



July 1, 2008

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Dear Dr. Berndt:

Subject: Final Report Entitled "Proof-of-Concept Testing of a Novel Mercury Control
Technology for a Minnesota Taconite Plant"
Contract No. B12296; EERC Fund 9752

Enclosed is the subject final report, which details the scope of work and results related to testing a novel technology for mercury removal at a taconite plant. If you have any questions, please feel free to contact me by phone at (701) 777-5268, by fax at (701) 777-5181, or by e-mail at jpavlish@undeerc.org.

Sincerely,

John H. Pavlish
Senior Research Advisor

JHP/dte

Enclosure

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PROOF-OF-CONCEPT TESTING OF A NOVEL MERCURY CONTROL TECHNOLOGY FOR A MINNESOTA TACONITE PLANT

ABSTRACT

Mercury control tests using the Energy & Environmental Research Center (EERC) high-energy dissociation technology (HEDT) prototype test unit were completed at Minntac Plant Line 3. Four halogen compounds including NaBr, CaBr₂, NaCl, and NaCl–CaBr₂ mixture were tested in the HEDT unit to evaluate their effectiveness on mercury reduction in taconite flue gas. Mercury continuous mercury monitor (CMM) data for stack gases indicate moderate mercury oxidation by NaBr and CaBr₂ with the HEDT unit but no substantial decrease in mercury emissions. It is suspected that the compromised HEDT injection location, which provided a very short residence time of 0.2 seconds, is part of the reason for the ineffectiveness of mercury oxidation and capture with the existing venturi scrubber. In addition, it is possible that other components in the gas, including fine iron oxide particles and the limestone fluxing material, interfered with mercury oxidation and subsequent capture in the venturi scrubbers. Additional studies on Hg–Br–Fe oxide reactions in taconite flue gas are needed. Possible future HEDT experiments are suggested further upstream of the test location to maximize mercury–bromine reactions at favored flue gas conditions but downstream of the grate to avoid possible corrosion issues.

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INTRODUCTION

Concerns over bioaccumulation of mercury in tissues of various organisms (including humans) have led the U.S. Environmental Protection Agency (EPA) to determine that it is appropriate to regulate mercury emissions from coal-fired utility plants. Several states have filed state implementation plans to impose strict mercury control and have publicly committed to reducing mercury from all significant sources within their states in order to reduce the potential for mercury hot spots and to hopefully reverse the concentrations of mercury measured in fish tissues and other animals.

The state of Minnesota is targeting an overall mercury reduction of 90%. In order to achieve this level of reduction, all sources of mercury emissions and releases to the environment are being evaluated for potential reductions. In Minnesota, taconite plants are the second largest source of mercury emissions in the state. Mercury emissions result from taconite processing in two ways: those released from the fuel (which is a minor contribution since it only takes 20–30 lb of coal to process 1 long ton [Lt] of iron ore to green balls) and those from the actual processing of the ore, which is the major concern. The concentration of mercury in the unprocessed ore at the west end of the mining region 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 the Northshore facility (1). A working group of experts that includes scientists and engineers from the taconite industry, the Minnesota Department of Natural Resources (MNDNR), the Minnesota Pollution Control Agency, and research institutions (University of Minnesota and University of North Dakota) is seeking effective mercury emission reduction strategies that have minimal impacts to the industry, both from an operational standpoint and with respect to the components of the production facility. Discussions are under way to evaluate the most effective means of controlling mercury while minimizing impact on both the operations and economics of Minnesota's taconite plants.

All Minnesota taconite facilities, with the exception of the Northshore facility (which has wet electrostatic precipitators), utilize a wet venturi-type scrubber to control particulate matter emissions (versus removing sulfur compounds as in coal-fired combustors). (2) This scrubber can effectively capture particulate-bound mercury and oxidized mercury (Hg^{+2}), but allows elemental mercury (Hg^0) to be emitted. Therefore, a technology that can promote mercury oxidation should theoretically facilitate capture.

