Minnesota Taconite Mercury Control Advisory Committee: Summary of Phase One Research Results (2010-2012)

A final report submitted to the United State Environmental Protection Agency

Grant Number: *GL00E00655-0*

Project Title: *TACONITE MERCURY EMISSION CONTROL STUDIES: PHASE ONE*

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Nov 29, 2012

Summary

The Minnesota Taconite Mercury Control Advisory Committee (MTMCAC), a group of industry, state, and academic technical experts, was formed in 2009 to help the taconite industry achieve a 75% reduction in industry-wide stack gas mercury emissions by 2025. Research conducted by this group from 2010-2012 focused on testing activated and brominated carbon sorbents to improve mercury capture in existing taconite processing plants. Six projects were selected and conducted using combined funds from the Minnesota Department of Natural Resources' Environmental Cooperative Research Program (ECR), six Minnesota participating taconite companies, and the US Environmental Protection Agency, Great Lakes Restoration Initiative (EPA-GLRI).

Two of the studies tested direct injection of powdered activated and brominated carbon directly into process gas streams upstream from existing wet scrubbers. A third study evaluated the capacity of several carbon-based sorbents to remove mercury in gases from active processing plant wet scrubbers. A fourth study used powdered activated and brominated carbon sorbents and a baghouse as a post wet-scrubber polishing process to remove mercury. A fifth study involved adding carbon and brominated carbon to "greenballs" and heating in a laboratory setting to determine if this method could increase oxidation and capture of mercury in process gases and wet scrubbers, respectively. A sixth study, also performed in the laboratory, evaluated the corrosive effects of bromide on grate materials used in taconite processing plants. Of the methods considered, direct carbon injection, fixed bed reactors, and post-scrubber bag houses were all found to have the potential to control mercury at levels needed for the industry to achieve its 75% reduction goal. Direct injection of activated and brominated carbons into process gas streams is considered to be the least expensive of these methods, however, precise cost estimates for application of these technologies for taconite furnaces have not been determined. Future mercury control research efforts will focus on further evaluation of technical and economic feasibility of using this technology to control mercury emissions from Minnesota's taconite industry.

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Introduction

Taconite mining is a major industry in Northeastern Minnesota that provides the United States with most of its domestic supply of non-recycled iron. Most taconite ore in this region is mined from the Biwabik Iron formation, a thick continuous layer of sedimentary rock that is over 100 miles long and composed of iron oxides, carbonates, silicates and trace mercury. Mercury has been identified as an issue within the last decade because a portion of it is released into the air when ore is concentrated and converted to pellets during taconite processing.

Most of the mercury in taconite ore is diverted to the tailings basin during a mineral separation process that separates the economic mineral, magnetite, from other minerals in the raw ore (Berndt, 2003). The mercury in tailings appears not to be leached into the environment. However, the mercury that remains with the magnetite is converted mostly to elemental mercury and released to the atmosphere during a high-temperature process referred to as induration. Induration is a necessary process in the taconite industry because it converts the powdered magnetite "concentrate" into hardened hematite pellets that are suitable for shipping to sites around the Great Lakes Basin and are ready for conversion to steel in specially designed blast furnaces.

Between 2005 and 2008, the state and industry conducted many studies on mercury cycling in processing plants including mercury generation during induration (Berndt and Engesser, 2005a; Galbreath, 2005; Berndt et al., 2005), its speciation in stack gases (Laudal, 2007; Berndt, 2008); its capture by existing wet scrubbers (Berndt and Engesser, 2005b); and its subsequent cycling within taconite processing plants (Berndt and Engesser, 2005b; Benner, 2008). Laudal and Dunham (2007) evaluated taconite control methods for the industry and concluded that chemical oxidation and sorbent injection methods used or considered for mercury emission control by the power industry may be adapted for use by the taconite industry. This led to the widespread testing of bromide addition in various forms including direct addition of dry salts to greenball, injection of salt brines into process lines, and of heated bromide radicals into waste gas ducts (Berndt and Engesser, 2007; Berndt, 2008, 2011; Pavlish and Zhuang, 2008).

In 2009, the Minnesota Pollution Control Agency (MPCA) developed an Implementation Plan to reduce Minnesota's statewide mercury Total Maximum Daily Load (TMDL). As part of this plan, the taconite industry and the MPCA set a target of 75% reduction from its 2010 mercury air emission inventory of 841 lbs down to 210 lbs by 2025 (See Appendix A). The Minnesota Taconite Mercury Control Advisory Committee (MTMCAC) was subsequently formed to help the industry achieve this goal. Six Minnesota taconite processing facilities participated in and/or contributed funding to projects: U.S. Steel-Keetac, Hibbing Taconite, U. S. Steel-Minntac, ArcelorMittal Minorca Mine Inc., United Taconite LLC, and Northshore Mining. The MPCA and Minnesota Department of Natural Resources (MDNR) participated in MTMCAC meetings as did the University of Minnesota's Natural Resources Research Institute (UM-NRRI) and the University of North Dakota's Energy and Environmental Research Center (UND-EERC). Projects were selected using a rigorous competitive process involving issuance of a request for proposals by the MDNR in November 2009. A total of six projects were selected from among eleven proposals received. Projects were facilitated by the MDNR and coordinated by MTMCAC.

These projects tested carbon injection into the process gases upstream from wet scrubbers at two taconite processing plants, one which has a straight grate furnace and the other a grate kiln. These are the two types of induration furnaces used by the taconite industry in Minnesota. Carbon addition to greenball was also tested in the laboratory at the bench scale for samples provided by five processing plants. Slip stream tests were conducted involving a bag house located downstream from the scrubber at one of the plants. Capture of mercury in gases passed through fixed beds containing carbon sorbents (located downstream from the scrubber) was evaluated using slip stream studies conducted at three of the plants. A relatively comprehensive bench-scale laboratory study was also conducted to further evaluate the effect of halides (Br and Cl) on corrosion in taconite induration furnaces.

