A Brief Summary of Hg Control Test Results for Br Injection into Taconite Induration Furnaces

Prepared for the Minnesota Taconite Mercury Control Advisory Committee.

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Summary

This report summarizes stack testing data results for Hg control tests performed in 2007 to 2009 when solutions containing dissolved CaBr2 and NaBr were sprayed into indurating furnaces at five taconite processing plants. Unstable baseline Hg conditions were frequently encountered owing to plant upsets and to slow baseline recovery following injection. Nevertheless, baseline values were estimated to permit a general assessment of the mercury remaining in stack gases when the Br salts were applied. Initial Hg concentrations in stack gases ranged from 2.9 to 8.0 $\mu g/m^3$, with 12 to 22% of this Hg reported as oxidized Hg. The total Hg remaining in stack gases during tests ranged about 1.4 to 4.6 $\mu g/m^3$, 25 to 54% of which was oxidized. Thus, the total percentage of Hg remaining in the taconite processing stacks ranged from 27 to 88% of the base value, however, the percentage of mercury emitted in oxidized form increases with Br addition.

Introduction

The Minnesota Department of Natural Resources conducted numerous Hg control tests using Br salt addition to taconite processing plants. This document provides a brief summary of the stack gas Hg concentrations for these tests in graphical form. Numerous additional data accompanied the stack testing during these tests, including full scrubber water chemistry and greenball Hg concentrations. Major flow streams for the taconite processing plants were also provided when automatic readouts were provided. The purpose of this report is to provide the Minnesota Taconite Mercury Control Advisory Committee and research team members with an update on previous Hg testing results and data availability as the effort to find methods to control Hg continues into the future.

Methods

Hg concentrations were measured using CMM (Continuous Mercury Monitors) in stack gases at taconite processing plants before, during, and after spraying of bromide bearing salt solutions into the processing furnaces. For grate kilns, the Br salt addition occurred on the flame end of the kiln. For straight grates, the Br addition was into the second “down-comer” located above the preheat zone. All measurements were made by the Energy and Environmental Research Center (EERC) using their AWS system. While additional data is available on taconite gas process flows (e.g., scrubber water blow down, greenball

feed rate, pellet production, gas temperature, etc..,) and composition of the streams, these data are not reported here because the purpose of this document is only to provide a brief overview of the stack gas chemistry, however, these data are available upon request from the author. Furthermore, additional tests were also conducted at these taconite processing facilities involving addition of dry NaBr salt directly to the greenball feed or of NaClO2 to the scrubber water. Injection of Br salt solutions directly into the furnace typically provided superior results to these other tests and so only these results are presented here.

Results: Br addition tests are summarized in Table 1 and presented in Figures 1 through 6. Typically, two forms of Hg were evaluated: Total Hg and Elemental Hg. Elemental Hg is generally insoluble in water and is thus, not easily captured by taconite processing streams. The difference between the two values (Total minus Elemental Hg) is believed to be present in oxidized form. Initial Hg concentrations in stack gases ranged from 2.9 to 8.0 $\mu g/m^3$, with 12 to 22% of this Hg apparently present in oxidized form. The total Hg remaining in stack gases during the conductions of tests ranged from 1.4 to 4.6 $\mu g/m^3$, 25 to 54% of which was present in oxidized form. The total percentage of Hg remaining in the taconite processing stacks ranged from 27 to 88% of the base value, however, the percentage of mercury emitted in oxidized form increases with Br addition.

Table 1 Hg concentrations ($\mu g/m^3$) in stack gases at taconite processing facilities during Br injection tests conducted by the DNR from 2007 to 2009.

