Mercury Transport in Taconite Processing Facilities: (III) Control Method Test Results

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1. Summary

Short-term tests were conducted at taconite processing facilities as part of a long-term Minnesota DNR study designed to identify potential means to decrease mercury in stack emissions. Three of these tests involved addition of chloride and bromide salts to operating induration furnaces in an attempt to convert elemental mercury (Hg^0) to oxidized mercury (Hg^{+2}), the latter form of which can be captured by existing wet scrubbers. A series of experiments was also performed on “slip-stream” gases from an operating taconite processing plant to evaluate use of chemical oxidants added directly to water in wet scrubbers to enhance capture efficiency for elemental mercury.

NaCl addition to the greenball feed in a straight-grate facility decreased total mercury (Hg(T)) in stack-gases by 5 to 9%, depending on chloride application rate. Injection of NaCl and $CaCl_2$ salt solutions directly into the preheat zone of a straight-grate furnace decreased Hg(T) in stack-gas by 6 and 13%, respectively. In contrast, NaCl addition to the greenball feed at a grate-kiln facility at rates similar to those used in the straight-grate tests resulted in 18 to 32% decrease in stack-gas Hg(T). Differences in results for the two types of furnaces can be attributed to differences in gas composition in the preheat zones. HCl is thermally generated from NaCl deep in either type of furnace, but bypasses the preheat zone in straight-grate furnaces and passes directly through the preheat zone in grate-kiln furnaces.

Bromide salts were much more effective than chloride salts at oxidizing mercury in straight-grate furnaces. Injection of NaBr and $CaBr_2$ salt solutions into the preheat zone of a straight-grate furnace resulted in 62 and 64% decreases in Hg(T) in stack-gas. In addition, mercury passing through the wet scrubber was almost fully oxidized, as measured by a continuous mercury monitor on the stack. These results suggest that at least a portion of the injected Br salts were converted rapidly to highly reactive Br_2. This gas species effectively oxidized the majority of Hg^0 to Hg^{2+} and enhanced capture of mercury in the wet scrubber. However, Br_2 generation may lead to other corrosion and environmental issues that will need to be studied before this method can be used to control mercury in taconite processing plants.

In slip-stream tests, it was found that hydrogen peroxide (1500 ppm H_2O_2) solutions captured about 10-15% of the mercury in process gas, which was less than the baseline capture rates for weakly buffered $NaHCO_3$ solutions (2.5 mmolal). However, solutions containing approximately 100 ppm of a proprietary EPA oxidant resulted in mercury capture rates in excess of 80%, pointing to the need for a plant-scale test using this oxidant. A surprising result was that the fraction of mercury captured by $NaHCO_3$ solution in these tests was much greater than the fraction of mercury present in oxidized form in the raw waste gas. This suggests that an oxidizing component present in waste gas, possibly Cl_2, oxidizes Hg^0 upon contact of the gas with water.

2. Introduction

The taconite industry arose on Minnesota's Iron Range in the late 1940's and early 1950's as high grade "oxidized" ore declined and technologies to utilize the more extensive but lower grade "taconite" ore were developed. Today, Minnesota supplies approximately 40 to 50 million tons of taconite pellets to steel makers throughout the Great Lakes region each year. The primary iron source is magnetite (Fe_3O_4) which is concentrated from taconite ore by grinding and magnetic separation. This concentrate is combined with either bentonite or an organic binder, rolled into cm-sized balls (referred to as greenballs), and converted to hardened pellets of hematite (Fe_2O_3) by heating in air to high temperatures (2400F) in a process referred to as "induration". In some cases, a limestone fluxing agent, needed for steel making, is added to the greenball prior to induration.

All of Minnesota's existing taconite processing plants were built in the 1950's to 1970's, well before mercury was recognized as a global pollutant. It was only recently recognized that mercury present in taconite concentrate is released to process gases during induration and that the majority of this mercury is not captured by the plants' wet scrubbers, but released to the atmosphere. Collectively, taconite processing in Minnesota releases approximately 350 to 400 kg of mercury to the atmosphere each year (Engesser and Niles, 1997; Jiang et al., 2000; Berndt, 2003; MPCA, 2006). Although this amount is small compared to global emission rates, it represents Minnesota's second largest industrial source of mercury to the atmosphere. It appears, therefore, that reduction in this source will be needed for the state to reach future mercury reduction goals (MPCA, 2006).

This report is the third in a series of studies conducted by the Minnesota Department of Natural Resources in an attempt to find cost effective means to decrease mercury in taconite stack emissions. The first two reports evaluated the source and fate of mercury in taconite processing plants (Berndt and Engesser, 2005 a, b). This report provides results of short-term tests recently conducted at taconite processing facilities to evaluate potential mercury control methods. In addition, the Minnesota DNR commissioned a study by the University of North Dakota's Environment and Energy Research Center (EERC) to independently evaluate feasibility and cost of borrowing other technologies being developed for the coal-fired power industry (Laudal, 2007a). A third study commissioned by the DNR during this biennium was conducted by the University of Minnesota, Coleraine Minerals Research Laboratory, and involves characterization of scrubber solids to determine how best to separate mercury from recoverable iron oxides. The final results from that study were not available at the time this document was being prepared.

3. Background Information

3.1. Previous Research

The DNR conducted its initial study summarizing past data, research, and reports on mercury releases and distribution related to taconite mining in 2003 (Berndt, 2003). Berndt et al. (2003) also conducted a study of scrubber waters in taconite induration plants, showing that large amounts of mercury are captured by existing equipment, and that this mercury is present in both dissolved and particle-bound forms. Following capture from process gas, dissolved mercury decreases while particulate-bound mercury increases in scrubber water on a time scale of minutes to hours.

This study, and an earlier study by Benner (2001), indicated that some control of mercury at taconite plants might be achieved by eliminating the mercury-enriched scrubber solids from processing loops that can recycle solids (and adsorbed mercury) back to the furnace. Based on estimates of Berndt and Engesser (2005a), eliminating mercury recycle loops in taconite companies would remove from 0 to 30% of the mercury currently being emitted. Berndt and Engesser (2005b) and Benner (2007) have worked to identify cost effective means to separate mercury from recyclable iron units. For emission reductions above the 30% level, however, these mercury-recycle loops must be eliminated *and* scrubber capture efficiencies for mercury must be improved.

Berndt and Engesser (2005a) studied the release of mercury in taconite induration plants and found a correlation between capture rate in wet scrubbers and the rates at which HCl and scrubber dust were generated during induration. This study, along with thermal mercury release experiments conducted by Benner (2005) and Galbreath (2005), Mössbauer spectroscopic measurements for heated taconite pellets (Berquó, 2005), and experimental data on adsorption of mercury to maghemite (Galbreath et al., 2005), suggested mercury release during taconite induration is a relatively complex process. Mineralogic conversion of magnetite to maghemite and hematite is closely tied to release of mercury as either Hg^0 or $HgCl_2$, depending on availability of HCl in the process gas. This affects scrubber efficiency for mercury capture, since $HgCl_2$ and other oxidized mercury species are more easily captured by existing wet scrubbers than Hg^0. Mass balance estimates suggested approximately 10-15% capture of mercury was typical for straight-grates while approximately 30% capture was found at grate-kilns.

Berndt and Engesser (2005b) studied the fate of mercury captured by wet scrubbers in taconite processing plants. They determined that most of the mercury in scrubber waters adsorbs to non-magnetic particles, presumably hematite, and avoids the magnetic particles, maghemite and magnetite. This means that one manner to permanently reduce mercury emissions from taconite processing plants is to increase the fraction of mercury captured by the wet scrubbers and then use mercury adsorption and magnetic separation to focus the captured mercury into tailings basins where the tailings sequester the mercury.

Two primary means to increase oxidation of mercury that were suggested by bench-top exeriments included addition of HCl to process gas (Galbreath et al., 2005; Berndt and Engesser, 2005b) and addition of oxidizing compounds to scrubber water (Hutson and Srivistava, 2006). Other methods, such as ozone or activated carbon injection to process gas may also have application to the taconite industry (Laudal, 2007a), however, these methods appear to be more costly to test and implement and have, thus far, not been studied. In addition to HCl, other halide species in gases have been known to oxidize mercury in power plant applications. These include Cl, Cl_2 and especially Br_2 (Liu et el, 2007). Although these gas species are likely expensive and dangerous to inject, they are known to form by thermal decomposition of halide salts during coal combustion (Edwards et al, 2001; Benson, 2006; Liu et al, 2007; Agarwal et al, 2007).

Although similar and more extensive studies have been conducted at other types of facilities (e.g., coal-fired power plants, waste incinerators, gold mining facilities), the taconite industry is intrinsically unique from each of these industries, owing to the widespread occurrence of relatively reactive iron-oxides which have not only been shown to participate in reactions involving mercury transport but can also impact mercury measurement (Laudal, 2007b). The experiments detailed in this report are the first of their kind conducted specifically for the taconite industry, and were, thus, designed to test mercury control methods more on a conceptual level than on a specific practical level.

3.2. Induration Furnaces and Wet Scrubbers

Although all taconite companies use heat and air to oxidize greenballs in induration furnaces, there are two very different types of furnaces used on the Iron Range to accomplish this task: straight-grate and grate-kiln.

Hibbing Taconite, located near Hibbing, MN, and Mittal Steel, located near Virginia, MN, fire greenballs in straight-grate furnaces (Figure 3.2.1). Large combustion chambers located in the center of the furnace provide heat to pellets that move past the firing zone on a large grate. Outside air, heated as it cools the fired pellets in the second cooling zone, dries and heats fresh greenball in the up-draft drying zone. Meanwhile, air introduced in the combustion chambers and/or in the first cooling zone passes through the pellet bed in the firing and preheat zones, and then again in the down-draft drying zone. Northshore Mining, located in Silver Bay, MN, also has straight-grate furnaces, which were the first of their type to be built in Minnesota. These furnaces have a slightly different air flow pattern than do the Hibtac or Mittal straight-grate furnaces.

Keewatin Taconite, near Keewatin, MN, Minntac, near Mountain Iron, MN, and United Taconite, close to Eveleth, MN all operate grate-kiln furnaces (Figure 3.2.2). Most heating in this type of system is provided by a large burner that projects a flame up a large rotating kiln as greenballs, fed from a moving grate, spill through the kiln. Air used to cool pellets in the cooler is cycled into the drying zone, while hot gas from the kiln is passed through the pellet bed in the preheat zone and used ultimately to dry pellets in the down-draft drying zone.

Plants that produce fluxed pellets (Minntac and Mittal) find it necessary to add additional heat to convert the limestone flux to lime. This heat is added through burners located in the preheat zone. United Taconite and Hibtac add small amounts of limestone to the pellets in order to increase pellet strength but at rates much less than used in production of Minntac and Mittal fluxed pellets. Keewatin Taconite does not add limestone to its pellets.

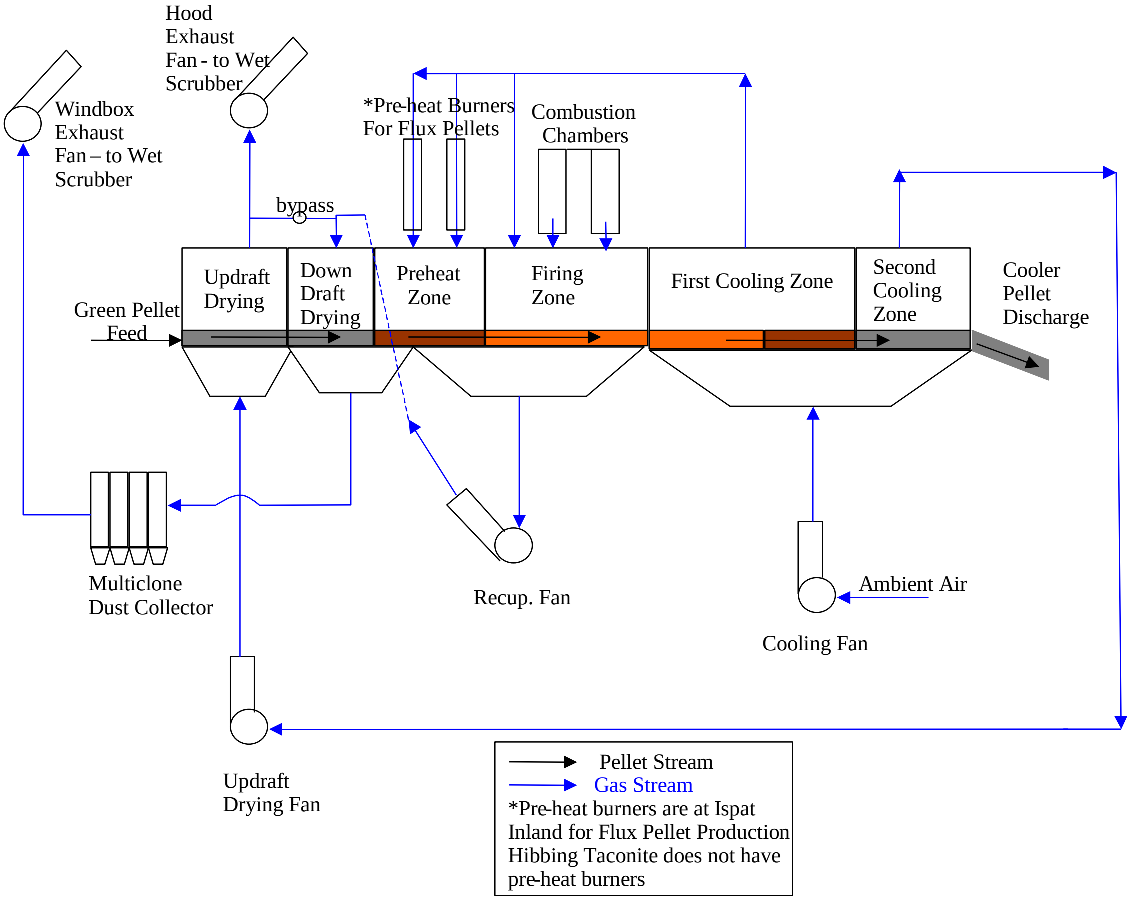

Figure 3.2.2: Diagram of a straight-grate induration furnace. Gases are passed numerous times through the pellet bed in order to dry, heat, and cool the pellets as they pass along a large grate. "Windbox exhaust" gases are derived from the down draft and preheat zones and passed through multiclone dust collectors before entering the wet scrubber/ exhaust system. "Hood exhaust" gases from the updraft drying zone originate from the second cooling zone and pass directly into the wet scrubber/ exhaust system.