A number of tests of limited duration, involving bench-, slipstream-, and full-scale unit, have been completed to evaluate the effectiveness of various noncarbon additives on mercury reduction in taconite flue gas (2, 3). Chloride and bromide salts have been directly added into the induration furnace, the green ball feed system, and the scrubber liquids in an attempt to convert Hg^0 to Hg^{+2} to facilitate mercury capture. Mercury removals with NaCl_2 and CaCl_2 showed some removal, as was expected; the grate kiln, which is the configuration for the Minntac Plant, showed better removals than straight-grate configurations. A series of experiments were also performed on slipstream gases from an operating taconite-processing

plant to evaluate the use of chemical oxidants added directly to water in wet scrubbers to enhance capture efficiency for elemental mercury.

Most mercury control technologies such as activated carbon injection and chemical additives were originally developed for the coal-fired utility industry and have been proven effective in coal combustion flue gas. However, these technologies may not be applicable to the taconite industry because the process and flue gas conditions for iron ore processing are vastly different (4). In particular, the chemistry and heat profiles of the taconite processes, as well as possible differences in fuel types, are likely to affect the performance of mercury control technologies somewhat differently than when applied to coal-fired utilities. Moreover, iron oxides have been shown to be particularly reactive with mercury in some settings and may, therefore, interfere with control technology applications. Consequently, technologies used by other industries (such as utilities) must be tested to determine their applicability and effectiveness for the taconite industry or new technologies may need to be developed.

The Energy & Environmental Research Center (EERC) at the University of North Dakota is heavily involved in mercury research, from developing protocols for sampling to cost-effective control technologies. The EERC has developed a number of technologies for use at coal-fired power plants that may prove effective for the taconite industry. Based on this experience, the EERC proposed proof-of-concept testing at the Minntac Plant to evaluate an EERC proprietary technology, high-energy dissociation technology (HEDT), for mercury control systems. The proposed technology is thought to have several benefits over standard in-furnace addition, especially in this application. For example, the potential for corrosion is significantly reduced because halogens are not added at locations where they can contact the grates at high temperatures. Instead, reactive halogens are generated at high temperatures outside of the taconite process and injected downstream of the grates at low temperatures within the ducts. The technology works by dissociating halogen salts, allowing the use of benign compounds to create halogen radicals that quickly oxidize Hg^0 to Hg^{2+} in flue gas. The oxidized mercury is theoretically removed in downstream equipment such as the wet scrubber. A key advantage of the technology is that injection of the dissociated halogen can occur anywhere in the system, allowing for optimization of injection location and minimization of impacts on system components. By comparison, other technologies require the addition of materials in the hot zone of the induration furnace, which may increase corrosion potentially throughout the entire system.

GOAL AND OBJECTIVES

The overall goal of this project is to evaluate a novel, proprietary EERC process (Patent Application US2007/0051239) by which mercury oxidation can be enhanced by injection of radical halogen species which are created from dissociating halogen salts. Specific objectives are as follows:

- Obtain baseline mercury removals in taconite flue gas.
- Inject variable rates of dissociated halogens to determine improvements in mercury capture and reduction.

- Assess applicability of the halogen dissociation technology to the taconite industry, particularly for a grate–kiln configuration.
- Evaluate initial/potential balance-of-plant impacts that may result from the use of this technology at Minntac and generalize results to other plants.

EXPERIMENTAL DESCRIPTION

The testing that was performed built on and was compared to previous tests that have been conducted under the leadership of Michael Berndt of MNDNR. The on-site evaluation of this technology was conducted at the Minntac Plant Line 3. This facility has a grate–kiln configuration (see Figure 1) that moves high-temperature air counter to the movement of the green balls through the system. Figure 1 shows the configuration for Lines 6 and 7, which are similar in process to Line 3. Line 3 is considerably smaller and is equipped with a recirculating, pH-controlled wet scrubber and updated cyclone for dust collection prior to the scrubber.