Research into mercury control for taconite industries is an on-going process. This document provides edited summaries for each of the studies completed between 2010 and 2012 and then uses an objective means to represent, track, and compare research results in a series of research status tables. Each of the full reports for the projects is available electronically at the following website: http://www.dnr.state.mn.us/lands_minerals/dnr_hg_research.html .

Project Summaries

Project 1: Evaluation of Scrubber Additives and Carbon Injection to Increase Mercury Capture

http://files.dnr.state.mn.us/lands_minerals/reclamation/benson_nasah_2012a.pdf

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August 2012

Project 1 was conducted by the University of North Dakota (UND) and Envergex LLC team with support from IAC International and Western Kentucky University. The goals of Project 1 included:

-Increasing the degree of oxidation of elemental mercury that is released during induration through the use of additives.

-Maximizing the capture of mercury in the scrubber and preferentially sequestering to the solid non-magnetic portion of the scrubber slurry, providing possible options for further separating and discharging 'mercury-rich' non-magnetic solid fraction.

The scope of work involved bench, pilot and full scale testing to examine the efficiency of various additives to oxidize and sequester the mercury.

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

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

Baseline total mercury stack emissions (during the testing period) from Minntac Line 3 ranged from 3.5 to 8.2 μg/m^3; with most values between 4.0 and 6.2 μg/m^3. Particulate mercury emissions during baseline operation (during test periods) were minimal, with most values below 3% of the total mercury emitted. The predominant form of mercury in the stack emissions was elemental; values ranged between 83 and 90%, with the exception of one measurement.

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

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

Project 2: Mercury Control for Taconite Plants Using Gas-Phase Brominated Sorbents

http://files.dnr.state.mn.us/lands_minerals/reclamation/miller_zerangue_2012.pdf

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Albemarle Environmental Division.

July 2012

In 2011, Albemarle Environmental Division personnel conducted a field trial at Hibbing Taconite to demonstrate the effectiveness of gas-phase brominated sorbents in controlling mercury emissions from taconite facilities. There was a preliminary site visit in March 2011 followed by pre-trial testing in early June 2011. The pre-trial testing determined that the mercury sorbent would have to be injected into both the Windox Exhaust flue gas stream and the Hood Exhaust flue gas stream to achieve the desired 75% mercury removal from the baseline condition.

The equipment was prepared for the trial and the demonstration conducted in September and October 2011. The parametric testing demonstrated that the 75% Hg removal target could be achieved with a gas-phase brominated sorbent injection rate of about 3 lb/MMacf (126 lb/hr). It was demonstrated in a two-week continuous injection run that this removal rate could be achieved over time. This injection rate is higher than expected to achieve the 75% mercury removal but it does not appear to be a problem of the control technique. Rather, the sorbent distribution was sub-optimal due to project limitations. It is believed that better mercury removal results could be achieved with improved sorbent distribution.

Grab samples of green balls, multiclone dust and scrubber water were taken to identify any trends. The green ball mercury content averaged about 15 ng/g and varied randomly by nearly a factor of two from high to low concentration measured. Sorbent was injected before the multiclone and there was a concern that some sorbent would be captured there and decrease the overall Hg removal rate. It was discovered that some sorbent was captured by the multiclone but that its impact on the mercury removal rate was probably small. The Hg content of the scrubber water did not increase during the trial and varied between the high and low levels observed in the baseline testing. Filtering the scrubber water greatly reduced the mercury content since the sorbent contained in the scrubber solids still had Hg capacity.

Project 3: Developing Cost-Effective Solutions to Reduce Mercury Emissions from Minnesota Taconite Plants

http://files.dnr.state.mn.us/lands_minerals/reclamation/schlager_amrhein_2012a.pdf

http://files.dnr.state.mn.us/lands_minerals/reclamation/schlager_amrhein_2012a.pdf

http://files.dnr.state.mn.us/lands_minerals/reclamation/schlager_amrhein_2012a.pdf

Richard Schlager, Jerry Amrhein and Kyle Bowell

ADA-Environmental Solutions

September 2012

ADA Environmental Solutions (ADA) proposed a project to The Minnesota Department of Natural Resources (MnDNR) to develop cost-effective solutions to meet the industry goal by reducing mercury emissions from taconite plants by 75%. ADA was contracted to determine if activated carbon (AC) was a viable sorbent to control mercury in process gas from taconite plants when used in a fixed-bed application. There were four main tasks defined in the Work Scope: (1) Slipstream screening tests evaluating relative performance of test materials in actual process gas, impact of relative humidity on performance, and impact of process gas on mercury capture performance compared to controlled laboratory conditions; (2) develop a full-scale, integrated fixed-bed process concept; (3) pilot-scale fixed-bed design, and (4) techno-economic analysis of mercury control options;

Screening at each plant was conducted using the Mercury Index Method (MIM), a tool based on EPA Reference Method 30B that was developed by ADA for the project. Stack gas from a taconite process was drawn through tubes containing AC sorbents for time periods ranging between 1 and 10 hours. Each tube contained two sections, the first containing the AC under evaluation mixed with sand, and the second containing a standard EPA Method 30B AC. The Method 30B AC was sufficient to capture all the mercury contained in the sample gas for several days to weeks. The effectiveness of the test AC was determined by measuring the mercury captured in both sections and determining the fraction that passed through the first section into the section containing the Method 30B AC.

Sorbent Screening Slipstream Testing

Results indicated that all test AC sorbents were effective for mercury removal. Test sorbents included a sulfonated, granular, coconut shell-based carbon; an untreated, pelletized, anthracite-coal based carbon; and a sulfonated, pelletized, anthracite-coal based carbon. The material that comparatively captured the most mercury at all three plants was the sulfur treated coconut-shell (CR612C-Hg). Performance sensitivity to changes in process conditions will affect the full-scale design. Therefore, CR612C-Hg was tested in process gas with relative humidity between 50% and 70% at Hibbing Taconite, 50 to 81% at Arcelor Mittal, and 50 to 67% at United Taconite. There was no significant impact in mercury capture performance as a result of changes to the relative humidity. Also, mercury removal results from laboratory testing in dry nitrogen were very similar to results from slipstream tests at all three plants, indicating that nothing in the process gases negatively impacted the mercury removal effectiveness.