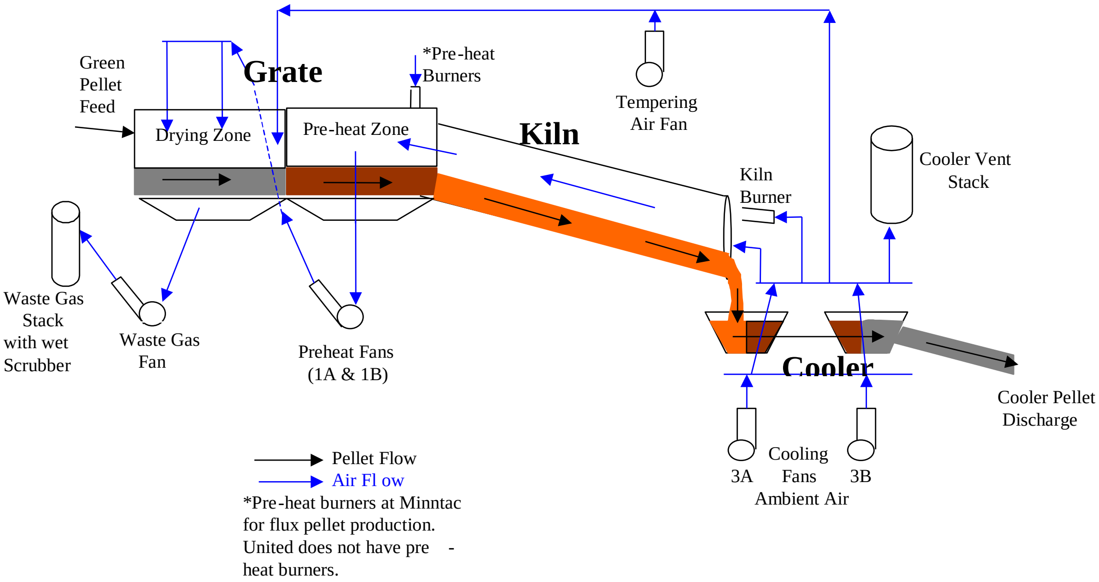

Figure 3.2.2: Diagram of a grate-kiln induration furnace. Combustion gases for heating the pellets are directed up a large rotating kiln and then down through the pellet bed in the preheat zone. The gases are then used for initial heating and drying of the greenball (or pellet) feed. Gases used for cooling the hot pellets are also used to dry and heat the pellets. Depending on the operation, the waste gases are passed through either one or two wet scrubbers and vented through one or two separate stacks.

In addition to differences in furnace types and pellets produced, the facilities use somewhat different methods for removing particles and pollutants from process gas (Table 3.2.1). Keewatin Taconite, United Taconite, and Mittal Steel all have recirculating scrubbers, while Hibbing Taconite has a single-pass scrubber. Minntac has four single-pass scrubbers and one recently built recirculating scrubber. Keewatin Taconite adds lime to control pH in its recirculating scrubber as does Minntac in its new recirculating scrubber. Northshore Mining Co uses wet-wall electrostatic precipitators (WWESPs) and does not use wet scrubbers.

Table 3.2.1: Taconite processing facilities on Minnesota's Iron Range.

Plant	*Lines*	*Furnace type*	*Pellets*	*Scrubber type*
US Steel, Keewatin Taconite	1	Grate-Kiln	Standard	Recirculating, Lime added
Hibbing Taconite	3	Straight-Grate	Standard	Single Pass
US Steel, Minntac	5	Grate-Kiln	Standard/ Fluxed	4 Single Pass 1 Recirculating, Lime added
United Taconite	2	Grate-Kiln	Standard	Recirculating
Mittal Steel	1	Straight-Grate	Fluxed	Recirculating
Northshore Mining Co.	3	Straight-Grate	Standard	Wet Wall ESP

4. Methods

4.1. NaCl Addition to Greenball: Hibbing Taconite and United Taconite

Galbreath (2005) achieved approximately 90% oxidation of Hg^0 released from greenball in bench scale tests by adding 100 ppmv HCl to the carrier gases. Although direct addition of HCl to taconite process gas is probably an unreasonable approach, these results suggest that one means to limit mercury emissions during taconite processing is to add components to greenball that can decompose to form HCl during taconite processing. Berndt and Engesser (2005a) showed that Cl salts present in greenball (dissolved in pore fluid) are volatilized quantitatively during induration, most likely as HCl, and carried to the wet scrubber where it is captured along with particles and other water-soluble gases. These results suggested that addition of NaCl to greenball should generate HCl and potentially lead to decreased mercury in stack emissions.

This method was tested at two plants: one (Hibtac) a straight-grate and the other (United Taconite) a grate-kiln plant. These plants were selected specifically because the background Cl^- in their processing waters and greenball is lower than at either Mittal or Minntac, and because, at the time these studies were being conducted, Keewatin Taconite's wet scrubber was relatively new and untested. The NaCl addition method may be limited by the potential for corrosive effects of alkali chloride salts on grate bars (Mohanty and Shores, 1993). If the tests for NaCl addition yielded positive results for mercury control, then corrosion studies would be required before mercury control by this method would be considered a viable alternative.

4.1.1. Straight-Grate (Hibbing Taconite)

In this test, NaCl was added to the filtered concentrate (filter-cake) at Hibbing Taconite's Line 3. The advantage of adding NaCl by this method is that the NaCl would be reliably mixed throughout the pellet bed as greenballs enter the induration furnace. It was estimated that between one and two hours would be required for NaCl added to filter cake to reach steady-state concentration in the greenball feed to furnaces. This is because filter cake is stored in day-bins, and because considerable cycling takes place in the balling drum circuit owing to transfer inefficiencies associated with greenball sizing. Thus, each test was conducted for a period of three hours: two hours for steady-state NaCl concentration to be achieved in greenballs, and one hour to allow for samples to be collected.

Two tests were conducted, the first adding NaCl at a rate of 25 lbs per hour and the second adding NaCl at a rate of 50 lbs per hour. The greenball feed rate was 500 long tons per hour during these tests and, thus, the application rates were equal to approximately 0.5 and 1.0 lbs of NaCl for every 10 long tons of greenball. Baseline samples for evaluating background concentrations of mercury, chloride, and other elements were collected before the tests were started and following completion of the tests after the added NaCl was cleared from the system.

This plant vents gas through four stacks (Stacks A, B, C, and D) for each production line. Because it was cost prohibitive to measure mercury using continuous mercury monitors (CMMs) (see section 4.4.1) on all four stacks, continuous monitoring was only performed in the stack with the highest mercury concentration. Non-continuous stack-gas mercury measurements were also made using Flue-gas Absorbent-trap Mercury Speciation traps (FAMS; see section 4.4.1) on both stacks A and B during the tests and on all four stacks when the plant was operating under baseline conditions on the day following the Cl-addition tests.

4.1.2. Grate-Kiln (United Taconite)

Owing to much longer residence time for filter cake in the large “day bins” at United Taconite (compared to Hibbing Taconite), NaCl was added at this plant directly to the top of greenballs that had already been formed, rather than to the filter cake feeding the balling drums. The NaCl was added before the balls were tumbled onto the grate, however, to permit as least some distribution of NaCl throughout the pellet bed. All testing at this plant was performed on “Line Two”.

NaCl was added at rates of 30 and 60 lbs per hour. The greenball feed rate was approximately 600 long tons per hour so, as was the case at Hibbing Taconite, application rates were approximately 0.5 and 1.0 lbs of NaCl per 10 long tons of greenball. Baseline samples of scrubber water and greenball were collected to monitor mercury and chloride both shortly before NaCl addition began and again in the morning following completion of the tests. Similar to the straight-grate tests at Hibbing Taconite, each NaCl addition test was run for a period of three hours: two hours for steady-state to be achieved and one hour for measurements to be conducted.

Unlike Hibbing Taconite, which has four stacks releasing gas from one large wet scrubber, United Taconite’s Line Two has two independent scrubbers each venting through its own stack. Beneath each stack is a thickener which helps eliminate particulates in water that recirculates to the scrubber. A sampling port located at the base of each thickener allows sampling of water and scrubber solids from these sites (the “underflow”).

Scrubber thickener underflow water was sampled for both stacks during the tests and analyzed for mercury, cations, and anions. However, gases were monitored by CMM (See section 4.4.1) for only one of the two stacks (2B). This stack was found to have higher Hg concentration than the other stack (2A) during previous visits to the plant. FAMS (See Section 4.4.1) measurements were made on both stacks throughout the tests for comparison purposes.

4.2. Focused Halide Injection at Hibbing Taconite

Halide salts exposed to elevated temperatures in coal-fired utitilities generate other gases (HCl, Cl_2, HBr, and Br_2) that can help to oxidize elemental mercury (Edwards et al, 2001; Benson, 2006; Liu et al, 2007; Agarwal et al, 2007). Because little experience exists on the subject of halide behavior in taconite furnaces, a third set of tests was conducted whereby NaCl, NaBr, $CaCl_2$, and $CaBr_2$ salts were added directly into the preheat zone at a straight-grate (Hibbing Taconite’s line three). The chemical and physical behavior of salt solutions sprayed into a taconite furnace is virtually unpredictable, owing to rapid heat transfer and changes in temperature, unknown gas-flow patterns, high vaporization and thermal expansion rates of the resulting steam, and unknown rates for key chemical reactions. Rather than attempt to test or model all of these parameters, it was decided to directly test the method in an operating induration furnace using “best guesses” on flow and spray parameters.

Each of the four salts was sprayed into the furnace at approximately 50 lbs per hour, all dissolved in water as 10 wt% solutions. Because these salts were added directly to the furnace, response was expected to be nearly immediate and so test-periods were shortened to one hour. Following an initial baseline period during which no salt was sprayed, NaCl was first added for a period of one hour. Greenball and scrubber water samples were collected 30 minutes into the test to monitor the behavior of Hg, Cl, Br, and other anions and cations such as Ca and Na in the scrubber water. Following NaCl addition, the other salts were tested sequentially in the order: NaBr, $CaCl_2$, $CaBr_2$. Each test followed a one hour period of time during which no salt was sprayed into the furnace. Scrubber water and greenball samples were collected beginning 30 minutes after addition of the salt had begun.

As was the case for NaCl addition to greenball at Hibbing taconite, the CMM was employed on Stack A. This stack was found to have the highest mercury during previous testing at this plant. FAMS was not used to measure mercury in this case because the CMM was considered a more reliable means to assess mercury for this specific application.

It is important to note that halide addition method may be limited by the potential for corrosive effects of alkali chloride salts on grate bars (Mohanty and Shores, 1993). If the tests for halide addition yielded positive results for mercury control, corrosion studies and cost analysis would be required before mercury control by this method would be considered a viable alternative.

4.3. In-Scrubber Oxidation: Slip-Stream Test at Keewatin Taconite

A number of studies have suggested that adding oxidizing chemicals directly to scrubber water (rather than to process gas) may provide an alternative means to control mercury in stack emissions for coal-fired power plants that have wet scrubbers (Overcamp, 1999; Korrell et al, 2003; Hutson and Srivistava, 2006). A preliminary assessment of potential control methods was made based on likely cost, effectiveness, and environmental impact of the oxidants. H_2O_2 was selected as one potential oxidant based on its low cost, widespread availability, its known ability to oxidize mercury at high concentrations, and reported success when using H_2O_2 to control mercury along with other additives in relatively specialized applications (Laudal, 2007a). In addition, H_2O_2 and ferric iron are known, in some cases, to have a synergistic effect on oxidation processes by generating highly oxidizing hydroxyl radicals (e.g., Fenton’s reagent). Another chemical, referred to here as EPA_{OX} was selected following consultation with Nick Hutson, (e.g., Hutson and Srivistava, 2006) after it was determined that this proprietary reagent is also inexpensive, widely available, and likely to decompose to harmless chemicals in the environment.

A special system was designed to screen oxidants for their effectiveness in capturing mercury from taconite process gases (Fig. 4.3.1). This system, referred to here as the Quench Liquid Injection Probe (QLIP) was configured specifically to prevent clogging and interference from accumulating particulates in a frit and to maximize contact between slip-stream gas and the liquids being tested. During a test, the scrubbing solution (with or without oxidant) is continuously circulated to the tip of the sampling probe using a peristaltic pump, and then sucked along with the process gas back into the liquid reservoir. Oxidized mercury and particulates are captured by the liquid, while insoluble gases pass through the system. Any mercury not collected by the "scrubber" solution is collected and speciated by a series of separate dry sorbent traps in the FAMS system (see section 4.4.1).

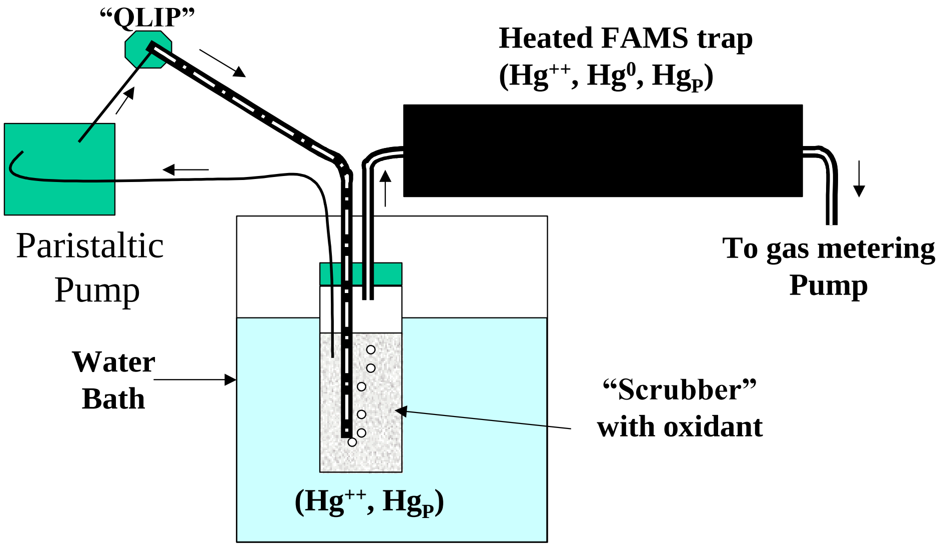

Figure 4.3.1 Quick Liquid Injection Probe (QLIP) designed for use in a slip-stream study. A peristaltic pump injects the scrubber solution containing oxidants into a sampling probe that is inserted into the ductwork at an operating processing facility. This liquid returns to the sampling jar with gases being pumped from the duct. Oxidized mercury is captured in the scrubber while any mercury remaining in the process gas is captured and speciated by the FAMS traps (see section 4.4.1).