Test	Base THg Conc	Base Elem. Hg	Base % Oxidized	Test Hg Conc	Test Elem. Hg	Test % Ox	% THg Remaining
Keewatin Taconite Ln 2	**5.5**	**4.4**	**20%**	**2.4**	**1.1**	**54%**	**44%**
Hibbing Taconite Line 3	**8**	**6.5**	**19%**	**3.1**	**NA**	**NA**	**39%**
Minntac Line 3	**5.2**	**4.6**	**12%**	**1.4**	**0.9**	**36%**	**27%**
ArcelorMittal	**2.9**	**2.5**	**14%**	**2**	**1.5**	**25%**	**69%**
United Taconite							
Line 2 Stack A	**5.2**	**4.5**	**13%**	**4.6**	**2.5**	**46%**	**88%**
Line 2 Stack B	**4.6**	**3.6**	**22%**	**3.2**	**1.8**	**44%**	**70%**

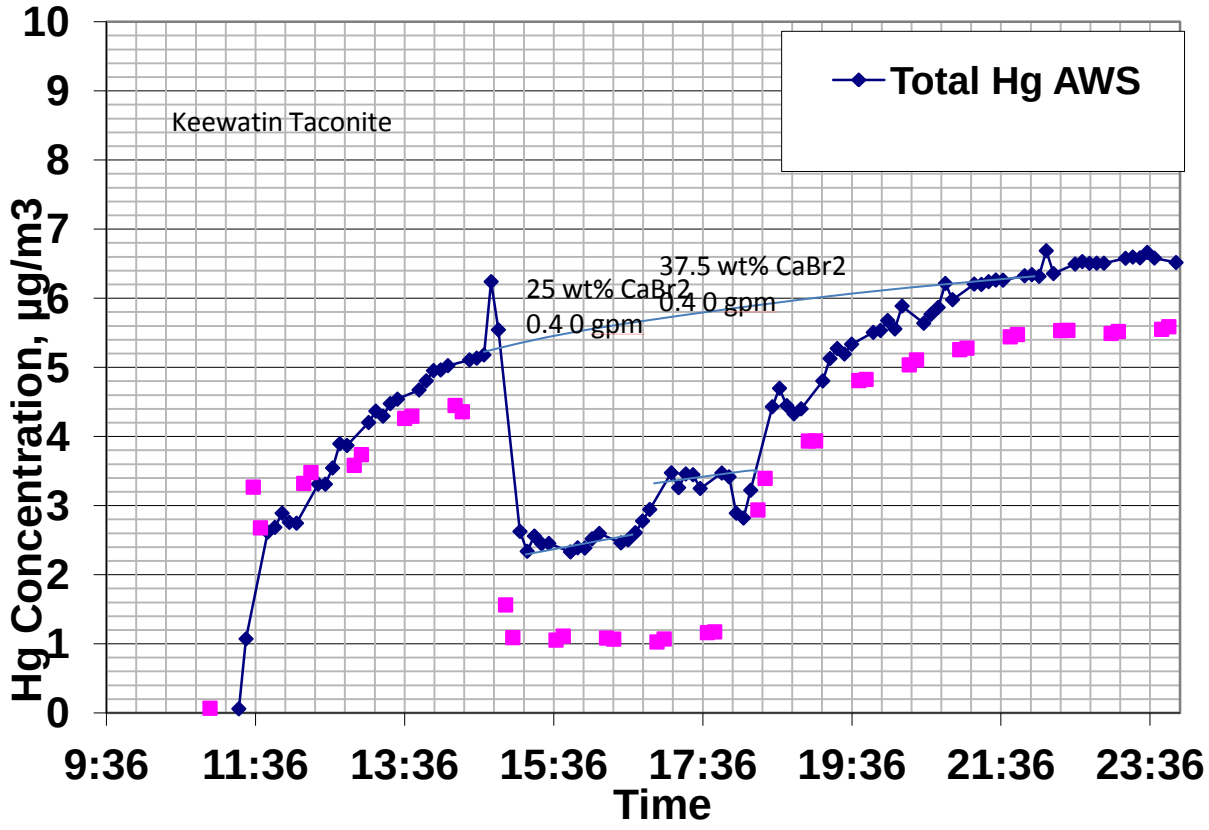

Fig 1. Keewatin Taconite test results. Dark blue diamond shapes represent total Hg. Pink squares represent elemental Hg. A plant upset occurred immediately in the morning when tests were about to begin. The plant came on line again and the test was begun approximately three hours later. It was found that 25 wt% $CaBr_2$ injection at 0.4 gpm provided better Hg capture than injection of 37.5 wt% $CaBr_2$ solution at the same rate.

