hr; and injection was at the pre-heat fan location. Baseline OHM showed low stack Hg^{VT} of just 3.44 µg/m³, the lowest baseline during the entire test duration (table 10). CMM baseline was even lower at 2.11 µg/m³. Injection with PAC showed very little reduction on the OHM measurements; meanwhile CMM data suggested almost no reduction (Figure 34). PAC is effective in oxidizing mercury and capturing it if there are oxidizing components such as halogens, present in the flue gas (33,34,17). However, mercury oxidation in taconite processing is believed to be caused by not just chlorides in the waste gas, but also reactive iron oxides (25,26). So it is unsure if the little or no oxidation is as a result of no halogens present or because of a different mechanism for oxidation than that seen in coal combustion systems (39).

On the other hand, Hg^P did not increase during PAC injection (table 10) as compared with ESORB-HG-11. There are two possible reasons for this: PAC did not capture any significant mercury species - it is not halogenated, so Hg^P should be low; or, PAC, which is a coarser grain than ESORB-HG-11, was more easily captured by the scrubber over ESORB-HG-11. However, inspection of the filters for the OHM and CMM probes after sampling showed very little carbon deposited on the filter, as was seen when testing ESORB-HG-11. With no significant results observed for PAC injection, no further testing was done using PAC.

Table 10: OHM and CMM concentrations during PAC injection testing at pre-heat fans

Date		OHM	OHM	OHM	OHM	CMM		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)	S.D.	Hg ^{VT} (µg/m ³)	S.D.
20 th	Baseline	3.14	3.44	0.03	3.47	1.56	0.14	2.11	0.38
	100 lb/hr	2.51	2.75	0.03	2.78	1.48	0.07	1.97	0.15
	150 lb/hr	2.31	2.57	0.04	2.61	1.23	0.26	1.68	0.42

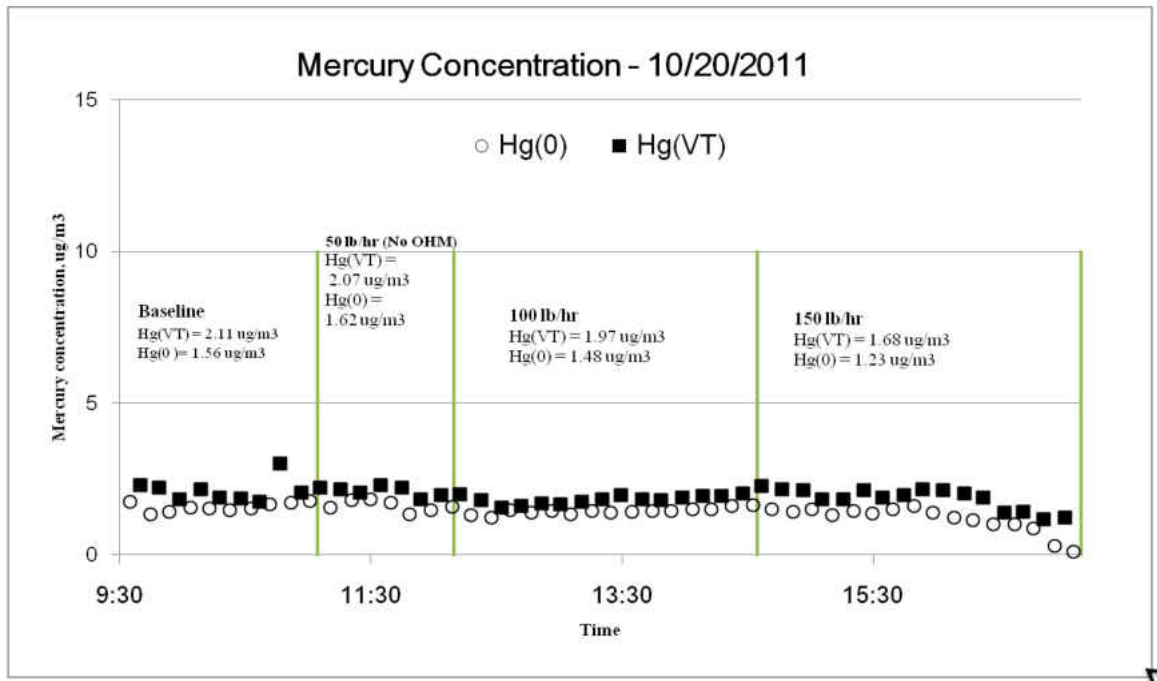


Figure 34: CMM data for the 20th showing injection results for PAC at pre-heat fan location

Sequestration Results

ESORB-HG-11 Results

Sequestration potential of ESORB-HG-11 was determined during injection tests for determining oxidation and capture. Injected ESORB-HG-11 ended being captured by the scrubber slurry, meaning any Hg²⁺ present in the slurry would be sequestered by the

captured ESORB-HG-11. Oxidation/capture testing using ESORB-HG-11 was done on 7 different days for both injection locations. However, sequestration was investigated only on the days when injection was at the pre-heat fan location: 14th, 17th, 18th, 21st, and 24th. Sequestration testing involved collecting scrubber samples during injection, filtering them and sending the filtrate and filter cake for analysis. Unfortunately, errors were encountered with filter cake sample analysis results. Consequently, only the results for the filtrate samples, Hg^D, is reported and discussed.

On the 14th, scrubber slurry samples were collected during OHM measurement for the baseline and 100 lb/hr injection rate. The filtrate from the baseline sample gave a Hg^D of 1100 ng/l; meanwhile, the filtrate during 100 lb/hr injection gave a non-detect (Hg^D < 0.2 µg/l) (Figure 35). Recall that in the sampling section above, it was mentioned that the filtrates from the slurry samples 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 the non-detect samples. The decrease suggests sequestration of the mercury by ESORB-HG-11 to the solid portion of the slurry. Unfortunately, solid samples results are not available to confirm the sequestration. Approximately 300 lbs of ESORB-HG-11 were injected, producing a scrubber slurry concentration of approximately 1400 mg/l.

On the 17th, the results mirrored those obtained on the 14th with a high dissolved Hg^D of 4000 ng/l during baseline OHM, which also decreased significantly with injection of ESORB-HG-11 to non-detect levels (Figure 36). Approximately 900 lbs of ESORB-HG-11 was injected on this day. This produced a maximum slurry concentration of approximately 4000 mg/l in the scrubber recirculation tank.

