

June 7, 2007

Dr. Michael E. Berndt  
Research Scientist III  
Minnesota Department of Natural Resources  
Division of Lands and Minerals  
500 Lafayette Road, Box 45  
St. Paul, MN 55155-4045

Dear Dr. Berndt:

Subject: Technical Report Entitled "Mercury Control Technologies for the Taconite Industry"; Agreement No. A85811; EERC Fund 9301

Please find enclosed the subject report. I have incorporated your comments into the final report for the project. Please distribute to the plants for their comments. I will be glad to incorporate any changes they feel are necessary. Please let me know as soon as possible if any changes are needed.

If you have any questions or comments, please contact me by phone at (701) 777-5138, by fax at (701) 777-5181, or by e-mail at [dlaudal@undeerc.org](mailto:dlaudal@undeerc.org).

Sincerely,

Dennis L. Laudal  
Senior Research Advisor

DLL/kal

Enclosure

# **MERCURY CONTROL TECHNOLOGIES FOR THE TACONITE INDUSTRY**

Technical Report

*Prepared for:*

Michael E. Berndt

Minnesota Department of Natural Resources  
Division of Lands and Minerals  
500 Lafayette Road, Box 45  
St. Paul, MN 55155-4045

Agreement No. A85811

*Prepared by:*

Dennis L. Laudal  
Grant E. Dunham

Energy & Environmental Research Center  
University of North Dakota  
15 North 23rd Street, Stop 9018  
Grand Forks, ND 58202-9018

June 2007

## **EERC DISCLAIMER**

LEGAL NOTICE. This research report was prepared by the Energy & Environmental Research Center (EERC), an agency of the University of North Dakota, as an account of work sponsored by the Minnesota Department of Natural Resources. Because of the research nature of the work performed, neither the EERC nor any of its employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement or recommendation by the EERC.

# TABLE OF CONTENTS

LIST OF FIGURES .....	ii
LIST OF TABLES .....	iii
1.0 INTRODUCTION.....	1
1.1 Project Objectives.....	2
1.2 Taconite Industry Background .....	2
2.0 MERCURY CONTROL TECHNOLOGIES BEING CONSIDERED FOR COAL-FIRED UTILITIES .....	5
2.1 Precombustion Technologies.....	5
2.2 Sorbent Technologies .....	6
2.3 Mercury Oxidation Technologies.....	14
3.0 POTENTIAL MERCURY CONTROL TECHNOLOGIES FOR THE TACONITE INDUSTRY .....	18
3.1 Precombustion Technologies.....	18
3.2 Sorbent Technologies .....	19
3.3 Oxidation Technologies.....	20
4.0 ECONOMICS OF MERCURY CONTROL FOR TACONITE PLANTS.....	24
5.0 RECOMMENDATIONS .....	26
6.0 REFERENCES.....	27

## LIST OF FIGURES

1	Mechanistic model for mercury capture by activated carbon .....	8
2	Mercury removal (%) vs. sorbent injection rate (lb/Macf) for tests at three sites.....	9
3	Mercury removal as a function of sorbent injection rate at a plant burning a PRB coal with an ESP .....	10
4	Mercury removal as a function of sorbent injection rate at a plant burning lignite with a FF.....	10
5	Mercury removal as a function of sorbent/additive injection rate at a plant burning a PRB coal with an ESP .....	11
6	Mercury removal at a plant with high (>30 ppm) SO <sub>3</sub> .....	12
7	Impact of SO <sub>3</sub> concentration on mercury removal.....	13
8	Proposed mechanism for Hg <sup>2+</sup> reduction to Hg <sup>0</sup> in a wet scrubber.....	14
9	Bench-scale tests using EPA's proprietary oxidant .....	17
10	Schematic of mercury testing at a straight-grate plant using NaCl.....	21
11	Schematic of testing at a grate kiln plant using NaCl .....	22
12	Schematic of testing for mercury at a straight-grate plant using bromine and chloride salts.....	23
13	Relative cost for mercury control technologies.....	26

## LIST OF TABLES

1	Summary of the Minnesota Taconite Plants .....	4
2	Mercury Concentrations at Power Plant Firing a High-Sulfur Eastern Bituminous Coal ..	15
3	Fate of Scrubber Materials .....	23
4	Distribution of Mercury in Scrubber Slurry .....	24
5	Summary of Costs Associated with ACI for Mercury Control at a Taconite Plant .....	25

# MERCURY CONTROL TECHNOLOGIES FOR THE TACONITE INDUSTRY

## 1.0 INTRODUCTION

Mercury is a naturally occurring element that is ubiquitous in the Earth's crust. However, both anthropogenic activities such as combustion and mining processes and natural sources such as volcanoes release mercury into the atmosphere. Through transport and deposition, some mercury enters the aquatic systems, resulting in an increase in mercury loading in fish. Over the past 15 years, there has been a concerted effort by national and state agencies to reduce mercury emissions from all sources. In 2005, the U.S. Environmental Protection Agency (EPA) issued the Clean Air Mercury Rule (CAMR) that for first time regulated mercury emissions from coal-fired power plants. In addition, a number of states, including Minnesota, are issuing mercury rules that would be more restrictive than those promulgated by EPA. As it became clear that EPA would eventually regulate mercury, the utility industry, the Electric Power Research Institute (EPRI), and the U.S. Department of Energy (DOE) began funding programs to develop and test potential mercury control technologies for coal-fired boilers.

Although utilities are the largest source of anthropogenic mercury, they are not the only source. States are also reviewing the potential of reducing mercury from these other sources as well. In Minnesota, one of these sources is the taconite industry. It has been estimated that these plants emit 250–350 kg of mercury per year into the atmosphere (1). In 2003, EPA stated “Since specific controls for mercury are not currently present in the industry and operating practices that effectively reduce mercury emission have not been identified, we are selecting no emission reduction as new source MACT” (2). This ruling was controversial, and there is continued pressure on the Minnesota Pollution Control Agency (MPCA) to potentially regulate mercury emissions from taconite plants.

As a result, the Minnesota Department of Natural Resources (MDNR) has been working with MPCA staff, taconite industry personnel, and several research laboratories, including the Energy & Environmental Research Center (EERC), to evaluate the sources, concentrations, chemistry, and potential control strategies for mercury from these facilities. This document is a direct result of these collaborations. In addition to visiting and touring each of the facilities discussed in this document, the EERC participated in frequent mercury research discussions between MDNR research staff and mining personnel. Moreover, the EERC was given full access to data as they were being generated by all of the groups involved in the MDNR research program. Beginning in July 2006, the EERC became an active participant in these studies by providing continuous mercury monitors (CMMs) to measure mercury in the stack gases during four plant-scale tests conducted at taconite-processing facilities. In this report, the EERC draws on its long history of mercury research at coal-fired utilities and its more recent experiences with the taconite industry to provide insights on the feasibility of transferring mercury control technologies between the two industries. The MDNR plant-scale tests for taconite facilities are also discussed briefly, but the results of those tests will be presented in more detail in a forthcoming MDNR report.

## **1.1 Project Objectives**

The overall goal of the project is to provide MDNR and the taconite industry with the information necessary to both assess the current state of mercury control technologies and define the mercury control strategies that are most applicable to the taconite industry. Specific objectives of the effort are to:

- Identify and describe mercury control technologies that are currently being considered for coal-fired electric generator plants.
- Collect and compile the relevant data from each of the taconite plants to aid in determining mercury control options.
- Assess to what degree each of the identified technologies may be applicable to the taconite industry.
- Assess potential balance-of-plant impacts that may occur as a result of installing a mercury control technology.
- Complete a preliminary economic evaluation for potential mercury control technologies that could reasonably be implemented.
- Determine the nature of any waste products that may be formed as a result of each potential control technology and the short- and long-term impacts of these waste products on the environment.
- Provide recommendations as to testing that may be necessary before permanent implementation of mercury control technology can take place. This may include laboratory testing and/or full-scale demonstrations.

## **1.2 Taconite Industry Background**

Six taconite facilities are located in Minnesota, as listed below:

- United States Steel (USS) Keewatin Taconite (Keetac) – located near Keewatin, Minnesota
- Hibbing Taconite Company (Hibtac)– located near Hibbing, Minnesota
- USS Minntac (Minntac) – located near Mountain Iron, Minnesota
- Mittal Steel Minorca Mine – located near Virginia, Minnesota
- United Taconite (U-Tac) – located near Eveleth, Minnesota
- Northshore Mining – located near Silver Bay, Minnesota

Taconite processing has two potential sources of mercury: mercury released from processing the ore and mercury released from the fuels used when the ore is processed. Unlike coal-fired utilities, the major source of mercury is not the combustion fuel but the processing of the ore into taconite pellets. Even for those facilities that fire coal, it only takes 20–30 lb of coal



to process 1 long ton (Lt) of green balls. The concentration of mercury in the unprocessed ore is related to the ore's geographical location in the Biwabik Iron Formation. The mercury concentration in the ore at the west end of the district is about 20 ppb and gradually increases eastward to a maximum of 32 ppb then decreases gradually to less than 1 ppb in the ore at Northshore (3). Although some of the information presented in this report may be relevant to Northshore Mining, this facility was not considered part of this study as the mercury concentration is very low.

Another difference between the two industries that could potentially impact the choice of mercury control technology is that all taconite facilities, with the exception of Northshore which has wet electrostatic precipitators (ESPs), utilize a wet venturi-type scrubber to control particulate matter emissions. This is compared to utilities, which most commonly have ESPs or fabric filters (FFs).

In addition to economic issues, a major constraint is that most taconite plants have severe space limitations that may preclude installing large sorbent injection systems, FFs, etc. At some sites, it may be possible to build these components outside of the existing plant. However, even installing the necessary ducting could be a problem for others.

Finally, taconite plants are much more market-driven than power plants. Depending on the worldwide supply and demand for steel, these plants are more susceptible to boom/bust cycles. Therefore, any mercury control technology selected must have a reasonable cost. If onerous mercury controls were required, economics may dictate closing the plant.

Although each plant is unique in its configuration and operation, there are several general factors that will determine the effectiveness of various mercury control strategies. These include the following:

- Type of induration – straight grate or grate kiln
- Mercury concentration and species generated in the process
- Recycle in the scrubber (both water recycle and recycling the collected dust material back to the processing facility)
- Type of pellets being manufactured – flux or acid pellets (flux pellets have limestone added to the pellets)
- Temperature in various zones of the process
- Fuel

Table 1 provides a summary for each of the plants.

**Table 1. Summary of the Minnesota Taconite Plants (1)**

Plant (line)	Line Type	Production, Lt/hr	Pellets	Fuel	Airflow Rate, kscfm
Minntac <sup>1</sup>					
3	Grate kiln	200–250	Acid	Natural gas	180–250
4	Grate kiln	400–450	Flux/acid	60% wood–40% natural gas	370–450
5	Grate kiln	400–450	Flux/acid	60% wood–40% natural gas	370–450
6	Grate kiln	400–450	Flux	PRB <sup>2</sup> coal	370–450
7	Grate kiln	400–450	Flux	PRB coal	370–450
Hibtac					
1	Straight grate	300–350	Acid	Natural gas	350–400
2	Straight grate	300–350	Acid	Natural gas	350–400
3	Straight grate	300–350	Acid	Natural gas	350–400
United Taconite <sup>3</sup>					
1	Grate kiln	200–250	Acid	Natural gas	180–250
2	Grate kiln	400–450	Acid	50%–50% petcoke–eastern bit.	450–600 <sup>4</sup>
Mittal Steel	Straight grate	350	Flux	Natural gas	350
Keetac <sup>5</sup>	Grate kiln	700	Acid	PRB coal	550–650

<sup>1</sup> Lines 1 and 2 are not operational.