Based on a site visit and several follow-up discussions with Minntac personnel, the EERC installed the HEDT field unit at the inlet of the waste gas fan, shown as Location 2 in Figure 2, in which the dissociated halogens were conveyed into the flue gas of Line 3. Location 2 is not optimal since it only provides a nominal ~0.2-second residence time for formed reactive halogen in the taconite flue gas before being scavenged with wet scrubbers. The residence time was estimated based on duct dimensions including duct cross-sectional area, duct length from the HEDT injection location to the scrubber inlet, and typical flue gas flow rate at Line 3. However, other possible injection locations such as Location 1 in Figure 2 were not accessible during the time frame of the project.

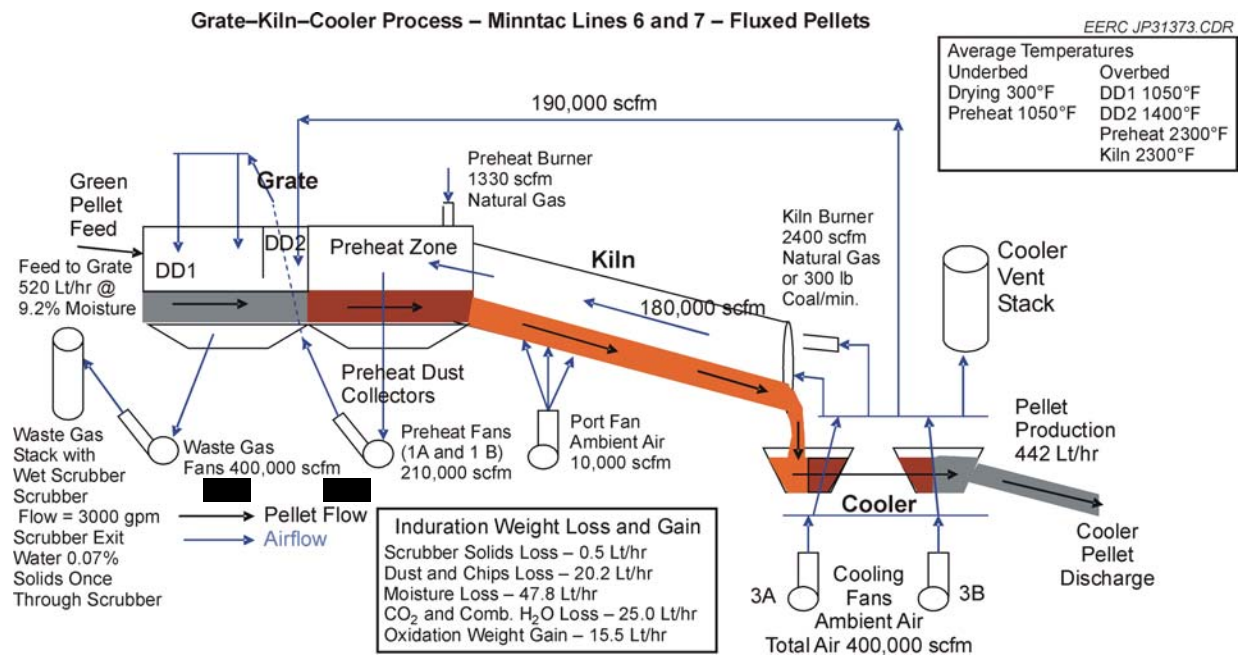


Figure 1. Configuration of Minntac Plant Lines 6 and 7, similar in process to Line 3.