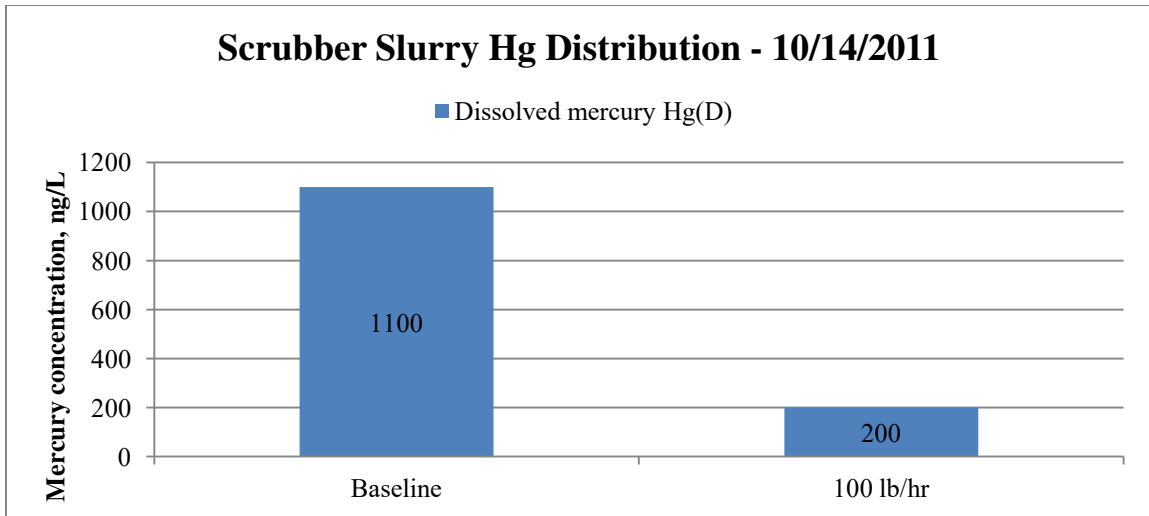


Figure 35: Scrubber Hg^D concentrations during OHM measurements on the 14th. Hg^D for 100 lb/hr (200 ng/l) not actual concentration but method detection limit.

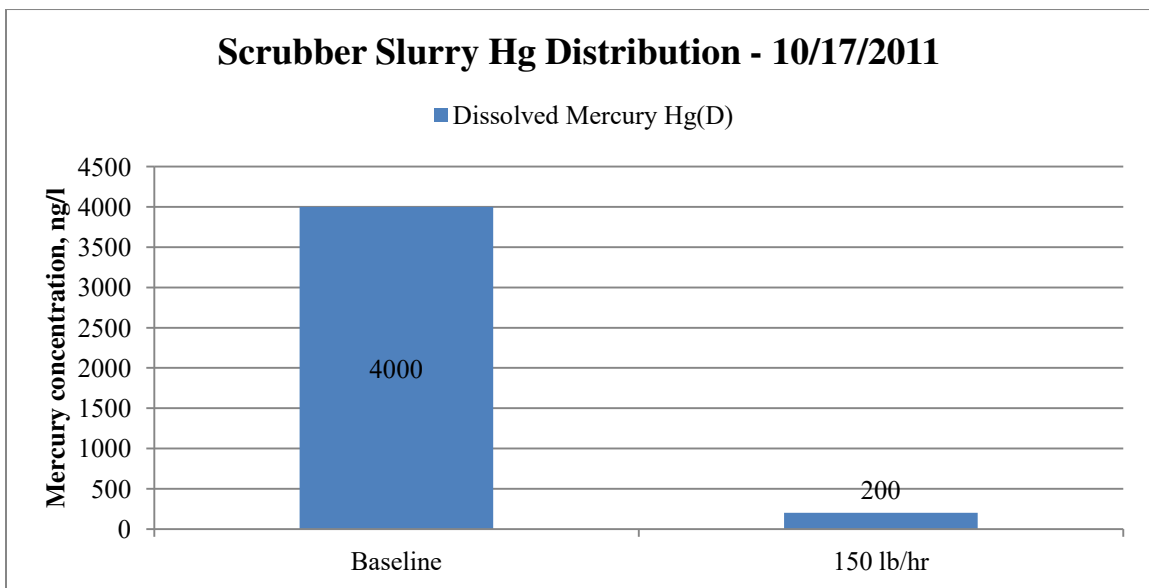


Figure 36: Scrubber Hg^D concentrations during OHM measurements on the 17th. Hg^D for 150 lb/hr (200 ng/l) not actual concentration but method detection limit.

The 18th was the next day on which ESORB-HG-11 testing was performed (100 lb/hr). The first important observation from the results was that the baseline filtrate

sample was 600 ng/l, which was lower than previous baseline values (Figure 37). Further investigation suggested that ESORB-HG-11 injected previously was still in the recirculation tank, but had reduced to smaller levels. If this was the case, some level of sequestration was still taking place in the recirculation tank. The Hg^D in the scrubber filtrate during sorbent injection decreased to very low values, 44.6 ng/l (this value was analyzed using EPA method 1631); further confirming the sequestration ability of ESORB-HG-11.

The 21st, which was a Friday, showed baseline Hg^D even lower than on the 18th. Analysis of the samples was done using EPA Method 1631, and baseline Hg^D was 82 ng/l. PAC was tested on the previous day, suggesting that trace amounts of PAC were still left in the system were responsible for the very low Hg^D. Even with such a low baseline Hg^D, injection of ESORB-HG-11 (750 lb of ESORB-HG-11 was injected) still resulted in further reduction of the Hg^D to 20 ng/l (Figure 38).

Finally, on the 24th – a Monday, baseline Hg^D for the filtrate increased to 4370 ng/l. This confirmed the suggestion that residual sorbent in the recirculation was still performing sequestration, because over the weekend, any residual sorbent in the scrubber recirculation tank would definitely be eliminated. If that is the case, baseline Hg^D should return to high levels as observed on the 17th, which was the case (Figure 39). Hg^D decreased once injection with 75 lb/hr of ESORB-HG-11 was started. At least 300 lbs of ESORB-HG-11 had been injected when the scrubber was sampled for analysis. Surprisingly, the Hg^D did not drop as significantly as it did on previous days after sorbent injection (599 ng/l). This unexpected observation coupled with the high Hg^P observed during stack testing is the reason for the suggestion that scrubber operation was not

optimal during the last week of testing. However, slurry samples collected on the 25th and 26th were not analyzed, so the observation cannot be confirmed.

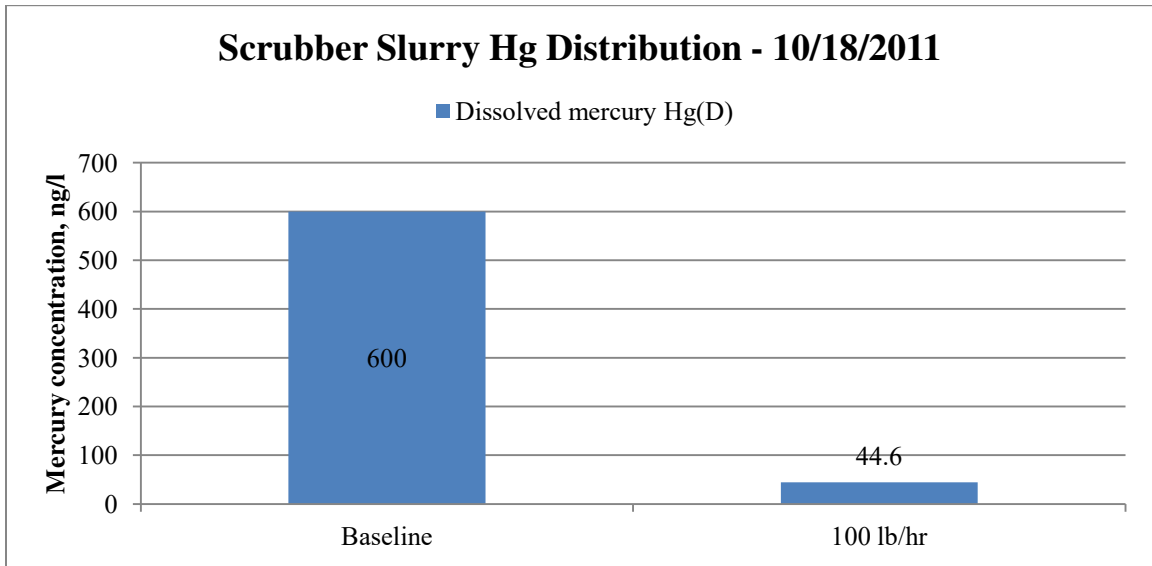


Figure 37: Scrubber Hg^D concentrations during OHM on the 18th.