Tests were conducted sequentially and side-by-side in the order shown in Table 4.3.1. All scrubber solutions tested were weakly buffered at near-neutral pH conditions using 2.5 mmolal $NaHCO_3$. Baseline conditions were assessed both by using $NaHCO_3$ solutions with no oxidant added and also by conducting tests with no "scrubber" solution added to the QLIP. In between baseline evaluations, solutions containing the same concentration of $NaHCO_3$ and either 1500 ppm H_2O_2 or approximately 100 ppm EPA_{OX} were tested in the apparatus. Following each test, a five ml aliquot of the reactant solution was collected and sent to the University of Minnesota Geochemistry laboratory for analysis by anion chromatography (Cl, Br, NO_2^-, NO_3^-, SO_4^-). Following a final measurement of pH, the remaining solution was preserved with BrCl and shipped to Cebam, Inc., Seattle, WA, for measurement of total captured mercury. The University of Minnesota, NRRI, supplied the constant temperature water bath and FAMS apparatus, including the gas pump. This group also performed mercury analysis on sorbents in the FAMS traps.

Table 4.3.1: Additives used for slip-stream tests at Keewatin Taconite. Baseline tests ($NaHCO_3$ with QLIP) were conducted in parallel with tests conducted without the QLIP apparatus.

ID	*"Scrubber" Solution*	*Parallel FAMS test w/o QLIP?*
Baseline-1	*0.0025 M $NaHCO_3$*	Yes
H_2O_2-1	*0.0025 M $NaHCO_3$+1500 ppm H2O2*	No
EPA_{OX}-1	*0.0025 M $NaHCO_3$ + 100 ppm EPA_{ox}*	No
Baseline-2	*0.0025 M $NaHCO_3$*	Yes
H_2O_2-2	*0.0025 M $NaHCO_3$+1500 ppm H2O2*	No
EPA_{OX}-2	*0.0025 M $NaHCO_3$ + 100 ppm EPA_{ox}*	No
Baseline-3	*0.0025 M $NaHCO_3$*	Yes

4.4. Measurement Methods

Extensive sampling and analysis of solids, liquids, and gases was performed prior to and during these tests to evaluate the best means to measure and monitor mercury in various components of the taconite process. However, chemical analysis is a non-trivial issue for mercury measurement in taconite process gases and scrubber waters owing to its relatively low concentrations, the presence of reactive gaseous species in taconite processing streams (such as Br_2, Cl_2, SO_2), and the ubiquitous occurrence of iron-oxide particles that can react with mercury in several ways (Berndt and Engesser, 2005a, 2005b; Laudal, 2007b). These issues will be discussed briefly in this report but are also the subject of continued research in other on-going studies.

4.4.1. Stack-gas Hg Measurement

Two primary methods were used to analyze the composition of stack-gases in this study: CMMs (continuous mercury monitors) and FAMS (flue gas absorbent-trap mercury speciation). CMMs systematically collect and automatically analyze either gaseous elemental mercury, referred to as Hg(0) or Hg^0, or total mercury, Hg(T), every few minutes. CMMs are the preferred method for gas analysis during plant tests because they provide virtually instantaneous feed-back that is needed when relating changes in process to change in stack-gas chemistry. However, FAMS analysis is a much less expensive method that provides an average value for gas concentration over a period of time and additionally reports values for three forms of gaseous mercury: particulate Hg(P), oxidized gaseous (Hg^{2+}), and elemental (Hg°). If FAMS could be proven reliable for measuring mercury in taconite stack-gases, it could be used to assess gas composition for plant balance and monitoring applications and to assess mercury speciation in applications where speciation is important.

Several CMM methods were tested and/or used to analyze gases during these tests. The first method, involved filtering the stack-gas at the sampling duct followed by transport to the analytical shed for processing and analysis. This method was used for analyzing mercury in gases during NaCl addition to greenball at Hibbing Taconite and United Taconite. A second method that was considered involved sampling gases through an ISP (Inertial Separation Probe) that effectively eliminates particles from entering the tubing by increasing the velocity of the gas at the sampling point. This method was tested at a taconite processing facility, but appeared to provide inferior results and so was not used in this study (Laudal, 2007b). A third method involved injecting a conditioning liquid into the duct at the gas sampling site and transporting the resulting gas/liquid mixture through heated tubing to the analytical shed. This method was also tested at a taconite processing facility by Laudal (2007b), and then subsequently used at Hibbing Taconite during the focused halide injection tests.

Collection of samples for FAMS analysis was performed using three different methods. The normal method involved inserting a heated vessel containing the FAMS sorbent train directly into the duct. This method eliminates condensation effects and allows any particulates in the gas phase to collect in a dry filter in the front end of the FAMS trap. This method was used to sample stack-gases when NaCl was added to greenball at the straight-grate and grate-kiln facilities.

The second FAMS method is depicted in Figure 4.3.1. This method involves placing a heated FAMS trap at the end of a liquid injection/trap system (QLIP = Quench Liquid Injection Probe) that removes particulate and oxidized mercury from the process gas during transport to the FAMS device. This system was developed to minimize sampling artifacts related to oxidation and capture of mercury by taconite dust in the sampling tubes. The FAMS method, in this case, only quantifies and speciates mercury that remains in the gas after passing through the QLIP. This method was only used for the slip-stream tests at Keewatin Taconite, although limited testing was also performed under baseline conditions at Hibbing Taconite prior to the focused halide injection tests.

In the third FAMS method, the system was connected to the sampling port by a one-meter long unheated Teflon tube. No effort was made to prevent condensation from occurring in the tube connecting the port to the FAMS. However, the FAMS was kept at high temperature to prevent condensing water from interfering with the material in the dry sorbent traps. This method was only used to provide results to compare to tests conducted when the QLIP system was used.

In all cases, the FAMS sorbent train contains three individual compartments for isolating different forms of mercury. Particulate mercury is isolated using a quartz fiber filter, oxidized mercury is trapped on a solid KCl sorbent material, and elemental mercury is collected with a chemically impregnated solid carbon sorbent. The solids from each compartment are digested and analyzed separately to provide the speciation. All FAMS testing in the study was performed by the University of Minnesota, Coleraine Minerals Research Laboratory.

4.4.2. Scrubber Water Sampling and Analysis

In all cases, scrubber water sampling ports were chosen at locations that provided the freshest sample of scrubber water possible. Hibbing Taconite, for example, combines scrubber water effluent from three lines into one stream flow that leads back to the concentrator. The line tested in this case, Line 3, has its own valved outlet for sampling of the blow-down water before it is added to the larger single stream.

United Taconite recirculates scrubber water using thickeners located beneath the wet scrubbers. The sample ports for scrubber water at United Taconite permit collection of the underflow water from each of its scrubber thickeners. Water from the top of the thickeners is pumped back to the scrubber and reused. This recirculation and thickening of scrubber water results in a much larger amount of suspended solids in United Taconite scrubber water compared to Hibbing Taconite blow-down water. Moreover, the contact time between water and particles prior to sampling is greater at United Taconite compared to single-pass scrubbers such as at Hibbing Taconite.

Scrubber water sampling at Keewatin Taconite is similar to that at United Taconite. There are valves located beneath the scrubber water thickener permitting sampling of the underflow, whereas water from the top of the scrubber is reused by the wet scrubber.

All water samples for mercury analyses were collected using “clean-hands, dirty-hands” procedures, whereby the clean bottles were placed into sealed plastic bags prior to leaving the laboratory and not opened except during sampling, and then again later when the analysis was being conducted. Only the designated clean-hands person, wearing clean plastic gloves (powder-free), handled the sample bottles when they were outside of the plastic bag. All other sample processing was conducted quickly and efficiently by the so-called “dirty-hands” person. These procedures were implemented to minimize the risk of contamination from plant dust and of cross-contamination between samples.

In addition to these special precautions, procedures were consistently evaluated using blanks to assess the degree of mercury contamination associated with filtration and sampling. Procedural blanks were collected at each site during each visit. One bottle was filled at the sampling site with deionized water brought from the laboratory. In addition, deionized water was filtered at the sampling location and both the water and the filter were saved for analysis. The level of contamination introduced by our procedures was insignificant relative to the concentration of mercury found in samples analyzed in this study.

Samples were analyzed by Cebam Analytical, Inc., located in Seattle, Washington. Filtered water samples were digested with BrCl over night, and then analyzed by $SnCl_2$ reduction, gold trap collection, and CVAFS detection (modified EPA1631). This laboratory participates in many round-robin blind sampling programs and routinely ran duplicates and standards to ensure accuracy.

Mercury concentration of the suspended solids, Hg(P) (in ng/g on a dry particle basis), was determined by analyzing the scrubber solids filtered from the water. Filters containing scrubber solids from the above procedures were dried at 104ºC for analysis, weighed, and digested in hot acid (HCl/HNO_3, 3/1). Mercury was analyzed using $SnCl_2$ reduction and gold trap collection, followed by CVAFS detection (modified EPA1631). Certified reference materials WS-68, NIST2709, and GSR-2 were used to assess recovery and analytical accuracy. As was the case for water samples, solids were digested and analyzed by Cebam Analytical, Inc., located in Seattle, Washington.

A new method was developed for analysis of total mercury in unfiltered waters containing suspended solids. This method was developed by Cebam, Inc., when lab personnel noticed that emptied sampling bottles left to dry over a period of time took on a reddish color. This reddish color was believed to be due to adherence of fine iron-oxide dust particles to the glass. The new method was developed to allow all of the mercury in a sample, including that on particles adhering to the surface of the bottle, to be analyzed with a single mercury analysis.

By this method, the visible suspended solids were allowed to settle from solution and the bulk of the water containing only the smallest particles was then decanted and treated with BrCl to oxidize the mercury. The remaining slurry was then digested in hot acid (HCl/HNO_3, 3/1) added directly to the sampling jar where it could dissolve mercury from both the visible solids as well as from any mercury on solids adhering to the surface of the sampling bottle. The contents of the jar were then added to the decanted portion and total mercury in the mixture was analyzed by $SnCl_2$ reduction, gold trap collection, and CVAFS detection (modified EPA 1631).

Importantly, it was found during the study that some scrubber waters contain components that are capable of reducing oxidized mercury to elemental mercury during sample storage. Elemental mercury is lost from the solution when this occurs and will be missed in the analysis. BrCl was routinely added to fix the samples prior to shipment, but not until after it was found that some of the samples in this study had potentially lost mercury due to this reduction process. This will be discussed further in relation to specific tests where it was thought mercury loss occurred (NaCl addition to a straight-grate at United Taconite).

4.4.3. Greenball Analysis

Greenball samples were commonly collected as a means to assess mass balance with respect to components entering and leaving the furnace (Cl and Hg, in particular). The sample collection point, in all cases, was at the front end of the induration furnace, just prior to the point where the greenball is fed onto the grate. The samples were collected using a spatula and placed into clean, acid-washed 20 ml bottles with Teflon-lined lids. The damp greenball samples, which contain approximately 9 to 10% moisture by weight, were shipped to Cebam, Inc., for drying and analysis of mercury. Greenball Hg concentrations were determined on a dry-weight basis by Cebam, Inc., using the same technique described above (Section 4.4.2) for solids filtered from scrubber water.

For Cl addition to straight-grates, the effectiveness of Cl addition to greenball was tested by leaching fresh greenballs with water and analyzing the water by Ion Chromatography. For these tests, 100 grams of dry greenball material was leached for approximately one week in 100 grams of deionized water. The water was then filtered and analyzed by ion-chromatography at the University of Minnesota, Department of Geology and Geophysics. The resulting concentrations were reported as water-leachable salts on a dry weight basis for the pellets.

4.5. Estimating Mercury Capture Efficiency For Wet Scrubbers

Ideally, estimating mercury capture efficiency for wet scrubbers would involve comparing simultaneously measured mercury concentrations in process gas at the scrubber inlet and outlet. The change in mercury concentration across the scrubber could be divided by the mercury concentration in gas entering the scrubber to obtain the capture efficiency. Unfortunately, this straight-forward method is not possible at Hibbing Taconite or United Taconite where the plants tests were performed. United Taconite does not have a suitable gas sampling port in the ducts leading to its wet scrubber. Hibbing Taconite has two ducts with sampling ports leading to the wet scrubber from different parts of the furnace, but the gases from these ducts mix into a common manifold from which four stacks vent waste gas. Gas flow rates and mercury concentrations from both scrubber-inlet ducts and all four stacks would be required to accurately measure scrubber efficiency for mercury at this plant.

An alternative approach that might be considered to measure capture efficiency at taconite processing plants is the mass balance approach used by Engesser and Niles (1997) and Berndt and Engesser (2005a, b), whereby Hg entering the furnace with greenball is compared to mercury exiting the furnace in scrubber water. However, data provided by Berndt and Engesser (2005a) indicate that mercury has a relatively long residence time in furnaces during taconite induration owing to adsorption and desorption of mercury on the surfaces of pellets, dust particles, and ductwork. Owing to this effect, the mercury entering the furnace may be temporarily out of sync with mercury concentrations in gases and scrubber water exiting the furnace. Thus, the mass balance approach is insufficient for estimating scrubber efficiency for short-term tests such as those conducted here, and likely requires the averaging of fluxes of mercury in major components for inputs and outputs to the furnace over a long term to accurately represent an averaged scrubber efficiency.