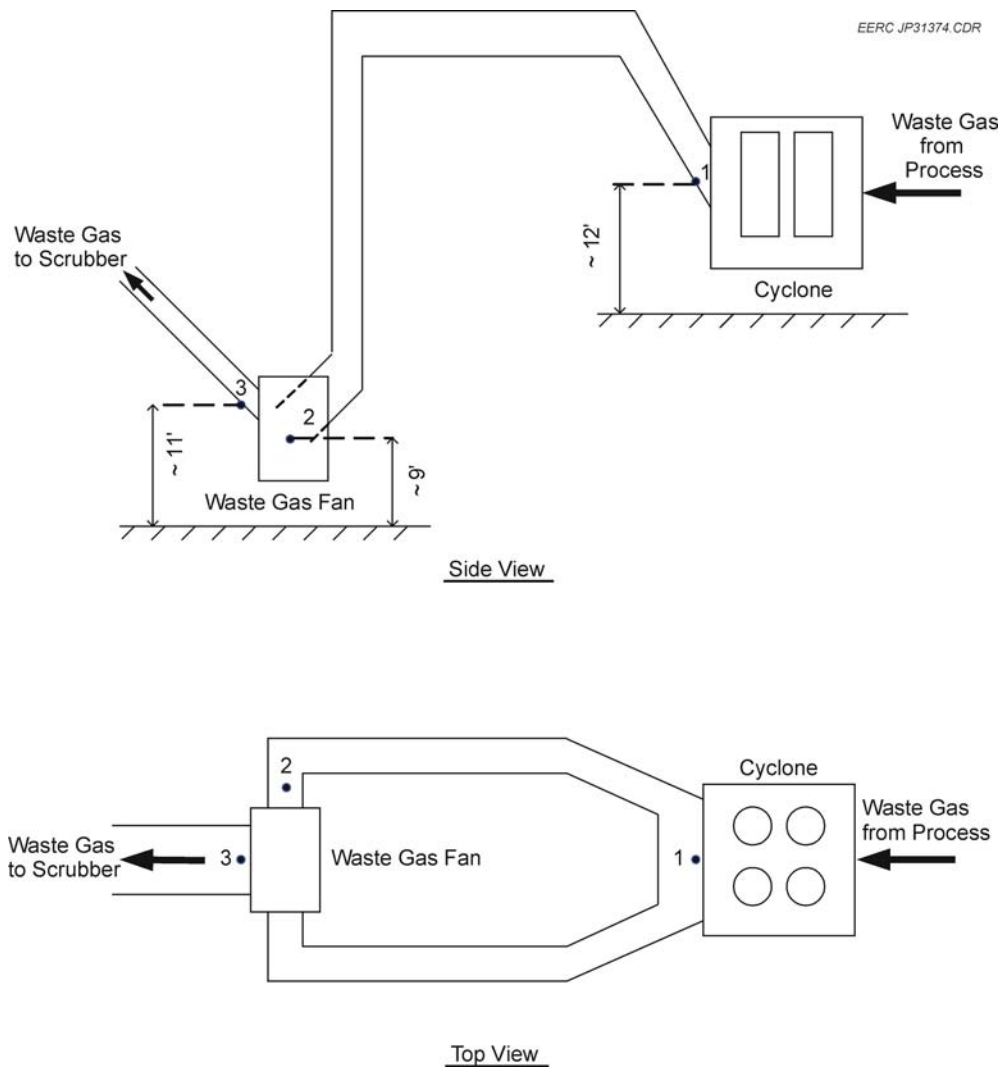


Figure 2. Possible injection locations within the Minntac Plant Line 3 ductwork.

The EERC HEDT field unit, as shown in Figure 3, was shipped to the Minntac Plant and installed at Location No. 2 on Line 3 to test the effectiveness of this technology to generate disassociated halogen radicals for improved mercury oxidation and particulate-bound mercury for subsequent removal by the existing venturi scrubbers.

Sodium bromide, calcium bromide, sodium chloride, and a 50% calcium bromide–50% sodium chloride mixture were evaluated separately for mercury reduction in taconite flue gas using the HEDT unit. The injection rates for each tested chemical additive are listed in Table 1. During the testing period, Minntac was generating fluxed pellets on Line 3, which is different from previous MNDNR test conditions when calcium bromide solution was injected into the kiln (3). In order to evaluate possible interferences on mercury–bromine reactions introduced by the added limestone and changed heating profiles associated with fluxed pellet production, a calcium bromide solution was again injected into the kiln (by DNR personnel) at the end of the EERC tests to compare with previous MNDNR testing results (3).



Figure 3. EERC HEDT field unit.

Table 1. Test Matrix Completed at Minntac Plant Line 3

Test No.	Chemical Additive	Injection Rate, lb/hr	Injecting Location
T-1	NaBr	5, 25	Waste gas fan
T-2	CaBr ₂	5, 14, 25	Waste gas fan
T-3	CaBr ₂ /NaCl	14, 25	Waste gas fan
T-4	NaCl	25	Waste gas fan
A-1*	CaBr ₂ solution	25	Hot zone in kiln

* For comparison, done outside of this project.

