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Mercury Transport in Taconite Processing Facilities: (II) Fate of Mercury Captured by Wet Scrubbers

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1 Abstract

The taconite industry in northern Minnesota emits approximately 300-400 kgs of mercury to the atmosphere each year. Most of this mercury is emitted as a result of induration, a process where magnetite concentrate from the ore is heated to high temperatures and oxidized to hematite. Hg(0) is released in the process and emitted to the atmosphere. Oxidized mercury (Hg(II)) is also generated during induration, but this species forms water soluble molecules and/or particulate-bound compounds that can be captured by the plants' wet scrubbers. This report details the mercury concentration in scrubber waters, and provides empirical experimental data needed to understand how the captured mercury partitions during subsequent reintroduction to mineral processing lines.

Concentrating iron at taconite plants involves grinding the ore to a fine grain size followed by magnetic separation to release the primary ore mineral, magnetite, from the more abundant non-magnetic gangue minerals (silicates, carbonates, hematite, goethite). Because magnetic separation is the primary means used to concentrate iron from taconite ore, experiments were conducted to determine how mercury partitions between magnetic and non-magnetic minerals. Mercury bound to nonmagnetic minerals will be rejected from the process and report to tailings basins, while mercury associated with magnetic minerals will be agglomerated into greenballs and re-volatilized during induration.

Results indicate that mercury in scrubber waters adsorb predominantly to non-magnetic minerals during taconite processing. This indicates that introducing scrubber waters and solids back into the taconite processing lines before magnetic separation will result in routing of the majority of captured mercury to tailings basins. Several taconite processing plants could cut mercury in stack emissions by sending scrubber waters and/or solids to the concentrator rather than to the agglomerator. The cost of implementing such changes and the likely savings in mercury emissions is dependent on a number of plant-specific parameters requiring further study.

2 Introduction

Stack emissions from taconite plants represent Minnesota's second largest contributor of mercury to the atmosphere. The emissions occur when the magnetic concentrate from taconite ore (magnetite) is heated to high temperatures in a process known as induration (hardening of taconite pellets). Trace mercury in the concentrate is volatilized mostly to Hg(0) which cannot be captured by the existing wet-scrubbers at taconite processing plants. However, a portion of the mercury volatilized during induration is oxidized to Hg(II) and transported as molecular or particulate-bound species that can be captured by wet scrubbers. This is the second report in a two-part series on control of mercury emissions in taconite processing facilities. The first report addressed mercury oxidation and capture during induration while this paper is concerned with the fate of the mercury following its capture in wet scrubbers.

Berndt et al. (2003) showed that mercury in scrubber waters from taconite plants is both dissolved (Hg(D)) and particle-bound (Hg(P)). The behavior of this captured mercury during taconite processing depends, to a large extent, on the minerals in the scrubber water that adsorb mercury and the routing of those minerals within the plant. A key parameter affecting mercury transport during taconite processing is the relative tendency for the element to adsorb to magnetic (magnetite and maghemite) versus non-magnetic minerals (hematite, quartz, Fe-silicates, and Fe-carbonates, binders or limestone flux). Magnetic separation is the primary method used to concentrate magnetite and reject silicate and carbonate minerals. Thus, mercury adsorbing to magnetic minerals will be directed to the induration furnaces and volatilized. Mercury adsorbing to non-magnetic minerals, meanwhile, will report to tailings basins where, based on low levels of dissolved mercury in tailings waters, disposal appears to be permanent (See Berndt, 2003). This paper provides mercury data from scrubber waters collected over a period of time from four taconite plants and empirical experimental data indicating that most mercury in scrubber waters adsorbs to non-magnetic minerals. This indicates that existing magnetic separators can route most of the captured mercury to tailings basins while selectively recapturing the magnetic iron units from scrubber solids.

3 Background

3.1 Taconite Processing on Minnesota's Iron Range

Taconite is a very hard, relatively low-grade ore that forms the basis of the iron mining industry in Minnesota. In 2005, six taconite companies were active in Minnesota, all of which mined ore on the Mesabi Iron Range. These include, from west to east: US Steel Minnesota Ore Operations-Keewatin Taconite (Keetac), near Keewatin; Hibbing Taconite Company (Hibtac) near Hibbing, US Steel Minnesota Ore Operations-Minntac Plant (Minntac), near Mountain Iron, United Taconite Mines (U-Tac), near Eveleth, Mittal Steel USA Minorca Mine (Mittal; formerly Ispat-Inland Mining Company), near Virginia, and, finally, Northshore (NS) Mining Company, with mines located near Babbitt and ore processing facility located in Silver Bay. All of these taconite plants were built decades ago to process low-grade iron ore, at a time when Hg was not an issue. Thus, atmospheric Hg emissions from taconite processing have grown with the industry, exceeding 100 kg/yr in the late 1960's, and ranging between approximately 200 and 400 kg/yr ever since (Engesser and Niles, 1997; Jiang et al., 1999; Berndt, 2003).