For the present case, the goal of the experiments was not to estimate scrubber efficiency, but rather to evaluate changes in mercury emission that occurred as a response to addition of a chemical. For this purpose, we relied on changes in the CMM-measured mercury concentrations in a single stack to evaluate cause/effect relations for the tests. For example, if mercury concentration measured in stack-gases is 6.0 $\mu g/m^3$ before a control method is applied and 4.0 $\mu g/m^3$ during activation of the control method, and then subsequently returns to 6.0 $\mu g/m^3$ following the test period, this suggests that the technique decreased the existing emissions by 33% compared to baseline emissions. However, the true efficiency of the wet scrubber could be significantly higher than this, since monitoring only a change in emission does not take into account the fact that some mercury is already removed by the wet scrubber under baseline conditions. Furthermore, true capture efficiency for the scrubber could be lower than this, owing to possible unaccounted for processes, such as increased adsorption to duct walls taking place during the test period. Non-scrubber related adsorption can temporarily remove mercury at locations upstream from the scrubber and, thus, cause the method used in this study to over-estimate long-term scrubber efficiency in short-term tests. In effect, the results from these short-term plant-scale tests represent an intermediate step in a long-term research process;

control method potential must be evaluated in the presence of process parameters not easily simulated in bench –scale tests before longer-termed tests can be designed.

5. Results

5.1. NaCl Addition to Greenball (Hibbing Taconite and United Taconite)

5.1.1. Straight-Grate (Hibbing Taconite)

Baseline mercury concentration in Stack A before and after NaCl was added to greenball at Hibbing Taconite was approximately 4.3 $\mu g/m^3$ total mercury (Figure 5.1.1.1), although a plant upset shortly before the test resulted in considerable scatter just prior to testing. This concentration dropped to about 4.1 and 3.9 $\mu g/m^3$ after addition of 25 and 50 lbs/hr of NaCl to greenball, respectively, indicating 5% and 9% reduction in mercury emission compared to baseline mercury removal from gases in Stack A.

FAMS measurements for Stacks A and B were also made before, during, and following the NaCl addition test (Table 5.1.1.1) while Stacks C and D were only monitored for comparison purposes after all testing was completed. Although the FAMS results for total mercury in Stack A are similar to those indicated by the CMM, all of the values were approximately 10% lower. Furthermore, the FAMS Hg(T) measurements for Stack B showed an increase from 2.00 before NaCl addition was started to 2.74 and 2.79 ng/l during the NaCl injection tests. When NaCl addition to greenball ceased, the FAMS Hg(T) in Stack B increased to 3.57 $\mu g/m^3$. These data do not follow the Hg trend for Stack A. Because of this, and because there are known interferences for FAMS measurements made in taconite processing gases (Laudal, 2007b), these FAMS data are not considered sufficiently reliable for purposes of drawing conclusions in this report. Full FAMS results for this test, including speciation, are provided in the appendix.

A potential complication for interpretation of these data is that the mercury concentration in the greenball feed to the furnace decreased unexpectedly during the testing period (Table 5.1.1.2). Total mercury in greenball averaged 20.4 ng/g for five samples collected just before NaCl addition began, decreased to 15.8 for the first test period, and finally dropped again to 12.0 ng/g for five samples collected during the second testing period. The average mercury concentration in greenball was 11.9 for five samples collected in the morning on the day following the NaCl addition tests. If stack emissions responded directly and immediately to the mass of mercury entering the furnace, a 40% decrease in mercury concentration would have been expected during the testing period even without NaCl addition. These data provide strong evidence that mercury concentrations in gases exiting the furnace responded much more quickly to changes in the chemistry and conditions of the process gas than they did to changing concentration of mercury in the greenball feed.

The total mercury concentration in scrubber water from Line 3 increased during the tests from 738 ng/l before Cl addition began, up to a maximum of 880 ng/l during the second testing period, and then returned back to 827 ng/l on the day following the tests (Table 5.1.1.2). This small increase in the concentration of mercury in scrubber water during testing provides confirmation that NaCl addition to greenball in a straight-grate slightly improves the mercury capture efficiency of wet scrubbers.

Na and Cl concentrations in scrubber water are reported along with greenball Cl concentration in Table 5.1.1.3. The increase in dissolved Cl, but not Na, in scrubber water during these tests indicates that the Cl from NaCl is volatilized, most likely as HCl and/or Cl_2, in the furnace and carried to the wet scrubber and captured. Na, meanwhile, is not volatilized to a significant degree, but stays with the pellet product. Full chemical data on anions, cations, and pH in scrubber waters during these tests are provided in the appendix.

Table 5.1.1.1 FAMS measurements for total mercury in Hibbing Taconite stacks A through D ($\mu g/m^3$). Each value represents the average of three separate measurements. The complete data set for individual samples is available in Appendix I.

Hg(T)	*Stack A*	*Stack B*	*Stack C*	*Stack D*
Baseline	3.90	2.00		
Cl Test 1	3.49	2.74		
Cl Test 2	3.55	2.79		
Baseline	3.83	3.57	1.54	1.19

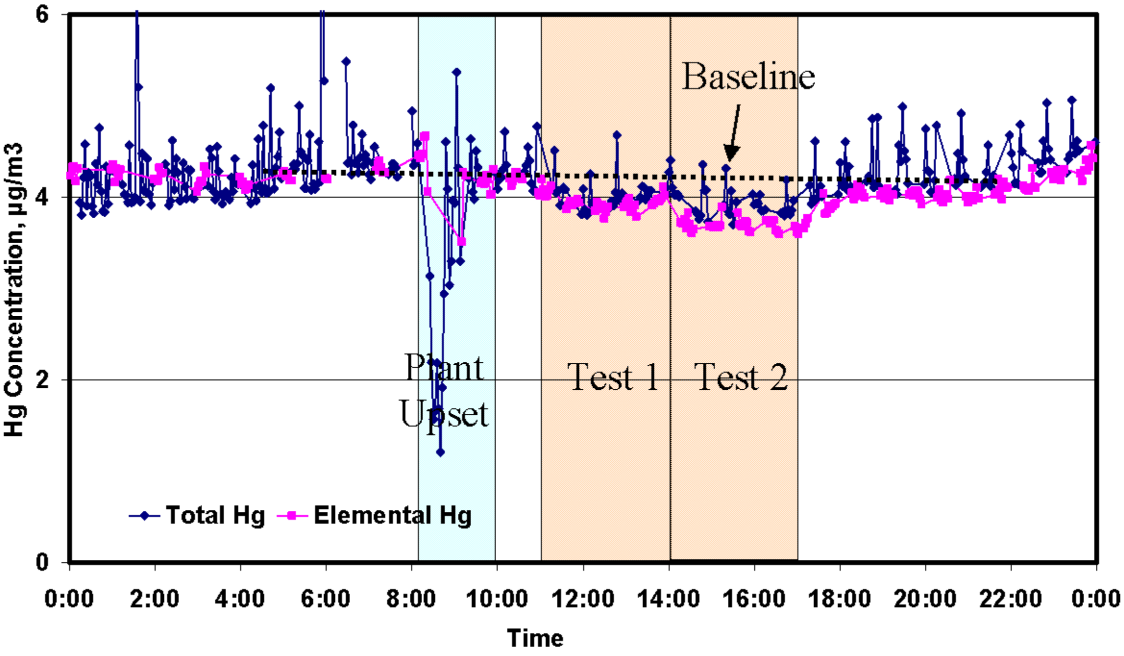

Figure. 5.1.1.1 Total and elemental mercury concentrations as a function of time during addition of NaCl to greenball at a straight-grate (Hibbing Taconite). There was a plant upset (blue) just before the tests were conducted but conditions were stable after that.

Table 5.1.1.2: Mercury concentration in greenballs and scrubber water during the NaCl addition tests performed at Hibbing Taconite. The full data set is provided in Appendix I.

Sample ID	*Greenball Hg (ng/g)*	*Hg(T) (ng/l)*	*Hg(D) (ng/l)*	*Hg(P) (ng/g)*
Baseline	20.4	738	439	1209
NaCl Add 1	15.8	742	499	1266
NaCl Add 2	12.0	880	587	1394
Baseline	11.9	827	561	1553

Table 5.1.1.3. Greenball Cl concentrations during Cl addition tests at Hibbing Taconite and resulting concentrations for Na and Cl in scrubber water. All concentrations are in units of ppm.

	Greenball Cl (H_2O leachable)	*Sodium*	*Chloride*
Make-up	-	-	66.0
Baseline	6.2	60.3	70.4
Cl Addition Test 1	21.0	60.0	75.4
Cl Addition Test 2	42.3	60.2	81.3
Baseline	6.2	60.3	70.7

5.1.2. Grate-Kiln (United Taconite)

As was the case for NaCl addition to Greenball at Hibbing Taconite, there was a plant upset shortly before the NaCl addition test began at United Taconite (Figure 5.1.2.1). There was considerable scatter in the CMM data for Stack 2B, following this time period, but based on concentrations measured shortly before the plant upset and soon after completion of the tests, baseline total mercury concentration in the stack-gas was estimated to be 5.7 μg/m^3. This concentration dropped to about 4.7 and 3.9 μg/m^3, respectively, during the two test periods, suggesting that the Cl-addition to the grate-kiln led to a reduction in mercury emissions from this stack of 18 and 32%, respectively. These changes are significantly higher than those observed for similar levels of NaCl addition to greenball at Hibtac's straight-grate (5 and 9%).

FAMS measurements were collected for both Stacks 2A and 2B during these tests (Table 5.1.2.1). The concentrations measured by FAMS for Stack 2B did not agree well with those reported for the same stack by the CMM. The first baseline FAMS set of samples had an average total mercury concentration of 2.9 μg/m^3, which is about half the value reported by the CMM. Subsequent samples agreed more closely with the CMM data, although total concentrations were generally lower and the oxidized fraction reported by the FAMS is higher than would be expected based on the CMM measurements.

As was the case for the tests at Hibbing Taconite, a close look at the accompanying greenball and scrubber water data present difficulties for data interpretation (Table 5.1.2.2). First, the greenball mercury concentration appeared to increase from 14.5 ng/g before the tests began up to 18.8 by the end of the second test period. It is unknown whether this effect was due to recycling of excess mercury captured during the test period or if it was due to a change in the concentration of mercury in the concentrate. However, it was also found that the concentration of mercury in the particulates that were being captured by the scrubber for Stack 2B increased from 465 ng/g before the tests began up to 823 ng/g during the first test period and, finally, up to 1165 ng/g by the end of the second test period, before decreasing again to 330 ng/g on the following day. Solids in thickener underflow water for Stack A showed similar increases in the Hg(P) from an initial value of 341 ng/g up to 578 ng/g and 625 ng/g during NaCl addition, and then decreased again to 246 ng/g in the morning of the day after testing was completed. These data suggest that there must have been a relatively large increase in mercury capture rate associated with NaCl addition to greenball at this site.

Unfortunately, mercury concentration in unfiltered scrubber water (Hg(T)) collected during times when mercury should be the highest (since more mercury was being removed from the process gases), turned out to be lower than in unfiltered scrubber water collected under baseline conditions. It is suspected that this was a sampling artifact because most of the mercury in United Taconite's scrubber waters is adsorbed to suspended particles and, thus, the decrease in Hg(T) is inconsistent with the simultaneously measured large increase in Hg(P) values. The conditions for these samples are consistent with those reported previously to cause reemission of Hg from wet scrubbers in the power industry (Currie, 2006): low pH and high SO_2. SO_2 dissolves in water as H_2SO_3, which reacts with dissolved Hg^{2+} by converting it to Hg^0. Hg^0 has low solubility in water and volatilizes. If this process affects United Taconite scrubber water samples collected during the tests and shipped to Cebam, then dissolved and particle-adsorbed mercury Hg^{2+} in unfiltered samples and dissolved mercury in filtered samples could be lost during shipping as Hg^0. The only samples that reflect the true mercury concentration in the scrubber water during the tests would be Hg(P) because filtration and drying of the suspended solids separates the Hg^{2+} from the H_2SO_3 before the two species can react with each other. Thus, the increases in Hg(P) observed during these tests are strong indicators that NaCl addition to greenball resulted in enhanced mercury capture by the wet scrubbers, consistent with the large decrease in Hg(T) in stack-gases reported by the CMMs.

Following this test, BrCl preservative was added to samples right after sampling, rather than after shipment to the analytical laboratory. Addition of BrCl insures that all mercury present in a sample remains oxidized during shipping.

Na and Cl concentrations in scrubber water are reported for both scrubbers in Table 5.1.2.3, along with pH and concentrations of other selected cations and anions (Ca, Fe, and SO_4). More complete data for cations and anions for these experiments are provided in the appendix.

As expected, Cl concentrations in the waters from both scrubbers increased during the experiments, while Na concentrations did not. Sodium concentration, in fact, appeared to decrease with increasing Cl. Interestingly, Ca in scrubber water increased with Cl during NaCl addition to greenball, while Fe concentrations, which are elevated at the low pH values for these scrubbers, decreased with increasing Cl. These data suggest that addition of NaCl to grate-kilns results in generation of HCl which, in turn, either changes the transport of other elements to the wet scrubber or affects the adsorption and precipitation equilibria among the other compounds within the scrubber.