<sup>2</sup> Powder River Basin.

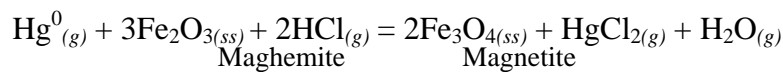
<sup>3</sup> Plant uses an organic binder to produce acid pellets.

<sup>4</sup> The plant has two waste gas fans.

<sup>5</sup> Scrubber adds lime to enhance SO<sub>2</sub> removal.

As stated earlier, all of the above plants have rod-type venturi scrubbers. The primary purpose of the scrubbers is to remove particulate matter. However, as is shown in Table 1, the new scrubber installed at Keetac was designed to reduce SO<sub>2</sub> by about 70% by adding lime to the slurry. Mittal, Hibtac, and Keetac also have multiclones to aid in reducing particulate matter.

During taconite processing, wet “green balls” consisting predominantly of magnetite and, possibly, other components (limestone flux, organic or bentonite binder, trace nonore components) are conveyed into a furnace and heated to approximately 1200°–1300°C in the presence of air. Data have suggested that magnetite is first converted to a magnetite/maghemite solid solution which attracts and collects mercury released from green balls deeper in the furnace (4). Mercury release occurs when magnetite and/or magnetite/maghemite solid solutions are heated past 450° or 500°C and converted to hematite. Wet scrubbers collect oxidized mercury (Hg<sup>2+</sup>) from flue gases, but not volatile Hg<sup>0</sup>(g). Wet scrubbers sometimes capture over 40% of the mercury released during induration, implying that extensive generation and transport of Hg<sup>2+</sup> can occur. On the other hand, scrubber efficiency can also be less than 10% for mercury, indicating that conditions needed for mercury oxidation are not always present. Plants having the highest capture rates for mercury also appear to have the highest Cl and particulate fluxes, suggesting a relationship such as the following controls mercury oxidation rates during induration:



## 2.0 MERCURY CONTROL TECHNOLOGIES BEING CONSIDERED FOR COAL-FIRED UTILITIES

Because of the likelihood of mercury regulations and subsequent promulgation of CAMR, the coal-fired electric utility industry has been the catalyst for most mercury control research. This section will define the technologies that are currently being considered for coal-fired boilers irrespective of their transferability to the taconite industry. Section 3.0 will discuss those technologies that would be applicable to the taconite industry. All mercury control technologies/strategies can then be grouped, based on maturity, into the following three main categories:

- *Commercially available technologies.* These technologies have been tested at the bench-, pilot-, and full-scale level and will be, or could potentially be, commercially available by 2009.
- *Commercially emerging technologies.* These technologies have been tested at the bench- and pilot-scale level and are currently being, or will be, demonstrated at the full-scale level during the next 1–3 years. Some of these technologies may be available by 2009, depending on test schedules and degree of technical and economic success.
- *Developing technologies.* These technologies are defined as those that have had only limited testing at the bench-scale or pilot-scale level but appear to have the potential for removing significant (>50% to 90%) mercury. It is not expected that sufficient demonstration of these technologies would be completed by 2009; therefore, they would not be commercially available until after 2010.

For utilities, mercury control can be accomplished in three fundamental ways:

- *Precombustion technologies.* This can be as simple as changing to a lower-mercury fuel or utilizing complex coal-cleaning techniques.
- *Sorbent technologies.* This strategy uses materials that will adsorb the mercury. The compounds can be injected into the flue gas (i.e., powdered activated carbon injection [ACI]) and then removed by a particulate collection device or utilized as part of a fixed-bed reactor.
- *Oxidation technologies.* These technologies take advantage of the fact that chemically reacted  $\text{Hg}^{2+}$  is water-soluble and readily removed by a wet scrubber. Therefore, by converting elemental mercury ( $\text{Hg}^0$ ) to  $\text{Hg}^{2+}$ , the wet scrubber will provide increased mercury removal.

### 2.1 Precombustion Technologies

Obviously, one method of reducing mercury from coal-fired power plants is to change to a fuel with lower or no mercury, such as natural gas or renewables. In general, in today's market, this is a very limited option or one economically unattractive for existing plants.

Coal cleaning for mercury control could be a very attractive option as it would have limited balance-of-plant impacts. Modifications would not be required for either the combustion process or emission control equipment. However, to date, no economically feasible process for consistently removing >50% of the mercury from all types of coals has been developed and commercialized. Generally, conventional coal cleaning has been limited to bituminous coals, and the process only removes, on average, about 30% of the mercury (5). Technologies have been tested on a limited basis that have the potential to remove >50% of the mercury; however, these technologies are clearly in the developmental stage and include the following:

- Magnetic separation
- Advanced froth flotation
- Selective agglomeration
- Chemical methods
- Biological methods

One precombustion technology that does show promise at the pilot-scale level and will be tested at the full-scale level in 2008 is the Western Research Institute's (WRI's) thermal treatment of coal (6). In this process, the fuel goes through two heating stages. In the first stage, the moisture in the fuel is driven off; in the second stage, coal is heated by nearly inert gas, resulting in significant removal of coal-bound mercury. The inert gas flow is an order of magnitude lower than the combustor flue gas and, hence, the stripping of mercury in the effluent streams becomes easier. The product coal is cooled and then directly fed into the boiler plant pulverizer. Preliminary tests have shown mercury removal of 60%–80%. It is expected that there will be significant reductions in  $\text{NO}_x$  as a cobenefit of the technology.

## 2.2 Sorbent Technologies

The most commercially advanced mercury-specific technologies are those using mercury sorbents, specifically ACI. The most important factor influencing the effectiveness of ACI to control mercury emissions resulting from coal combustion is the oxidation state of the mercury in the flue gas. Therefore, the effectiveness of ACI is related to the constituents in the flue gas, in particular, halogens,  $\text{SO}_3$ , temperature, and residence time. Based on the bench-scale work that has been completed, the following was concluded (7):

- Increasing temperature results in decreased equilibrium adsorption capacity.
- Physical adsorption is not the dominant mechanism, and based on the EERC model, chemisorption of  $\text{Hg}^{2+}$  to a basic site on the carbon is believed to be the binding site.
- Sorbent particle size determines the minimum sorbent mass requirement necessary to effect mass transfer from the bulk gas to sorbent particles.
- Any water vapor in flue gas decreases the equilibrium sorption capacity because of interactions with  $\text{NO}_x$  and  $\text{SO}_x$  species. Water vapor is always present, and there do not appear to be any concentration effects.

- Cl increases the reactivity of activated carbon for mercury.
- SO<sub>2</sub> in the absence of NO<sub>x</sub> reduces the equilibrium adsorption capacity dramatically for Hg<sup>0</sup> and mercuric chloride. The effect of a combination of SO<sub>2</sub> and NO<sub>2</sub> reduces the capture of Hg<sup>0</sup> even more severely.
- NO<sub>x</sub> (10% NO<sub>2</sub> and 90% NO) has an impact on Hg<sup>0</sup> capacity in the presence of SO<sub>2</sub> and HCl. The equilibrium sorption capacity of Hg<sup>0</sup> is minimal in the absence of both NO<sub>x</sub> and HCl, and it increases as NO<sub>x</sub> alone increases. In the presence of HCl, the capacity for Hg<sup>0</sup> drops as NO<sub>x</sub> increases. Bench-scale tests suggest that HCl and NO<sub>x</sub>/NO<sub>2</sub> can promote the oxidation and capture of Hg<sup>0</sup>, and little chemisorption capture appears to occur in the absence of mercury oxidation.
- The equilibrium sorption capacity for Hg<sup>0</sup> increases with increasing levels of oxidation occurring across the carbon test bed, as determined by changing the concentrations of HCl and SO<sub>2</sub>. This indicates that mercury oxidation is an essential step in capturing mercury on sorbents.

From the bench- and pilot-scale work completed, a heterogeneous model has been constructed to explain the activated carbon–Hg behavior in coal-fired flue gas shown in Figure 1 (8). Although mercury reactions are complex, essentially Hg<sup>0</sup> must first be catalytically oxidized by chloride ions and/or NO<sub>2</sub> on the basic carbon sites, thus resulting in mercury capture. Capture continues until the binding sites are used up and breakthrough occurs. However, in the presence of both SO<sub>2</sub> and NO<sub>2</sub>, compounds are formed which effectively blind the active sites, preventing long-term mercury capture. Although the mercury is no longer captured, the mercury that breaks through the carbon bed is no longer Hg<sup>0</sup> but Hg<sup>2+</sup>.

In 1999, DOE issued a request for proposal (RFP) to test mercury control technologies at the full scale. The near-term goal of the RFP was to evaluate technologies that could achieve 50%–70% mercury removal at a cost of less than three-quarters of the estimated cost of \$50,000–\$70,000/lb mercury removed. The longer-term goal was to develop technologies that could provide up to 90% control at a cost of half to three-quarters of ACI technology by the year 2010. Two projects were selected under this RFP:

- Scrubber enhancement – McDermott/Babcock & Wilcox (B&W)
- Activated carbon injection – ADA-ES

The projects were short-term (1–2 weeks) tests that were completed at several different plants. The McDermott/B&W project was to test several additives in attempt to prevent mercury reemission. This project is discussed in Section 2.3. The ADA-ES project was designed to test ACI at plants burning different coals and having different air pollution control equipment. The results of these tests are shown in Figure 2 (9). As was expected, the use of a FF with ACI at the Gaston Plant provided the best mercury removal at the lowest ACI rate. For the same type of coal (low-sulfur bituminous), much higher levels of activated carbon were needed

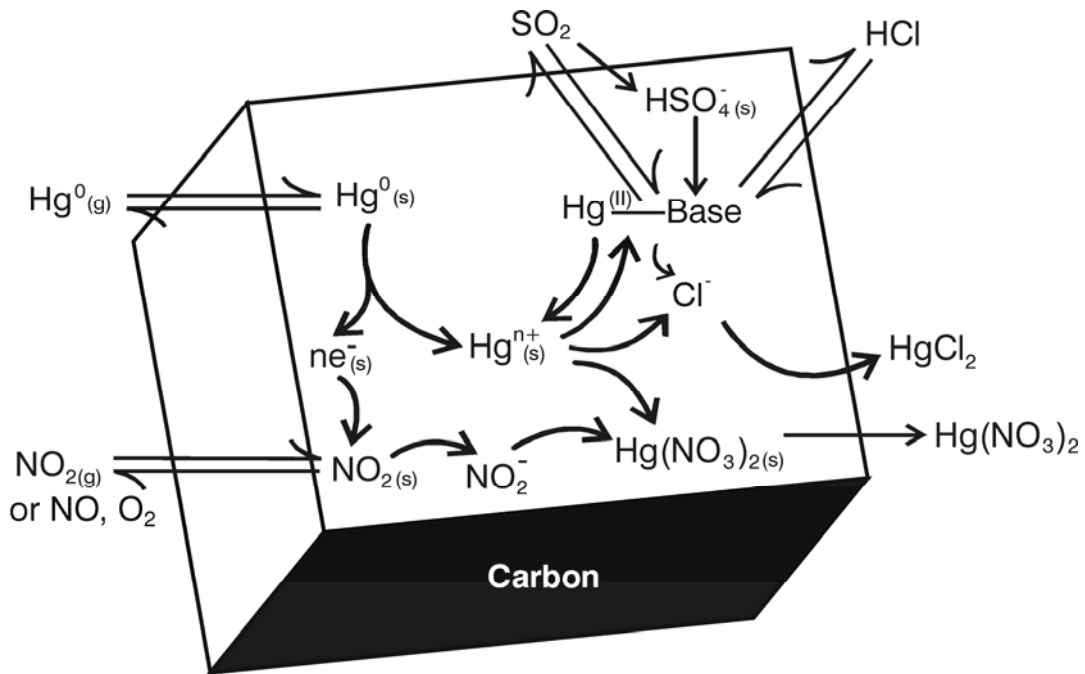


Figure 1. Mechanistic model for mercury capture by activated carbon (8).

to achieve the same level of control when only an ESP was present. For the PRB subbituminous coal with an ESP (Pleasant Prairie), the maximum mercury removal was 66%, regardless of the ACI rate. This clearly demonstrates the effect of fuel type and particulate control device on the effectiveness of ACI for mercury control.