During processing, ore is ground to a fine grain size and magnetite is magnetically separated from other solids producing an iron-rich "concentrate". This concentrate is "rolled" with other minor components (fluxing agents, binders) into wet, friable 1-cm balls (greenballs) in a process known as "agglomeration". The greenballs are then dried and heated to high temperatures during "induration", a process that converts the soft greenballs to hardened pellets composed mostly of hematite. These pellets are durable for shipping and ideal for use in steel-making blast furnaces.

3.2 Mercury Emissions and Capture During Induration

An understanding of mercury release during taconite processing is needed for development of effective control measures for mercury in taconite stack emissions. In Part I of this series, Berndt and Engesser (2005) indicated how mercury release from taconite is distinct from the combustion-related processes that dominate mercury release in coal-fired power plants. First and foremost, the primary source of mercury released during taconite processing on Minnesota's Iron Range is the ore and not the coal or other fuel (Berndt, 2003). Relatively few taconite processing companies use coal to fire their pellets and, for those that do, it only takes about 20 to 40 lbs of coal to fire one long ton of pellets.

Another important difference from coal-fired power plants is that mercury released during induration in taconite companies is exposed to large masses of iron-oxide minerals in the pellet bed as well as in dust transported with the volatiles. This is significant because iron oxides are believed to promote oxidation and capture of Hg^0 especially in the presence of HCl (Galbreath and Zygarlicke, 2000; Zygarlicke, 2003; Pavlish, 2003, Galbreath et al., 2005; Berndt and Engesser, 2005, Berndt et al., 2005; Galbreath, 2005). Indeed, Berndt and Engesser (2005) found that taconite plants having the highest apparent capture efficiencies for mercury (by wet scrubbers) also had the highest Cl and particulate fluxes in process gases, and proposed a relationship such as:

$$Hg^0_{(g)} + \underset{\text{Maghemite}}{3Fe_2O_{3(ss)}} + 2HCl_{(g)} = \underset{\text{Magnetite}}{2Fe_3O_{4(ss)}} + HgCl_{2(g)} + H_2O_{(g)} \qquad (3.2.1)$$

to account for mercury oxidation. By this process, maghemite/magnetite solid solutions (indicated by the subscript "*ss*") created during induration mediate the oxidation of $Hg^o_{(g)}$ in the process gas, and Cl from $HCl_{(g)}$ combines with oxidized mercury to generate a water soluble molecule ($HgCl_{2(g)}$). Bench scale heating experiments confirmed a relationship like Equation 3.2.1 for release of oxidized mercury from taconite and demonstrated, further, that most of the reaction takes place at temperatures less than 450 or 500ºC (Benner, 2005; Galbreath, 2005; Berndt and Engesser, 2005). This release temperature is well below the high temperatures associated with mercury release in coal combustion plants (e.g., approximately 1600ºC). Thus, the high- temperature radicals thought important for mercury oxidation in coal-fired power plants (e.g., Edwards et al., 2001) play a subordinate role compared to low-temperature, iron oxide-influenced reactions during taconite processing.

Regardless of the source of mercury in wet scrubbers at taconite plants, its fate during mineral processing depends on a number of factors including plant routing and adsorption to particles in the process stream. Mercury in scrubber waters is initially present as both dissolved and adsorbed species, but adsorption of the dissolved component is progressive and rapid in scrubber waters. Berndt at al. (2003), for example, measured dissolved and adsorbed mercury on samples that were filtered either immediately upon collection or several days later at the analytical facility. Dissolved mercury at one of the taconite plants (Hibtac) was close to 300 ng/l for samples filtered in the field, but dropped to only 13 ng/l for samples filtered at the analytical laboratory. A corresponding increase in particulate mercury was observed indicating that the dissolved mercury had adsorbed to the suspended solids. The meta-stable nature of mercury distribution in scrubber waters complicates the study of mercury fate during mineral processing and obviates the need to consider and note the relative timing between sample collection and filtration.