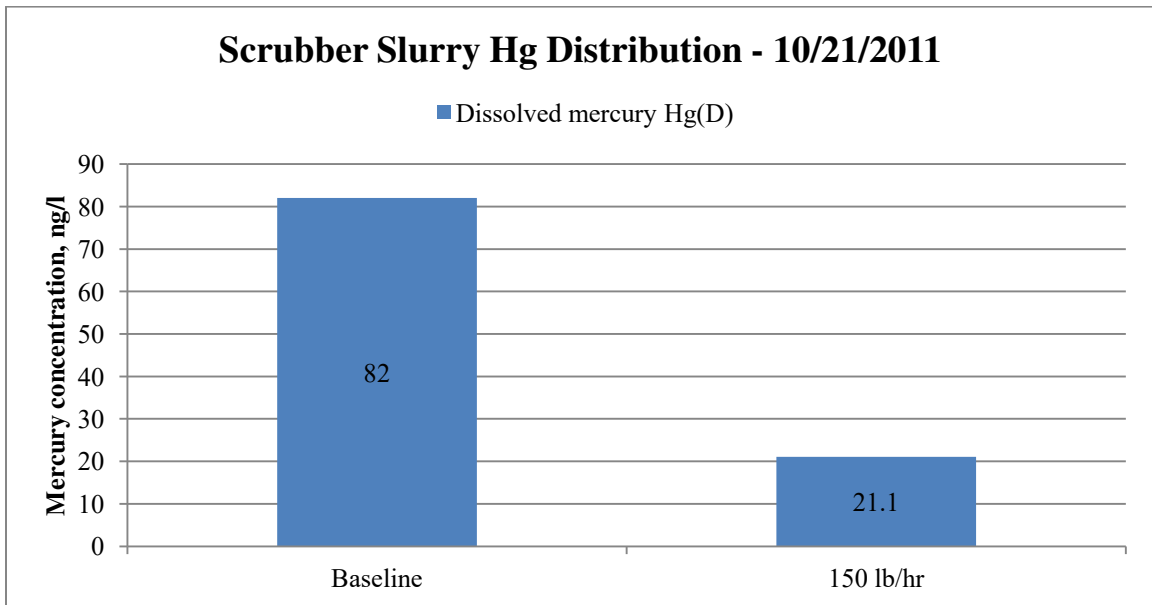


Figure 38: Scrubber Hg^D concentrations during OHM on the 21st.

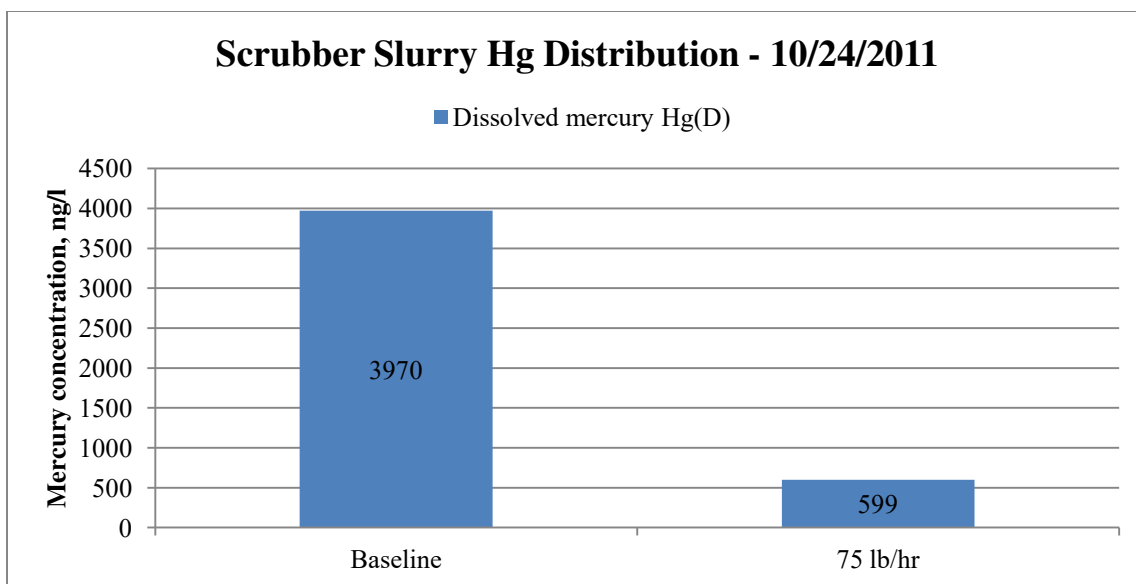


Figure 39: Scrubber Hg^D concentrations during OHM on the 24th.

To conclude, other than on the 24th, significant reduction in Hg^D was observed when ESORB-HG-11 was added to the scrubber recirculation tank through injection into the waste gas. Reductions in Hg^D ranged from 74% to 95% as a result of addition of ESORB-HG-11. The concentrations of ESORB-HG-11 in the scrubber recirculation tank were significantly high by the end of the injection, with the lowest being on the 14th and approximately 1000 mg/l. These concentrations are a lot higher than those investigated during bench- and pilot-scale tests, so it is no surprise that the reductions were so high. Another important fact observed was the residual effect of the injected sorbent hours after injection stopped. The long time it took for concentrations to return to previous baseline values (estimated to be 24 to 48 hr), suggested that ESORB-HG-11 was effective at lower concentrations in the scrubber tank, just as observed in the bench-scale tests.

PAC Results

Field sequestering capabilities of PAC have already been mentioned during sequestration results of the 21st. Analysis of scrubber samples collected during testing confirmed that even though PAC did not show any significant reduction in stack mercury emissions, it still showed sequestration of Hg^D. Baseline Hg^D for this test was analyzed using EPA method 7470 and returned a non-detect value (ESORB-HG-11 was injected on previous day), so a default baseline Hg^D of 200 ng/l was assumed. All other samples on this day were analyzed using low level mercury analysis (EPA Method 1631) by Pace Analytical Laboratories. Hg^D decreased during injection of PAC, confirming bench and pilot testing that PAC effectively captures and sequesters mercury from the liquids. Figure 40 summarizes the results obtained during PAC injection.