Two continuous mercury monitors (CMMs) were used during the tests to measure gaseous mercury species upstream of the HEDT injection location and downstream from the wet scrubber at the stack. To protect the CMM, a filter assembly was installed in the CMM sampling line at the scrubber inlet to capture particulate matter (primarily iron oxide). In doing so, mercury oxidation most likely occurred when elemental mercury came in contact with the iron oxide filter cake. As a result, mercury species sampling at the scrubber inlet had biased low elemental mercury and total gaseous mercury concentration.

RESULTS AND DISCUSSION

Plotted in Figures 4–6 are the temporal variations of gaseous mercury for stack gases for the entire test period. The collected CMM data were then averaged and replotted in Figure 7 to summarize the changes of mercury emissions at the stack when halogen additives were added as defined in Table 1. Mercury CMM data at the stack indicate no significant decrease of mercury emissions but with improved mercury oxidation when dissociated halogens were added into the taconite flue gas. At an injection rate of 25 lb/hr, both NaBr and CaBr₂ enhanced

mercury oxidation by increasing the fraction of oxidized mercury in flue gas: from 8.9% in baseline to 13% for NaBr injection and from 13% in baseline to 38% for CaBr₂ injection. Injections of NaCl and a mixture of CaBr₂-NaCl did not appreciably change mercury speciation in stack flue gas.

The dissociated bromine radicals affect mercury species and subsequent capture by either homogeneously oxidizing elemental mercury followed by adsorption onto particles such as iron oxide or heterogeneously oxidizing mercury on fine particles contained within taconite flue gas. The gas-to-particle transportation is potentially a mass transfer-limiting process, meaning that the residence time for bromine radicals contacting flue gas is very critical. Unfortunately, compared to the ~2 minutes of residence time of bromine species in flue gas when bromide compounds were added into the hot zone of the kiln, only 0.2 seconds of residence time was available during the HEDT tests, which may have been too short for capture by the venturi scrubber.

In addition, since the gas-to-particle transportation rate is inversely correlated with particle size, most of the adsorbed mercury would be enriched within the fine fraction of particulate matter. Allowing adequate residence time, these Hg-enriched fine particles would coagulate with other particles to form large-sized agglomerates that are more easily removed by venturi scrubbers. Coagulation between particles has been recognized as one of the main mechanisms for particle growth in high-dust-loading flue gas, which has been extensively studied elsewhere (5). However, as a result of the short residence time in the current test configuration, the particulate-bound mercury, if formed, would likely remain fine in size and escape the venturi scrubber, which is known for its low collection efficiency for fine particles. Therefore, the Hg-enriched fine particulate matter, most likely in the submicron range, would not be captured and would exit the stack. Additionally, the fine-sized particulate-bound mercury would also travel into the CMM mercury conversion unit in which the particulate-bound mercury would be released, detected, and reported by the CMM as oxidized mercury, adding to the total mercury concentration. It should be noted, that for these tests the CMM was not equipped with an inlet filter as most of the large particulate is scrubbed out by the venturi scrubber.

In order to further evaluate the effect of adding limestone as a fluxing agent, a repeat test injecting CaBr₂ solution into the kiln hot zone was performed (by MNDNR personnel) at the end the HEDT test period. The CMM data are plotted in Figure 6, and averaged data are summarized in Figure 7. It shows mercury emission was reduced to 2.8 µg/m³ with 2.2 µg/m³ of elemental mercury, compared to a decrease of total mercury in stack gases from 5.1 to 1.4 µg/m³ attained in previous MNDNR tests during the production of standard pellets and using the same CaBr₂ injection. From these results, it can be concluded that the added limestone and changed thermal regimes associated with generation of fluxed pellets has a significant negative effect on mercury-bromine chemistry reactions. However, the fact that stack gas mercury decreases occur when CaBr₂ is injected into the kiln while no change or even slight increases of mercury emission occurred when similar species are injected into the duct indicates a fundamental need for more detailed work with Hg-Br-Fe oxide reactions at various temperatures.