Based on the Phase I results, it appeared that mercury control was going to be more problematic for western lower-rank fuels, lignites, and PRB subbituminous coals. In general, lignites and PRB coals contain significantly lower levels of chlorine and have a much higher concentration of alkali components compared to bituminous coals. As a result, most of the mercury generated is in the form of  $Hg^0$ , which is more difficult to remove. A major focus of DOE Phase II projects was to improve mercury control for these low-rank fuels. Under the Phase II program, the following projects were selected:

- Evaluation of Sorbent Injection for Mercury Control – ADA-ES
- Amended Silicates for Mercury Control – Amended Silicates
- Sorbent Injection for Small ESP Mercury Control – URS Group
- Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems – URS Group
- Evaluation of MerCAP for Power Plant Mercury Control – URS Group

- Enhancing Carbon Reactivity in Mercury Control in Lignite-Fired Systems – EERC
- Mercury Oxidation Upstream of an ESP and Wet FGD – EERC
- Advanced Utility Mercury-Sorbent Field-Testing Program – Sorbent Technologies

Of these projects, five are attempts to improve mercury capture using various sorbents at plants burning low-rank fuels, including using treated carbons and various additives to improve mercury control. The results of these demonstration programs (Figures 3 and 4) showed that the most effective control methods were to use brominated activated carbon (B-pac from Sorbent Technologies or DARCO Hg-LH from NORIT Americas) or halogenated additives with ACI (9). Although a higher level of mercury control can be achieved at lower ACI rates when a FF is present (Figure 3), a high level of control at reasonable rates can also be achieved with only an ESP when brominated carbons are used (Figure 2).

Rather than using treated carbons, the same improved mercury control was also achieved by using chemical additives with ACI. This provides for more flexibility in that the injection rates of one or both can be controlled. Parametric results for a plant burning a PRB coal with only an ESP are shown in Figure 5 (10). The results shown are similar to those obtained using the treated carbon (Figure 2).

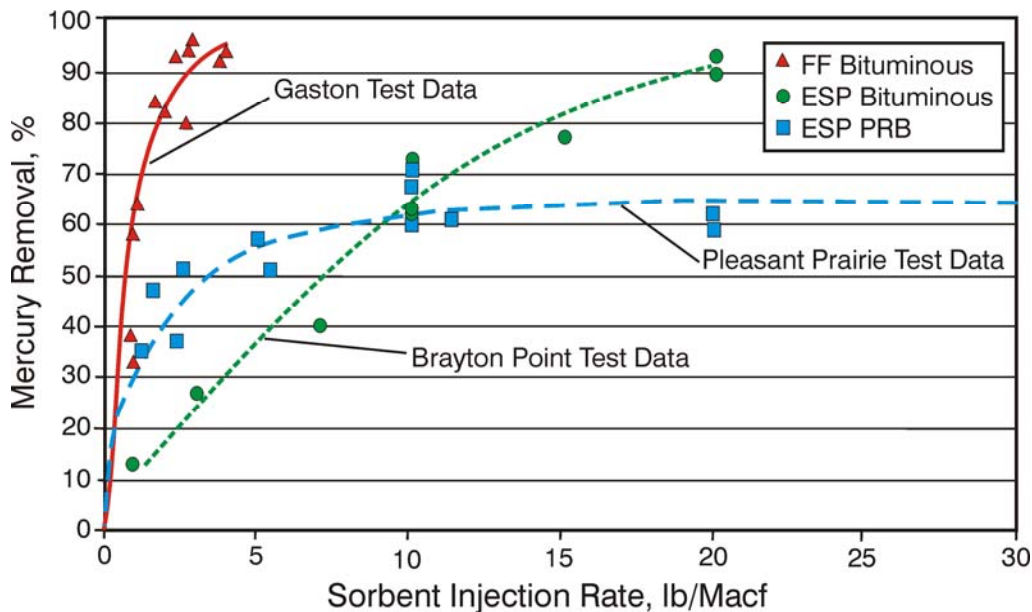


Figure 2. Mercury removal (%) vs. sorbent injection rate (lb/Macf) for tests at three sites (9).

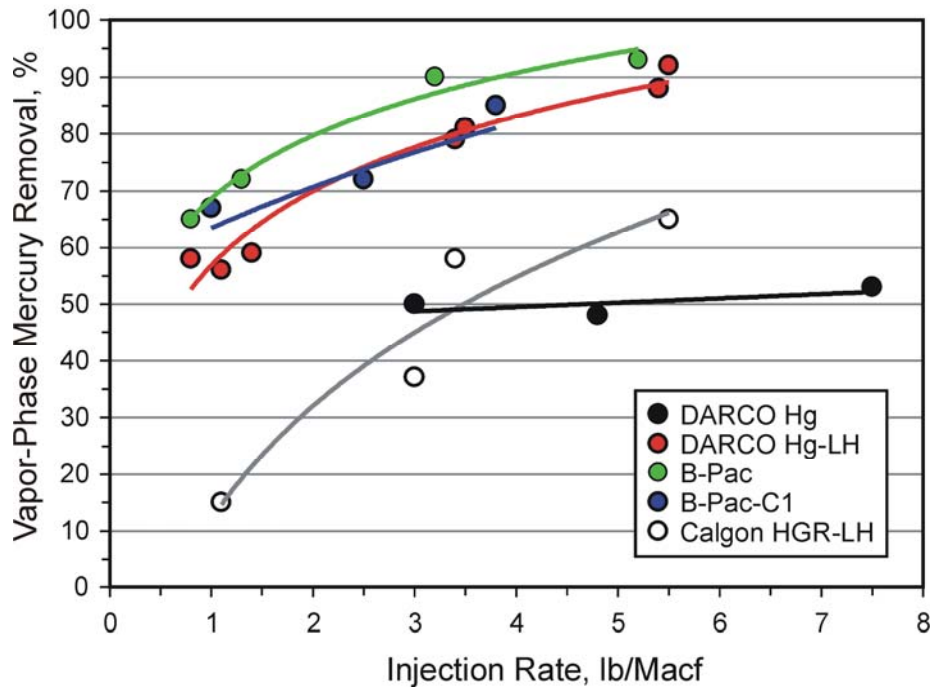


Figure 3. Mercury removal as a function of sorbent injection rate at a plant burning a PRB coal with an ESP (9).

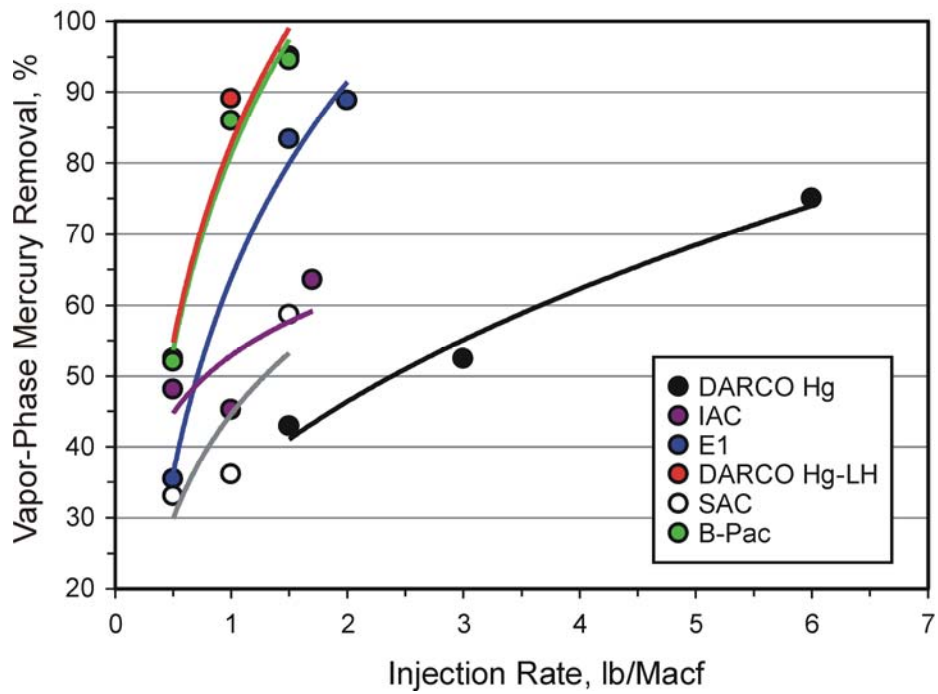


Figure 4. Mercury removal as a function of sorbent injection rate at a plant burning lignite with a fabric filter (9).



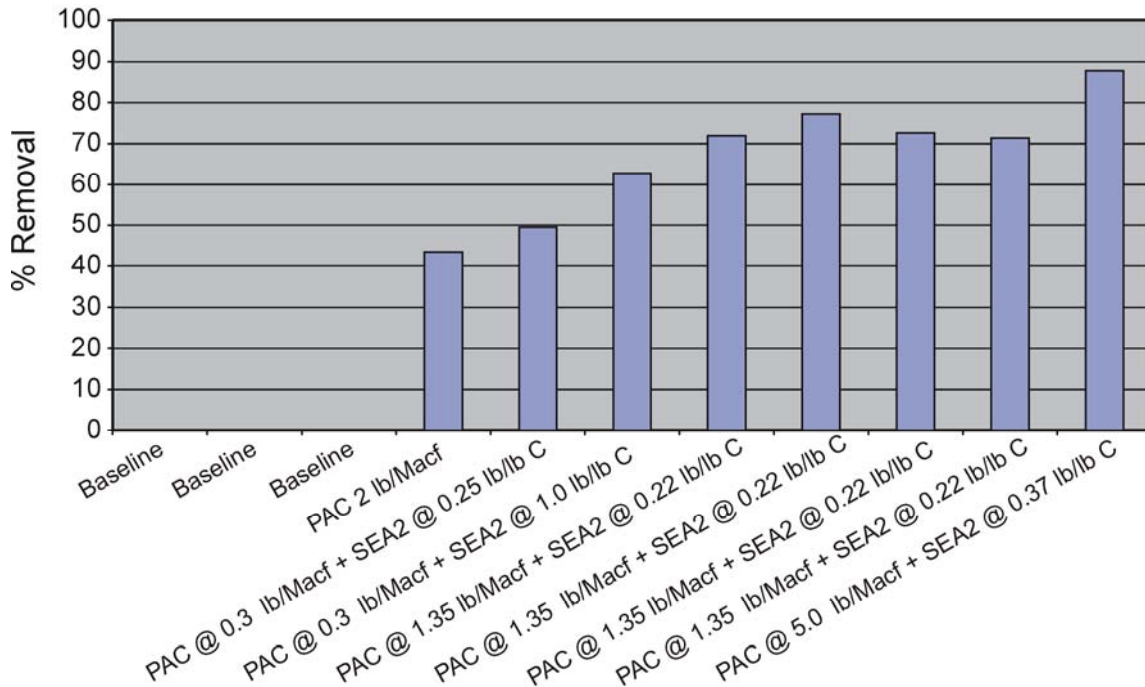


Figure 5. Mercury removal as a function of sorbent/additive injection rate at a plant burning a PRB coal with an ESP (10).