Development of Full-Scale, Integrated Fixed-Bed Process Concept

Task 1 screening results and full-scale design criteria were used to develop a full-scale fixed-bed conceptual design using design flows of 756,000 ACFM at Hibbing Taconite, 854,000 ACFM at Arcelor

Mittal, and 493,000 ACFM at United Taconite[1]. The design incorporates 18, 19, and 11 vessels, respectively, for the plants. Vessels contained beds of carbon that are each 47 feet long and 12-feet wide and 3 feet deep. An estimated 1,252,080 lbs of AC would be required to fill the beds at Hibbing Taconite, which compares to 1,377,288 lbs at Arcelor Mittal, and 813,850 lbs at United Taconite . The estimated pressure drop across the beds in each case is 6 to 12 inches of water. The amount of carbon that would be used per year to maintain 100% mercury capture was projected to be 200,208 lbs at Hibbing Taconite, 117,403 lbs at Arcelor Mittal, and 138,108 lbs at United Taconite. This initial concept design would need to be validated through longer-term pilot testing.

Pilot Plant Design

The estimated cost of a pilot-scale fixed-bed system appropriate to collect detailed information required for a robust full-scale design is $50,000. All testing costs would be in addition to the cost of the equipment. Task 1 results indicate fixed-beds of activated carbon can reliably achieve the taconite industry’s goal of 75% mercury control. However, based on the concept design and the techno-economic analysis (below), a fixed-bed approach to control mercury from the process gas at either HibTac, ArcelorMittal, or UTac is expected to be more costly than other approaches and require multiple, large, interconnected vessels. Therefore, ADA does not recommend continued development and testing of fixed-bed technologies for mercury control from the process gas at these plants.

Techno-Economic Analysis

The relative technical and economic characteristics of seven mercury control technologies were compared using a Kepner-Tregoe (KT) decision-making approach by Stantec Consulting Ltd. The fixed-bed method to control mercury was determined to provide good performance but at relatively high cost compared to other options. The high cost was a result of several factors including the number of vessels required and the associated plant integration, and the expected pressure drop across the beds. AC injection was identified as the most promising technology using this approach.

[1] In a later review of this report, this flow rate was thought to be too low for those typically encountered during normal operation at this plant. A higher flow rate would result in increased costs compared to those estimated in the report.

Project 4: Evaluation of a slipstream baghouse for the taconite Industry

http://files.dnr.state.mn.us/lands_minerals/reclamation/laudal_2012.pdf

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January 2012

The Energy & Environmental Research Center tested a mercury control technology utilizing a slipstream baghouse with activated carbon injection at the United States Steel Corporation, Minnesota Ore Operations – Keetac Plant. The EERC slipstream baghouse is a trailer-mounted baghouse that was transported to the test site and connected in slipstream fashion to allow for testing "real" flue gases under actual operating conditions. Because the slipstream baghouse was located after a wet scrubber, the flue gas at the inlet was saturated at about 132°F. To avoid wetting the bags and fan, an additional drip leg and heating elements were installed to raise the inlet flue gas temperature to about165°F. For a full-scale unit, it would be expected that a portion of the flow (prior to the wet scrubber) would be routed to the baghouse to maintain a temperature above the water dew point. For the Keetac test, the baghouse was operated at a nominal air-to-cloth ratio of 6 ft/min (actual ft^3/min of gas per ft^2 of cloth). Ports were installed so that the mercury concentrations at both the baghouse inlet and outlet could be measured using continuous mercury monitors (CMMs) and sorbent traps. Results showed that by using as little as 2.2 lb/Macf of standard activated carbon or 1.1 lb/Macf of a treated carbon >75% mercury removal can be achieved.

Mercury removal of >75% can be achieved at Keetac with either standard or bromine-treated activated carbon. 2.0 lb/Macf of standard activated carbon and 1.1 lb/Macf of bromine-treated activated carbon are needed when natural gas is used as the fuel. Only 0.6 lb/Macf of bromine-treated activated carbon is needed when a PRB coal is fired. Very low particulate emissions can be achieved in either case.

Because of the relatively high cost of installing a fabric filter, the most economical installation would be for those taconite facilities that require fuel flexibility and/or where additional particulate control is needed. If a baghouse is to be installed at Keetac, 18%–20% flue would need to bypass the wet particulate scrubber to prevent wetting of the bags. Overall, the slipstream baghouse and CMMs operated well during the test period. However, it appears that if the ACI is turned off, there is the potential of (temporarily) high mercury emissions as a result of reemission.

If this is to be a viable technology, the following recommendations are made for future testing: (1) Longer-term testing is needed to determine the resultant steady-state pressure drop across the baghouse as a function of air-to-cloth ratio. (2) Longer-term tests are also needed to ensure that required mercury control will be maintained. (3) It appeared that the bromine-treated activated carbon worked better when firing coal compared to natural gas. The same may be true using standard activated carbon. Therefore, additional coal tests are needed. (4) The economic evaluation presented in this report is based on the utility requirements and may or may not be the same for a taconite plant. Therefore, more specific economic data are needed. (5)There may be a need to evaluate or update the existing wet scrubber mist eliminators.

Project 5: Evaluation of a Low Corrosion Method to Increase Mercury Oxidation and Scrubber Capture

http://files.dnr.state.mn.us/lands_minerals/reclamation/benson_lentz_2012b.pdf

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September 2012

Green balls produced from concentrate/filter cake and additives obtained from five of the taconite facilities operating on the Mesabi Iron Range were combined with trace amounts of ESORB-HG-11. ESORB-HG-11 is a proprietary brominated powdered activated carbon. The green balls containing ESORB-HG-11 were then subjected to laboratory heating experiments to determine the mercury oxidation potential of the additive.