CONCLUSIONS AND RECOMMENDATIONS

Experimental data collected at Minntac Plant Line 3 indicate that limited mercury oxidation occurred when reactive bromine species were generated with the EERC HEDT, but with no decrease in total mercury emission at the stack. An increase of oxidized mercury of 4% and 25% was achieved for NaBr and CaBr₂, respectively, at a 25-lb/hr injection rate. The current HEDT injection location, which provided a residence time estimated at 0.2 second, may be one of many factors that limit HEDT performance. Other components in flue gas, including fine iron oxide particles and the limestone fluxing material, may also interfere with mercury oxidation and subsequent capture in the venturi scrubbers.

The repeat MNDNR tests proved that the added limestone and changed thermal regimes associated with generation of fluxed pellets have a significant negative effect on mercury–bromine chemistry reactions.

The EERC HEDT field testing at Minntac Plant Line 3 demonstrated the importance of time–temperature profile on mercury oxidation and/or adsorption in taconite flue gas. The data suggest a need for better understanding of reactions between iron oxides, Br, and Hg as functions of temperature and residence time.

It is recommended that future testing with the HEDT technology be at an injection location further upstream of the location tested for this project, but downstream of the grate to avoid corrosion concerns. For example, at Minntac Plant Line 3, a suggested location would be at the inlet of the fly ash drop box which is upstream of the multicyclone collector.

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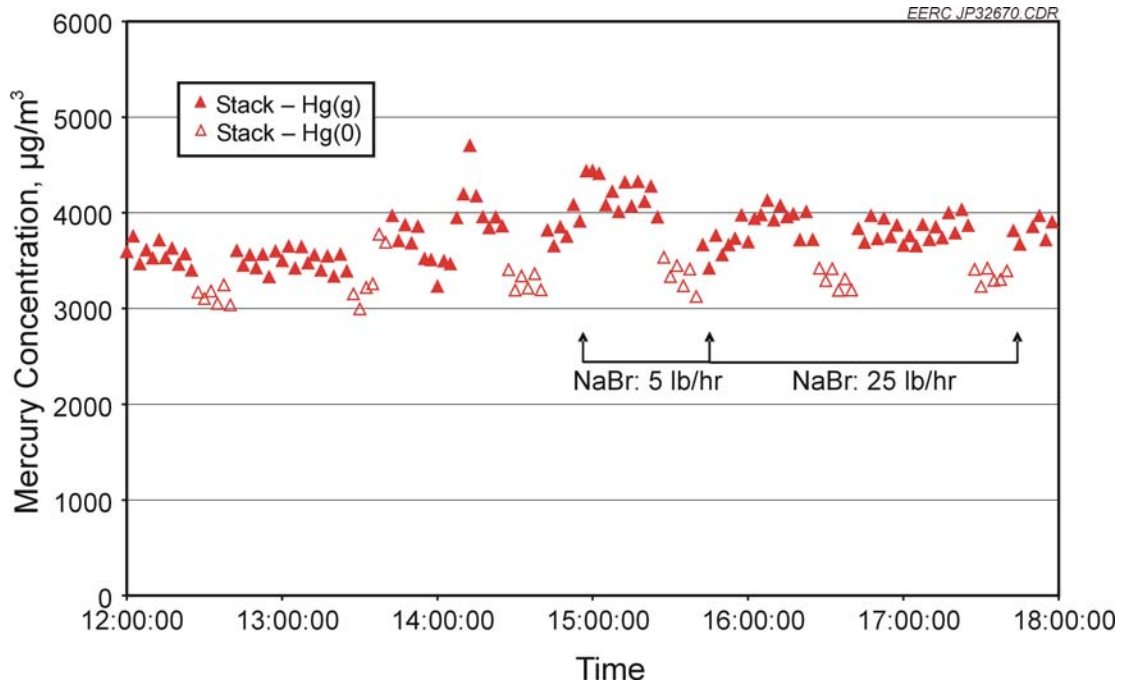


Figure 4. Continuous mercury measurement at Minntac Plant Line 3 when NaBr was used with the HEDT.