A wide range of non-carbon-based materials have also been tested at the bench-scale level to determine if they are effective in removing mercury. A partial list of these sorbents includes the following:

- Sodium tetrasulfide ( $\text{Na}_2\text{S}_4$ )
- Amended silicates
- Calcium-based sorbents
- Zeolites
- Metal oxide-based sorbents

Although none of these materials are expected to provide substantially better mercury control over carbon-based sorbents, because carbon can limit the resale of fly ash, the materials may find a market at some point in the future.

From the Phase II results it is expected that 80%–90% mercury control can readily be achieved for plants burning low-rank fuels using brominated carbons or halogen additives with ACI. However, it has been found that for high-sulfur eastern bituminous coals achieving a high level of mercury control may be exceedingly difficult. It has been shown that  $\text{SO}_3$  greatly decreases the removal efficiency of carbon-based sorbents. As shown in Figure 6, there is at best only a 25%–35% improvement in mercury removal over baseline conditions even using brominated carbons (11). Figure 7 shows that even at low  $\text{SO}_3$  concentrations there is an impact on mercury removal (11). Current mercury control research is focusing on methods on minimizing the impact of  $\text{SO}_3$  on ACI.

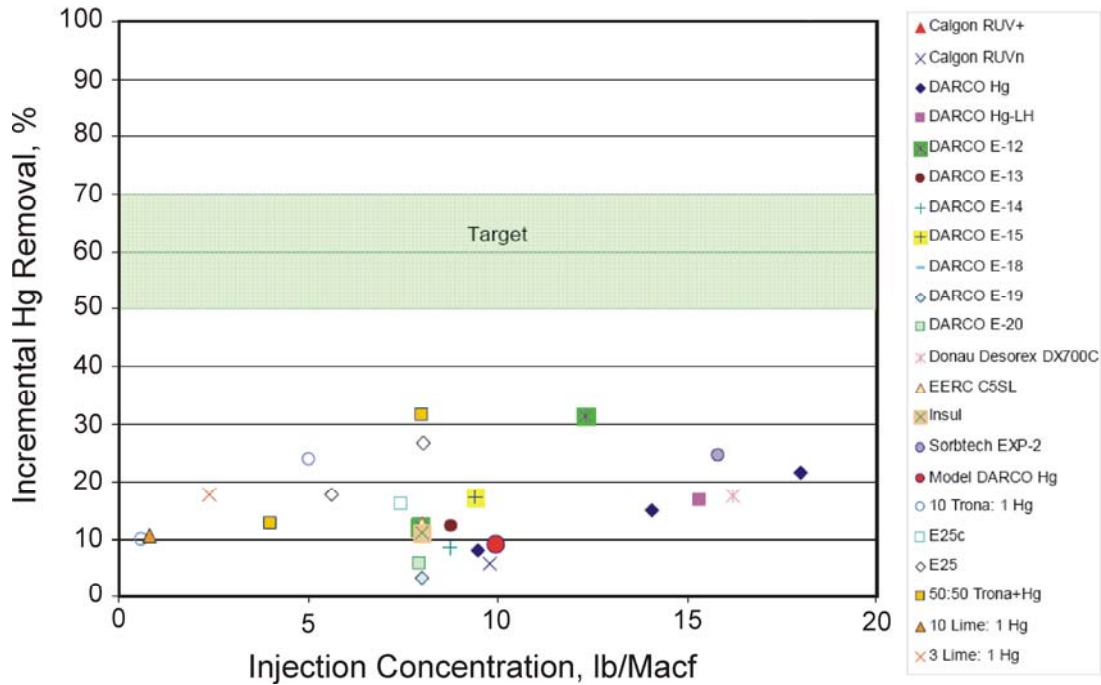


Figure 6. Mercury removal at a plant with high (>30 ppm) SO<sub>3</sub> (11).

Rather than injecting a sorbent into the flue gas, a fixed-carbon reactor can also be used. These systems have been extensively used for mercury control for waste-to-energy systems, particularly in Europe (12). Carbon filter beds have also been used in power plants in Germany since the late 1980s. The primary purpose of these filters is to remove residual SO<sub>2</sub> downstream of a wet flue gas desulfurization (FGD) system and to prevent ammonium sulfate formation in the low-dust selective catalytic reduction (SCR) units. Although not the primary purpose, reduction of mercury is inherent to the control system. A mercury level below 1 µg/dscm has been guaranteed by one vendor (typical power plants have uncontrolled mercury emissions of 5–10 µg/m<sup>3</sup>).

The most common type of system is the cross-flow filter. In this design, the flue gas flows horizontally through the filter bed. Typically, each filter bed module contains three layers with a total thickness of about 1 meter. Each layer is separated by perforated plates. Fresh carbon is conveyed to and distributed within the bed by a screw conveyor on top of the bed. Discharge cylinders at the bottom allow extraction of carbon from each layer. Pressure drop is usually the parameter that determines the rate of carbon removal. Typically, the pressure drop across the whole system is 305 mm of water (12 inches). Based on typical removal rates, the whole carbon bed is replaced approximately once a year. Note that the bed replacement rate could be expected to increase in the absence of a wet FGD system.

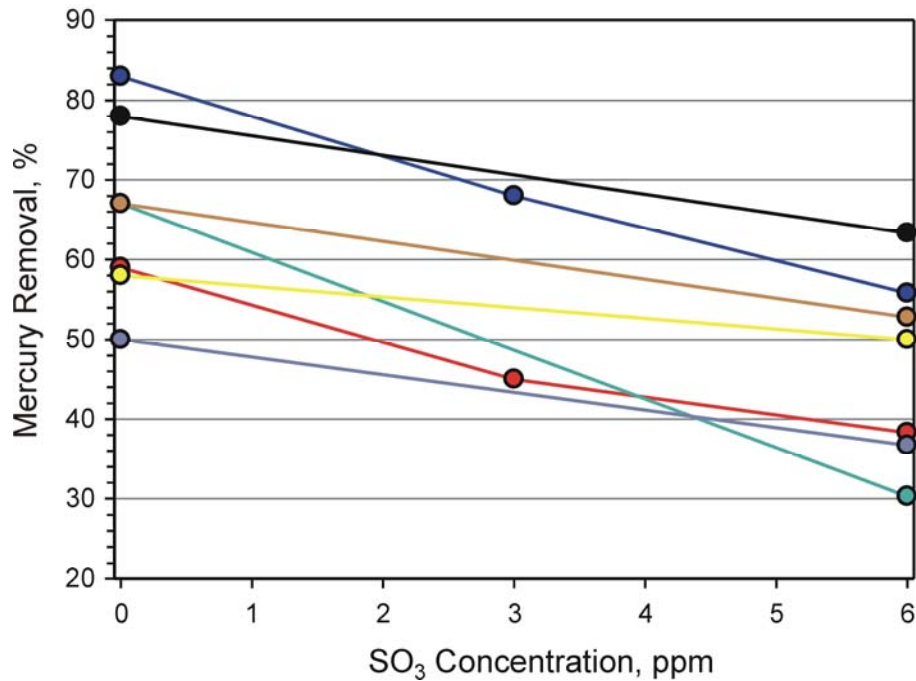


Figure 7. Impact of SO<sub>3</sub> concentration on mercury removal (11).

The primary advantages of a fixed-carbon bed are as follows:

- It is much more flexible, because the mercury removal efficiency does not depend on the type of particulate control device.
- There is the possibility of regenerating the sorbent, reducing costs.
- With a wet FGD system and a fixed-carbon bed, very high mercury removals (>90%) can potentially be achieved. At temperatures typically encountered following a wet FGD, carbon has a high affinity for mercury.

However, there is a strong aversion to widely installing these types of systems on coal-fired electric utilities for the following reasons:

- Flue gas flow rates for utilities are an order of magnitude greater than typical waste-to-energy facilities. This requires substantially more space, and coal-fired utilities are often space-limited.
- Small additional pressure drop is very costly to a large utility.
- To prevent desorption of mercury, a very high level of SO<sub>2</sub>, NO<sub>x</sub>, and HCl control must be accomplished or the bed replacement rates would need to be increased.

### 2.3 Mercury Oxidation Technologies

$\text{Hg}^0$  is insoluble, and little if any is removed by wet scrubbers. Therefore, technologies that can result in a higher percentage of the mercury reaching the wet scrubber as  $\text{Hg}^{2+}$  will provide a greater level of control, but there is a caveat: it must stay captured. There are two primary methods of improving wet scrubber mercury removal efficiency. The first, as mentioned above, is to provide a higher concentration of  $\text{Hg}^{2+}$  to the scrubber by using a mercury oxidation technology. The second is to ensure that once mercury is captured by the wet scrubber, it remains captured and not reemitted.

Up until the late 1990s, it was assumed that  $\text{Hg}^{2+}$  was effectively captured by wet scrubbers (>90%), but it was observed that in a number of cases mercury removal was less than expected based on the concentration of  $\text{Hg}^{2+}$  measured at the inlet to the scrubber. In addition, the concentration of  $\text{Hg}^0$  at the scrubber outlet was greater than the scrubber inlet. Initially, this was assumed to be a bias in the measurement because of particulate matter collecting on the filter. This was not the case, however, as it was shown that, depending on scrubber conditions, some of the captured  $\text{Hg}^{2+}$  can be reduced in the scrubber to  $\text{Hg}^0$  and reemitted (13). These mercury reduction reactions are very complex and are not fully understood. A proposed mechanism was developed by URS Corporation and is shown in Figure 8 (14).