Heating tests of the green balls from four of the facilities gave mercury oxidation levels ranging between 43% and 78%, with averages of 52% (±8%) and 58% (±11%) for additive amounts of 0.1 weight% and 0.5wt%, respectively. Baseline oxidation percentages measured in the laboratory averaged 18% (±6%), while oxidation in green balls mixed with ESORB-HG-11 averaged 42% (±9)% and 48% (±13)% for the 0.1 wt% and 0.5 wt% additive loading experiments respectively. The results confirm preliminary results obtained in Phase 1 of this project, and indicate that the 0.1 weight% ESORB-HG-11 loading is optimal for mercury oxidation, and is recommended for any potential future work involving the technology. The results obtained from a fifth facility, United Taconite, were not included in determining the averages, as they showed significantly lower mercury oxidation increases for ESORB-HG-11-containing green balls. The oxidation levels observed were approximately 10% to 15% lower than those observed for the other plants. The possible reason for this difference was not conclusively established during the testing.

The green balls were produced by the Coleraine Minerals Research Laboratory (CMRL) of the Natural Resources Research Institute (NRRI). They were then subjected to industry-standard, batch balling tests to determine the possible effects that the additive might have on the physical properties of the green balls. The physical properties investigated consisted of the moisture content, wet drop number, and dry compressive strength. For the samples with 0.1 weight% additive, no significant difference due to addition of ESORB-HG-11 was observed with respect to the baseline standard during the batch balling tests. Slight differences from the baseline standard were observed with the 0.5 weight% additive loading, suggesting that the 0.1 weight% is the optimal additive loading.

Preliminary tests performed during Phase 1 of this project determined that there was little or no gas-phase mercury oxidation occurring during tests performed using the bench scale apparatus. This suggests that the mercury oxidation observed during these tests is a solid phase phenomenon occurring most likely on the carbon surface and within the green ball. Previous work indicates that gas-phase mercury oxidation does occur in taconite facilities with bromide addition to the green ball which enhances baseline (no bromide addition) mercury oxidation values. Consequently, a full-scale demonstration of the technology might result in higher levels of mercury oxidation than observed during the bench scale tests in this project. No tests were performed in this project to determine the impact of the carbon additive on the physical and metallurgical properties of fired taconite pellets; this aspect should be investigated in future testing.

Project 6: Corrosion Potential of Bromide Injection Under Taconite Operating Conditions

http://files.dnr.state.mn.us/lands_minerals/reclamation/zhuang_dunham_2012.pdf

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June 2012.

The overall goal of this project was to characterize bromine-induced corrosion on taconite processing equipment under simulated but representative taconite processing conditions. Specific objectives of this project included the following: determine Br-induced corrosion on grate bars (metal alloys) and on ductwork materials (low carbon steel) in simulated taconite flue gas containing HBr under thermal cycling conditions, compare the corrosion rates induced by bromine and chlorine, and estimate the life span of test coupons in taconite flue gas containing bromine species.

Comparisons between bromine- and chlorine-induced metal corrosion were made under simulated taconite operating conditions. Blisters and/or pinholes observed on the surface of the grate bar metals indicate that volatile compounds were formed, mainly iron chloride or iron bromide compounds. Temperature is very critical to corrosion, and the maximum temperature seems to be the most important factor.

Active oxidation appears to be the main corrosion mechanism for grate bar samples under elevated temperatures of 500°–950°C, while HBr showed a higher corrosion rate than HCl under similar simulated conditions. As a result, under the same level of halogen exposure with the same thermal cycles, both the Minntac and Minorca grate bar showed more microfracture and weight loss under the bromine condition compared to chlorine, while the main reasons for the weight loss can be ascribed to depletion of iron.

Based upon the measured data, the projected weight loss of Minntac and Minorca grate bar metals over 3 years of operation under HBr conditions is marginal. Minorca grate bar is expected to have 0.84 mm of material depletion in comparison to 0.01 mm of material loss with Minntac grate bar.

By comparison, no significant corrosion was observed for the low-carbon steel from ducts since it only experienced low temperatures of 50°–200°C. The project weight loss of this metal over a 3-year operation under HBr conditions is minimal.

Note that the completed corrosion exposure tests were carried out in a bench-scale experimental system that cannot precisely simulate actual operating conditions in the taconite process. Therefore, the project results can be regarded as a first-step effort to address the potential bromine-induced corrosion as bromine is applied to the taconite facility for mercury reduction. Large-scale field testing is recommended in the future to account for the difference between bench-scale and full-scale systems.

Technology Status (September 2012)

Processing plants and test methods vary so it can become difficult to compare and assess results from competing control methods tested at a variety of processing plants. Some of the variables that need to be considered include furnace type, pellet type produced, binder used in greenballs, scrubber type used to control particulates, fuel type burned, and the number of stacks per line (See Appendix II).

Thus, the MTMCAC adopted a standardized approach to track research status for several different technologies being considered for Hg control by the taconite processing industry. First, each of the contractors performing tests for MTMCAC was required to provide and report the specific details of the equations and extrapolations used to estimate reductions achieved by their methods. These equations and reports were reviewed and validated by an independent third party (Barr Engineering, Minneapolis, MN) to ensure that the reports contained all information and assumptions needed to reproduce the control estimates. Tables 1 to 5 were then constructed to provide a direct comparison of results and to record assumptions made, testing locations and type (e.g., conducted on a bench – slip stream, pilot, or short, or long-term full-plant scale). Results were also extrapolated to other plants to assess the potential Hg reductions that might be realized if the technology were applied on an industry-wide basis. The methods used to make these extrapolations are also tracked in the tables.

The five technologies evaluated include $CaBr_2$ injection into the process gas stream (Table 1, tested prior to the present study), addition of brominated carbon sorbents to greenball feed (Table 2 – Project 5 in this report), brominated carbon sorbent injection into process gas streams upstream from wet scrubbers (Table 3 – Projects 1 and 2), capture by fixed beds containing several activated carbon types and located downstream from wet scrubbers (Table 4 – Project 3), and post-scrubber injection of sorbents downstream of the scrubber but upstream from a baghouse (Table 5 – Project 4). The mercury reductions were computed from annual baseline values estimated for 2010 (see Appendix 1) which estimated total industry emissions to be 840.6 lbs/year during that year. If a plant had more than one line, then the plant's inventory was partitioned among the separate lines according to their respective production capacities.