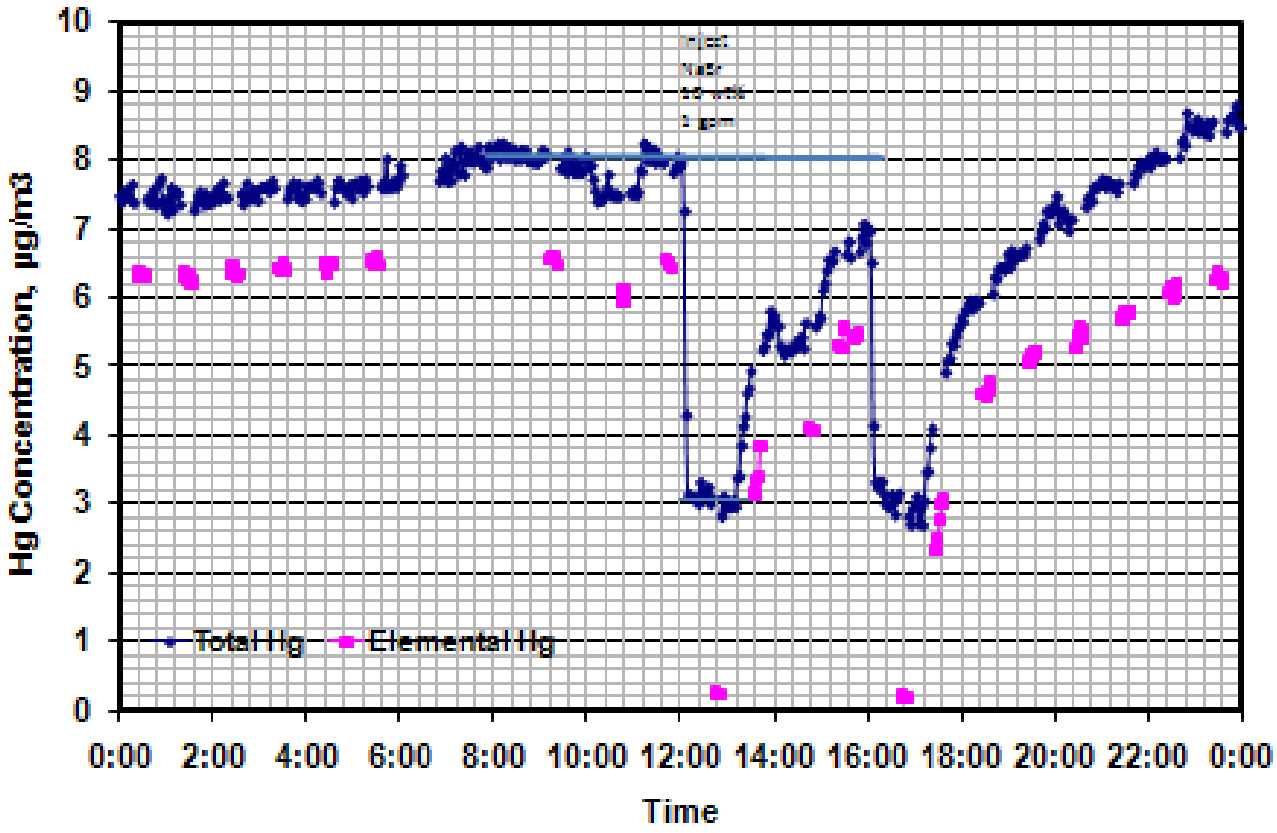

Fig 2. Hibbing Taconite Line 3 test results. Dark blue diamond shapes represent total Hg. Pink squares represent elemental Hg. Several tests were conducted at Hibbing Taconite over a period of approximately eight hours. Only the NaBr injection test, beginning at 12:00 and ending at 13:00 is evaluated here. The smaller dips beginning at 10:00 and 14:00 represent NaCl injection, and the large dip at 16:00 represents CaBr2 injection. Hg concentration recovery to the pre-test values in the stack gases at this site were very slow following the tests. Note that elemental Hg analysis suggest nearly all of the Hg in the stack gas was present in oxidized form during the Br tests (e.g., very low elemental Hg mercury), but this was later found to be due to an artifact of the method being used to measure Hg. This problem was corrected and is not believed to affect analysis at the other sites.