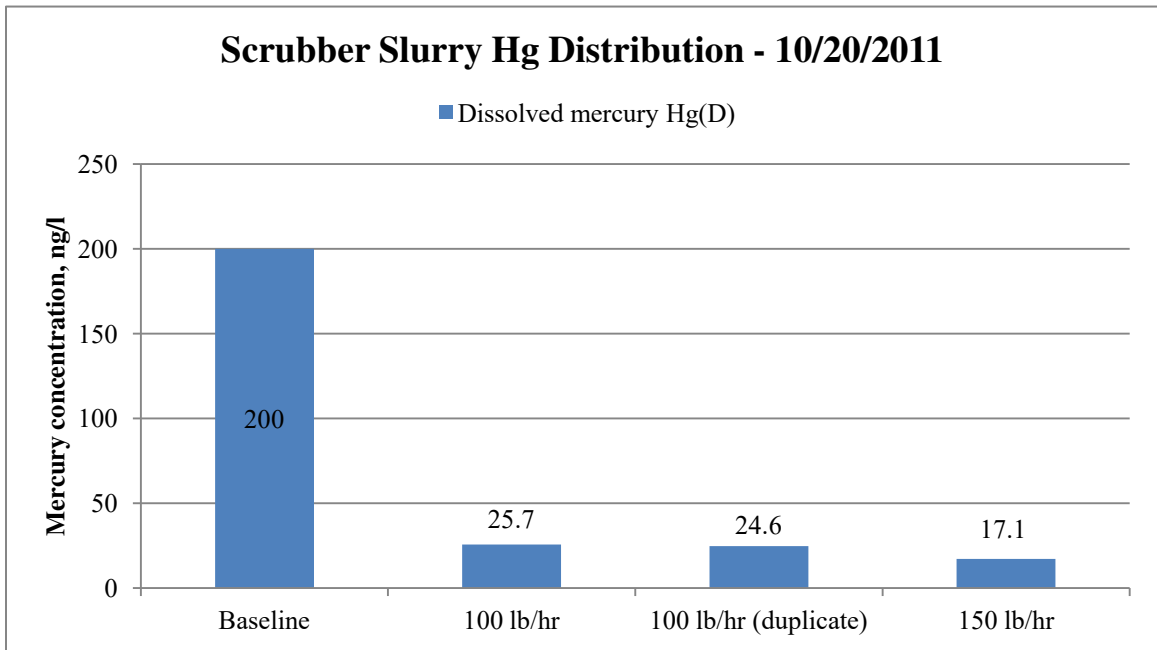


Figure 40: Scrubber HgD concentrations during PAC injection on the 20th. Hg^D for baseline (200 ng/l) not actual concentration but method detection limit.

As the baseline obtained was just an estimate, the percent reduction during PAC testing cannot be calculated, however, the decrease observed in Hg^{D} from 100 lb/hr to 150 lb/hr, suggests that PAC is still effective in mercury sequestration. This is further confirmed by the low baseline (82 ng/l) seen on the 21st.

DEDTC Results

The last technology tested investigated the addition of diethyl dithiocarbamate (DEDTC). The test was performed on the 19th. Recall that DEDTC is a mercury chelating agent used to improve oxidized mercury capture in the scrubber by reducing Hg^{D} concentration. Testing of DEDTC was performed in two steps: first, testing the DEDTC alone to see if this improved capture of oxidized mercury (if any) that is not captured by the scrubber; and second, increase oxidation of mercury species upstream of the scrubber using ESORB-HG-11 (at 50 lb/hr injection rate) and observe the difference from results obtained from the injection of ESORB-HG-11 by itself on the 17th.

For the first step, DEDTC was added to the scrubber recirculation tank by dosing to first maintain a concentration of 0.7mg/l, then 1.4 mg/l, and finally, 7.0 mg/l. Scrubber slurry was sampled at least one hour after dosing the recirculation tank. Stack mercury concentration data and slurry analysis during this test period showed no impact of DEDTC (Figure 41 and 42). On the contrary, the dissolved mercury concentration Hg^{D} increased from low baseline values, suggesting that ESORB-HG-11 in the system from injection on the 18th was reducing to insignificant levels while the DEDTC was not forming chelates with the Hg^{D} (Figure 42).

In the second test, 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 (Figure 41). However, the reduction in mercury emission was similar with and without the addition of DEDTC to the scrubber slurry, indicating that the entire impact on the mercury concentrations was most likely from the injection of ESORB-HG-11 (Figure 41). Injection of ESORB-HG-11 also decreased the dissolved mercury in the scrubber slurry filtrate significantly after just two hours of injection (Figure 42). To summarize, injection of the scrubber additive DEDTC did not improve mercury capture or mercury sequestration.

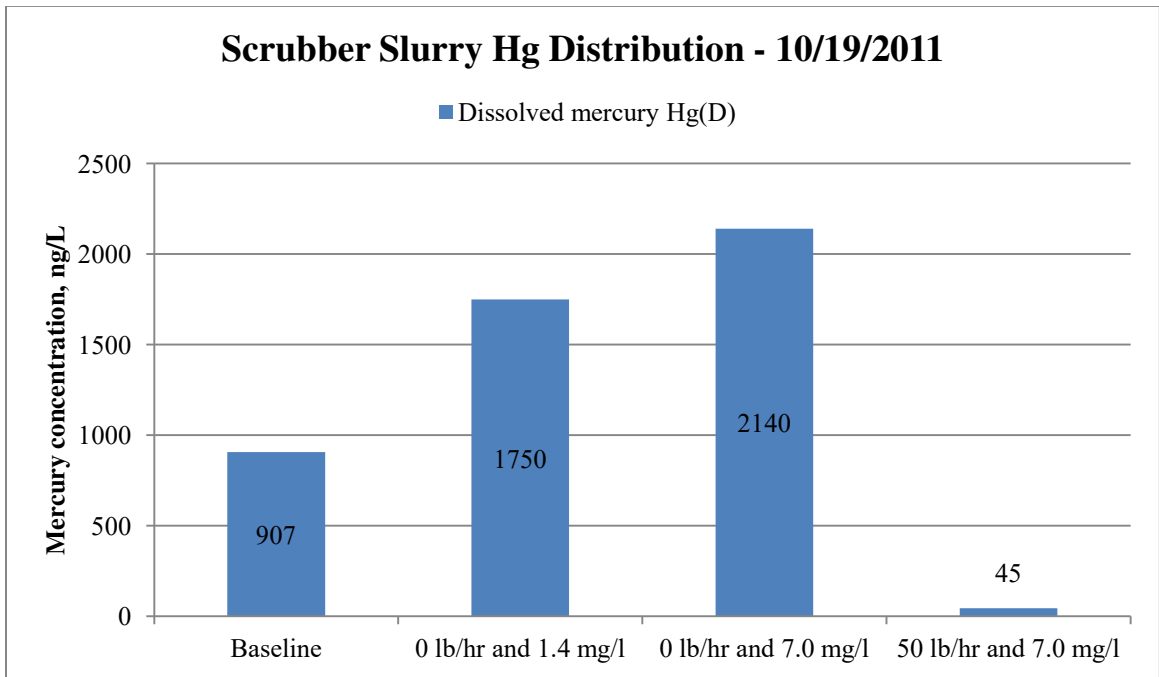


Figure 41: Scrubber Hg^D concentrations during dosing with DEDTC and injection of 50 lb/hr ESORB-HG-11 on the 19th