A common, but non-universal practice among taconite processing plants is to mix the scrubber solids with the concentrate prior to greenball agglomeration. This slightly increases the overall efficiency of the plant in terms of iron unit recovery but potentially reintroduces previously captured mercury into the induration furnace. This study investigates magnetic separation as a means to selectively reject mercury-bearing minerals but still recover iron units from the scrubber solids. Little is known about the relative adsorption of mercury to magnetite and other minerals such as hematite, silicates, and carbonates in the taconite-processing stream. The empirical data provided herein permits assessment of the relative efficiency of iron recovery and mercury rejection from scrubber waters for companies sending scrubber waters suspended solids to the plants' concentrator.

4 Methods

Four taconite processing plants participated in the present study: Hibbing Taconite (Hibtac), US Steel-Minntac (Minntac), United Taconite (U-Tac), and Mittal Steel (Mittal). These plants were selected based on the concentration of mercury in stack emissions and the presence of wet scrubber systems. Keewatin Taconite (Keetac) was eliminated based on lack of a wet scrubber during the study period. Keetac has since installed a wet scrubber system that began operation in October 2005. Northshore Mining was eliminated from this study because this company has low mercury emissions owing to low mercury concentrations in their ore. The four plants participating in this study were the same four companies that participated in Part I of the study (Berndt and Engesser, 2005).

4.1 Scrubber Waters: Hg(D), Hg(P), Hg(T) and Other Components

Scrubber water samples were collected routinely as part of both this and the previous study (see Berndt and Engesser (2005)). For all but one plant, scrubber waters were accessed by opening a valve and temporarily diverting part of the flow from a much larger pipe. Minntac, Line 7, was the exception. Scrubber water samples from this plant were collected from a dedicated hose that continuously diverted a small portion of the scrubber water stream into an accessible spot above the concentrate thickener.

Hg(D) in this report represents the concentration of dissolved mercury (ng of mercury per liter of solution) which is, in this case, the mercury concentration remaining in the water after filtration through a 0.45-micron filter (Pall Corporation). Hg(P) represents the concentration of mercury in the filter cake (ng of mercury divided by grams of filter cake). Hg(T) represents the total mercury concentration (in ng per liter) which could be determined in one of two ways. The preferred method for calculating Hg(T) is using the formula:

$$\mathrm{Hg(T)} = \mathrm{Hg(D)} + \mathrm{TSS} \times 10 \times \mathrm{Hg(P)} \qquad (4.1.1)$$

where TSS (Total Suspended Solids) is in units of wt%, Hg(D) and Hg(T) are in units of ng/l , and Hg(P) is in units of ng/g. An alternative method to determine Hg(T) is to simply process and analyze unfiltered water samples for mercury, however, this method is less desirable because the 250 ml sample may contain a less representative fraction of suspended solids than the larger sample used for measurement of TSS (see below). Most of the mercury in taconite scrubber systems is usually present as species that are adsorbed on the suspended solids.

Although the concentration of mercury in scrubber waters is typically much higher than in waters from lakes and rivers, all water samples for Hg(D), Hg(P), and Hg(T) analyses were collected using "clean-hands, dirty-hands" procedures. Clean acid-washed bottles were placed into sealed plastic bags prior to leaving the laboratory and not opened except during sampling. Only the designated clean-hands person, wearing clean plastic gloves, handled the sample bottles when they were outside of the plastic bag. All other sampling procedures were conducted quickly and efficiently by the so-called "dirty-hands" person. These procedures were implemented to minimize the risk of contamination from plant dust or from cross-contamination between samples.

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

Filters containing scrubber solids from the above procedures were dried at 104ºC for analysis, weighed, and digested in hot acid (HCl/HNO_3, 3/1). Particulate mercury was analyzed using $SnCl_2$ reduction and gold trap collection, followed by CVAFS detection (modified EPA1631). In most cases, the entire filter was processed with the filter cake to ensure that all of the mercury was analyzed and to prevent sampling bias that might result from scraping the filter cake from the filter paper. The filter papers used as procedural blanks typically contained undetectable mercury (<1 ng) or only a tiny fraction of the mercury found in the scrubber solids. Hg(P) could be calculated by dividing the total mercury detected during total digestion of the filter and filter cake by the net weight of the solids (filter plus solids minus filter weight). However, for samples with relatively high TSS, such that digestion of the entire mass was unwieldy, only a portion of the solids was analyzed without the filter.