These tables include emissions from two companies that did not participate in the present research: Essar Steel and Mesabi Nugget. These companies have permits requiring that they conduct their own research on mercury emission control methods. However, Essar Steel is building a straight-grate taconite processing facility. Therefore, MTMCAC provided estimates for the amount of control they might expect, using each of the five technologies considered here. Results for the studies presented in this report, are not applicable to Mesabi Nugget due to the differences in processing techniques. It was assumed, therefore, that Mesabi Nugget would reach a 75% mercury reduction goal using control methods designed specifically for their process.

Each of the inventories also includes several smaller sources where mercury is unlikely to be controlled or practicable: Northshore, where only 7.3 lbs of Hg is emitted annually from three process lines, and sources unrelated to taconite processing furnaces that emit 1.2 lbs of mercury annually. The inventories presented in Tables 1 through 5 do not assume any control of mercury from these sources.

Estimated annual emissions are provided for each processing line both with and without the technology in place and the total emissions are summed. Costs were evaluated using a relative scale, whereby the technologies were ranked L, M, or H, respectively for those with lowest, medium, or highest estimated costs. Techno-Economic Analysis conducted by Schlager et al. (2003) (Project 3 above) greatly aided this process.

Injection of dissolved $CaBr_2$ into taconite processing lines (Table 1). Prior to the tests presented in this research summary, extensive testing was conducted to determine whether injection of Br salts into taconite processing furnaces impacts Hg emissions. Test methods involved the direct injection of calcium bromide ($CaBr_2$) brine into the processing line at rates of approximately 20 to 50 lbs/hr on a dry salt weight basis. The water evaporates and the salts decompose to yield HBr and Br_2, which can oxidize the mercury. This method was first studied at the Hibbing Taconite processing plant by Berndt and Engesser (2007) and was eventually tested at five processing plants (summarized by Berndt, 2011).

Other methods of Br-salt injection have been tried (addition directly to the greenball feed (Berndt, unpublished data) or direct injection of fired halogens into process gas in the waste gas ducts (Pavlish and Zhuang, 2008), but these methods proved to be less effective than direct injection of $CaBr_2$ salt solutions into the process gases within the induration furnaces.

Initially, a primary criticism of this method was that the addition of halide salt to the process lines may result in enhanced corrosion and shortened life of furnace grates. Two laboratory studies conducted by Zhuang et al. (2009, 2012 – see summary for Project 6 of this report) on grate materials supplied by industry revealed that although Br addition enhanced corrosion, the rates were relatively slow and would likely have minimal impact on the life spans of the grates.

With or without a corrosion issue, the method was unable to reliably reach the desired 75% capture rate at most of the plants studied (Table 1; Berndt, 2011). It is estimated that although some applications approached 75% capture (Line 3 at Minntac and Line 3 at HibTac), use of this technology would capture only about half of the mercury currently emitted by the industry. Although the cost of this method is considered to be the lowest of those studied, the MTMCAC does not believe it can be used to reach its target reduction goals.

Addition of brominated carbon to greenball feed (Table 2). This process was not tested at any plants but was tested in the laboratory using freshly produced greenball feed from five taconite processing plants (Benson et al., 2012b – See summary for Project 5 of this report). The addition of the brominated carbon to the heated greenball causes an increase in oxidation for Hg released during the induration processes. To estimate the effect of this method on mercury control at taconite processing furnaces, MTMCAC assumed that the increased capture in the wet scrubbers would be proportional to the increased oxidation in the mercury released from the greenball.

Based on this estimation method, none of the companies would reach 75% control of their emissions and the annual total range-wide mercury emissions would drop from approximately 840.6 lbs/year down to 522.6 lbs/year, well short of the 210 lb/year target. Benson et al. (2012) believe that actual control might be better than those estimated by this method due to reactions between bromine and Hg in the gas phase so it is possible that, with further testing at a plant scale, this technique might achieve the 75% reduction level at some plants.

This method has a lower anticipated cost than other sorbent carbon methods but effect on the quality of fired pellets has not been fully evaluated. Engesser (2004), for example, found that addition of 0.6 and 1.0 wt% carbon to greenballs caused a decline in compression strength of the fired pellet.

Injection of gas-phase brominated sorbents into process gas, upstream from wet scrubbers (Table 3). This method involves the injection of brominated carbon-based sorbents into taconite process gases, downstream of the location where the mercury is released, upstream from the wet scrubbers that control particulate emission. This method, which is widely used to control mercury at coal-fired power plants, was tested here at two taconite processing plants: Minntac Line 3 (Benson et al., 2012a; see summary for Project 1) and HibTac Line 1 (Miller et al., 2012; See summary for project 2). Both tests demonstrated that a large percentage of the mercury in taconite stack gases can be removed. Non-brominated activated carbon (PAC) sorbents provided less control of mercury in stack gases but the amount of carbon needed was greatly increased compared to brominated carbon-based sorbents.

It is important to note that Benson et al. (2012a) observed that mercury control by this method at Minntac was accompanied by an increase in particulate mercury emission that was associated with the activated carbon. Total reduction from these tests was approximately 71%, slightly short of the 75% target. It is estimated, therefore, that the technology can reach a 75% or greater mercury control level with improved particulate capture. Tests by Miller et al. (2012) at Hibbing Taconite exceeded the 75%

control goal but they reported that test limitations on injection port locations meant that the amount of sorbent needed to control mercury emissions was larger than expected.

To estimate control levels for the industry, it was simply assumed that the companies would optimize their individual mercury control processes to achieve a 75% (or better) mercury reduction level. In both cases, it appeared that a 75% or greater reduction goal can be achieved using brominated sorbents at taconite plants, and that the total emissions for the industry could potentially be reduced from 840.6 lbs/year to less than 216 lbs/year. Minntac, ArcelorMittal, and United Taconite would also be required to eliminate mercury recycling loops in their induration furnaces (Keetac already discards scrubber solids and the non-magnetic scrubber solids, including the injected sorbent, will be routed to the tailing basins at Hibbing Taconite).