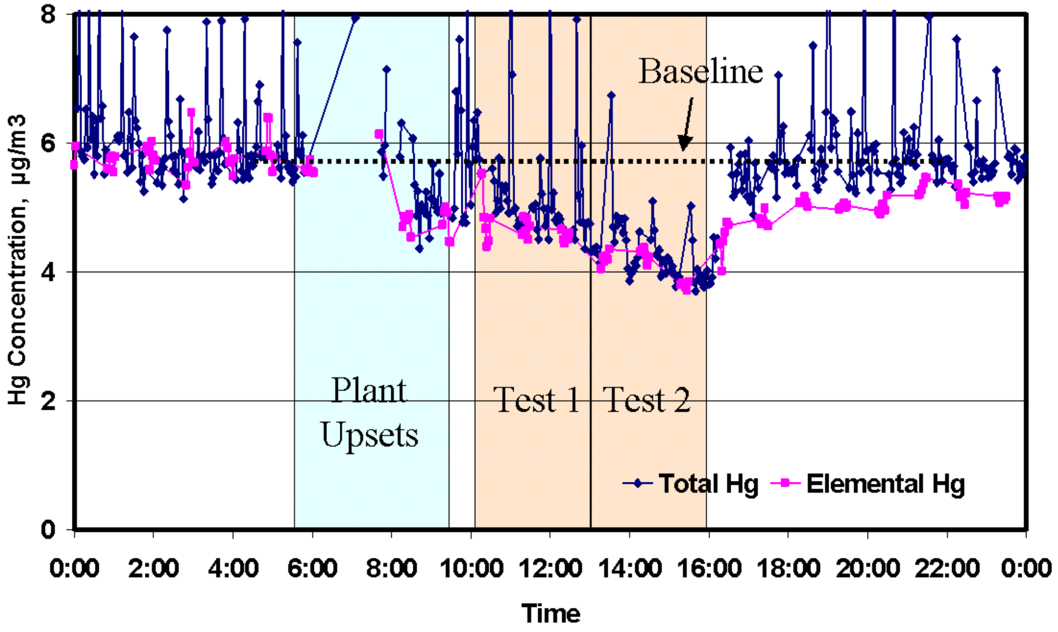

Figure 5.1.2.1 CMM mercury data collected during Cl addition to greenballs at United Taconite's grate-kiln furnace. The measurements were made on Stack 2B. A plant upset (indicated by blue) occurred just prior to conduction of the tests.

Table 5.1.2.1 FAMS mercury data for Stacks 2B and 2A the United Taconite. CMM data are provided for comparison purposes.

Stack-gas concentrations ($\mu g/m^{3)}$	*Hg(P)*	*Hg^{+2}*	*FAMS Hg°*	*FAMS Hg(T)*	*CMM Hg°*	*CMM Hg(T)*
<u>Stack 2B</u>						
Baseline	0.18	0.70	2.02	2.90	5.5	5.7
Cl-Test-1	0.20	0.79	2.87	3.86	4.6	4.7
Cl-Test-2	0.15	0.50	3.11	3.75	3.9	3.9
Baseline	0.09	0.88	3.94	4.90	4.8	5.7
<u>Stack 2A</u>						
Baseline	0.21	0.52	4.42	5.15		
Cl-Test-1	0.28	0.25	4.19	4.71		
Cl-Test-2	0.16	0.13	3.61	3.90		
Baseline	0.10	0.19	4.98	5.27		

Table 5.1.2.2 Mercury concentration in greenball and scrubber water during NaCl addition to greenball at United Taconite.

	Hg GB *ng/g*	**Hg(T)* *ng/l*	**Hg(D)* *ng/l*	*Hg(P)* *Ng/g*
Stack 2B				
Baseline	14.7	7790	32	465
Cl-Add I	14.5	7916	38	823
Cl-Add 2	18.8	5451	56	1165
Baseline	18.5	7678	144	330
Stack 2A				
Baseline	14.7	4954	187	341
Cl-Add I	14.5	5237	125	578
Cl-Add 2	18.8	3356	99	625
Baseline	18.5	5985	763	246

*Suspect that these samples lost mercury during shipping of samples to the analytical laboratory.

Table 5.1.2.3 Concentration of selected elements in scrubber waters collected during NaCl addition to greenball at United Taconite.

	pH	*Na* *(ppm)*	*Ca* *(ppm)*	*Fe* *(ppm)*	*Cl* *(ppm)*	*SO4* *(ppm)*
Stack 2B						
Baseline	3.19	113	62	25	85	614
Cl addition-1	3.12	-	-	-	106	589
Cl addition-2	3.13	110	76	17	113	580
Baseline	3.37	-	-	-	88	726
Stack 2A						
Baseline	3.75	116	56	21	84	497
Cl addition-1	3.73	-	-	-	106	479
Cl addition-2	3.88	112	69	10	112	451
Baseline	4.43	-	-	-	91	577

5.2. Focused Halide Injection at Hibbing Taconite

The focused halide injection test at Hibbing Taconite (a straight-grate facility) delivered 10 wt% halide salt solutions directly into the preheat zone as a mist. Stack-gas mercury concentrations during each period of injection decreased within minutes of salt injection and increased rapidly right after injection was stopped (Figure 5.2.1). However, the stack-gas mercury concentration did not always return to the original baseline level when the salt addition was stopped. This created a need to adjust the baseline for latter experiments; particularly following injection of the bromide salts.

Initial injection of NaCl resulted in a 6% decrease in stack-gas mercury concentration from baseline conditions. This decrease is similar to that found when NaCl was added to greenball at this plant, but small compared to the 62% decrease in stack-gas Hg(T) that occurred within minutes of injecting the NaBr solution into the preheat zone. In fact, Hg^0 reported by the CMM all but disappeared from the emissions during NaBr injection, suggesting the nearly all mercury reaching the detector was oxidized to Hg^{2+}. This suggests either that (1) essentially all mercury passing through the wet scrubber did so as an oxidized species or (2) elemental mercury became oxidized some time after passing through the wet scrubber but before it could be analyzed by the detector. The importance of this distinction will be discussed in greater detail in Section 6.1 of this report.

Once NaBr injection stopped, the concentrations of both elemental and total mercury in stack-gases (Stack A) rapidly increased, though not to the original baseline levels. Thus, a new baseline pattern was assumed for $CaCl_2$ injection and the total mercury in stack-gas declined by approximately 13% from the adjusted baseline. Stack-gas mercury rapidly returned to the projected baseline levels when $CaCl_2$ salt injection was stopped.

Subsequently, stack-gas Hg(T) and Hg^0 response to $CaBr_2$ injection was equally impressive to that observed when NaBr was injected. For $CaBr_2$ there was an estimated 64% decrease in stack-gas total mercury concentration compared to the adjusted baseline conditions (Fig.5.2.1). When $CaBr_2$ addition was stopped, there was a rapid rebound in mercury concentration, but, as was noted following injection of NaBr, the concentration did not reach the pre-injection level. Moreover, Hg(T) continued to increase gradually to values above the original baseline, and not decreasing to the original baseline values until after approximately a 12 hour period (not shown) of slightly increased emission. Interestingly, stack-gas Hg^0 concentration, as reported by the CMM, decreased to low levels during injection, but, unlike Hg(T), never exceeded the original baseline level once bromide injection stopped. This component increased gradually before leveling off at the original baseline value about six hours after the last halide injection test was completed.

Mercury concentration in greenball stayed relatively constant throughout the tests, but the concentrations were generally higher than they were for most of the previous test period when NaCl was added to greenball at this plant. Scrubber water mercury concentrations, meanwhile, increased in approximate proportion to the sequential mercury decreases observed during the series tests (Table 5.2.1). This is consistent with greater capture in the scrubber water leading to reduced mercury emissions in the stack-gases, especially during bromide salt injection.

Na, Ca, Cl, and Br concentrations for scrubber water before, during, and after the test periods are shown in Table 5.2.2. As expected, Na and Ca concentrations changed little during the injection periods, while Br and Cl increased when their respective salts were injected into the preheat zone. This indicates that the cations (Na,Ca) dissociated from Br and Cl during the tests, and combined with solids in the pellets. Only the Cl and Br were volatilized and transported to the wet scrubber. Full chemical data for the scrubber waters in these tests are presented in Appendix 3.

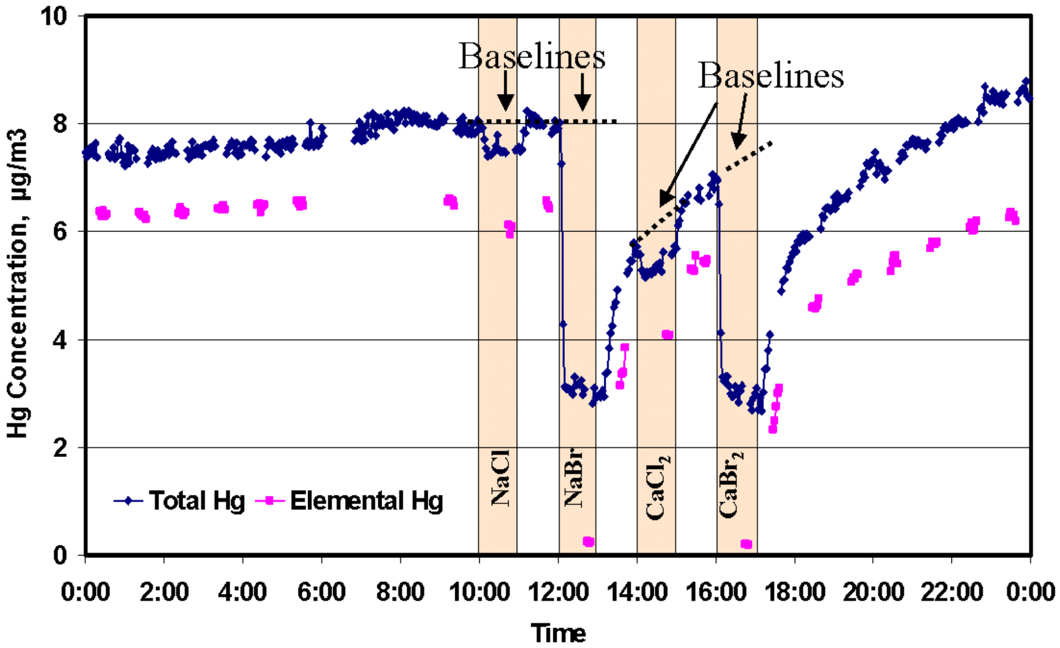

Figure 5.2.1 CMM mercury concentrations reported during halide injection tests at a straight-grate facility (Hibbing Taconite).

Table 5.2.1 Reported mercury concentrations for samples collected during halide injection experiments at Hibbing Taconite.

	Hg GB *ng/g*	*Hg(T)* *ng/l*	*Hg(D)* *ng/l*	*Hg(P)* *ng/g*
Base1	19.0	1288	1127	162
NaCl	23.9	1453	1210	244
NaBr	19.4	2950	2630	319
CaCl2	18.7	1665	1484	181
CaBr2	18.7	3072	2799	273
Base2	17.6	1528	1316	212

Table 5.2.2 Concentrations of selected elements in scrubber waters observed during baseline conditions and during injection of halide salts at Hibbing Taconite.

	pH	*Na* *(ppm)*	*Ca* *(ppm)*	*Cl* *(ppm)*	*Br* *(ppm)*
Baseline	6.74	49.1	35.9	67.6	0.24
NaCl Injection	6.75	49.8	36.1	78.3	0.24
NaBr Injection	6.77	49.3	36.0	67.1	12.4
$CaCl_2$ Injection	6.64	49.2	36.1	79.6	0.42
$CaBr_2$ Injection	6.71	49.2	36.0	68.4	13.8
Baseline	6.79	49.2	36.0	67.8	0.61

Table 5.2.3 Concentrations of potential oxidation products for NO_x and SO_x in scrubber waters that were observed under baseline conditions and during injection of halide salts at Hibbing Taconite.

Concentrations (ppm)	*NO2-N*	*NO3-N*	*SO4*
Baseline	0.21	5.45	247
NaCl Injection	0.19	5.47	241
NaBr Injection	0.18	5.46	240
$CaCl_2$ Injection	0.19	5.48	242
$CaBr_2$ Injection	0.18	5.53	243
Baseline	0.19	5.64	241

Table 5.2.3 lists the dissolved concentrations of NO_2^-, NO_3^-, and $SO_4^=$ reported during these tests. The results indicate that the injection of halides has little or no effect on capture of NO_x and SO_2 from stack-gases.

5.3. In-Scrubber Oxidation: Slip-Stream tests at Keewatin Taconite

Mercury results for the "in-scrubber" oxidation bench scale tests are shown in Table 5.3.1 and Figure 5.3.1, computed in units of μg per cubic meter of gas that passed through the QLIP and FAMS apparatus. These units allow direct comparison to be made with the FAMS and CMM stack-gas measurements for the rest of this report. The "scrubber Hg" represents the mercury scrubbed by the wet portion of the apparatus, while the other amounts represent mercury in various forms that passed through the wet scrubber and adsorbed to the sequence of dry sorbents in the FAMS trap (See section 4.4.1). The experiments labeled "no scrubber" were run in parallel with the $NaHCO_3$-only tests, but with an unheated Teflon tube leading from the sampling port to the heated FAMS trap.

An unexpected result was that fraction of mercury identified as particulate and/or oxidized mercury when no solution was used in the QLIP was much less than that trapped by the $NaHCO_3$ "scrubber" solution in any of the other test. For example, approximately 23% of the mercury was captured in the scrubber portion of the apparatus when no oxidizing compound was added to the solution, but only a tiny fraction was captured when there was no solution. The total mercury measured in these experiments was virtually identical and the tests were conducted over exactly the same time period. These data suggest either that mercury in taconite process gas becomes oxidized when it contacts the water in the QLIP device, or that oxidized mercury is quickly reduced to elemental mercury in empty Teflon tubing. This is a critical observation since it potentially affects interpretation of all mercury data from taconite stacks and wet scrubbers.

Perhaps even more surprising than the high degree of capture by weak $NaHCO_3$ solutions (compared to the no-scrubber configuration) is the fact that adding H_2O_2 to the $NaHCO_3$ solution resulted in even less capture of oxidized mercury than when $NaHCO_3$ solutions were used without an oxidant. A possible explanation for this was provided by the analyst at Cebam, Inc., who reported that the solutions containing H_2O_2 and received by the laboratory did not have the same amber color as the other solutions in the shipment. The amber color is produced by the preservative, BrCl. The laboratory reported that additional BrCl was added to the solutions but, each time they did this, the color faded with time. This indicated that a reaction was taking place between H_2O_2 and BrCl. The laboratory proceeded to measure mercury in the solutions, but indicated the concentrations may be low because of this apparent interference. Adding H_2O_2 to the scrubber test solutions led to a decrease in the solution's ability to oxidize and capture elemental mercury in taconite process gases, suggesting the possibility that minor Cl_2 is present in taconite process gas, and that its reaction with H_2O_2 *rather than* elemental mercury led to reduced mercury capture efficiency. It appears from these results that H_2O_2 is not a likely candidate for in-scrubber oxidation at taconite processing plants and that, perhaps, it even interferes with the background mercury oxidation process that takes place when no oxidant is added to the water.