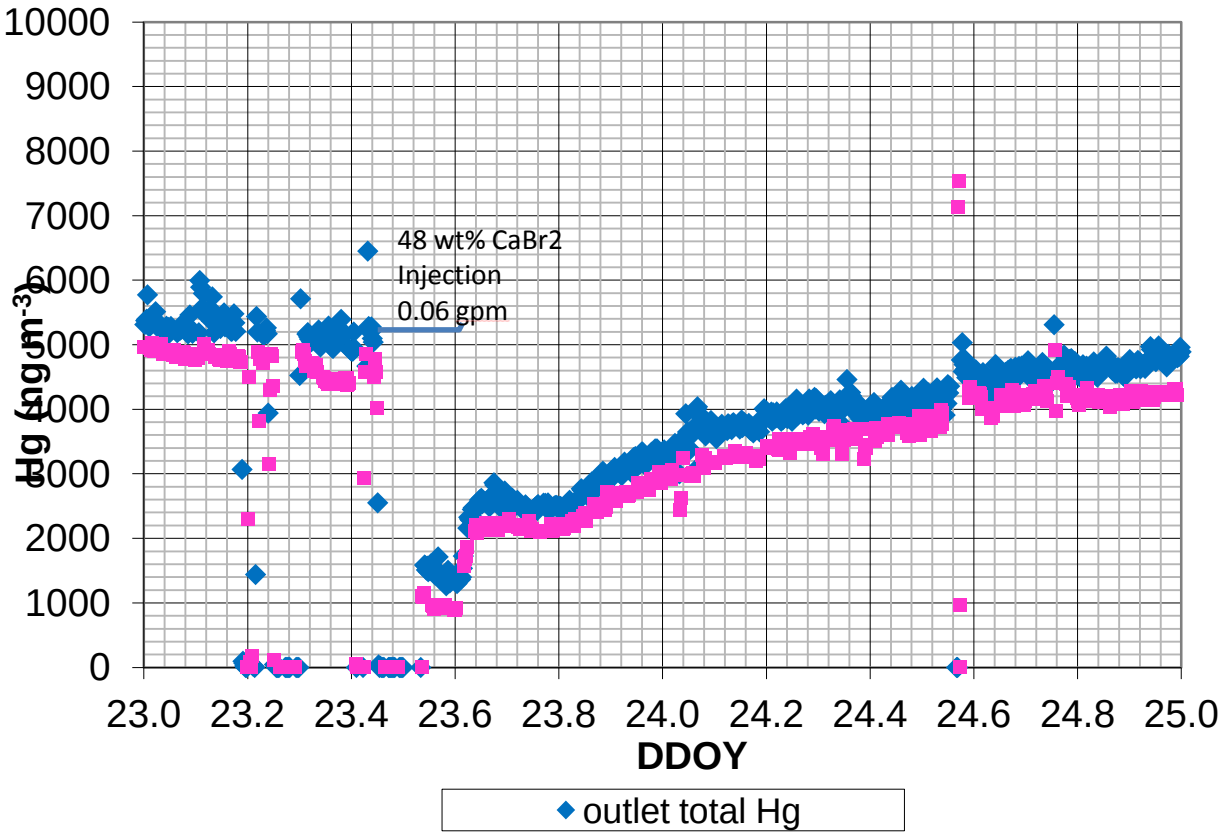

Fig. 3: Hg concentrations resulting from Hg tests conducted on **Minntac Line 3**. Dark blue diamond shapes represent total Hg. Pink squares represent elemental Hg. CaBr2 addition took place between 23.46 and 23.61 on this time scale (units are in digital days). A temporary monitor malfunction occurred just as the test was scheduled to begin but this was not immediately noticed. It was quickly fixed and readings resumed. As commonly occurred at the other taconite plants, the rebound in Hg concentration in stack gases following the test was very slow.