Injection of brominated carbon into process gas downstream of wet scrubbers but upstream from a baghouse (Table 4). The sorbents are injected following the wet scrubber in this polishing technique, and then captured by a baghouse. The sorbents that accumulate in the bag house provide an effective chemical trap for most of the mercury that would otherwise escape the scrubber. Advantages of this method include the fact that it does not interfere directly with the induration process nor does it introduce potentially corrosive bromide into the taconite processing lines. Pellet quality would not be threatened. The slipstream tests conducted by Laudal (2012; See Project 4 summary included in this report) at US Steel Keetac indicated that the method could remove greater than 75% of the mercury that remains in the gas after passage through the scrubber. However, the high initial capitalization and maintenance costs, space limitations, pressure drop across the bags (requiring additional process fans and energy), and the need for heating the process gas stream (or to bypass the wet scrubber with a fraction of the gas) to prevent condensation in the baghouse make this one of the most expensive control methods that was evaluated.

Fixed bed reactors containing activated carbon (Table 5). As with the post-scrubber bag house, this method is a polishing process for the waste gas and so does not interfere directly with the induration process itself and does not increase potentially corrosive bromine to process gases. This method was initially pioneered for taconite processing plants using simulated taconite process gases generated in the laboratory by Dunham and Miller (2009). Schlager et al. (2012 a, b, and c; See Project 3 summary in this report) tested the technique using packed beds exposed for 1 to 10 hrs to actual taconite processing gases at three taconite processing plants. The results suggested that this method could capture greater than 75% of the mercury in taconite processing streams and meet the industry's reduction goals. Furthermore, because it is a polishing technique, located post-scrubber, its use would avoid interference with the taconite induration process, nor would it introduce potentially corrosive bromide to the taconite processing lines. However, this method suffers from many of the same limitations as the post-scrubber baghouse: high initial capitalization and maintenance costs, space limitations, increased pressure drop, and the need for heating of the process gas stream to prevent condensation. It is considered the most expensive method tested.

Conclusions and Path Forward

Six studies were conducted to test a variety of potential carbon-based methods to control mercury levels in stack gases emitted from Minnesota taconite processing facilities. Five of the studies evaluated various activated and brominated carbon applications, while a sixth study evaluated the corrosive effects of halides (bromide and chloride) on the grates that are used in taconite processing facilities. Direct injection of brominated carbon appears to be the least costly of the methods that have been tested to date that has the potential to help the industry reach its stated goal of 210 lbs Hg emitted per year. Other methods, including ($CaBr_2$) addition to process gases (tested previously) and brominated carbon addition to greenball feed, are likely less expensive, but neither has been demonstrated to reliably achieve the necessary mercury reduction levels. Polishing techniques located after the scrubber worked well in slipstream experiments, but the costs associated with these techniques are much higher than methods relying on direct injection of brominated carbon to the process gas stream.

Based on mercury research project findings, from 2011 and 2012, the Minnesota taconite industry is planning to conduct long-term testing of gas-phase brominated sorbents. Further, it is the goal of industry to comply with the state of Minnesota's mercury TMDL and to identify a practical, feasible, and cost-effective technology that that not interfere with pellet quality and/or result in additional complex waste streams that will require management. Industry hopes to learn how furnace, fuel, binder and scrubber types may influence results as well the potential operational and capital costs.

Acknowledgements

The research represented in this document was funded, directed, guided, and completed through the combined efforts of a large number of participating groups and agencies. It could not have occurred without funding provided by the MDNR Environmental Cooperative Research program (ECR), the six cooperating Minnesota taconite operations (U.S. Steel-Keetac, Hibbing Taconite, U. S. Steel-Minntac, ArcelorMittal Minorca Mine Inc., United Taconite LLC, Northshore Mining), and especially the United States Environmental Protection Agency, through its Great Lakes Restoration Initiative (EPA-GLRI). John Pavlish (University of North Dakota), Anne Jackson and Mary Jean Fenske (MPCA), and John Engessser (MDNR) are thanked, along with all of the industry MTMCAC representatives who provided consistent and continuous support and encouragement throughout this effort. Keith Hanson and Julianne Hanson, Barr Engineering, are gratefully acknowledged for providing much needed logistical support, including the scheduling of monthly MTMCAC meetings and assistance with keeping all contractors on tight reporting schedules. Tim Russell and Aaron Aamold, Barr Engineering, Inc., are acknowledged for performing data quality verification of the EPA-funded projects. Matt Lindon (Minnesota Pollution Control Agency) provided important assistance in the area of data quality management, as well. Eric Osantowski, EPA, is acknowledged for guiding this project through the federal funding and reporting processes. Daniel Roark, MDNR, is also thanked for navigating the individual contracts through the state and federal funding processes.

Technology Research Status Tables

Table 1: Hg-reduction Technology Status for Injection of calcium bromide (dissolved in water) into the process gas stream. Estimated emissions are listed in pounds of mercury emitted annually with and without the technology in place.

Processing Line	Estimated Baseline Emission	Tests Conducted				Estimated controlled emission	Cost L/M/H	Footnotes
		Bench-Scale Laboratory	Slip Stream	Short Full-Scale	Long Full-Scale			
Keetac 2	105.8			46.6		46.6	L	1,7
HibTac 1	75.7					33.3	L	2,7
HibTac 2	75.7					33.3	L	2,7
HibTac 3	75.7			33.3		33.3	L	1,7
Minntac 3	26.5			7.2		7.2	L	1,7
Minntac 4	39.7					19.9	L	3,6,7
Minntac 5	39.7					19.9	L	3,6,7
Minntac 6	39.7					19.9	L	3,6,7
Minntac 7	39.7					19.9	L	3,6,7
Arc. Mittal 1	33.4			23.0		23.0	L	1,6,7
United Tac 1	66.8					52.8	L	2,6,7
United Tac 2	66.8			52.8		52.8	L	1,6,7
Northshore	7.3					7.3		8
Essar	77.0					41.6	L	4,6,7
Mesabi Nug	70.0					17.5		5
Other	1.2					1.2		9
Rangewide	**840.6**					**429.3**		