Results for EPA_{ox} are quite opposite from those obtained using H_2O_2. Not only did EPA_{ox} capture much more mercury than the other solutions, but only a small percentage of mercury in the slip-stream gas was able to elude capture by the EPA_{ox} scrubber solution to register a response in the FAMS sorbent traps. 80% and 87% capture was measured for the two experiments. This oxidant is, thus, a good candidate for further testing at taconite plants. It appeared, however, from the high total mercury concentration in all of the traps combined (Figure 5.3.1) that there was contamination in the EPA_{ox} traps, perhaps resulting from additional uptake of Hg^0 from air or another temporary source that came into contact with the solutions. Nevertheless, after discounting this additional source of mercury that greater than 70% of the total mercury in the slip-stream gas was oxidized and captured by water containing the oxidant.

In addition to mercury, the scrubber solutions were tested for NO_2-N, NO_3-N¸and SO_4, to determine if other pollutant species were oxidized along with elemental mercury (Table 5.3.2). Results showed that the EPA_{ox} solutions had the highest concentrations of each of these components indicating that other components in taconite processing gas could potentially interfere with the ability of EPA_{ox} to capture mercury. However, the concentrations of these species suggest recovery rates for NOx and SOx were relatively low in these tests.

Table 5.3.1 Mercury trapped from slip-stream gas at Keewatin Taconite during the “in-scrubber” oxidation experiments.

	*Scrubber Hg $\mu g/m^3$	**Hg(P) $\mu g/m^3$	**Hg^{2+} $\mu g/m^3$	**Hg° $\mu g/m^3$
No scrubber	-	0.07	0.13	5.56
No scrubber	-	0.09	0.21	5.78
No scrubber	-	0.07	0.13	5.68
$NaHCO_3$	1.27	0.00	0.02	4.23
$NaHCO_3$	1.27	0.01	0.03	4.37
$NaHCO_3$	1.41	0.02	0.04	4.56
H_2O_2 - $NaHCO_3$	0.53	0.03	0.02	4.83
H_2O_2- $NaHCO_3$	0.77	0.04	0.21	4.75
EPAox- $NaHCO_3$	6.21	0.06	0.07	0.73
EPAox- $NaHCO_3$	5.06	0.08	0.10	1.19

*Scrubber Hg is the total mass of mercury captured in the QLIP apparatus, divided by the total amount of process gas that passed through the system.

** Hg(P), Hg^{2+}, and Hg° are, in this case, the total amounts of mercury captured on sorbents in the appropriate FAMS traps divided by the total amount of gas passing through the system.

Table 5.3.2 Anion concentrations in “scrubber water” from slip-stream tests performed at Keewatin Taconite.

	F (ppm)	Cl (ppm)	NO2-N (ppm)	NO3-N (ppm)	SO4 (ppm)
NaHCO3 start	<0.005	0.08	<0.002	0.17	0.24
NaHCO3-1	1.26	2.22	0.12	0.25	25.9
NaHCO3-2	1.51	5.25	0.12	0.25	29.3
NaHCO3-3	1.46	5.30	0.10	0.14	26.9
H2O2 – start	<0.005	0.151	<0.002	0.20	0.37
H2O2 – 1	1.276	2.292	0.12	0.11	25.8
H2O2 – 2	1.35	4.08	0.11	0.26	26.2
EPAox –start	0.09	12.4	<0.002	0.11	0.37
EPAox –1	1.39	37.7	0.32	1.10	28.3
EPAox –2	1.61	28.5	0.09	0.84	26.4

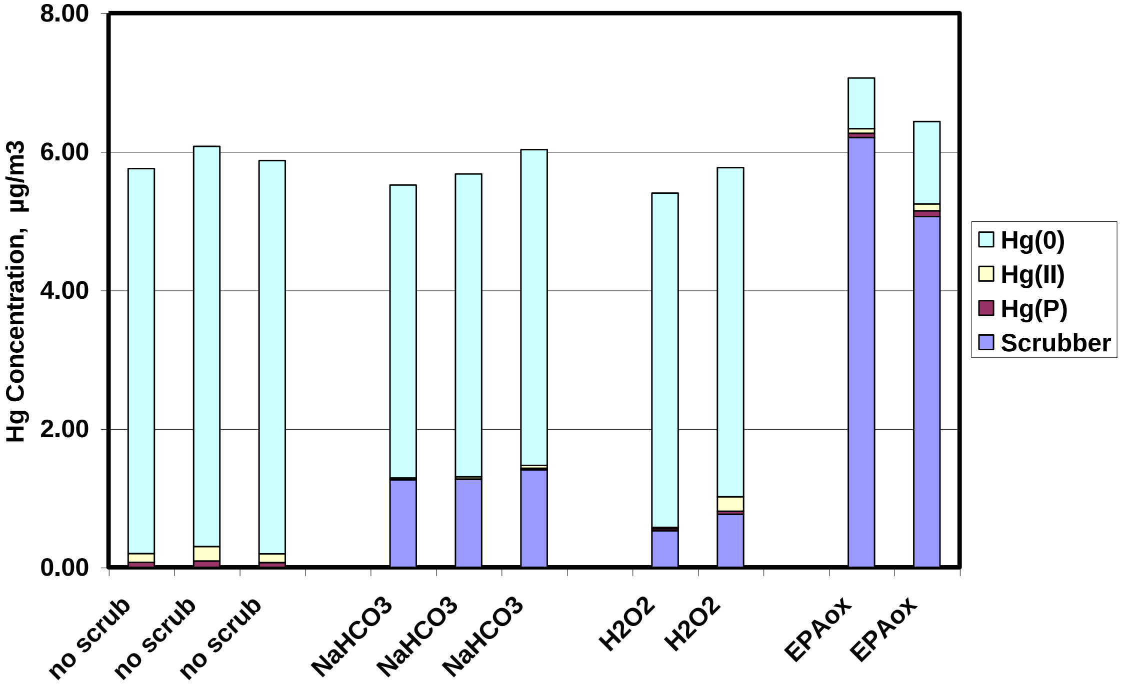

Figure 5.3.1 Mercury captured from slip-stream gas at Keewatin Taconite using the QLIP-FAMS testing system described in section 4.3.

6. Discussion

While it is tempting to begin to analyze potential costs associated with the most promising techniques, such endeavors carried out at a serious level are likely premature as the tests conducted here were short-term and it is likely that improvements in measurement and control methods will be made as experience increases. The tests presented in this study merely reveal that several promising approaches exist for controlling mercury emissions at taconite processing plants. Final evaluation of whether a method is a viable alternative must wait until the time when longer tests can be performed and other hazards of using the techniques can be identified and assessed.

It is important to note that in the process of performing these tests that the empirical relationships obtained between halide addition or injection and mercury oxidation, capture, and measurement are of value regardless of whether they lead directly to a viable control method. A more careful analysis of these results can lead to greater understanding of the physical and chemical processes affecting mercury transport at taconite processing plants needed for future applications. In this regard, at least three results stand out as significant from both practical and conceptual perspectives:

(1) Addition of NaCl to greenball was more effective at decreasing mercury in stack-gases at the grate-kiln facility than it was at the straight-grate plant, but neither method worked as well as injecting bromide salts into the preheat zone of a straight-grate furnace;

(2) Elemental mercury in process gas was oxidized and captured upon contact with an aqueous solution, even when no oxidant was added to the solution; and,

(3) Oxidants added to solutions, EPA_{ox} in particular, have the capacity to oxidize and remove large fractions of the elemental mercury from taconite process gases.

The sodium chloride addition experiments were designed based on models and data presented by Berndt and Engesser (2005a), who found that magnetite is first converted to a magnetite/maghemite solid-solution in the preheat zone, and that this phase plays an important role in regulating mercury capture and release in taconite induration furnaces. In that study, it was found that full mercury release in the absence of added NaCl did not occur until magnetite and/or magnetite/maghemite solid-solutions were heated past approximately 450 or 500º C and converted to hematite. However, mercury released from hotter zones in the furnace could partially collect in the cooler zones where it came into contact with maghemite. This maghemite need only coat the outer surface of a magnetite grain to absorb mercury and, thus, high mercury concentrations are generally found in iron-oxides within the preheat zones of taconite induration furnaces.

Experimental and field data presented by Berndt and Engesser (2005a) suggested that the degree to which Hg was volatilized as either Hg^0 or $HgCl_2$ in this zone depended, to some degree, on the availability of HCl, as described by the following reaction:

$$Hg^0_{(g)} + \underset{\text{Maghemite}}{3Fe_2O_{3(ss)}} + 2HCl_{(g)} = \underset{\text{Magnetite}}{2Fe_3O_{4(ss)}} + HgCl_{2(g)} + H_2O_{(g)} \quad (1)$$

where the subscripts, "*g*" and "*ss*", represent gaseous and solid-solution components for process gas and iron-oxides, respectively. According to this reaction, increasing HCl in the process gas in the zone of active maghemite generation (e.g., the preheat zone), should lead to increased transport of $HgCl_2$ to the wet scrubber. This is the presumed dominant volatile form of oxidized mercury, Hg^{2+}, which is the form of mercury most easily captured by wet scrubbers.

Cl is present to some extent in all greenball produced on the Iron Range. It is released both from the ore minerals and limestone flux during processing, although most Cl entering an induration furnace at any one time is dissolved in the process water pore fluid of the greenball, which makes up about 10% of the mass of the greenball at the time it enters the furnace. Drying of the greenball in the preheat zones during induration leads to evaporation of the water and residual salt in the greenball pore spaces. These salt components break down into volatile and labile components upon heating to high temperatures. Typically, the most volatile components from these residual salts are the halides, Cl^-, Br^-, and F^-, which are thought to combine with H^+ to generate mobile acid species HCl, HBr, and HF. These species are generally soluble in water and, as a consequence, are captured by wet scrubbers. Adding NaCl to greenball in the straight-grate experiments was intended to generate HCl which, upon contact with maghemite and adsorbed mercury in the preheat zone, would mobilize the mercury to the wet scrubber as $HgCl_2$ (Reaction 1).

While chloride addition increased mercury capture when NaCl was added to the greenball or directly to the preheat zone, the method worked considerably better in the grate-kiln facility compared to at a straight-grate. One important clue for this, perhaps, is provided by considering the somewhat limiting constraint imposed by Reaction (1) requiring HCl generated by the process to directly contact greenball in the preheat zone. More specifically, if HCl fails to contact greenball in the zones where active maghemite formation is occurring (e.g., the preheat zone), then it will not result in significant improvement in the capture of mercury at taconite processing plants.

Examination of the geometry and ducting for straight-grate and grate-kiln furnaces provides a possible explanation for the large difference in mercury capture rates for the two types of plants. At United Taconite, the grate-kiln plant, NaCl addition resulted in 18 and 32% improvement to capture rates which, added to baseline capture rates, suggests that as much as 40 to 50% total recovery of mercury may be achieved (using the estimated normal capture rates reported by Berndt and Engesser, 2005b). It is important to note, however, that any HCl generated in the kiln (e.g., the firing zone) portion of a grate-kiln plant is transported directly to the preheat zone where the gases are passed through the pellet bed. Thus, assuming Reaction 1 is the primary process in this case, and assuming further that HCl (rather than, Cl_2 or other species) is generated in the kiln, this is an ideal situation for using NaCl addition to greenball to control mercury.

By contrast, HCl generated by NaCl degradation in a straight-grate furnace has two potential pathways through which gases eventually reach the wet scrubber, one leading through the preheat zone, and the other not. Gases generated in the firing zone are transported to the downdraft drying zone, while gases generated in the first cooling zone are fed into the preheat zone. Thus, HCl generated in the firing zone will generally miss the zone of active maghemite formation and proceed directly to a drying zone. This difference can account for the relatively low level of mercury control found when NaCl was added to greenball at the straight-grate facility (Hibbing Taconite).

It was hoped that adding NaCl or $CaCl_2$ solutions directly to the preheat zone as a mist might better utilize Reaction 1 as a means to control mercury emission at a straight-grate facility in at least one of two ways. First, since the top of the pellet bed in the preheat zone is much hotter than the bottom of the bed, this method of adding NaCl or $CaCl_2$ should lead to earlier formation of HCl compared to the case where NaCl is distributed throughout the pellet bed. Second, if HCl is generated at the top of the pellet bed, it would be driven through the lower portion of the pellet bed where Reaction 1 may be taking place. This, in turn, could lead to increased oxidation and capture of mercury by the wet scrubber.

The fact that focused injection of chloride salts did not significantly improve mercury capture rates compared to addition of NaCl to greenball indicates that either the HCl was still generated too deeply in the furnace to make use of Reaction 1 or that only a small portion of the pellet bed was contacted by the NaCl or $CaCl_2$ mist in the preheat zone. Whatever the cause, the results suggest that addition of chloride salts is a relatively ineffective means to control mercury at straight-grate facilities.

During the course of this study, an alternative pathway for mercury oxidation related to chloride addition was also considered, based on an entirely different reaction pathway compared to Reaction 1. Edwards et al. (2001), for example, showed that other chloro-based gas species, such as Cl and Cl_2, can oxidize Hg^0 at rates that are orders of magnitude more rapid than reactions with HCl. It is unknown whether such meta-stable species exist in taconite processing gases. However, exposure of NaCl to high temperatures during induration could conceivably generate at least some of these species. Moreover, data presented and summarized by Radermakers et al, 2002, suggest that reaction of NaCl with iron oxides can lead to heterogeneous reactions that generate Cl_2, as follows:

$$2NaCl + Fe_2O_3 + 1/2O_2 = Na_2Fe_2O_4 + Cl_2 \qquad (2)$$

$$6NaCl + Fe_3O_4 + 2O_2 = 3Na_2Fe_2O_4 + Cl_2 \qquad (3)$$

Generation of Cl_2 by this or any other reaction would almost certainly impact mercury capture since Cl_2 can react directly with mercury by:

$$Cl_2 + Hg^0 = HgCl_2. \qquad (4)$$

This reaction has been found to be especially rapid when Cl_2 and Hg^0 come into contact with water (Linak et al, 2001; Roy, 2003).