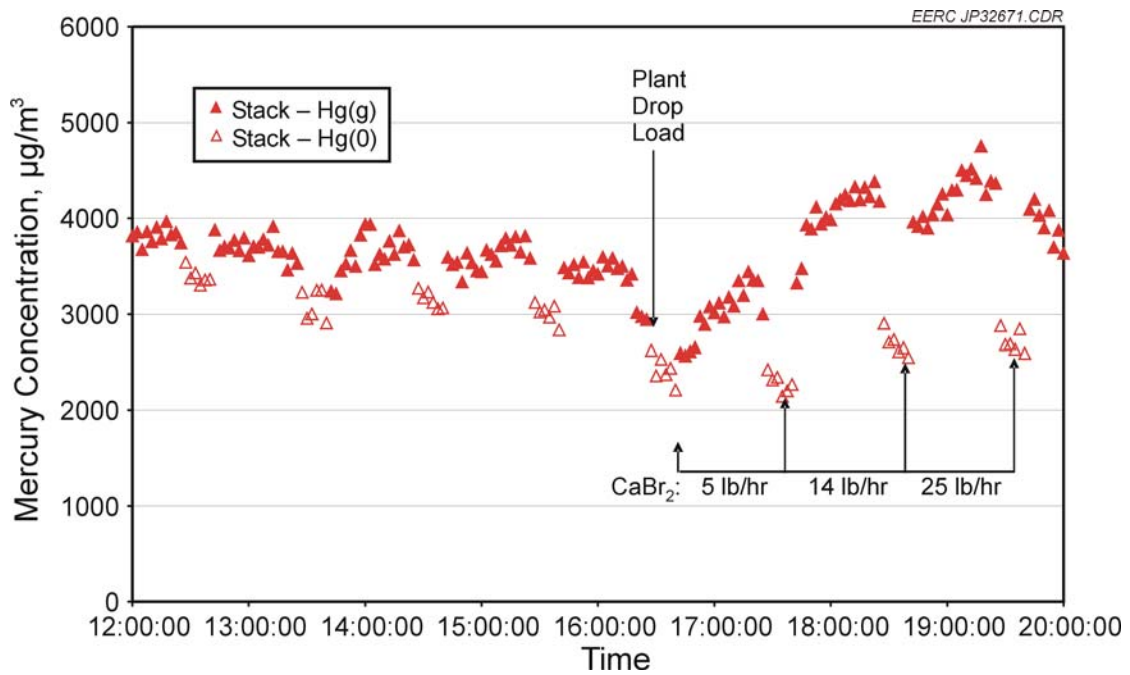


Figure 5. Continuous mercury measurement at Minntac Plant Line 3 when CaBr_2 was used with the HEDT.