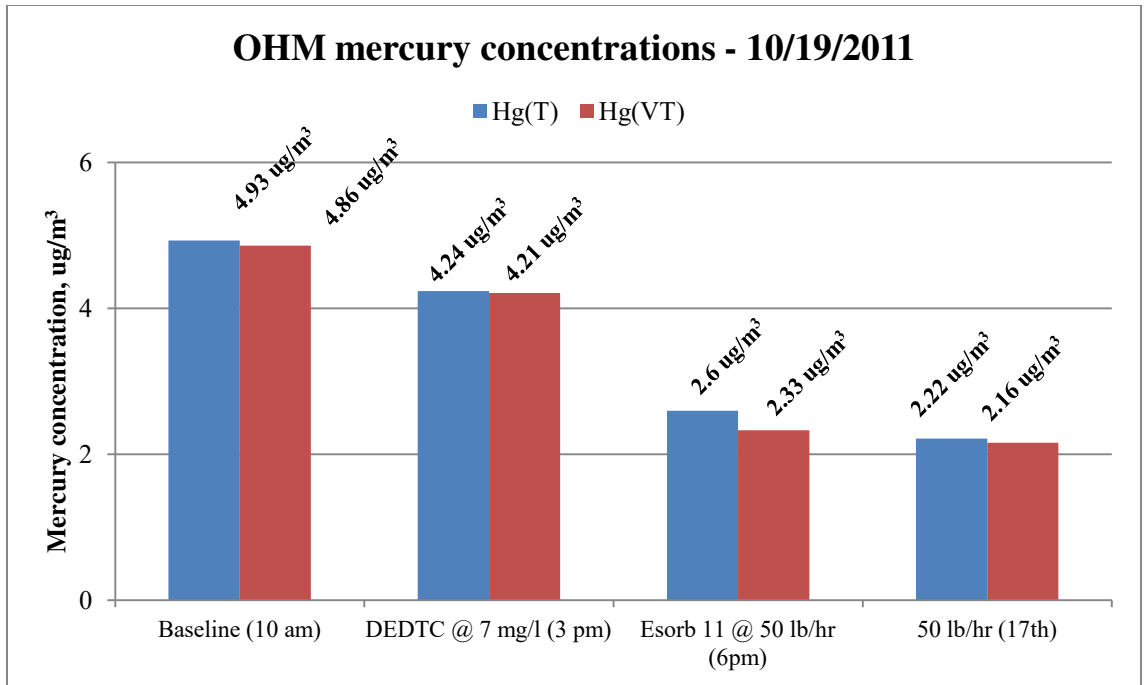


Figure 42: Stack mercury concentrations during DEDTC dosing and injection of 50 lb/hr ESORB-HG-11

CHAPTER VII

CONCLUSION AND RECOMMENDATIONS

Conclusion

Bench-scale tests investigated the sequestration performance of the sorbents: PAC and ESORB-HG-11; and the chelates: DEDTC and TMT-15®; when added to a slurry solution spiked with Hg^{2+} as HgCl_2 . Of these four additives, ESORB-HG-11, a halogenated powdered activated carbon supplied by Envergenx LLC of Sturbridge, MA, was the most effective at sequestration, constantly achieving more than 98% reduction in Hg^{D} when tested on three concentration levels. Its sequestration capabilities were further confirmed during pilot-scale and field tests, where for the pilot-scale tests, it improved the driving force for Hg^{2+} capture by scrubber waters with little or no capability of capturing any more mercury. During field tests, analysis of the scrubber filtrate showed decreasing Hg^{D} concentrations from baseline values once ESORB-HG-11 was added to the slurry. The ability of ESORB-HG-11 to sequester mercury from the liquid to solid portion of scrubber slurry should have a three-fold advantage: First, concerns such as re-emission of Hg^{D} are most likely to be eliminated as re-emission is believed to occur largely from reduction of Hg^{2+} in scrubber slurry to Hg^0 that is not soluble (46). Secondly, and most important, sequestering most of the captured mercury to one phase of the slurry facilitates removal and disposal of that mercury from the process loops.

Thirdly, sequestration using a non-magnetic, low density additive introduces a possible method for separating the mercury from the valuable portion of the scrubber solids allowing the possibility of solids recycle.

Other additives (PAC, DEDTC, and TMT-15®) also showed promise during bench and pilot-scale tests, but their performance was not effective enough to warrant any recommendation for further work. Impregnation of PAC with TMT-15® showed promise for a 20 and 90 parts per thousand concentration of TMT-15® on PAC, prepared at a lower temperature. However, the lower temperature used for preparation resulted in longer preparation times, so this new additive was not tested further. DEDTC used in scrubber slurry for Hg sequestration showed no observable effect, even though the concentration was increased to 7 times the pilot concentration. Possible reasons for this could be the chemistry of the slurry during field test (temperature, effective pH, other constituents not yet adsorbed to solid portion) could be hindering the effectiveness of DEDTC. Also, it is possible that there was heavy metal partitioning in the scrubber slurry, where other metals were competing with Hg^{2+} for DEDTC, reducing effectiveness of DEDTC loading significantly. Unfortunately, investigating concentrations higher than 7.0 mg/l raised the risk of introducing a new problem to the system, sulfur concentrations. Sulfur levels in Minntac discharge waters are regulated, so sulfur concentrations are controlled using limestone. Any additional source of sulfur to their system would probably require further studies to ensure a new problem is not created.

On the other hand, field testing also investigated oxidation and capture potential of sorbent technologies: PAC and ESORB-HG-11. Once more, ESORB-HG-11 proved to be the most promising technology, achieving total stack mercury reductions higher than

70%. The reduction potential on the line could even be improved further if particulate capture potential of the scrubber was improved to capture fine particles such as ESORB-HG-11. If improving particulate control is not feasible, then certain measures, as pointed out in the recommendation section below, might be needed.

PAC testing showed very little capture, with the capture observed probably not a function of the injected PAC. However, it is important to observe that during PAC testing, baseline Hg emissions were very low ($3.44 \mu\text{g}/\text{m}^3$), the lowest for the entire test period. It is possible that the lower baseline biased the effectiveness of the PAC in mercury oxidation and capture; however, even if that is the case, it just goes further to support the observation that PAC might not be suitable for mercury control in Taconite facilities.

Recommendations

Recommendations for future work focuses mainly on the field test. The first recommendation will be to investigate injection of PAC alongside an oxidation technology such as a sodium bromide (NaBr) solution which was shown to achieve a 62% oxidation when injected in the pre-heat zone (29). This combination was also suggested by Laudal (22), based on the fact that PAC is believed to improve oxidation of Hg^0 in the presence of halogens (38).

The second recommendation would be to investigate the redesign and/or operation of the scrubber to capture finely powdered activated carbon effectively. ESORB-HG-11 was extremely effective in oxidizing and capturing vapor phase mercury. However, the scrubber was not fully effective in removing the fine sorbent particles

loaded with the captured mercury. Better particulate capture by the scrubber may be achieved by increasing the pressure drop through the scrubber, using finer droplets for particulate capture, and/or minimizing the bypass or sneackage of the flue gas through the scrubber. The use of another halogenated sorbent using coarser PAC grains may also be investigated. The goal here would be to take advantage of the observation that PAC testing did not exhibit any significant increase in Hg^P or particulate emission. It must be noted that the benefit of fine particle size on mercury oxidation and capture is well established (17) and the approach of using larger particles may be counterproductive.

The third recommendation involves testing ESORB-HG-11 and the recommended technologies above at other Taconite facilities. Minntac-Line 3 has a lot more duct work when compared to the lines of other facilities. Considering that duct work is believed to play a positive role in the capture of mercury, it would mean that lines with less duct work might require higher injection rates. The only way to verify this would be to perform tests on the other lines.

The fourth recommendation focuses on the sequestration results obtained. First, if sequestration tests are performed at any other line, then extra measures should be taken to ensure that the solids mercury data is not compromised. Secondly, separation tests should be performed on taconite scrubby slurry containing ESORB-HG-11 and process solids. The goal should be to confirm the ease of separation of the ESORB-HG-11 from the valuable scrubber solids. The tests should look at magnetic separation and/or density based separation, as scrubber solids are very dense.