Reaction 4, in fact, may help to account for two unusual results obtained from the in-scrubber oxidation experiments with slip-stream gases: (1) significant mercury was captured from taconite waste gas containing only a small fraction of oxidized mercury even when no oxidant was added to the aqueous solution and (2) H_2O_2 addition to the scrubber actually impeded mercury capture compared to the case where no oxidant was added. If we infer the presence of minor Cl_2 in the slip-stream gas used in those experiments, then Reaction (4) can account for both of these unusual observations. First, Cl_2 in the process gas would behave as a mercury oxidant when the gas contacted the aqueous solution as discussed and shown by Roy (2003). Moreover, it is quite possible that H_2O_2 consumes Cl_2 as effectively as it consumed the similar compound BrCl that was used as a preservative (see section 5.3). In effect, the Cl_2 oxidizes the H_2O_2 to O_2 while it is itself converted to much less reactive (with respect to Hg^0) HCl. If so, then addition of H_2O_2 to the scrubber water interferes with, rather than enhances capture of mercury from waste gas containing Cl_2. However, this is only indirect evidence for a role for Cl_2 during mercury capture by taconite wet scrubbers. Better data on mercury, chloride, and chlorine gas species in taconite process gases are needed to confirm this mechanism.

Regardless of the mechanism controlling oxidation of mercury by chloride or chlorine in taconite process gases, the tests clearly revealed that bromide salts out-performed chloride salts in terms of increasing mercury capture upon injection into the preheat zone at straight grate facilities. It is apparent that injection of NaBr or $CaBr_2$ into induration furnaces leads to formation of a very reactive oxidant, most likely Br_2. As was the case for injection of NaCl and $CaCl_2$, analysis of scrubber waters during injection of bromide salts into the preheat zone revealed no detectable increases in Na or Ca suggesting that the salts were not transported to the scrubber as aerosols containing NaBr or $CaBr_2$. The salts injected must have been converted to other Br-bearing species such as HBr or Br_2. Rademakers *et al.* (2002), in a review of the literature on Br speciation, suggest that Br_2 gas forms rapidly from HBr oxidation in "almost entirely a homogeneous reaction" at temperatures between 490˚C and 635˚C. Thermocouples placed in the area into which the bromide salts were injected into Hibbing Taconite's furnace registered temperatures close to 750˚C which implies this zone was certainly hot enough to heat the injected solutions to the temperature range needed for Br_2 formation.

Whether or not Br_2 or HBr is generated in induration furnaces is important for two reasons. First, Br_2 is a strong oxidant that can cause corrosion in equipment that it contacts and, second, it can pass through the wet scrubber systems and be emitted to the atmosphere. The latter effect may account for the relatively high apparent oxidation state of mercury reported by the CMM during the Br-salt injection tests. Any Br_2 passing through the wet scrubber would be collected with Hg^0 by the wet injection probe used to sample gases for the CMM during the halide injection tests. Once sampled, the stack-gases were transported in a bubble train through a heated 25 ft hose before being processed for gas analysis by the Tekron instrument used for mercury analysis. If this amount of reaction time is sufficient for Br_2 to oxidize Hg^0 to Hg^{2+}, then it would cause the CMM to over-report oxidized mercury while still reporting a correct value for Hg(T). Thus, although it is possible that the highly oxidized nature of mercury in the stack-gas during bromide injection is real, a more realistic interpretation is that most of the mercury in the stack was unoxidized Hg^0 that passed through the wet scrubber, but this mercury was oxidized during transport from the stack to the instrument.

The proposed explanation for the mercury data collected during the bromide salt injection tests, therefore, is that the following overall reactions occurred and dominated mercury transport upon bromide injection to the preheat zone:

$$1/2O_2 + 2NaBr = Na_2O + Br_2 \qquad (5)$$

$$Hg^0 + Br_2 = HgBr_2 \qquad (6)$$

Br_2 is thermally generated from NaBr in the furnace (Reaction 5), perhaps catalyzed by iron-oxides in the pellet bed. This Br_2 oxidized a majority of the Hg^0 being transported in process gas, either by gas-phase reactions or following contact with water in the wet scrubber. The data suggest that some of the Br_2 that formed by the process escaped the wet scrubber and continued to oxidize most of the remaining Hg^0 that also passed through the wet scrubber. This latter oxidation step may have occurred either before or during entrapment by the wet sampling device used by the CMM, in a manner analogous to the Cl_2 and Hg^0 capture mechanism explored by Roy (2003).

It is somewhat disconcerting that our efforts to speciate taconite stack-gases are still somewhat uncertain. The relative fates of oxidized and elemental mercury from stack emissions make speciation of stack-gas an important unresolved issue. Hg^0 remains in the atmosphere for long periods of time and is deposited globally, whereas oxidized mercury in the gas emissions is deposited locally and could lead to generation of local mercury hot-spots if the emitted gases were composed predominantly of oxidized mercury. The interpretation of the gas measurements associated with the stack testing, therefore, has added significance, not only as a means to asses control feasibility, but also if the data are to be used to evaluate environmental consequence of the control method. At the very least, further testing is needed to resolve whether the high oxidation state for mercury indicated by the CMM used in the bromide salt injection tests is an artifact of the method or an indication of a potential secondary environmental issue.

Considering the relatively small increases in mercury capture efficiencies demonstrated for chloride salt addition in straight-grate furnaces, and the potential for corrosion should bromide be injected into taconite furnaces for long periods of time, perhaps the most promising technology studied here is in-scrubber oxidation using EPA_{ox}. Not only was this oxidant effective, but this method does not appear to result in unwanted by-products in stack emissions (such as Br_2), nor does the method introduce corrosive agents to the grates, kiln, or ductwork leading to the scrubber. The instrumentation required to implement in-scrubber oxidation is inexpensive and straight forward since it involves only a tank containing the oxidant and a small pump to feed the material into the scrubber system. However, the potential breakdown products of the chemical to be used and the potential for oxidizing and capturing other components along with mercury must be evaluated before it can be considered a viable mercury reduction method.

The breakdown products for EPA_{ox} will be evaluated in future studies, however, experiments conducted by Hutson and Srivistava (2006) have already indicated that this oxidant can also react extensively with NO_x and SO_x. It is unknown why application of EPA_{ox} in the tests conducted during the present study were much less effective at oxidizing these components in the taconite process gases. It likely results from differences in contact time between water and process (or carrier) gas. If plant-scale application is better approximated by the apparatus used by Hutson and Srivistava (2006), then it implies both a higher consumption rate for the oxidant and a potential for high NO_3^- in the scrubber effluent, which may lead to an eventual water treatment problem that could add further to the cost of using EPA_{ox} to control mercury in taconite plants.

7. Conclusions

Addition of NaCl to greenball provided a more effective means to control mercury emissions at a grate-kiln facility than at a straight-grate facility. Injection of bromide salts into the preheat zone of a straight-grate worked much better to control emissions than chloride injection at either facility. The difference can be attributed to different predominant pathways for dissociation and reaction of chloride and bromide salts in taconite induration furnaces. The results suggest that addition of chloride salt by any method leads to volatilization mostly of less reactive HCl but possibly minor Cl_2 during taconite induration. Bromide salt injection, on the other hand, appears to generate a large amount of much more reactive species such as Br_2, capable of oxidizing a large fraction of the mercury in taconite process gases.

One important observation is that elemental mercury in process gas appeared to be oxidized upon contact with water in one set of experiments. Although this observation was used to infer presence of Cl_2 in process gas, the relative distribution of HCl and Cl_2 was not measured.

Slip-stream experiments indicate that addition of a proprietary reagent, EPA_{ox}, has the capacity to remove a large fraction of elemental mercury from taconite process gases. Other gaseous oxidation products from pollutants such as NO_x and SO_x were generated in the experiments, but not to the degree observed by Hutson and Srivistava (2006) owing, most likely, to differences in gas/liquid contact time. Plant-scale tests should be conducted to determine effectiveness of this method with the actual gas/liquid contact time for wet scrubbers under normal use conditions.

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10. Appendices – Miscellaneous Data

10.1. Appendix I: Hibbing Taconite NaCl-Addition To Greenball

July 18-19, 2006

Stack-gas Chemistry: Stack A

Gas composition - Stack A

Time	% O2	Ppm NO	ppm NOx	ppm NO2	ppm SO2	ppm CO
7:45:35	19.05	107	107	0.3	3	6
7:49:08	19.05	101	101	0	2	7
7:54:05	19.07	104	104	0	2	6
8:04:51	19.05	104	104	0	6	6
8:10:07	19.06	106	106	0	8	6
8:25:16	19.14	105	105	0	8	5
8:37:30	19.09	108	108	0	8	7

FAMS Analysis: Pre-injection baseline, 7/18/06

Stack A	Particulate	Oxidized	Elemental	Total
	0.01	0.37	3.38	3.75
	0.07	0.45	3.13	3.65
	0.08	0.24	3.97	4.29
Average	0.06	0.35	3.49	3.90
STD/AVE	0.733735	0.290023	0.123	0.088531

Stack B	Particulate	Oxidized	Elemental	Total
	0.06	0.42	1.20	1.69
	0.07	0.71	1.06	1.84
	0.10	0.63	1.74	2.47
Average	0.08	0.59	1.34	2.00
STD/AVE	0.239927	0.250434	0.269477	0.20743

FAMS Analysis: Hibbing Taconite Cl-addition I, 7/18/06

Stack A	Particulate	Oxidized	Elemental	Total
	0.13	0.38	2.95	3.46
	0.12	0.34	2.92	3.38
	0.11	0.27	3.26	3.64
Average	0.12	0.33	3.04	3.49
STD/AVE	0.080651	0.17286	0.061804	0.03819

Stack B	Particulate	Oxidized	Elemental	Total	
	0.13	0.62	1.89	2.64	
	0.18	0.62	2.04	2.84	
	0.15	1.52	3.75	5.41	eliminated
Average	0.15	0.62	1.96	2.74	
STD/AVE	0.208615	0.006669	0.053706	0.051795	

FAMS Analysis: Hibbing Taconite Cl-addition II, 7/18/06

Stack A	Particulate	Oxidized	Elemental	Total
	0.11	0.35	2.81	3.27
	0.17	0.29	3.21	3.67
	0.11	0.30	3.31	3.72
Average	0.13	0.31	3.11	3.55
STD/AVE	0.266218	0.103336	0.084496	0.069163

Stack B	Particulate	Oxidized	Elemental	Total
	0.12	0.55	2.27	2.94
	0.08	0.53	1.85	2.46
	0.09	0.46	2.43	2.97
Average	0.10	0.51	2.18	2.79
STD/AVE	0.206246	0.094606	0.136568	0.103436

FAMS Analysis: Hibbing Taconite Post-Cl-addition baseline, 7/19/06

Stack A	Particulate	Oxidized	Elemental	Total
	0.11	0.35	3.44	3.90
	0.11	0.27	3.19	3.57
	0.10	0.36	3.56	4.03
Average	0.11	0.33	3.40	3.83
STD/AVE	0.049284	0.153162	0.056145	0.061714

Stack B	Particulate	Oxidized	Elemental	Total
	0.17	0.81	2.54	3.53
	0.21	0.70	2.47	3.38
	0.17	0.60	3.04	3.81
Average	0.18	0.71	2.69	3.57
STD/AVE	0.119711	0.150422	0.114967	0.061496

Stack C	Particulate	Oxidized	Elemental	Total
	0.07	0.17	1.17	1.41
	0.12	0.13	1.33	1.58
	0.09	0.13	1.40	1.63
Average	0.09	0.14	1.30	1.54
STD/AVE	0.22701	0.147173	0.09129	0.073395

Stack D	Particulate	Oxidized	Elemental	Total	
	0.07	0.30	0.82	1.20	
	0.06	0.29	0.84	1.19	
	0.06	0.28	1.44	1.79	eliminated
Average	0.07	0.30	0.83	1.19	
STD/AVE	0.084852	0.034837	0.012738	0.004712	

Scrubber water anion concentrations (ppm) compared to makeup water during Hibbing Taconite Cl-addition tests.

	Fluoride	Chloride	Bromide	Sulfate	Nitrite-N	Nitrate-N
Baseline	11.41	5.38	0.02	46.60	0.06	0.15
Cl-ADD I	11.23	10.43	0.02	47.10	0.05	0.42
Cl-ADD 2	11.13	16.36	0.02	44.80	0.04	0.27
Baseline	11.26	5.72	0.02	50.20	0.06	0.14

Scrubber water major and trace cation concentrations during Hibbing Taconite Cl-addition tests

	Na Ppm	Mg ppm	Si ppm	K ppm	Ca ppm
Baseline	60.26	74.32	11.50	19.78	43.04
Cl-ADD I	59.99	74.38	11.52	19.81	43.08
Cl-ADD 2	60.24	74.83	11.77	19.79	43.11
Baseline	60.28	74.65	11.61	19.71	43.01

	Li ppb	B ppb	Al ppb	P ppb	Cr ppb	Fe ppb	Mn ppb	Co ppb	Ni ppb	Tl ppb	Pb ppb	U ppb
Baseline	15.18	116.70	0.00	2.58	0.24	131.00	5.15	0.34	9.23	0.58	0.50	1.65
Cl-ADD I	16.43	107.10	0.00	2.52	0.28	77.17	4.60	0.35	8.18	0.37	0.44	1.71
Cl-ADD 2	17.82	120.30	0.19	4.75	1.38	62.60	4.73	0.37	3.69	0.38	0.53	1.79
Baseline	17.73	123.33	0.00	4.73	0.54	44.55	4.56	0.35	4.47	0.29	0.52	1.75

	Cu ppb	Zn ppb	As ppb	Se ppb	Rb ppb	Sr ppb	Mo ppb	Cd ppb	Cs ppb	Ba ppb	W ppb	Tl ppb	Pb ppb	U ppb
Baseline	3.0	21.6	59	21	14.5	162	27.6	0.09	1.10	21	0.34	0.58	0.50	1.65
Cl-ADD I	3.6	9.1	34	23	15.2	170	28.0	0.09	1.15	22	0.24	0.37	0.44	1.71
Cl-ADD 2	3.2	6.7	38	26	15.9	179	29.5	0.09	1.19	24	0.23	0.38	0.53	1.79
Baseline	3.4	20.5	52	25	15.7	176	29.7	0.10	1.17	23	0.21	0.29	0.52	1.75

Averaged Total (Hg(T)) and Dissolved (Hg(D)) mercury in scrubber waters during NaCl addition to greenball at Hibbing Taconite.