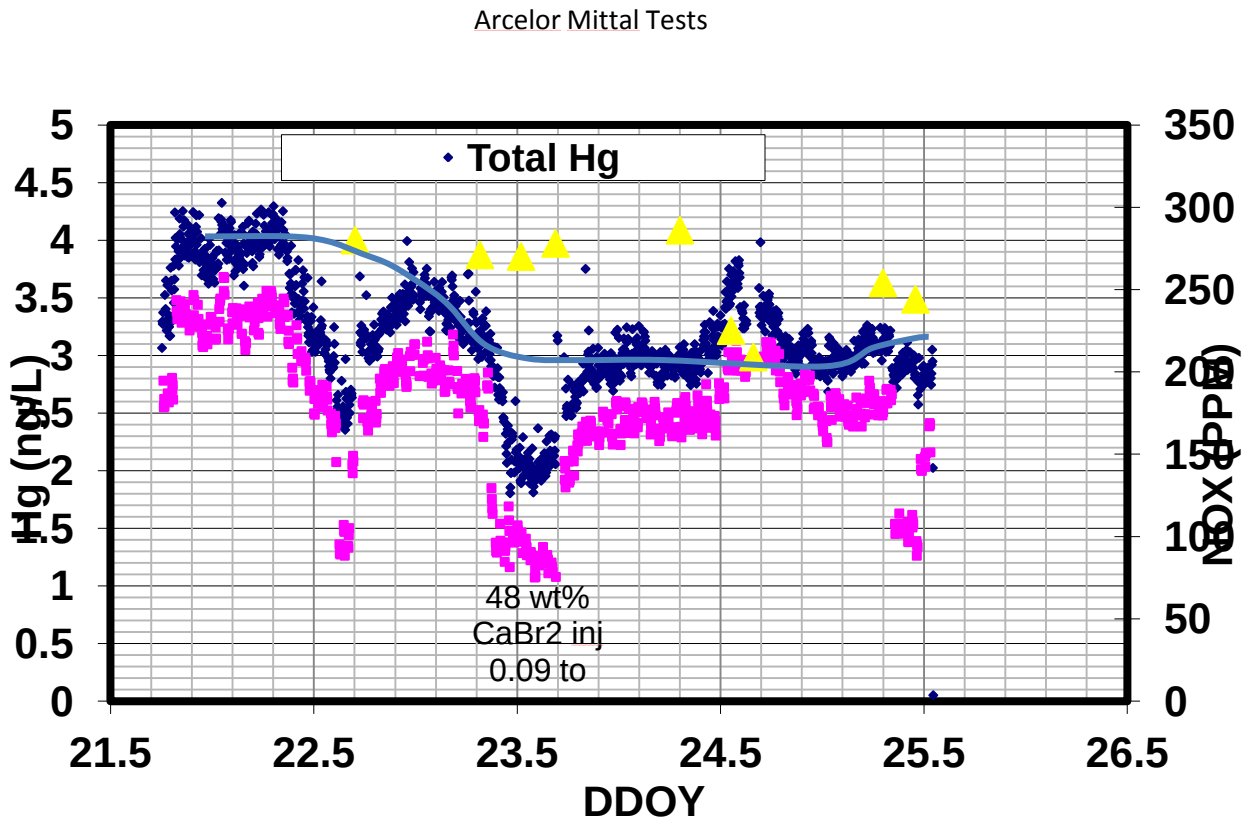

Fig. 4: Hg concentrations resulting from Hg tests conducted on **ArcelorMittal.** Dark blue diamond shapes represent total Hg. Pink squares represent elemental Hg. (yellow triangles are NOX measurements). The baseline shifted greatly prior to this test. Sometime before 22.5, the plant began wasting their scrubber water as a part of the test. Actual CaBr2 injection occurred between 23.3 and 23.7 on this time scale (digital days).