1 Estimate based on full-plant test results from Berndt and Engesser (2007) and Berndt (2011).
2 Based on tests conducted on identical processing lines by Berndt and Engesser (2011) and Berndt (2011).
3 Calculated using average test result from grate kiln furnaces (50% Hg remained)
4 Calculated using average test result from straight grate furnaces (54% Hg remained)
5 No applicable results available, but assumes company will reach 75% TMDL Hg reduction goal
6 Scrubber solid recirc loop must be eliminated and this could result in improved capture rates.
7 Consult Zhuang et al. (2012) to evaluate potential for grate corrosion.
8 Small source compared to size of operation, Hg control unlikely to be practicable
9 "0ther" small sources unrelated to taconite furnaces-Thunderbird and Babbitt boilers

Table 2: Hg-reduction Technology Status for addition of brominated carbon to greenball. Estimated emissions are listed in pounds of mercury emitted annually with and without the technology in place.

Processing Line	Estimated Baseline Emissions	Tests Conducted				Estimated controlled emissions	Cost L/M/H	Footnotes
		Bench-Scale Laboratory	Slip Stream	Short Full-Scale	Long Full-Scale			
Keetac 2	105.8	67.7				67.7	L	1,5,6,9
HibTac 1	75.7	43.1				43.1	L	1,5,6,9
HibTac 2	75.7	43.1				43.1	L	1,5,6,9
HibTac 3	75.7	43.1				43.1	L	1,5,6,9
Minntac 3	26.5	13.5				13.5	L	1,5,6,9
Minntac 4	39.7	20.2				20.2	L	1,5,6,8,9
Minntac 5	39.7	20.2				20.2	L	1,5,6,8,9
Minntac 6	39.7	20.2				20.2	L	1,5,6,8,9
Minntac 7	39.7	20.2				20.2	L	1,5,6,8,9
Arc. Mittal 1	33.4	19.7				19.7	L	1,5,6,8,9
United Tac 1	66.8	54.1				54.1	L	1,5,6,8,9
United Tac 2	66.8	54.1				54.1	L	1,5,6,8,9
Northshore	7.3					7.3		2
Essar	77.0					43.1	L	3,5,6,8,9
Mesabi Nug	70.0					17.5		4
Other	1.2					1.2		7
Rangewide	**840.6**					**488.3**		

1 Based on bench-scale tests conducted by Benson et al (2012b)
2 Small source compared to size of operation, Hg control unlikely to be practicable
3 Assumed average for test results from other operations.
4 No applicable results available, but assumes company will reach 75% TMDL Hg reduction goal
5 This technology is likely to have low cost.
-costs could be higher if Brominated C interferes with pellet quality
6 Consult Zhuang et al. (2009, 2012) to assess corrosion potential
7 "0ther" small sources unrelated to taconite furnaces-Thunderbird and Babbitt heating boilers
8 Scrubber solid recirc loop must be eliminated and this could result in improved capture rates.
9 Engesser (2004) found addition of 0.6 and 1.0% carbon to greenball decreased pellet strength

Table 3: Hg-reduction Technology Status for injection of brominated carbon sorbents into process gas stream. Estimated emissions are listed in pounds of mercury emitted annually with and without the technology in place.

Processing Line	Estimated Baseline Emissions	Tests Conducted				Estimated controlled emissions	Cost L/M/H	Footnotes
		Bench-Scale Laboratory	Slip Stream	Short Full-Scale	Long Full-Scale			
Keetac 2	105.8					<26.5	L	4,6,7
HibTac 1	75.7			<18.9		<18.9	L	1,5,6,7
HibTac 2	75.7					<18.9	L	3,6,7
HibTac 3	75.7					<18.9	L	3,6,7
Minntac 3	26.5			<6.6		<6.6	L	2,6,7
Minntac 4	39.7					<9.9	L	4,6,7,8
Minntac 5	39.7					<9.9	L	4,6,7,8
Minntac 6	39.7					<9.9	L	4,6,7,8
Minntac 7	39.7					<9.9	L	4,6,7,8
Arc. Mittal 1	33.4					<8.4	L	4,5,6,7,8
United Tac 1	66.8					<16.7	L	4,6,7,8
United Tac 2	66.8					<16.7	L	4,5,6,7,8
Northshore	7.3					7.3		10
Essar	77.0					<19.3	L	4,7,8
Mesabi Nug.	70.0					17.5		9
Other	1.2					1.2		11
Rangewide	**840.6**					**<216.6**		

1 Based on short term tests conducted by Miller et al. (2012) that showed >75% capture could be achieved

2 Based on short term test conducted by Benson et al. (2012a) that showed >75% capture could be achieved

3 Based on test results from identical process lines by Miller et al. (2012)

4 Based on results from other taconite processing line but no testing was completed on this line.

5 Slip stream tests performed on carbon sorbent reactivity this line by ADA-ES (Schlager et al., 2012 a,b,c).

6 Adjustment to wet scrubber may be needed to control particulate mercury emissions (Benson et al., 2012a)

7 Consult Zhuang et al. (2009, 2012) to evaluate potential for grate corrosion.

8 Scrubber solid recirc loop must be eliminated and this could result in improved capture rates.

9 No applicable results available, but assumes company will reach 75% TMDL Hg reduction goal

10 Small source compared to size of operation, Hg control unlikely to be practicable

11 "Other" small sources unrelated to taconite furnaces-Thunderbird and Babbitt boilers

Table 4: Hg-reduction technology status for fixed carbon beds. Estimated emissions are listed in pounds of mercury emitted annually with and without the technology in place.