Certified reference materials WS-68, NIST2709, and GSR-2 were used to assess recovery and analytical accuracy. As was the case for water, solids were digested and analyzed by Cebam Analytical, Inc.

Procedures were consistently evaluated using blanks to assess the degree of mercury contamination associated with filtration and sampling. Procedural blanks were collected at each site during each visit. One bottle was filled at the sampling site with deionized water brought from the laboratory. In addition, deionized water was filtered at the sampling location and both the water and the filter were saved for analysis. The level of contamination introduced by our procedures was usually insignificant compared to the relatively high concentrations of mercury found in scrubbers. The exceptions to this were when the mass of solids available for measurement of Hg(P) was exceptionally small or when the concentration of mercury was exceptionally low. These samples were considered on an individual basis as discussed in the results.

Total suspended solids (TSS) were analyzed by filtering a two-liter sample of scrubber water collected specifically for this purpose. Solids from this sample were collected on a glass fiber filter (0.7µ), dried at 104ºC overnight, and weighed.

Other samples were routinely collected for measurement of temperature, pH, and conductivity on site. Temperature and pH were measured using a Beckman Model 11 meter with a Ross Model 8165BN combination pH electrode and a Beckman Model 5981150 temperature probe, while specific conductance was measured with a Myron L EP series conductivity meter. For cation (Ca^{++}, Mg^{++}, K^+, Na^+, etc..) analyses, samples were filtered and acidified with nitric acid in the field and then analyzed by inductively coupled plasma mass spectrometry (ICP-MS) at the University of Minnesota, Department of Geology and Geophysics. For anions (Cl^-, Br^-, $SO_4^=$, etc..), samples were stored in clean plastic bottles and analyzed using ion-chromatography (IC, Dionex Ion Chromatograph fitted with a GP40 gradient pump, CD20 conductivity detector, and two AS4 anion exchange columns) at the University of Minnesota, Department of Geology and Geophysics. Chemical data for pH, Ca, and Cl were reported in Part I of this study, and complete data on other elements can be obtained by contacting the authors of this report.

Other Considerations: Previous sampling at taconite companies revealed that considerable variability could be found for samples collected from the same source during the same trip. Two sets of preliminary tests were conducted for this study to evaluate whether this uncertainty is due to sampling difficulty (e.g., scrubber waters are meta-stable and heterogeneous mixtures of solids and water) or if it is due to imprecision or inaccuracy in the laboratory analysis. The first test examined potential errors associated with analysis of Hg(P) by complete digestion of filters and solids. Three filters containing filter cake from a single sample were cut in half and sent to the analytical facility to be processed independently. Although cutting the filters introduced additional weighing errors, analysis of Hg(P) for the two halves from each filter agreed to within 3.4, 4.2, and 8.4 %, respectively. This suggests errors in Hg(P) greater than about 5 to 10% can be attributed to real variation in Hg(P) in the sample being tested.

A second test evaluated the effect of sample residence time (prior to filtration) on analysis of Hg(D) and Hg(P). In this case, a single two-liter sample of scrubber water was collected, and mixed continuously by hand for a two-hour period. 250 ml aliquots were periodically drawn from the bottle, filtered, and analyzed for Hg(D) and Hg(P). Results are displayed in Figure 4.1.1.

The initial sample from this test contained 0.0136 wt% solids with Hg(P)= 2800 ng/g suspended in a solution containing 300 ng/l Hg(D) for a total Hg concentration, Hg(T), of approximately 700 ng/l. Hg(D) decreased to nearly 200 ng/l within 15 minutes and to 130 ng/l within 2 hrs. Hg(P) simultaneously increased to over 3800 ng/g mercury (not shown), but when multiplied by TSS to calculate total mercury on a per/liter basis (Hg(adsorbed) in Figure 4.1.1) it can be seen that the increase in adsorbed mercury mirrored the decrease in Hg(D). Hg(T) remained nearly constant throughout the experiment, allowing for minor mercury adsorption onto the walls of the plastic bottle. Thus, even though this sample contained only 0.0136 % solids, adsorption processes dramatically affected mercury distribution within minutes of sampling. This test illustrates the important role that sample residence time plays on controlling the mercury distribution in scrubber water samples. Although scrubber waters sampled in the present study were filtered at the sampling sites within minutes of sample collection, variation in residence time within the scrubber system can cause significant change in mercury distribution.