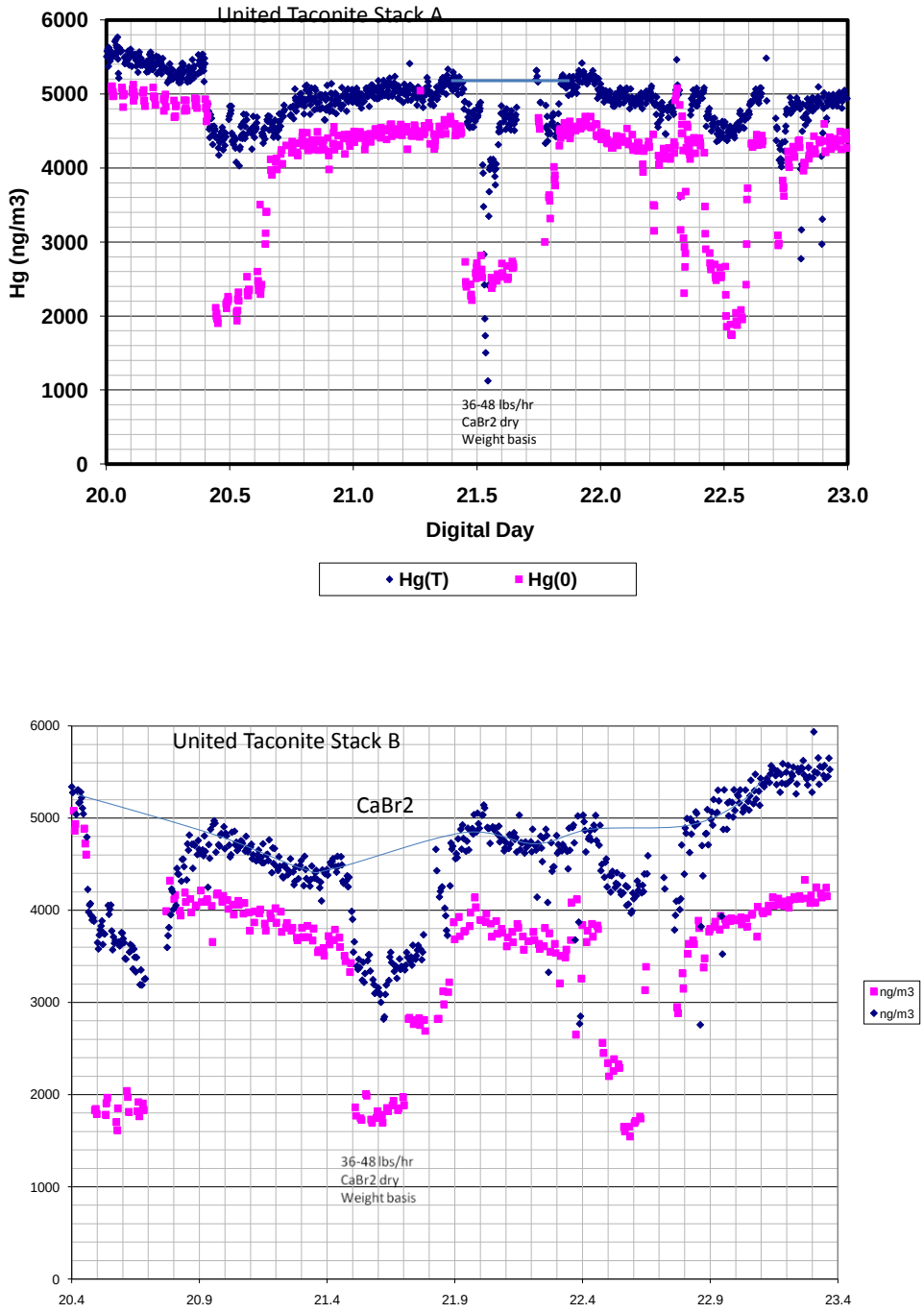

Figure 6. Hg concentration in United Taconite stack emissions during Br injection tests. Dark blue diamond shapes represent total Hg. Pink squares represent elemental Hg. Upper graph is for Stack A and lower graph is for Stack B. CaBr2 injection occurred between 21.4 and 21.65 on this time scale.