An extreme example of reemission is shown in Table 2. The data was generated from a plant burning a high-sulfur bituminous coal that had an SCR, ESP, and wet scrubber. Based on

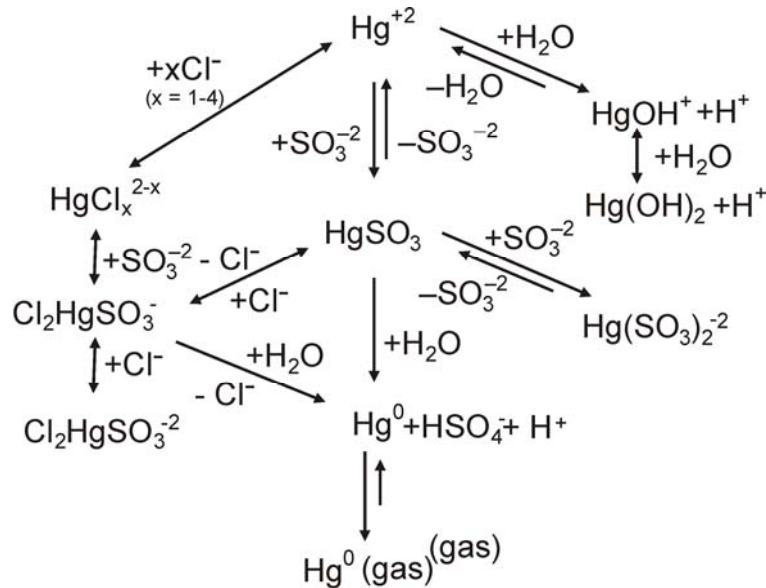


Figure 8. Proposed mechanism for  $\text{Hg}^{2+}$  reduction to  $\text{Hg}^0$  in a wet scrubber (14).

**Table 2. Mercury Concentrations at a Power Plant Firing a High-Sulfur Eastern Bituminous Coal\***

Sample Location	SCR Inlet, $\mu\text{g}/\text{Nm}^3$	SCR Outlet, $\mu\text{g}/\text{Nm}^3$	Wet FGD		Reduction, %
			Inlet, $\mu\text{g}/\text{Nm}^3$	Stack, $\mu\text{g}/\text{Nm}^3$	
Hg <sup>p</sup>	0.02	0.03	0.00	0.00	
Hg <sup>0</sup>	8.32	2.83	0.33	3.97	
Hg <sup>2+</sup>	0.94	5.05	7.60	0.54	
Hg <sub>total</sub>	9.27	7.90	7.93	4.50	43.3

\* All data are corrected to 3% O<sub>2</sub>.

the percentage of Hg<sup>2+</sup> at the wet FGD inlet (>95%), it would be expected the scrubber would provide a very high level of mercury removal, but only 43.3% was removed as a result of mercury reemission as Hg<sup>0</sup>.

As mentioned in Section 2.2, one of the technologies selected under DOE's Phase I program was a project proposed by McDermott/B&W to enhance wet scrubber performance by reducing mercury reemission. Tests were conducted at two different power plants. One had a forced oxidation scrubber, and the other had a magnesium/lime scrubber. McDermott/B&W sprayed a sulfide-containing salt (potassium sulfide, sodium sulfide, and thioacetamide) into the scrubber, which greatly reduced the reemission from the forced oxidation scrubber but had little impact on the magnesium–lime-based scrubber. Since that time, other additives have been studied for preventing mercury reemission from the scrubbers. These include Degussa's TMT-15 additive (15), chelating agents such ethylenediaminetetraacetic acid (EDTA), solid oxides such as aluminum, magnesium and iron oxides, and vanadium pentoxide (16).

The second method for improving mercury removal in a wet scrubber is to use additives or catalysts to increase the concentration of Hg<sup>2+</sup> in the gas stream or in the scrubber slurry. Any technology that can result in a higher percentage of the mercury reaching the wet scrubber as Hg<sup>2+</sup> will improve the overall mercury removal efficiency of the system. The following is a list of technologies that have been tested at least at the pilot scale:

- Addition of additives including halogenated compounds
- MercOx process
- Multipollutant control technologies
  - BOC LoTOx™
  - ECO™/PowerSpan
  - EnviroScrub Pahlman™ Process
  - EPA's Multipollutant Scrubber for SO<sub>2</sub>, NO<sub>x</sub>, and Hg control
  - Airborne Process – sodium bicarbonate scrubbing
- PCO™ Process

- Catalytic oxidation
  - SCR
  - Low-temperature catalytic oxidation (metal oxides and noble metals)

As part of a DOE test program, the EERC sprayed a 30% solution of  $\text{CaCl}_2$  onto North Dakota lignite. Full-scale results showed a decrease in  $\text{Hg}^0$  from 82% to 65% as a result of adding the equivalent of 500 ppm chloride in the coal (17). At another North Dakota plant, the EERC added a proprietary additive (SEA2) to the coal. The result of injecting this additive was an increase in mercury removal by the wet scrubber from near zero to 45% at an add rate of 100 ppm (10). As was discussed previously, these additives are also being used in conjunction with ACI with very high levels of mercury removal being achieved, particularly for low-rank coals.

A process is being successfully developed in Germany called the MercOx process (18). The process is designed to convert  $\text{SO}_2$  to sulfuric acid and  $\text{Hg}^0$  to  $\text{Hg}^{2+}$ . To do this, the MercOx utilizes hydrogen peroxide to oxidize  $\text{Hg}^0$  in a specialized scrubber. The scrubber is a packed tower, and flue gas is passed counter to the scrubber liquid (water and hydrogen peroxide). Using a proprietary additive, the mercury is precipitated out as  $\text{HgS}$ .

The multipollutant control systems are complex and expensive as they are designed to control  $\text{NO}_x$ ,  $\text{SO}_2$ , and mercury emissions. Of the three systems listed above, the most commercially advanced system is the PowerSpan reactor (19). A full-scale system is currently being installed at a utility. The PowerSpan process generates high-energy electrons that initiate chemical reactions that lead to the formation of oxygen and hydroxyl radicals.  $\text{Hg}^0$  vapor is oxidized to form  $\text{HgO}$ , which is removed by the wet scrubber/wet ESP.

The BOC LoTOx system is a  $\text{NO}_x$  removal system that injects ozone into the flue gas stream to oxidize insoluble  $\text{NO}_x$  to soluble oxidized compounds (20). The mercury removal is achieved by oxidizing  $\text{Hg}^0$  with ozone to produce soluble  $\text{HgO}$ , which is captured in a downstream wet scrubber. The process is very effective for  $\text{NO}_x$  but the reactions between ozone and mercury are relatively slow and, therefore, the mercury removal is low.

The EnviroScrub Pahlman process uses a regenerated manganese compound to adsorb  $\text{SO}_2$  and  $\text{NO}_x$ . The technology consists of a single-stage, dry system that essentially replaces the wet FGD for  $\text{SO}_2$  scrubbing, SCR for  $\text{NO}_x$  removal, and ACI for mercury reduction (21). High capture percentages coupled with the single-stage capabilities of the system make the technology attractive compared to the standard alternatives of wet FGD, SCR, and ACI systems. Mercury control results from slipstream testing at the Minnesota Power Boswell Station and at Detroit Edison's River Rouge Plant show mercury removals of  $\text{Hg}^0$  were achieved up to 99%. Total mercury removals of 94% were also obtained.

The work that is being done by EPA is interesting in that it utilizes a typical lime-based wet scrubber but uses a proprietary oxidant that is added to the scrubber solution to ensure that a high percentage of the mercury is oxidized and that reemission is prevented (22). Bench-scale results are shown in Figure 9. This process is currently being tested at the pilot-scale level.

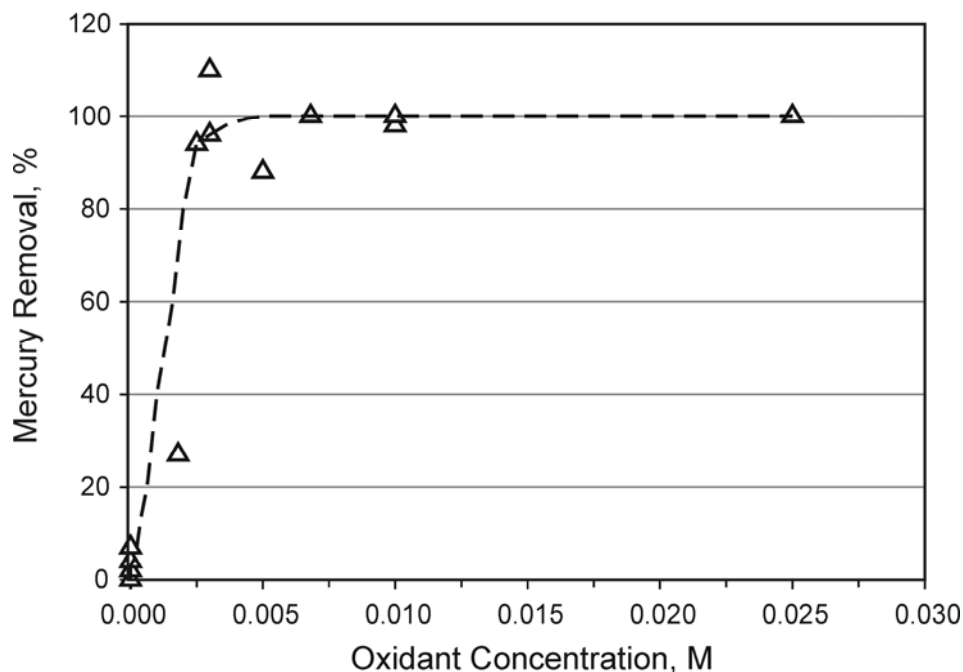


Figure 9. Bench-scale tests using EPA's proprietary oxidant (22).

Airborne Pollution Control's Airborne Process is an advanced pollution control process that employs a sodium bicarbonate scrubbing solution for combined  $\text{NO}_x$ ,  $\text{SO}_x$ , mercury, and particulate emission reduction. The sodium bicarbonate-based scrubbing is used in conjunction with Airborne's process for the regeneration of the sodium bicarbonate reagent and the production of a high-grade fertilizer by-product. The process has been demonstrated at the 5-MW scale (500 lb/hr of sodium bicarbonate) at Kentucky Utilities' Ghent Generating Station (Ghent, Kentucky), which burns a high-sulfur coal (23). The scrubbing agent was sodium bicarbonate, and the effluent from the oxidizer was predominantly a 20% aqueous solution of sodium sulfate. The regeneration system used ammonium bicarbonate to convert the sodium sulfate into sodium bicarbonate. Mercury control at Ghent depended on the mercury speciation. Particulate mercury was collected in the ESP, and  $\text{Hg}^{2+}$  was captured in the wet scrubber, as would be expected. Airborne is further investigating the use of an oxidant to convert  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  for improved total mercury capture. The fate of mercury during the regeneration process has not been reported.

The DOE National Energy Technology Laboratory (NETL) has developed a technology to photochemically oxidize mercury in coal-fired power plants. The process is intended to serve as a low-cost mercury oxidation technology that will facilitate  $\text{Hg}^0$  removal in a downstream scrubber, wet ESP, or FF. PowerSpan Corporation has licensed the technology and has completed bench- and small-scale pilot testing (24). The technology uses 254-nanometer ultraviolet light to produce an excited mercury species state in the flue gas, leading to oxidation of  $\text{Hg}^0$ . Bench-scale testing has indicated that oxidation levels of 86% to 91% can be achieved

using 100%  $Hg^0$  in a simulated flue gas. The technology is in the early stages of development, and the following issues must still be addressed:

- The practicality of using this approach on very large ducts is uncertain.
- How to maintain a long ultraviolet (UV) path length in a flue gas with ash.
- The fate of the mercury within the scrubber or wet ESP.