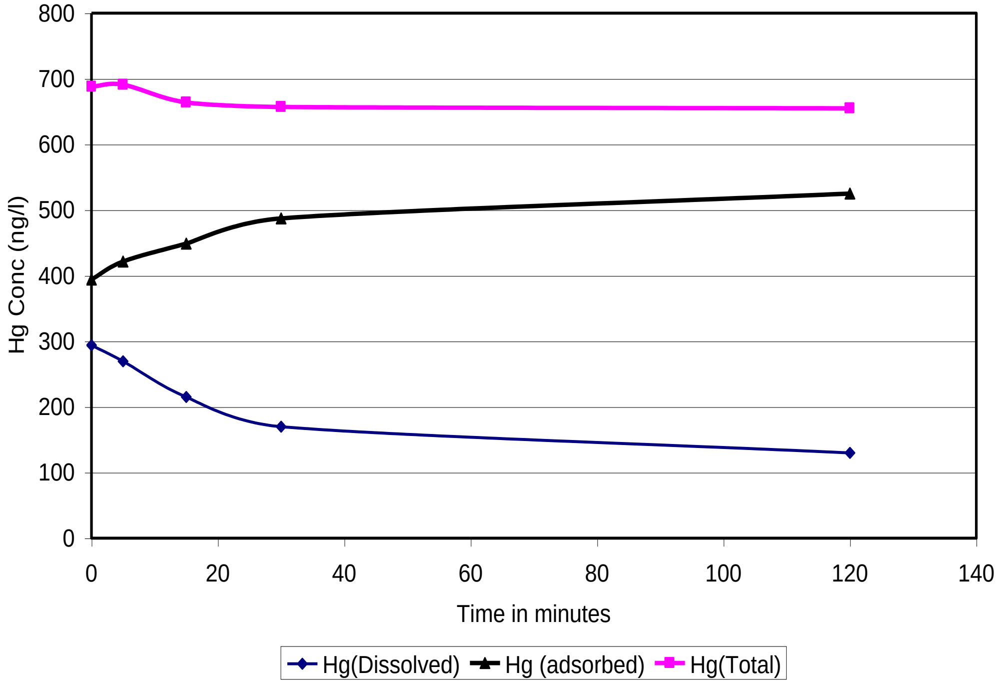

Figure 4.1.1 Results of preliminary time series test from Hibtac. Results demonstrate the rapid transfer of mercury from solution to solids that takes place in scrubber waters. Hg(adsorbed), in this case, is the concentration of adsorbed mercury per liter of water.

4.2 Adsorption Experiments

An important component of this study was to evaluate the relative fractions of mercury adsorbed to magnetic and non-magnetic minerals during mineral processing. Mercury adsorbed to magnetic minerals will follow magnetite through the taconite concentration process, eventually adding to the mercury inventory of "greenballs" that are fed to the taconite induration furnaces while mercury associated with non-magnetic minerals will be rejected from the concentrate and routed to tailings basins. To evaluate the final destination of mercury captured by wet scrubbers, a series of experiments involving mixtures of scrubber waters and tailings was performed and the resulting solids were magnetically separated, filtered, and analyzed for mercury. Scrubber solids are composed mostly of magnetite and other iron oxides containing high mercury, whereas, tailings are essentially composed of non-magnetic minerals containing low mercury. By evaluating the relative distribution of mercury in magnetic and non-magnetic fractions of tailings/scrubber water mixtures, we can establish how mercury captured during induration will behave when introduced to concentrators during taconite processing.

Experiments were performed by placing the reactants in 250 ml acid-washed glass bottles (Teflon lined lids). The bottles were placed on a bottle-roller overnight prior to separation and/or filtration. The bottles were rotated at approximately 14 revolutions per minute, a speed that appeared adequate for keeping solids in suspension and solutions well mixed.

In all cases, experiments were conducted using reactants immediately after they were collected from the processing plants (scrubber waters and suspended solids, freshly produced tailings slurries). Drying and storage of solid samples potentially changes the composition and reactivity of mineral surfaces, while storage of water samples prior to use can lead to precipitation of super-saturated compounds (e.g., fluorite) and/or a change in oxidation state and speciation of dissolved components. Thus, to most closely approximate processes that can be expected to occur within processing plants, only fresh solutions and solids were used as reactants in experiments.