More testing would be required before this testing can be recommended as a mercury control technology for the Taconite industry of the Minnesota range. Continuous injection and monitoring for several days would be necessary to confirm that the above technology would permanently reduce mercury emissions as well as verify that the use of this technology doesn't create additional issues such as increased particulate emissions.

APPENDICES

APPENDIX A

Field Test Results Raw Data

Table 11: Field test raw OHM data

Date		Hg ⁰ (µg/m ³)	Hg ^P (µg/m ³)	Hg ^{VT} (µg/m ³)	Std Dev
20111026	Baseline	3.84	0.10	4.09	0.30
	100 lb/hr-E-HG-11	1.65	1.09	2.05	0.3
20111025	Baseline	3.35	0.20	3.81	0.39
	75 lb/hr-E-HG-11	1.91	0.60	2.18	0.11
20111024	Baseline	4.38	0.08	4.98	0.41
	75 lb/hr-E-HG-11	1.91	0.77	2.21	0.08
	75 lb/hr-E-HG- 11	1.5	0.99	1.71	0.13
20111021	Baseline	4.50	0.02	5.04	0.13
	150 lb/hr-E-HG-11	0.61	0.67	0.83	0.07
20111020	Baseline	3.14	0.03	3.44	0.38
	100 lb/hr-PAC	2.51	0.03	2.75	0.15
	150 lb/hr-PAC	2.31	0.04	2.57	0.42
20111019	Baseline	4.63	0.07	4.86	0.15
	7 mg/l-DEDTC	3.9	0.03	4.21	0.28
	50 lb/hr-E-HG-11	2.09	0.27	2.33	0.12
20111018	Baseline	5.35	0.03	6.17	n/a
	100 lb/hr-E-HG-11	1.4	0.33	1.77	0.11
	100 lb/hr-E-HG-11	1.07	0.55	1.4	0.14
20111017	Baseline	5.82	0.02	8.22	0.88
	50 lb/hr-E-HG-11	1.71	0.06	2.16	0.21
	150 lb/hr-E-HG-11	1.14	0.59	1.22	0.29
20111014	Baseline	5.86	n/a	6.69	0.08
	100 lb/hr-E-HG-11	2.36	0.13	2.85	0.57
20111013	Baseline 1	3.70	n/a	4.45	0.41
	Baseline 2	3.98	n/a	4.93	0.30
	Baseline 3	4.64	0.00	5.19	0.32

Table 12: Field raw CMM data

Date		Hg ⁰		Hg ^{VT}	
		(µg/m ³)	Std Dev	(µg/m ³)	Std Dev
20111026	Baseline	4.03	0.37	4.55	0.30
	100 lb/hr-E-HG-11	1.81	0.21	2.3	0.3
20111025	Baseline	3.11	0.29	4.39	0.39
	75 lb/hr-E-HG-11	1.57	0.07	2.30	0.11
20111024	Baseline	3.56	0.16	5.11	0.41
	75 lb/hr-E-HG-11	1.26	0.08	2.11	0.08
	75 lb/hr-E-HG-11	1.16	0.04	2.05	0.13
20111021	Baseline	3.12	0.50	3.96	0.13
	150 lb/hr-E-HG-11	0.33	0.05	0.61	0.07
20111020	Baseline	1.56	0.14	2.11	0.38
	100 lb/hr-PAC	1.48	0.07	1.97	0.15
	150 lb/hr-PAC	1.23	0.26	1.68	0.42
20111019	Baseline	4.08	0.13	5.19	0.15
	7 mg/l-DEDTC	2.68	0.27	4.29	0.28
	50 lb/hr-E-HG-11	1.68	0.11	2.43	0.12
20111018	Baseline	n/a	n/a	n/a	n/a
	100 lb/hr-E-HG-11	1.22	0.15	1.53	0.11
	100 lb/hr-E-HG-11	0.80	0.10	1.15	0.14
20111017	Baseline	5.12	0.30	7.08	0.88
	50 lb/hr-E-HG-11	2.12	0.16	2.93	0.21
	150 lb/hr-E-HG-11	0.53	0.06	1.07	0.29
20111014	Baseline	4.26	0.10	5.65	0.08
	100 lb/hr-E-HG-11	1.16	0.25	1.98	0.57
20111013	Baseline 1	2.32	0.26	4.24	0.41
	Baseline 2	2.58	0.13	3.88	0.30
	Baseline 3	2.78	0.08	4.1	0.32

Table 13: Field raw results for multiclones solids analysis

Date	ID	Time	ng/g
10/17/2011	MS1	1:00PM	139
10/17/2011	MS2	4:00AM	82
10/17/2011	MS3	6:00PM	42
10/18/2011	MS5	950AM	212
10/19/2011	MS7	1030AM	45
10/19/2011	MS8	230PM	15
10/19/2011	MS9	410PM	26
10/19/2011	MS10	555PM	90
10/20/2011	MS11	850AM	90
10/20/2011	MS13	2PM	182
10/20/2011	MS14	420PM	451
10/21/2011	MS15	1115AM	65
10/21/2011	MS16	405PM	86
10/24/2011	MS17	10AM	47
10/24/2011	MS19	330PM	40

Table 14: Field raw results for scrubber filtrate analysis and TSS

		Injection rate (lb/hr)	ID	Hg ^D (ng/l)	TSS (%)
10/13/2011	Baseline	n/a	SS3	5000	0.68
	Baseline	n/a	SS 5	5000	0.68
10/14/2011	None	Baseline	SS3	1100	0.68
	E-HG-11	150	SS 5	200	0.68
10/17/2011	None	Baseline	SS8	4000	0.67
	E-HG-11	150	SS14	200	0.59
10/18/2011	None	Baseline	SS17	600	0.86
	E-HG-11	100	SS 19	45	0.65
10/19/2011	DEDTC	Baseline	SS 23	907	0.39
	DEDTC	1.4 mg/l	SS 25	1750	0.78
	DEDTC	7.0 mg/l	SS 27	2140	0.99
	DEDTC & E-HG-11	7.0 mg/l & 50	SS 29	45	1.04
10/20/2011	PAC	Baseline	SS 31	200	0.76
	PAC	100	SS 36A	25.7	0.69
	PAC	100	SS 36B	24.6	0.69
	PAC	150	SS 38	17.1	0.67
10/21/2011	E-HG-11	Baseline	SS 41	82	0.59
	E-HG-11	150	SS 43	21.1	0.46
10/24/2011	E-HG-11	Baseline	SS 46	3970	0.77
	E-HG-11	75	SS 51	599	0.80

APPENDIX B

Horiba DM-6B Operation and Maintenance

The following section focuses on operation with the wet-chemistry pretreatment in batch and not continuous mode. For continuous mode operation see Hrdlicka, 2006 (43). To setup the wet solution conditioning system, four 500 ml modified Greenburg-Smith impingers are used. Two are for the elemental mercury side and two are for the total mercury side. The two sides are setup into parallel impinger trains using two impingers for each train. The outlets of the trains are connected to the DM-6B mercury analyzer. Quarter inch socket joints ordered from HS Martin are used with quarter inch PFA unions (from Swagelok) to connect the impingers to the outlet and inlet tubing. The right impinger ball joints should be connected to the tubing going to the Horiba DM-6B to prevent the solutions in the impingers from being sucked by the Horiba DM-6B into the sample lines.