Metal oxides have been known to be effective for  $SO_2$  and  $NO_x$  control (25). SCR of  $NO_x$  using vanadium/titania catalysts has been shown to be an effective method of enhancing mercury oxidation for eastern bituminous coals (26, 27), thereby improving overall mercury capture in wet FGD systems. It appears that the chloride concentration in the flue gas is an important factor. It was thought that other metal oxides may have some potential for oxidizing or removing mercury as well. Although mercury breakthrough occurs very rapidly when acid gases, HCl,  $SO_2$ , and  $NO_x$  are present, the mercury is nearly 100% oxidized. Metal oxides that have been evaluated include copper, iron, manganese, zinc, and titanium. Noble metals that have been used include gold, palladium, and silver. A slipstream pilot-scale catalytic reactor is currently being tested at five sites (28), including plants burning lignites from North Dakota and Texas, a PRB site, and a site firing an eastern bituminous coal. Depending on the coal type, 50% to 80% mercury oxidation was achieved using noble metal catalysts. These materials are expensive; therefore, to be cost-effective, they must be regenerated.

### **3.0 POTENTIAL MERCURY CONTROL TECHNOLOGIES FOR THE TACONITE INDUSTRY**

There are significant differences between the different taconite facilities and even within lines at the same facility that may impact mercury emissions. As previously stated, the mercury content in the ore is related to the geographic location of the mine. Also, depending on the plant, either a “straight grate” or “grate kiln” operation is used. The fuel to provide the energy for the induration process varies from plant to plant. The primary fuel is either natural gas or coal, but some plant lines use biomass and petroleum coke. Therefore, as is the case for coal-fired power plants, most likely there will not be one technology to fit all plants to reduce mercury emissions.

#### **3.1 Precombustion Technologies**

It is highly unlikely that precombustion technologies used for coal (i.e., coal cleaning) will be useful to the taconite industry. Any coal cleaning will have limited value, as the mercury in the coal accounts for only a minor portion of the total mercury emissions. The magnetic separation techniques currently used by the taconite industry to process the ore already remove >80% of the mercury from the raw ore (3). If the overall efficiency of the milling process can be improved, it would not only increase plant efficiency but may also reduce mercury emissions.



### 3.2 Sorbent Technologies

Using sorbents to remove mercury from the gas stream is a technology that will need to be considered for the taconite industry. Using powdered activated carbon (PAC) or treated PAC injection has several advantages:

- Because mercury control is being done after induration, nothing is added to the pellet-making process to interfere with the iron chemistry, including the initial magnetic separation step, making the green balls, and the induration process.
- To a great degree the effectiveness of the sorbents would be independent of type of furnace, straight grate or grate kiln.
- The technology has been tested extensively for coal-fired systems so the mercury/sorbent chemistry is reasonably well known.
- With the exception of the injection lances, no additional ductwork would be necessary, and the equipment (PAC silo and feeder) could be placed outside of the process building.
- All equipment can be purchased directly from vendors and is very reliable. Depending on the amount of carbon used the annual labor cost for operating and maintaining the equipment can be quite low.

The disadvantages of PAC or treated PAC injection for taconite plants are as follows:

- Although several plants do have multicyclones, the primary particulate control device for the taconite industry is a wet scrubber. Although it is expected that 50%–60% mercury control can be achieved with PAC, all of the removal will be in-duct capture. This will increase the amount of PAC needed to achieve the same level of control as would be the case when an ESP or FF is present. The greater distance upstream of the scrubber the PAC is injected, the better (greater residence time).
- Because of the high-level concentrations of  $\text{Hg}^0$  generated at taconite plants, more expensive treated (brominated) carbons may be needed to achieve the desired mercury control at a reasonable cost. The long-term balance-of-plant impacts with these materials is still unknown.
- If a plant is currently concerned about particulate emissions, additional carbon could exacerbate the problem.
- Some plants recycle scrubber solids in the manufacture of the green balls to improve overall iron utilization. Most likely wastewater streams would need to be rerouted to prevent the captured mercury from recycling back to the furnace.

- To ensure good distribution of the PAC, a flow profile of the duct will be needed, and it may be necessary to do modeling of the flow to determine the proper location of the lances.

As an option to using PAC injection, a fixed-bed sorbent reactor could be considered for taconite plants. Almost all the disadvantages of PAC injection no longer pertain:

- The fixed-bed sorbent reactor is much more flexible because the mercury removal efficiency does not depend on the type of particulate control device.
- There is the possibility of regenerating the sorbent, reducing costs.
- With a wet FGD system and a fixed-carbon bed, very high mercury removals (>90%) can potentially be achieved. At temperatures typically encountered following a wet FGD, carbon has a high affinity for mercury.
- Increased particulate emissions would not be a problem.
- There is no impact on the scrubber or recycle of solids.
- There are vendors who currently supply fixed-bed reactors for mercury control.

The disadvantages are as follows:

- A fixed-bed reactor would add 8–14 in. H<sub>2</sub>O pressure drop, possibly requiring additional fan power.
- The fixed-bed reactor capital costs will be higher than these PAC injection systems.
- The fixed-bed reactor would require duct modification. Most likely, because of space limitations, the fixed-bed reactor would need to be housed in a separate building located near the process plant. Therefore, additional duct work will be needed from the scrubber to the stack.

Another option that would allow for more flexibility and increased particulate control would be to install a pulse-jet baghouse either in addition to the wet scrubber or as a replacement. Most likely a high level of mercury control could be achieved with a relatively low amount of sorbent. A FF provides an excellent contacting surface for mass transfer for mercury to the carbon. This would be the most expensive option both in capital investment and operating costs. However, if a new plant were to be built, it should be considered a viable option.

### **3.3 Oxidation Technologies**

As all taconite plants have scrubbers for particulate control, it clearly would be advantageous to increase the percentage of Hg<sup>2+</sup> or particulate-bound mercury at the inlet to the

scrubber. The number of mercury oxidation technologies that could be considered for use within the taconite industry is rather limited. Most likely, multipollutant control technologies that increase  $Hg^{2+}$  such as SCRs and ECO™/PowerSpan would not be considered economically viable for the taconite industry. Therefore, the most likely candidates are the addition of chemical additives. Chemical additives that may have potential are as follows:

- Sodium and calcium chloride
- Sodium and calcium bromide
- Hydrogen peroxide
- EPA’s proprietary oxidant
- EERC’s proprietary additive
- Ozone
- Sodium bicarbonate

Beginning in July 2006, MDNR, in collaboration with the EERC and Coleraine Minerals Research Laboratory began conducting plant-scale and bench-scale tests at taconite facilities to evaluate the viability of several of these oxidation technologies. Limited testing has been done with chloride and bromide salts, hydrogen peroxide, and EPA’s proprietary oxidant.

Plant tests were completed at United Taconite (grate kiln) and Hibtac (straight grate), evaluating the impact of adding sodium chloride both directly to the green balls as a solid and adding it as solution to the firing zone at Hibtac and to the kiln at United Taconite. A schematic of the tests is shown in Figures 10 and 11. The results of these tests were somewhat

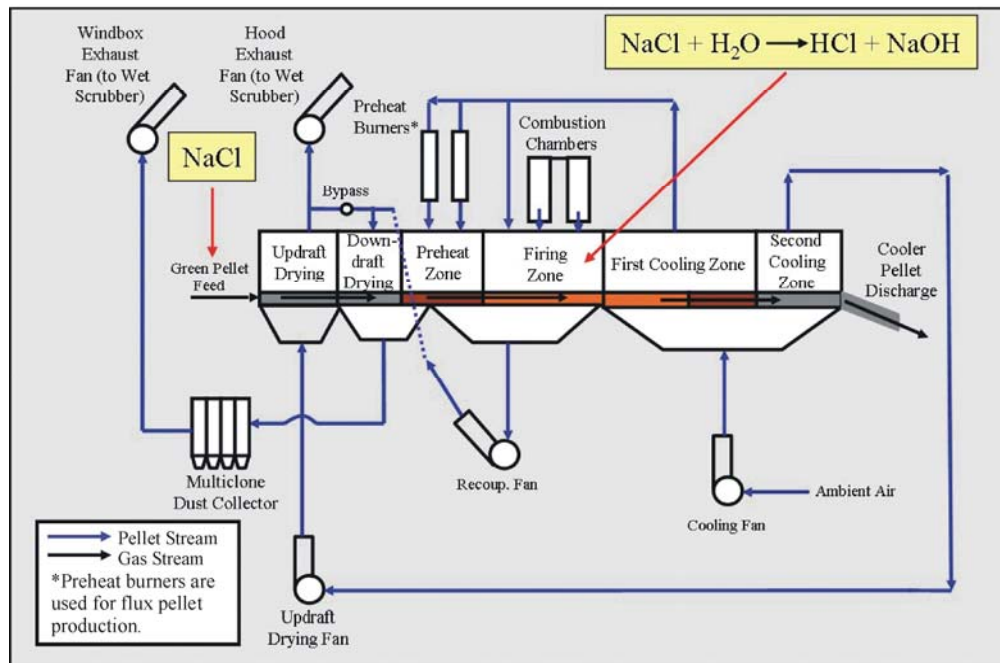


Figure 10. Schematic of mercury testing at a straight-grate plant using NaCl (29).

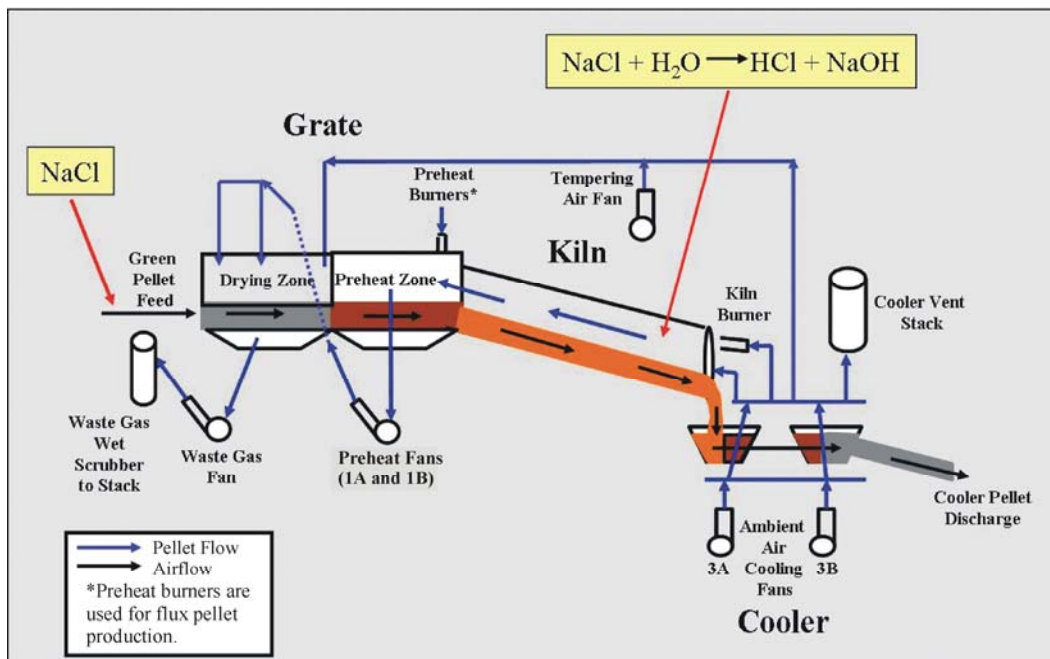


Figure 11. Schematic of testing at a grate kiln plant using NaCl (29).

disappointing at Hibtac but more promising at United Taconite (29). A major difference was that Hibtac had a straight grate compared to a grate kiln at United Taconite. It was believed that in the straight grate most of the mercury is liberated from the ore in the preheat zone (~1500°F).