Processing Line	**Estimated Baseline Emissions**	**Tests Conducted**				**Estimated controlled emissions**	**Cost L/M/H**	**Footnotes**
		Bench-Scale Laboratory	**Slip Stream**	**Short Full-Scale**	**Long Full-Scale**			
Keetac 2	105.8					<26.5	H	4,7
HibTac 1	75.7		<18.9			<18.9	H	1,7
HibTac 2	75.7					<18.9	H	4,7
HibTac 3	75.7					<18.9	H	4,7
Minntac 3	26.5					<6.6	H	4,7
Minntac 4	39.7					<9.9	H	4,7
Minntac 5	39.7					<9.9	H	4,7
Minntac 6	39.7					<9.9	H	4,7
Minntac 7	39.7					<9.9	H	4,7
Arc. Mittal 1	33.4		<8.4			<8.4	H	2,7
United Tac 1	66.8					<16.7	H	4,7
United Tac 2	66.8		<16.7			<16.7	H	3,7
Northshore	7.3					7.3		5
Essar	77.0					<19.3	H	4,7
Mesabi Nug	70.0					17.5		6
Other	1.2					1.2		8
Rangewide	**840.6**					**<216.6**		

1 >75% removal achievable based on slip stream test results (Schlager et al., 2012a)
2 >75% removal achievable based on slip stream test results (Schlager et al., 2012b)
3 >75% removal achievable based on slip stream test results (Schlager et al., 2012c)
4 Based on slip stream results from other processing lines by ADA-ES (Schlager et al., 2012 a,b,c).
5 Small source compared to size of operation, Hg control unlikely to be practicable
6 No applicable results available, but assumes company will reach 75% TMDL reduction goal
7 High cost relative to other technologies based on data available in ADA-ES.
-Large footprint needed to house exchangeable carbon beds
-Fans and electrical infrastructure needed to account for increased pressure drop
-Additional heat may be needed to prevent condensation
8 "Other" small sources unrelated to taconite furnaces-Thunderbird and Babbitt boilers

Table 5: Hg-reduction Technology Status for post-scrubber injection of brominated carbon with bag house. Estimated emissions are listed in pounds of mercury emitted annually with and without the technology in place.

Processing Line	Estimated Baseline Emissions	Tests Conducted				Estimated controlled emissions	Cost L/M/H	Footnotes
		Bench-Scale Laboratory	Slip Stream	Short Full-Scale	Long Full-Scale			
Keetac 2	105.8		<26.5			<26.5	H	1, 5
HibTac 1	75.7					<18.9	H	2, 5
HibTac 2	75.7					<18.9	H	2, 5
HibTac 3	75.7					<18.9	H	2, 5
Minntac 3	26.5					<6.6	H	2, 5
Minntac 4	39.7					<9.9	H	2, 5
Minntac 5	39.7					<9.9	H	2, 5
Minntac 6	39.7					<9.9	H	2, 5
Minntac 7	39.7					<9.9	H	2, 5
Arc. Mittal 1	33.4					<8.4	H	2, 5
United Tac 1	66.8					<16.7	H	2, 5
United Tac 2	66.8					<16.7	H	2, 5
Northshore	7.3					7.3		3
Essar	77.0					<19.3	H	2,5
Mesabi Nug	70.0					17.5		4
Other	1.2					1.2		6
Rangewide	**840.6**					**<216.6**		

1 Slip Stream test results conducted by Laudal (2012).

2 Estimated using slip-stream test results for Keetac Line 2 (Laudal, 2012)

3 Small source compared to size of operation, Hg control unlikely to be practicable

4 No applicable results available, but assumes company will reach 75% TMDL Hg reduction goal

5 Costs are estimated to be high relative to other technologies.
-Retrofit would require considerable re-engineering
-Large footprint required for bag house
-Fans and electrical infrastructure needed to account for increased pressure drop
-Heating or partial scrubber bypass needed to prevent condensation in bag house

6 "Other" small sources unrelated to taconite furnaces-Thunderbird and Babbitt boilers

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Appendix I: Annual taconite mercury emissions estimated during Minnesota's Mercury TMDL implementation stake holder process

This is Table 19 from REPORT ON THE MERCURY TMDL IMPLEMENTATION PLAN STAKEHOLDER PROCESS Prepared for the Minnesota Pollution Control Agency by the Minnesota Environmental Initiative July 7, 2008 CFMS Contract No. A99751 most recently downloaded from: http://www.pca.state.mn.us/index.php/component/option,com_docman/task,doc_view/

Facility	2005	2010	2018
Northshore Mining Co - Silver Bay	7.3	7.3	7.3
US Steel Corp - Minntac	185.3	185.3	185.3
United Taconite LLC - Thunderbird Mine	1.1	1.1	1.1
Hibbing Taconite Co	227.1	227.1	227.1
Ispat Inland Steel Mining - Minorca	33.4	33.4	33.4
US Steel - Keewatin Taconite	146.8	105.8	105.8
United Taconite LLC - Fairlane Plant	133.6	133.6	133.6
Minnesota Steel Industries (MSI)	0.0	77.0	77.0
Mesabi Nugget	0.0	70.0	70.0
Total	**734.8**	**840.6**	**840.6**

Note: Keewatin Taconite had pollution-control equipment installed in Oct 2005, which reduced Hg emissions by 28% after 2005

Appendix II. Data for individual taconite processing furnaces where MTMCAC mercury control studies were performed.

Location	Minntac Line 3	Hibbing Taconite	ArcelorMittal	United Taconite	Keetac
Furnace type	Grate-Kiln	Straight-Grate	Straight-Grate	Grate-Kiln	Grate-Kiln
Pellet type	~8% flux	High compression	~11% flux	~1% standard	~1% flux
Binder for greenballs	Bentonite	Bentonite	Bentonite	Organic	Bentonite
Line used for testing	Line 3	Line 1	Line 1	Line 2	Line 2
Scrubber type	Re-circulating, Discards solids	Single-pass, Solids sent to Concentrator	Re-circulating Solids recycled	Re-circulating, Solids recycled	Re-circulating, Discards solids
Fuel	Natural gas and biomass	Natural gas	Natural gas	Natural gas and coal	Natural gas and coal
No. of stacks/line	1	4	4	2	1