The chemicals used for the impingers would depend on what kind of gas is being sampled. For sampling of acidic gases, the elemental mercury side uses a solution of 1 M KCl and 1 M NaOH. The total mercury side uses a solution of 2% SnCl₂ and 1 M NaOH (43). Other possible solutions used can be obtained from Buitrago, 2011 (44); and Zhuang, 2011 (45). The chemicals must be reagent grade or trace metal grade and can be purchased from Fisher Scientific. Impingers are kept in an ice bath. Once the entire setup is connected, a leak test must be performed. Begin sampling and block the flow of the inlet of the conditioning unit. A vacuum will begin to develop in the system and can be monitored by the pressure sensors in the DM-6B analyzer. The vacuum in each impinger should be greater than 20 psig for each line after one minute. If it takes longer

than one minute to reach 20 psig, then there is most likely a leak. Fittings and impinger connections need to be checked.

Every time the equipment is turned on, a calibration should be performed. Perform a standard manual calibration with the MG-1 mercury generator as outlined in the user manual. Mercury concentration from the MG-1 can be verified by the Energy and Environmental Research Center – EERC. Before and after any major sampling episode, a calibration verification must be performed. To perform one, the calibration gas should be connected to the impinger inlets and allowed to reach a stable value. It takes at least 2 hrs for the MG-1 to reach steady state. So to prevent build-up of mercury concentration in the sampling line, the MG-1 should be fitted with a tee. One line from the tee should be connected to a fume hood and flow should NOT be restricted; meanwhile the other line should be used to calibrate the analyzer. This line can be equipped with a valve which is closed when system is not undergoing calibration or verification. If calibration verification is not successful, then another calibration should be performed, this time, bypassing the impinger solutions. If this verification also fails, then recalibrate the analyzer. If not, then there is either a leak in the impinger trains or the solutions need to be changed.

To start sampling begin measurement on the DM-6B mercury analyzer control panel. The analyzer will automatically perform a zero calibration every hour on the hour. To begin recording measurements open the DM-6B software and select run from the file menu. The software will begin recording measurements every 10 seconds and store the information a Microsoft Excel file. It is important to note that on the last day of the month, 30th or 31st, the data acquisition software does not work. A “run-time error” is

displayed when the software is turned on. When this happens, change the date on the Horiba DM-6B and set to a any other day other than the first or last day of the month, then restart acquisition.

The following paragraphs will discuss analyzer maintenance and highlight things to watch for during operation. The most important thing to monitor during operation is the pressure of the sample in the DM-6B pressure sensors. The pressure sensors monitor the amount of vacuum being pulled by the analyzer's sample vacuum pumps. The pressure should stay around some normal value on a daily basis. Depending on the type of work being done, the normal pressure will vary. Normal operating pressures for the work done in this thesis were between 1 and 3 psig.

If the pressure gets too high (>10 psig) then something in the system is plugging the sample flow. In this work, the most common source of this problem was the Teflon moisture filters. Directly at the inlet of the analyzer is a filter that is used to detect moisture in the sample gas. This filter can easily be plugged up with various contaminants or moisture. To replace this filter stop sampling, disconnect the tubing from the filter, and replace with a new one. The filters can be obtained from Savillex.

If the pressure is still too high then other sources of plugging need to be investigated. Check all tubing, fittings, and other equipment in the system. Start at the inlet of the analyzer and move to the inlet of the sample conditioning system. Checking each component separately will pinpoint the source of the plugging. Once the source is found, clean out the component and the pressure should decrease back to normal values.

Other problems could occur during operation of analyzer. For more information on maintenance, see Horiba DM-6B manual and Hrdlicka 2006 (43).

REFERENCES

1. GLIN. The Great Lakes. www.great-lakes.net/lakes/ (accessed February 16, 2012).
2. EPA. Great Lakes. www.epa.gov/glnpo/glwqa/1978/index.html (accessed February 16, 2012).
3. Chapter 1: Introduction and Purpose of the Lake Superior Lakewide Management Plan, 2006. USEPA - Great Lakes - Lake Superior 2006 LaMP. epa.gov/glnpo/lakesuperior/2006/ls_chapter1_2006.pdf (accessed February 2, 2012).
4. Executive Summary, 2006. USEPA - Great Lakes - Lake Superior 2006 LaMP. epa.gov/glnpo/lakesuperior/2006/index.html (accessed February 2, 2012).
5. L.S.W.G. Lake Superior Lakewide Management Plan (LaMP) 2000 - Summary edition, 2000. USEPA - Great Lakes - Lake Superior Binational Program. epa.gov/glnpo/lakesuperior/summaryeditionLaMP2000.pdf (accessed February 16, 2012).
6. EPA. Laws and Regulations - Clean Water Act. www.epa.gov/hg/regs.htm#water (accessed April 03, 2012).
7. L.S.W.G. Lake Superior Lakewide Management Plan (LaMP) - Stage 3 (Draft), 1999. USEPA - Great Lakes - Lake Superior Binational Program. www.epa.gov/glnpo/lakesuperior/stage3/stage3v15.PDF (accessed February 17, 2012).
8. MPCA. Developing a strategy for implementation of Minnesota's Statewide Mercury TMDL, 2009. Minnesota Pollution Control Agency - Mercury. www.pca.state.mn.us/index.php/view-document.html?gid=11650 (accessed February 17, 2012).

9. O.A.Q.P.S; O.R.D. *Mercury Study Report to Congress Volume I: Executive Summary*; Final report; U.S. environmental Protection Agency, 1997.
- 10 Jensen, R. R.; Karki, S.; Salehfar, H. Artificial neural network-based estimation of mercury speciation in combustion flue gases. *Fuel Processing Technology* **2004**, *85* (6-7), 451-462.
- 11 Coulter, A. S.; Buchanan, L. H. Mercury exposure in children: a review. *Toxicology and Applied Pharmacology* **2004**, *198* (2), 209-230.
- 12 Silbergeld, E. K.; Devine, P. J. Mercury - are we studying the right endpoints and mechanisms. *Fuel Processing Technology* **2000**, *65-66*, 35-42.
- 13 Clewell, H. J.; Crump, K. S.; Gentry, P. R.; Shipp, A. M. Site-specific reference dose for methylmercury for fish-eating populations. *Fuel Processing Technology* **2000**, *65-66*, 43-54.
- 14 Grandjean, P.; Weihe, P.; White, R.; Debes, F.; Araki, S.; Yokoyama, K.; Murata, K.; Sorensen, N.; Dahl, R.; Jorgensen, P. Cognitive deficit in 7-year-old children with prenatal exposure to methylmercury. *Neurotoxicology and Teratology* **1997**, *19*, 417-428.
- 15 Davidson, P.; Myers, G.; Cox, C.; Axtell, C.; Shamlaye, C.; Sloane-Reeves, J.; Cernichiari, E.; Needham, L.; Choi, A.; Wang, Y.; Berlin, M.; Clarkson, T. Effects of prenatal and postnatal methylmercury exposure from fish consumption on neurodevelopment: outcomes at 66 months of age in the seychelles child development study. *Journal of the American Medical Association* **1998**, *280*, 701-707.
- 16 Lebel, J.; Mergler, D.; Branches, F.; Lucotte, M.; Amorim, M.; Larribe, F.; Dolbec, J. Neurotoxic effects of low-level methylmercury contamination in the amazonian basin. *Environmental Research* **1998**, *79*, 20-32.
- 17 Pavlish, J. H.; Sondreal, A. E.; Mann, M. D.; Olson, E. S.; Galbreath, K. C.; Laudal, D. L.; Benson, S. A. Status Review of Mercury Control Options for Coal-fired Power Plants. *Fuel Processing Technology* **2003**, *82* (2-3), 89-165.
- 18 Celso, V.; Lean, D. R.; Scott, S. L. Abiotic methylation of mercury in the aquatic