Additional tests were later conducted at Hibtac where bromine and chloride salts were added as a solution in the preheat zone as shown in Figure 12 (29). The results from these tests showed nearly 70% mercury removal. The results of all tests will be presented in more detail in a report by MDNR.

Bench-scale tests using hydrogen peroxide and EPA’s proprietary oxidant in a simulated wet scrubber were also completed by MDNR. The results indicated that hydrogen peroxide did not work well but the EPA oxidant was very promising. It does appear that using additives to increase mercury oxidation and subsequent capture in the scrubber is a promising technology for the taconite industry. However, the overall impact of chemical additives on the induration process is very much an unknown, and additional testing is needed.

Based on the configuration of the taconite plants, high concentration of  $\text{Hg}^0$  in the gas stream, and gas temperature, EERC proprietary additive has the potential to provide a high level of mercury oxidation and be very cost-effective. In addition, the additive can be injected almost anywhere in the system, resulting in minimal plant impacts.

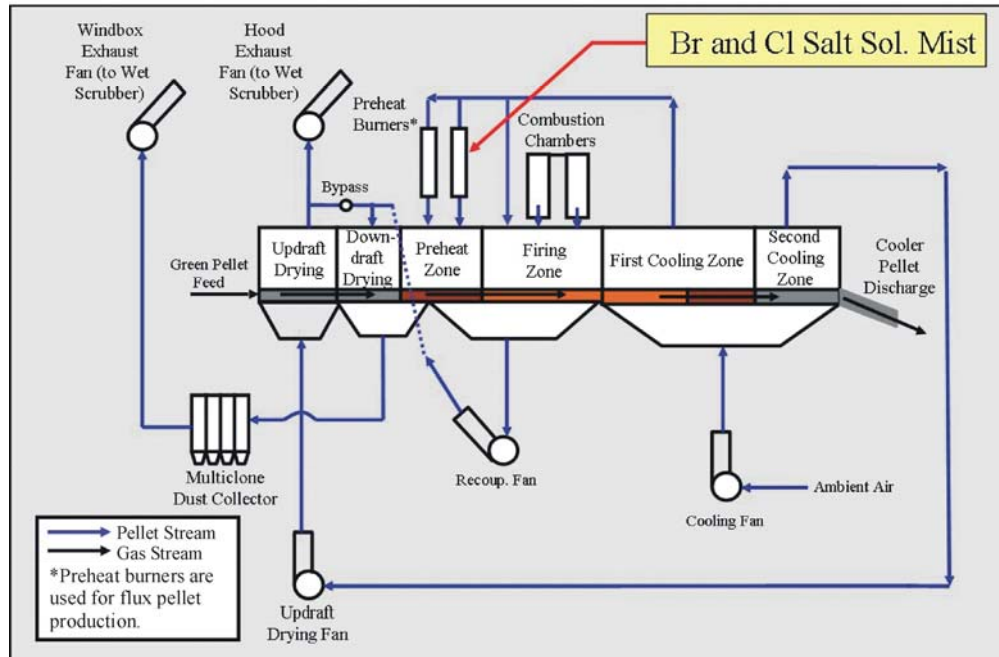


Figure 12. Schematic of testing for mercury at a straight-grate plant using bromine and chloride salts (29).

Another possibility is to use halogenated additives (or potentially others) in conjunction with ACI. By adding small amounts of these additives, the effectiveness of the PAC may be greatly enhanced, resulting in decreased costs. There are several concerns using chemical additives to enhance mercury oxidization. The first is that many of the taconite facilities recycle the scrubber water and send the scrubber solids back to the processing facility to improve the overall plant efficiency by recovering the iron that is in the solids. Table 3 shows how each plant treats the scrubber liquor. At most plants, even if the scrubber is removing the mercury from the gas stream, it is simply being recycled back into the system. Based on the MDNR results presented in a report to the Iron Ore Cooperative Research (4), it appears, with the possible exception of Hibtac, a high percentage (>80%) of the mercury removed by the scrubber reports to the solids. Even though the actual measured concentration is quite variable, the percentage in the solids stays relatively constant as is shown in Table 4. Recycling these solids creates the potential to generate very high mercury concentrations in the slurry, reducing the overall mercury removal. A second concern is the potential for corrosion and erosion. This is particularly true for the halogenated (chlorides and bromides) additives. However, other oxidants also may result in increased equipment maintenance over time. To date, these problems have been minimal in coal-fired boilers, but the tests have been relatively short term. Finally, the overall impact on iron chemistry is unknown.

**Table 3. Fate of Scrubber Materials**

Plant	No. of Lines	Induration Furnace	Scrubber Type	Scrubber Water	Scrubber Solids
Hibbing Taconite Co.	3	Straight grate	Once through	Grinding mills	Grinding mills
Keewatin	1	Grate kiln	Recirculating	Tailing basin	Landfill
United Taconite Co.	2	Grate kiln	Recirculating	Tailing thickener	Green ball feed
Mittal Steel	1	Straight grate	Recirculating	Tailing thickener	Tailing thickener
Minntac*	4	Grate kiln	Once through	Grinding mills	Green ball feed
Minntac*	1	Grate kiln	Recirculating	Tailing basin	Settling pond

\* Lines 4-7 are once through Line 3 is recirculating.

**Table 4. Distribution of Mercury in Scrubber Slurry (4)**

Plant	Hg(D) <sup>1</sup> , ng/L		Hg(P) <sup>2</sup> , ng/g		TSS <sup>3</sup> , %		Hg(T) <sup>4</sup> , ng/L		Hg in Solids, %	
	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.
Hibtac	325	164	2528	2525	0.019	0.011	671	314	51.1	9.07
Minntac (Line 4)	209	180	859	668	0.184	0.109	1540	826	86.4	7.39
Minntac (Line 7)	273	42	2470	563	0.070	0.024	1943	541	85.3	3.35
United Taconite	542	626	616	236	1.866	0.578	11550	5004	96.6	2.60
Mittal	1117	465	2305	1504	0.126	0.031	4368	1929	80.5	11.23

<sup>1</sup> Dissolved Hg in filtration liquid.

<sup>2</sup> Hg in filtration solids.

<sup>3</sup> Total suspended solids.

<sup>4</sup> Total mercury in scrubber slurry.

#### 4.0 ECONOMICS OF MERCURY CONTROL FOR TACONITE PLANTS

Until recently, very little mercury testing has been done at taconite plants. Almost all the testing that has been done has been proof of concept, short-term tests conducted by MDNR and Coleraine Minerals Research Laboratory. To obtain valid economic data, considerably more testing will need to be done, in particular for mercury oxidation technologies. The following information will be needed before a detailed economic study can be constructed for using oxidation technologies to reduce mercury emissions at taconite plants:

- Chemical additive to be used and the cost of the additive
- Amount of additive needed to obtain a specific result
- Feeding devices (solid vs. liquid)
- Impact on scrubber dust and liquid recycle
- Equipment maintenance
- Equipment installation requirements (ducting, utilities, labor)
- Effect on process chemistry, if any

A sensitivity analysis (based on the amount of PAC used) for ACI is shown in Table 5. The data presented in the table are based on an economic study that was done on data from a coal-fired power plant (10). Although the added cost (\$35/ton) of disposal because of the increase in dust due to the carbon is included, the loss of revenue from the disposal of scrubber

**Table 5. Summary of Costs Associated with ACI for Mercury Control at a Taconite Plant (Based on 2005 \$)**

	Case 1	Case 2	Case 3
Unit Size, kscfm	350	350	350
Particulate Removal	Venturi scrubber	Venturi scrubber	Venturi scrubber
Targeted Mercury Removal	60%	60%	60%
ACI Rate, lb/Macf	10	5	3
ACI Rate, lb/hr	390	145	90
<b>Capital Cost (\$)</b>			
Purchased Equipment	974,000	974,000	974,000
Installation	25,000	25,000	25,000
Total Capital Requirement	999,000	999,000	999,000
<b>Operating and Maintenance (\$/yr)</b>			
Operating Labor	32,000	32,000	32,000
Maintenance Labor	18,240	18,240	18,240
Supervision Labor <sup>1</sup>	4800	4800	4800
Replacement Parts <sup>2</sup>	19,480	19,480	19,480
Raw Materials (PAC)	1,312,854	656,427	393,856
Utilities	8775	8775	8775
Disposal of Scrubber Solids Because of Added Carbon	39,414	19,708	11,825
Overhead <sup>3</sup>	11,008	11,008	11,008
Taxes, Insurance, Administration <sup>4</sup>	29,970	29,970	29,970
Fixed Charges	185,571	185,571	185,571
<b>Levelized Annual Costs<sup>5</sup></b>			
Total Annual Cost, \$/yr	2,090,541	1,200,149	843,993
Mercury Reduction (\$/lb Hg removed)	61,189	35,128	24,703

<sup>1</sup> Based on 15% of operating labor.

<sup>2</sup> Based on 2% of purchase equipment.

<sup>3</sup> Based on 20% of labor costs.

<sup>4</sup> Based on 3% of total capital requirements.

<sup>5</sup> The sum of the levelized operating and fixed costs.

dust rather than recycling it back to the milling is not taken into account. Most likely this recycle would not be possible if carbon were to be injected in the scrubber. This also assumes 24-hour operation with 85% uptime.

Although no commercial fixed-carbon beds have been installed in the United States or Canada for mercury control, based on 1996 dollars, EPA estimates the cost for a coal-fired plant using a fixed-carbon bed to be \$37,800 per lb of mercury removed (12). Therefore, a fixed bed would be somewhat more expensive than simply injecting PAC. In general, the capital equipment costs will be higher and the operating costs will be higher because of relatively high pressure drops across the system. It would be expected that sorbent costs will be somewhat less as the filter bed is a better gas sorbent contactor than the venturi scrubber.

Figure 13 shows the relative cost for each of the different technologies, from least expensive to most expensive.

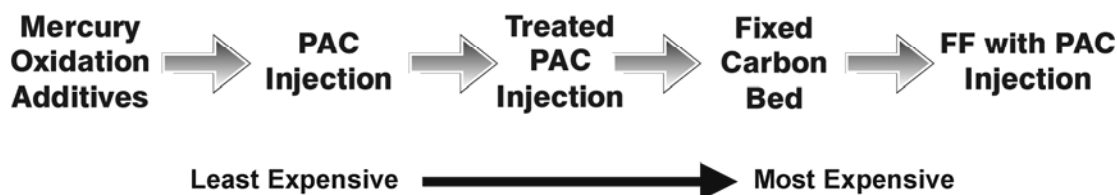


Figure 13. Relative cost for mercury control technologies.

## 5.0 RECOMMENDATIONS

Unlike the power plant industry, testing of mercury control technologies for the taconite industry is in the very early developmental stage. Although some of the results obtained from testing at coal-fired power plants are valid for taconite plants, there are substantial differences between the two industries that are going to impact on what technologies ultimately are implemented. As has been discussed, there are essentially two types of mercury control technologies that would most likely be considered for the taconite industry. These are mercury oxidization additives and mercury sorbents, of which the oxidation additives will most likely be the cheapest and, possibly, the most effective. However, there are a number of concerns that must be addressed by additional testing, both short and longer term.