	Hg(T)	Hg(D)	Hg(D)/Hg(T)
Baseline	738	439	0.60
Cl-ADD I	742	499	0.67
Cl-ADD 2	880	587	0.67
Baseline	827	561	0.68

Hibbing Taconite Chloride Addition to filter cake: field measurements.
Line 3, 7/18/06 and 7/19/06.

Line 3	Baseline	Test 1	Test 2	Baseline
Time	1000	1300	1600	0900
PH	7.28	7.19	7.00	7.01
Temperature(°C)	39.5	40.0	40.9	40.9
Conductivity(µS/cm)	1050	1050	1050	1050
Total suspended solids (%)	0.023	0.024	0.0235	0.0235

Note: The initial baseline and tests 1 and 2 were conducted on 7/18/06. The second baseline analysis was conducted on 7/19/06.

10.2. Appendix II: United Taconite NaCl-Addition to Greenball

Dates: Sept. 12-13, 2006

Gas Chemistry during NaCl-addition to greenball at United Taconite

9/12/2006 Stack 2B gas analyses

Time	Temp F	% O2	ppm NO	Ppm NOx	ppm NO2	ppm SO2	ppm CO
8:58:06	122.3	18.90	76	76	0	41	7
8:59:26	122.2	18.87	77	77	0	71	7
9:21:05	122.6	18.75	80	80	0	84	8
9:31:11	121.9	18.80	83	83	0	109	8
9:41:12	122.4	18.79	79	79	0	91	8
9:53:35	124.8	18.82	83	83	0	90	6
10:03:05	128.3	18.85	83	83	0	86	7
10:12:45	123.1	18.76	86	86	0	60	8
11:24:52	122.8	18.78	88	88	0	96	7
11:58:06	123.2	18.65	92	92	0	92	9
12:09:49	123.3	18.67	94	94	0	91	8
12:21:45	123.5	18.71	91	91	0	82	8
12:30:47	122.5	18.73	92	92	0	84	8
12:45:16	123.2	18.72	93	93	0	67	8
12:54:47	123.5	18.72	94	94	0	68	9
13:04:29	123.6	18.84	85	85	0	59	8
14:19:49	122.8	18.82	88	88	0	41	9
14:56:27	123.5	18.65	79	79	0	71	7
15:06:21	123.8	18.68	77	77	0	69	8
15:17:56	125.6	18.65	79	79	0	65	7
15:30:36	125.9	18.68	79	79	0	65	8
15:43:52	125.7	18.68	77	77	0.3	65	7
15:55:13	125.4	18.68	78	78	0	60	8
16:03:51	127.5	18.59	82	82	0	67	7
16:05:10	127.6	18.58	81	82	0.3	61	8

9/13/2006	Temp F	% O2	ppm NO	ppm NOx	ppm NO2	ppm SO2	ppm CO
8:59:10	123.7	18.22	105	105	0	133	9
9:09:15	123.2	18.29	99	99	0	120	8
9:21:47	124.2	18.29	99	99	0	109	8
9:31:15	124.9	18.29	101	101	0	114	9
9:46:37	125.2	18.33	100	100	0	101	7
9:55:43	125.4	18.38	101	101	0	109	8
10:07:40	124.9	18.52	92	92	0	83	8

FAMS Hg measurements during NaCl addition to greenball at United Taconite

9/12/2006

Stack	Sample	ng/l	Total ng/l	Percentage
2B	1 Particles	0.10		3.97
9:00	1 Oxidized	0.46		18.14
	1 Elemental	1.99	2.56	77.88
9:25	2 Particles	0.18		5.47
	2 Oxidized	0.87		26.93
	2 Elemental	2.18	3.22	67.60
9:51	3 Particles	0.26		8.89
	3 Oxidized	0.77		26.34
	3 Elemental	1.88	2.90	64.77
11:55	4 Particles	0.23		5.76
	4 Oxidized	0.92		22.42
	4 Elemental	2.93	4.08	71.82
12:19	5 Particles	0.15		3.97
	5 Oxidized	0.59		16.03
	5 Elemental	2.96	3.70	80.01
12:42	6 Particles	0.22		5.76
	6 Oxidized	0.85		22.42
	6 Elemental	2.73	3.81	71.82
2:55	7 Particles	0.13		3.54
	7 Oxidized	0.43		11.82
	7 Elemental	3.07	3.63	84.63
3:19	8 Particles	0.12		3.08
	8 Oxidized	0.64		16.24
	8 Elemental	3.18	3.95	80.67
3:42	9 Particles	0.20		5.32
	9 Oxidized	0.42		11.44
	9 Elemental	3.07	3.69	83.24
9/13/2006				
8:55	1 Particles	0.10		2.24
	1 Oxidized	0.78		17.25
	1 Elemental	3.63	4.51	80.51
9:19	2 Particles	0.07		1.35
	2 Oxidized	0.88		17.42
	2 Elemental	4.12	5.08	81.23
9:43	3 Particles	0.09		1.76
	3 Oxidized	0.97		18.88
	3 Elemental	4.07	5.12	79.36

9/12/2006

Stack	Sample	ng/l	Total ng/l	Percentage
2A	1 Particles	0.06		1.07
9:00	1 Oxidized	0.54		10.34
	1 Elemental	4.61	5.20	88.59
9:25	2 Particles	0.40		7.96
	2 Oxidized	0.32		6.42
	2 Elemental	4.33	5.06	85.62
9:51	3 Particles	0.17		3.33
	3 Oxidized	0.69		13.21
	3 Elemental	4.33	5.19	83.45
11:55	4 Particles	0.26		5.01
	4 Oxidized	0.27		5.26
	4 Elemental	4.59	5.11	89.73
12:19	5 Particles	0.24		5.13
	5 Oxidized	0.28		5.77
	5 Elemental	4.25	4.77	89.10
12:42	6 Particles	0.33		7.79
	6 Oxidized	0.20		4.80
	6 Elemental	3.72	4.25	87.41
2:55	7 Particles	0.13		2.91
	7 Oxidized	0.30		6.66
	7 Elemental	4.01	4.44	90.43
3:19	8 Particles	0.29		7.66
	8 Oxidized	0.04		1.18
	8 Elemental	3.42	3.76	91.15
3:42	9 Particles	0.05		1.41
	9 Oxidized	0.06		1.69
	9 Elemental	3.40	3.51	96.90
9/13/2006				
8:55	1 Particles	0.06		0.95
	1 Oxidized	0.13		2.23
	1 Elemental	5.81	6.00	96.82
9:19	2 Particles	0.08		1.51
	2 Oxidized	0.27		5.23
	2 Elemental	4.87	5.22	93.26
9:43	3 Particles	0.15		3.35
	3 Oxidized	0.18		3.92
	3 Elemental	4.27	4.61	92.73

Cation concentrations in scrubber water before and during Cl-addition to greenball at United Taconite

	Na ppm	Mg ppm	Si ppm	K ppm	Ca ppm	Fe ppm	Mn ppm	Sr ppb	Ba ppb
Baseline Stack B	113	58	11.6	20.7	62	25	2.8	379	39.6
During Cl-Addition Stack B	110	55	11.1	19.7	76	17	2.2	363	34.3
Baseline A	116	57	10.4	21.2	56	15	1.7	347	28.3
Cl-Addition A	113	55	10.0	20.1	69	10	1.3	335	24.5

Anion concentrations in scrubber water and in Cl-leach samples from greenball for NaCl addition to greenball at United Taconite

Stack 2B	F ppm	Formate ppm	Cl ppm	NO2-N Ppm	Br ppm	NO3-N ppm	SO4 ppm
Baseline	57.3	2.5	85	0.005	0.52	8.39	614
Cl addition-1	52.0	2.8	106	0.008	0.52	8.43	589
Cl addition-2	52.9	2.8	113	0.003	0.50	8.18	580
Baseline	54.4	3.2	88	0.010	0.55	8.40	726
Stack 2A							
Baseline	54.9	2.0	84	0.016	0.56	8.4	497
Cl addition-1	52.7	2.1	106	0.013	0.53	8.35	479
Cl addition-2	53.2	1.8	112	0.045	0.50	8.23	451
Baseline	53.8	2.8	91	0.018	0.57	8.21	577
UT1 MAKEUP	11.9	0.18	44.4	0.96	0.25	6.12	195
UT4 MAKEUP	11.8	0.18	45.1	1.03	0.25	6.23	196
Cl in Greenball (dry wt basis)	4.6	4.60	6.20	0.032	0.035	0.82	38
Cl in Greenball (dry wt basis)	4.8	8.34	6.37	0.018	0.031	0.73	34

Field data for NaCl addition to greenball at United Taconite

Stack 2B Thickener	Baseline	Test 1	Test 2	Baseline
Time	0900	1200	1500	0900
PH	3.19	3.12	3.13	3.37
Temperature(°C)	41.9	42.9	42.1	41.0
Conductivity(µS/cm)	2000	2050	2000	2200
Total suspended solids(%)	1.00	0.84	0.64	2.46

Stack 2A Thickener	Baseline	Test 1	Test 2	Baseline
Time	0915	1210	1510	0900
PH	3.75	3.73	3.88	4.43
Temperature(°C)	35.5	37.6	36.5	36.0
Conductivity(µS/cm)	1700	1700	1650	1900
Total suspended solids(%)	1.16	1.14	0.80	2.77

10.3. Appendix III: Hibbing Taconite Focused Halide Injection Tests

Dates: May 1-May 3, 2007

Hibbing Taconlite halide injection tests conducted on 5/2/07

Field data for focused halide injection tests at Hibbing Taconite

	Baseline	NaCl	NaBr	$CaCl_2$	$CaBr_2$	Baseline
Time	0845	1043	1245	1445	1646	1745
PH	6.74	6.75	6.77	6.64	6.71	6.79
Temperature(C)	35.6	35.6	35.5	36.3	36.2	35.6
Conductivity(S/cm)	1050	1050	1050	1050	1050	1050

Anion concentrations in scrubber water during focused halide injection at Hibbing Taconite

	F ppm	Cl Ppm	NO2-N ppm	Br ppm	NO3-N Ppm	SO4 ppm
Baseline	30.5	67.6	0.21	0.24	5.45	247
NaCl Injection	30.9	78.3	0.19	0.24	5.47	241
NaBr Injection	28.3	67.1	0.18	12.4	5.46	240
CaCl2 Injection	29.0	79.6	0.19	0.42	5.48	242
CaBr2 Injection	29.7	68.4	0.18	13.8	5.53	243
Baseline	28.4	67.8	0.19	0.61	5.64	241

Cation concentrations in scrubber water during focused halide injection at Hibbing Taconite

SAMPLE DESCRIPTION	Li ppm	Na ppm	NH_4 ppm	K ppm	Mg Ppm	Ca ppm
HT - H201	0.0147	49.1	1.04	12.8	66.0	35.9
HT – NaCl	0.0147	49.8	1.11	12.8	66.2	36.1
HT – NaBr	0.0149	49.3	0.99	12.8	66.3	36.0
HT - CaCl2	0.0149	49.2	0.96	12.8	66.1	36.1
HT - CaBr2	0.0146	49.2	0.91	12.8	66.1	36.0
HT - H202	0.0147	49.2	0.95	12.9	66.1	36.0

FAMS baseline sampling results from Hibbing Taconite immediately before focused halide injection tests were performed.

Sample	ppt	ng	l	ng/l	Total ng/l
HFT 1-1 base 1 particles	37.00	0.85	22.7	0.04	
HFT 1-1 base 1 oxidized	114.70	2.64	22.7	0.12	
HFT 1-1 base 1 elemental	5809.38	133.62	22.7	5.89	6.04
HFT 1-2 base 2 particles	22	0.51	23.4	0.02	
HFT 1-2 base 2 oxidized	138.70	3.19	23.4	0.14	
HFT 1-2 base 2 elemental	5492.58	126.33	23.4	5.40	5.56
HFT 1-3 base 3 particles	105.50	2.43	28.5	0.09	
HFT 1-3 base 3 oxidized	98.30	2.26	28.5	0.08	
HFT 1-3 base 3 elemental	8163.55	187.76	28.5	6.59	6.75

HFT1-1 NaHCO3 Scrubber		16.83	31.7	0.53	
HFT 1-1 QLIP 1 particles	7.80	0.18	31.7	0.01	
HFT 1-1 QLIP 1 oxidized	9.30	0.21	31.7	0.01	
HFT 1-1 QLIP 1 elemental	4504.31	103.60	31.7	3.27	3.81
HFT1-2 NaHCO3 Scrubber		17.66	27.1	0.65	
HFT 1-2 QLIP 2 particles	15.10	0.35	27.1	0.01	
HFT 1-2 QLIP 2 oxidized	165.80	3.81	27.1	0.14	
HFT 1-2 QLIP 2 elemental	4600.18	105.80	27.1	3.90	4.71
HFT1-3 NaHCO3 Scrubber		19.73	28.5	0.69	
HFT 1-3 QLIP 3 particles	16.30	0.37	28.5	0.01	
HFT 1-3 QLIP 3 oxidized	37.60	0.86	28.5	0.03	
HFT 1-3 QLIP 3 elemental	5499.63	126.49	28.5	4.44	5.17