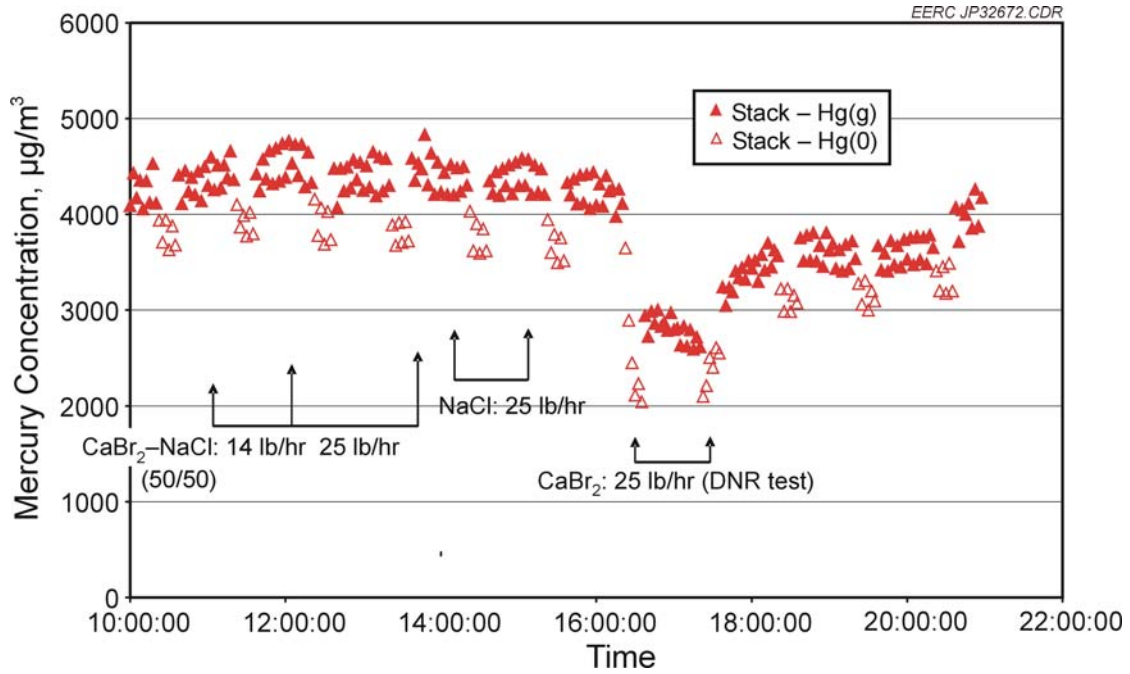


Figure 6. Continuous mercury measurement at Minntac Plant Line 3 when a CaBr₂-NaCl mixture and NaCl alone were used with the HEDT.

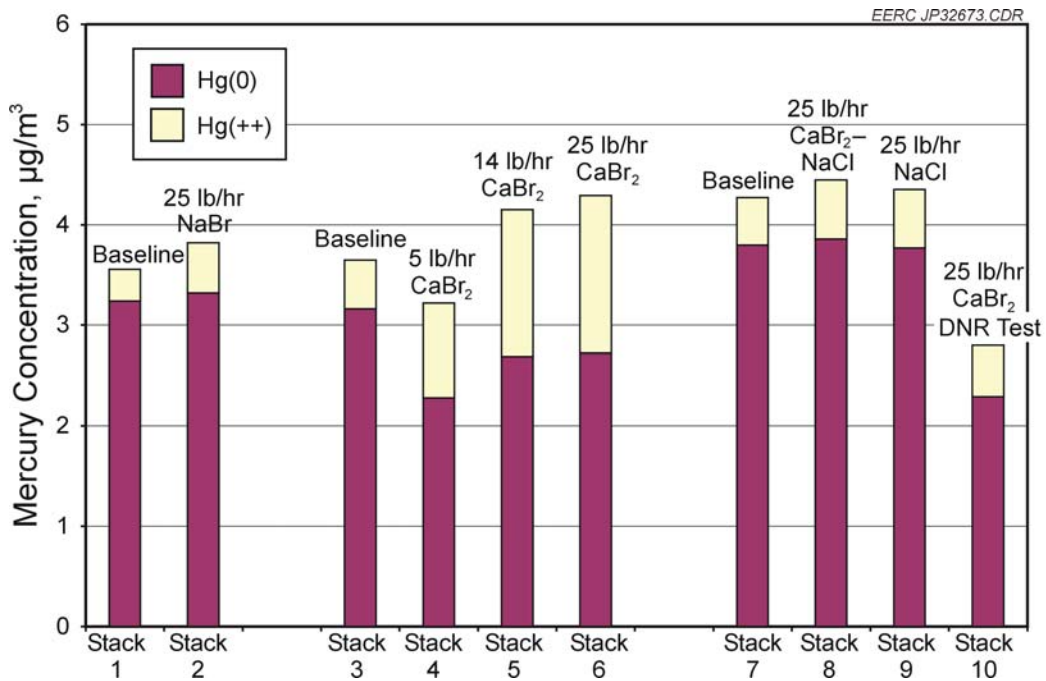


Figure 7. Summary of Mercury Testing at Minntac Plant Line 3.