A major concern of using oxidants to increase mercury removal in the scrubber is the potential increase in mercury concentration in the scrubber as a result of solids and water recycle loops. As was shown previously in Table 4, a high percentage of the mercury captured by the scrubber is associated with the solids; therefore, recycling the solids could result in very high (and increasing) levels of mercury being recycled. Although these data can only be obtained by conducting long-term testing (several months or more), it is important that the following be evaluated:

- The economics and the practicality of not recycling the solids/water.
- Potential for recycling only a percentage of the solids, thereby reaching some sort of equilibrium.
- Would there be an advantage to recycling the solids back to the grinding mill rather than the green ball feed? It is possible that the mercury-containing solids can be separated during processing. It has shown that the mercury tends to absorb to the nonmagnetic fraction of the scrubber dust. Thus, by sending the scrubber solids back to the grinding mill, the magnetic fraction of these solids without the mercury could be recovered while the high-mercury nonmagnetic fraction would be discarded (30).

Other potential concerns that must be studied are corrosion/erosion of piping and other equipment as a result of the oxidants and the overall impact on system chemistry.



Mercury oxidation is accomplished by either adding the oxidant prior to the scrubber, as would be the case for the EERC additive and halogens such as NaBr or NaCl, or changing the scrubber slurry, as would be the case when using hydrogen peroxide or the EPA oxidant. In either case, there is the potential to change the system chemistry with unknown consequences. If halogens are added, there is the possibility of exacerbating corrosion/erosion problems, resulting in additional system maintenance.

It does appear that the addition of NaBr to the green balls shows promise. Therefore, it is recommended that longer-term testing be completed using NaBr addition in both straight-grate and grate kiln facilities. Initially, testing would be for several days to ensure that the short-term results are valid. Once that is complete, longer-term testing for periods of up to a month should be done. During the longer-term testing, metal coupons will need to be installed to measure corrosion and erosion. During this period, it is essential that measurements be made to evaluate the effect of the water and solids recycle loops on mercury concentration in the scrubber.

Bench-scale testing to screen potential mercury oxidants should continue. In particular additional tests should be conducted utilizing the EPA oxidant, as initial preliminary tests show this additive has promise. If this technology or others continue to be promising, it may be advantageous to build a small slipstream scrubber. This way, tests can be conducted with minimal impact on plant operations.

For coal-fired boilers, the technology of choice appears to be standard ACI or using treated PACs. Depending on several factors, such as future state or federal regulations and the effectiveness and practicality of using mercury oxidants, this technology may need to be evaluated for the taconite industry as well. The effectiveness of these sorbents for removing mercury, the impact on the scrubber and system chemistry, and the impact on the level of particulate emissions is completely unknown at this time. Unfortunately, in order to obtain any meaningful results, testing would have to be conducted at the full-scale level.

One technology that must at least be considered by the industry is to install a carbon fixed bed at the outlet of the scrubber. Depending on fan capacity, this technology would have minimal impact on plant operation. In addition, it is possible to test a slipstream pilot unit to evaluate both standard and treated activated carbons. Although this option would most likely be more expensive than ACI, it could provide the highest level of comfort by not impacting the plant chemistry and recycle systems and at the same time achieve a high level of mercury control. It is possible that by using a halogenated carbon, >90% mercury control could be obtained. Along the same lines, for those facilities interested in reducing particulate emissions, tests could be completed using a slipstream FF with ACI.

## 6.0 REFERENCES

1. Berndt, M.; Engesser, J.; Johnson, A. *On Distribution of Mercury in Taconite Plant Scrubber Systems*; Submitted to the Minnesota Pollution Control Agency, Oct 2003.

2. Federal Register. National Emission Standards for Hazardous Air Pollutants: Taconite Iron Ore Processing, Final Rule, 40 CFR, Part 63; Oct 30, 2003.
3. Berndt, M. *Mercury and Mining in Minnesota*; Minerals Coordinating Committee Final Report, Oct 2003.
4. Berndt, M.; Engesser, J. *Mercury Transport in Taconite Processing Facilities: (I) Release and Capture During Induration*; Iron Ore Cooperative Research Final Report, April 2003.
5. Pavlish, J.H.; Laudal, D.L.; Holmes, M.J.; Hamre, L.L.; Musich, M.A.; Weber, G.F.; Hajicek, D.A. *Technical Review of Mercury Technology Options for Canadian Utilities – A Report to the Canadian Council of Ministers of the Environment*; Canadian Council of Ministers of the Environment Final Report; March 2005.
6. Brand, A. Pilot Testing of WRI’s Novel Mercury Control Technology by Pre-Combustion Thermal Treatment, In *Proceedings of the 2006 Mercury Control Technology Conference of Coal*; Pittsburgh, PA, Dec 2006.
7. Olson, E.S.; Laumb, J.D.; Benson, S.A.; Dunham, G.E.; Sharma, R.K.; Miller, S.J.; Pavlish, J.H. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **2003**, 48 (1), 30–31.
8. Pavlish, J.H.; Sondreal, E.A.; Mann, M.D.; Olson, E.S.; Galbreath, K.C.; Laudal, D.L.; Benson, S.A. *Status Review of Mercury Control Options for Coal-Fired Power Plants, Fuel* **2003**, 82, 89–165.
9. Feeley, T.J., III; Murphy, J.T.; Hoffmann, J.W.; Granite, E.J.; Renninger, S.A. *DOE/NETL’s Mercury Control Technology Research Program for Coal-Fired Power Plants*; EM 2003; pp 16–23.
10. Wocken, C.A.; Holmes, M.J.; Pavlish, J.H.; Thompson, J.S.; Hill Brandt, K.L.; Pavlish, B.M.; Galbreath, K.C.; Laudal, D.L.; Olderbak, M.R. *Enhancing Carbon Reactivity in Mercury Control in Lignite-Fired Systems*; Draft Final Technical Report for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement DE-FC29-03NT4189; Oct 2006; in preparation.
11. Sjostrom, S.M.; Wilson, C.; Bustard, J.; Spitznogle, G.; Toole, A.; O’Palko, A.; Chang, R. Full-Scale Evaluation of Carbon Injection for Mercury Control at a Unit Firing High Sulfur Coal. In *Proceedings of the Power Plant Air Pollutant Control “Mega” Symposium*; Paper No. 14, Baltimore, MD, Aug 2006.
12. U.S. Environmental Protection Agency. *Mercury Study Report to Congress*; Volume VIII: An Evaluation of Mercury Control Technologies and Costs, U.S. Environmental Protection Agency, EPA-452/R-97-010, Dec 1997.
13. McDonald, D.K.; Amrhein, G.T.; Kudlac, G.A.; Yurchison; D.M. *Full-Scale Testing Of Enhanced Mercury Control Technologies for Wet FGD Systems*; Draft Final Report for

- U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-00NT41006; May 2003.
14. DeBerry, D.W.; Blythe, G.M.; Pletcher, S.; Rhudy, R. Bench-Scale Kinetics Study of Mercury Reactions in FGD Liquors. In *Proceedings of the Power Plant Air Pollutant Control "Mega" Symposium*; Paper No. 47, Baltimore, MD, Aug 2006.
  15. Blythe, G.M.; Miller, C.E.; Rhudy, R.G.; Wiemuth, B.; Kyle, J.; Lally, J. Wet FGD Additive for Enhanced Mercury Control. In *Proceedings of the Power Plant Air Pollutant Control "Mega" Symposium*; Paper No. 36, Baltimore, MD, Aug 2006.
  16. Diaz-Somoano, M.; Unterberger S.; Hein, K.R. Using Wet-FGD Systems for Mercury Removal. *J. Environ. Monit.* **2005**, *9*, 906–909.
  17. McCollor, D.P.; Benson, S.A.; Holmes, M.J.; Libby, S.; Mackenzie, J.; Crocker, C.R.; Kong, L.; Galbreath, K.C. Large-Scale Mercury Control Technology Testing for Lignite-Fired Utilities – Oxidation Systems for Wet FGD. Presented at the 6th Power Plant Air Pollution Mega Symposium, Baltimore, MD, Aug 28–31, 2006.
  18. Korell, J.; Seifert, H.; Paur, H.R.; Anderson, S.; Bolin P. Flue Gas Cleaning with the MercOx Process. *Chem. Eng. Technol.* **2003**, *26* (7), 737–740.
  19. Alix, F.; Boyle, P.D. Commercial Demonstration of ECO<sup>®</sup> Multi-Pollutant Control Technology. Presented at the EUEC 7th Electric Utilities Environmental Conference, Jan 19–22, 2004.
  20. Jarvis, J.B., et al. LoTOx<sup>™</sup> Process Flexibility and Multi-Pollutant Control Capability. Presented at the Combined Power Plant Air Pollutant Control Mega Symposium, Washington, DC, May 19–22, 2003.
  21. Boren, R.M.; Hammel, C.F.; Harris, L.E.; Bleckinger, M.R. Pilot Test Results from Enviroscrub Technologies Multi-Pollutant Pahlman Process<sup>™</sup> Technology for NO<sub>x</sub>, SO<sub>2</sub>, and Mercury. Presented at the Combined Power Plant Air Pollutant Control Mega Symposium, Washington, DC, Aug 30–Sept 2, 2004.
  22. Hutson, N.; Srivastava, R. A Multipollutant Wet Scrubber for Capture of SO<sub>2</sub>, NO<sub>x</sub> and Hg. In *Proceeding of the 2006 Mercury Control Technology Conference of Coal*; Pittsburgh, PA, Dec 2006.
  23. Johnson, D.W.; Ehrnschwender, M.S.; Seidman, L. The Airborne Process – Advancement in Multi-Pollutant Emissions Control Technology and By-Product Utilization. In *Proceedings of the Combined Power Plant Air Pollutant Control Mega Symposium*; Washington, DC, Aug 30 – Sept 2, 2004.
  24. McLarnon, C.R.; Granite, E.J.; Pennline, H.W. Initial Testing of Photochemical Oxidation for Elemental Mercury Removal from Subbituminous Flue Gas Streams. Presented at the 19th Annual Western Fuels Symposium; Billings, MT, Sept 2004.

25. Hoffman, J.S.; Yeh, J.T.; Pennline, H.W.; Resnik, K.P.; Vore, P.A. Flue Gas Cleanup Studies with the Moving-Bed Copper Oxide Process. In *Proceedings of the Joint Power and Fuel Systems Contractor Review Meeting*; July 1996.
26. Laudal, D. *Effect of Selective Catalytic Reduction on Mercury, 2002 Field Studies Update*; Final Report; Energy & Environmental Research Center: Grand Forks, ND, Aug 2004.
27. Withum, J.A.; Tseng, S.C.; Locke, J.E. *Mercury Emissions from Coal-Fired Facilities with SCR-FGD Systems*, In *Proceedings of DOE/NETL's Mercury Control Technology R&D Program*; Pittsburgh, PA, July 12–14, 2005.
28. Machalek, T.; Olsen, B. Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems. Presented at Combined Power Plant Air Pollutant Control Mega Symposium; Baltimore, MD, Aug 28–31, 2006.
29. Berndt, M. E.; Engesser, J. E. Minnesota DNR's Coordinated Hg Research Effort. Presented at the Annual Society of Mining Engineers Meeting: Consolidation, Growth, Technology, Duluth, MN, April 17–18, 2007.
30. Berndt, M. E.; Engesser, J. *Mercury Transport in Taconite Processing Facilities: (II) Fate of Mercury Captured by Wet Scrubbers*; EPA: Great Lakes National Program Office Report, 2005.