One disadvantage of using fresh reactants, however, involves a difficulty in precisely controlling the relative amounts of water and solids used in the experiments. For example, many experiments that were conducted involved mixing of two suspensions: scrubber waters and tailings. While the relative amounts of suspensions used in the experiments could be controlled, the mass of solid (tailings or scrubber solids) added in each case was unknown until after the experiment was completed and the filtered solids had been dried and weighed.

Filtered solids were, in this case, analyzed using the same method as listed for Hg(P) in section 4.1. However, because total mass of solids or total mass of mercury on the solids was sometimes small, results are reported in terms of masses found in each fraction (total mass of solids and total mass of mercury for magnetic and nonmagnetic fractions, respectively) rather than concentration. For these experiments, Hg(P) values are of secondary importance compared to relative masses of mercury and solids that partition to the magnetic and non-magnetic fractions, respectively.

4.3 Davis-Tube Separation

Magnetic separations were performed using Davis Tubes located at the Coleraine Minerals Research Laboratory, University of Minnesota (CMRL). The tubes are composed of glass and mounted vertically to permit gravity flow. A powerful electromagnet, located near the center of the tube, prevents transport of magnetic minerals but permits transport of water and non-magnetic minerals through an outlet at the base of the tube. The tube was pre-loaded with water until the water line was located above the magnet. The entire sample including water and suspended solids was then loaded into the tube with the magnet in the “on” position. Additional deionized water was then added to transport all of the nonmagnetic minerals through the tube and into a waiting container. This was continued until all of the water beneath the magnet was visibly clear. The magnet was then deactivated and the remaining minerals were all rinsed into a clean bottle. The solids used for mercury analysis were retrieved by filtration of each fraction, magnetic and non-magnetic, onto separate pre-weighed filters.

5 Results and Discussion

5.1 Scrubber Water Chemistry

Scrubber water mercury chemistry is displayed in Table 5.1.1. Various components of scrubber water chemistry displayed include: Hg(D) in ng per liter of filtered water *(in this case, filtered immediately upon sampling)*; particulate mercury, Hg(P), in ng per gram of filter cake *(also for samples filtered immediately upon sampling)*, total suspended solids (TSS in wt %), and total mercury (Hg(T)). Note that Hg(T) in Table 5.1.1 does not always match what might be expected by application of Equation 4.1.1. This is because Hg(D), Hg(P), and Hg(T) were not always determined on the same set of samples.

One defining characteristic for scrubber water mercury chemistry at taconite plants is the wide variation that occurred throughout the study. For example, the standard deviation (σ) for Hg(D) values for Hibtac was nearly half of the average Hg(D) value. Hg(P) at Hibtac varied by even more, ranging from a low value of 604 ng/g up to a high of 8396 ng/g. Similar or even greater variability was found at all of the plants.

Part of this variability could certainly be attributed to the sampling of a heterogeneous and ever-changing process stream composed of water and suspended solids. However, a closer inspection of the data indicates that not all of the variability shown in Table 5.1.1 can be attributed to this. In particular, analysis of duplicate samples collected during the same visit to a plant usually agreed to much less than 25% of the reported value. Visits for those few times when $\sigma > 25\%$ are marked with an asterisk. The observed differences in mercury concentration and distribution through time at each plant are likely process related, and represent day to day changes in ore composition and plant operation. Any method to route captured mercury to tailings basins must be sufficiently robust to work for a wide range of scrubber water conditions.

Another important result suggested by the data in Table 5.1.1 is that the chemistry of scrubber water is generally different at different plants. United Taconite has generally low Hg(P) but high TSS compared to the other plants. Hg(D) at United and Mittal is more variable and reaches values that can be higher or lower than the less variable Hg(D) concentrations observed at Hibtac and Minntac. Hibtac scrubber water is generally lower in TSS and Hg(T) than scrubber water at the other plants. To account for the difference in mercury distribution at plants, we note that each plant in this study is unique in terms of furnace type and scrubber water handling procedures (Table 5.1.2).

Minntac and United use grate-kiln furnaces where the greenballs are dried and heated on a short grate before being dumped into a rotating kiln where they are fired. Hibtac and Mittal use a straight grate for drying, heating, and firing of the pellets. Abrasion of taconite pellets within the rotating kiln in grate-kilns likely generates more dust than simple transport of pellets along a straight grate. In addition, the straight grate plants use multiclone dust collectors to capture some of the dust prior to the wet scrubber. The result is higher particulate capture rate in grate-kilns as compared to straight-grates.