- . environment. *Science of the Total Environment* **2006**, 368 (1), 126-137.
- 19 Heller, K. B.; Yang, J.-C. *Taconite Mining and Processing Industry Profile*; Draft Report; U.S. Environmental Protection Agency: Research Triangle Park, 2001.
- 20 EPA. AP-42, CH 11.23: Taconite Ore Processing, 1997. USEPA - Emissions Factors & AP 42 - CH11: Minerals Products Industry. www.epa.gov/ttnchie1/ap42/ch11/final/c11s23.pdf (accessed February 17, 2012).
- 21 Berndt, M. E. *Mercury and Mining in Minnesota*; Final report; Minerals Coordinating Committee: St. Paul, 2003.
- 22 Laudal, D. L.; Dunham, G. E. *Mercury Control Technologies for the Taconite Industry*; Technical report; Minnesota Department of Natural Resources: St. Paul, 2007.
- 23 Berndt, M. E.; Engesser, J.; Johnson, A. *On the distribution of mercury in taconite plant scrubber systems*; Minnesota Department of Natural Resources: St. Paul, 2003.
- 24 Berndt, M.; Engesser, J.; Berquo, T. S. *Mercury Chemistry and Mossbauer Spectroscopy of Iron Oxides During Taconite Processing on Minnesota's Iron Range*; Final report; Minnesota Department of Natural Resources: St. Paul, 2005.
- 25 Galbreath, K. C. *Mercury Vaporization Characteristics of Taconite Pellets*; Final Report; Minnesota Department of Natural Resources: St. Paul, 2005.
- 26 Galbreath, K. C.; Tibbets, J. C.; Schulz, R. L.; Zygarlicke, C. J.; Grant, D. E. Effects of NO_x, alpha-Fe₂O₃, gamma-Fe₂O₃ and HCL on Mercury Transformations in 7-kW Coal Combustion System. *Fuel Process Technology* **2005**, 86 (4), 429-448.
- 27 Berndt, M.; Engesser, J. *Mercury Transport in Taconite Processing Facilities: (I) Release and Capture During Induration*; Final Report; Iron Ore Cooperative Research, 2005.
- 28 Berndt, M.; Engesser, J. *Mercury Transport in Taconite Processing Facilities: (II) Fate of Mercury Captured by Wet Scrubbers*; Final Report; EPA-Great Lakes National Program Office, 2005.

- 29 Berndt, M. E.; Engesser, J. *Mercury Transport in Taconite Processing Facilities: (III) . Control Method Test Results*; Final report; Minnesota Department of Natural Resources: St. Paul, 2007.
- 30 Berndt, M. E. *On the Measurement of Stack Emissions at Taconite Processing Plants*; . Progress Report; Minnesota Department of Natural Resources: St. Paul, 2008.
- 31 Benson, S. *Controlling Mercury Emissions for Utilities Firing Lignites from North . America*; Summary Report; University of North Dakota - Energy & Environmental Research Centers (UND - EERC): Grand Forks, 2007.
- 32 Senior, C.; Bustard, J. C.; Durham, M.; Baldrey, K.; Michaud, D. Characterization of . fly ash from full-scale demonstration of sorbent injection for mercury control on coal-fired power plants. *Fuel Processing Technology* **2004**, *85*, 601-612.
- 33 Carey, T. R.; Hargrove, O. W.; Richardson, C. F.; Chang, R.; Meserole, F. B. Factors . Affecting Mercury Control in Utility Flue Gas Using Activated Carbon. *Air & Waste Management Association* **1998**, *48*, 1166-1174.
- 34 Miller, S. J.; Dunham, G. E.; Olson, E. S.; Brown, T. D. Flue gas effects on a carbon- . based mercury sorbent. *Fuel Processing Technology* **2000**, *65-66*, 343-363.
- 35 Olson, E. S.; Thompson, J. S.; Pavlish, J. H. Trapping and Identification of Oxidized . Mercury Species in Flue Gas, 2000. Division of Energy & Fuels - American Chemical Society.
http://www.anl.gov/PCS/acsfuel/preprint%20archive/Files/45_3_WASHINGTON%20DC_08-00_0560.pdf (accessed March 12, 2012).
- 36 Olson, E. S.; Dunham, G. E.; Sharma, R. K.; Miller, S. J. Mechanisms of Mercury . Capture and Breakthrough on Activated Carbon Sorbents, 2000. Division of Energy & Fuels - American Chemical Society.
http://www.anl.gov/PCS/acsfuel/preprint%20archive/Files/45_4_WASHINGTON%20DC_08-00_0886.pdf (accessed March 12, 2012).
- 37 Dunham, G. E.; Miller, S. J. *Demonstration of Mercury Capture in a Fixed Bed*; Draft . Final Report; Minnesota Department of Natural Resources: St. Paul, 2009.
- 38 Pavlish, J. H.; Holmes, M. J.; Benson, S. A.; Crocker, C. R.; Galbreath, K. C.

- . Application of sorbents for mercury control for utilities burning lignite coal. *Fuel Processing Technology* **2004**, *85*, 563-576.
- 39 Galbreath, K. C.; Zygarlicke, C. J. Mercury transformations in coal combustion flue gas. *Fuel Processing Technology* **2000**, *65-66*, 289-310.
- 40 Hutson, N. D.; Ryan, S. P.; Touati, A. Assessment of PCDD/F and PBDD/F emissions from coal-fired power plants during injection of brominated activated carbon for mercury control. *Atmospheric environment* **2009**, *43* (26), 3973-3980.
- 41 Srivastava, R. K.; Hutson, N.; Martin, B.; Princiotta, F.; Staudt, J. Control of Mercury Emissions from Coal-Fired Utility Boilers. *Environmental Science & Technology* **2006**, *40* (5), 1385-1393.
- 42 Henke, K. R.; Robertson, D.; Krepps, M. K.; Atwood, D. A. Chemistry and Stability of Precipitates from Aqueous Solutions of 2,4,6-Trimercaptotriazine. Trisodium salt, Nonahydrate (TMT-55), and Mercury (II) Chloride. *Water Resources* **2000**, *34* (11), 3005-3013.
- 43 Hrdlicka, J. A. *Performance Testing of Mercury Oxidation Via Catalytic Barrier Filters*; Master Thesis; University of North Dakota: Grand Forks, 2007.
- 44 Buitrago, P. A. *Gas-Phase Mercury Oxidation: Effects of bromine, chlorine and SO₂ under air firing and oxy-fuel conditions, experimental and modeling study*; PhD Thesis; Department of Chemical Engineering - University of Utah, 2011.
- 45 Zhuang, Y.; Pavlish, J. H.; Lentz, N. B.; Hamre, L. L. Mercury measurement and control in a CO₂-enriched flue gas. *International Journal of Greenhouse Gas Control* **2011**, *55*, 5136-5142.
- 46 Wu, C.-L.; Cao, Y.; He, C.-C.; Dong, Z.-B. P. W.-P. Study of elemental mercury re-emission through a lab-scale simulated scrubber. *Fuel* **2010**, *89*, 2072-2080.