Another key difference is that United Taconite and Mittal Steel recirculate their scrubber waters while Hibtac and Minntac use "single-pass" scrubber systems.

Recirculating scrubbers allow mercury and dust to accumulate and react for greater periods of time than single-pass scrubber systems. Hg(T) values reflect both the total mercury capture rate of scrubber systems and the accumulation of mercury due to recirculation in some systems.

Averaged values for Hg(T) are lowest at Hibtac (736 ng/l) because this company has a relatively low capture rate compared to other companies (Berndt and Engesser, 2005) and because the company operates a single-pass scrubber. In contrast, Hg(T) is highest at United Taconite (9867 ng/l) owing to a relatively high mercury capture rate (Berndt and Engesser, 2005) and use of a recirculating scrubber system. Minntac, with an averaged Hg(T) value of 1540 ng/l for Line 4 and 2009 ng/l for Line 7, has a high capture rate but does not recirculate scrubber waters. Mittal, with average Hg(T) of 4867 ng/l has relatively low capture rates for mercury but *does* recirculate scrubber water. Thus, Hg(T) for the latter two companies is intermediate to the values measured at Hibtac and U-Tac.

Accounting for differences in the relative concentrations of individual components such as Hg(D) and Hg(P) is more complicated than accounting for difference in Hg(T). This is because Hg(D) and Hg(P) are affected by adsorption phenomena as described in the methods section (See Figure 4.1.1) and because the relative amount of dust generated and captured at each plant varies. Hg(P) values will increase with increasing Hg capture rates and residence times in the scrubber system, but decrease with increasing TSS. For example, Hg(P) in Hibtac scrubber water, which has low TSS (0.02 wt%), was high (2619 ng/g) compared to U-Tac (609), which had high TSS(1.6 wt%) over the study period. High TSS has a diluting effect on Hg(P) at U-tac; a large amount of captured mercury adsorbed to an even larger mass of suspended solids. Conversely, Hibtac's wet scrubber system has low TSS, and thus, any mercury that is captured adsorbs to fewer solids, and results in proportionately higher Hg(P). It is probably no coincidence that the highest Hg(P) for Hibtac was found on a day when TSS was the lowest.

Hg(D) values are much more variable at plants operating recirculating scrubbers (United Taconite and Mittal Steel) than they are in plants with "single-pass" scrubber systems (Hibtac and Minntac). This effect may be due to incomplete mixing processes in the recirculating scrubbers. If some samples contain water that has recently passed through the scrubber, while other samples contain water that has resided in a "dead" zone for a period of time, then Hg(D) will reflect variable amounts of adsorption within the scrubber system. Moreover, it is uncertain how many times water being sampled at any particular time has been exposed to gases in a recirculating scrubber. Such differences are less likely to occur in a single-pass scrubber system because all of the water passes through the scrubber only once.

Table 5.1.1: Scrubber Water Chemistry. Year 2003 samples are from Berndt et al. (2003). Number in parenthesis is the number of analyses that were averaged to obtain the shown value. A "*" before the value indicates averaged values with σ > 25%.

Plant	Date	Hg(D) (ng/l)	Hg(P) (ng/g)	TSS (wt%)	Hg(T) (ng/l)
Hibtac	2/20/2003	256(1)	1406(1)	0.010(1)	492(1)
	5/8/2003	339(2)	606(2)	0.033(3)	532(4)
	9/11/2003	231(2)	604(2)	0.038(1)	460(2)
	1/27/2004	292(2)	1484(2)	0.018(1)	556(2)
	5/12/2004	*237(2)	*2039(2)	0.013(1)	*502(2)
	7/27/2004	294(2)	2813(2)	0.014(2)	688(7)
	2/15/2005	721(2)	2874(2)	0.024(1)	1410(2)
	5/19/2005	234(3)	8396(3)	0.006(3)	731(3)
	8/15/2005	567(3)	3354(3)	0.021(1)	1250(4)
	Average	352	2619	0.020	736
	St. Dev.	173	2378	0.011	351
Minntac Line 4	2/19/2003	116(1)	1285(1)	0.058(6)	1167(6)
	5/9/2003	81(2)	160(2)	0.315(2)	578(4)
	9/10/2003	474(2)	434(2)	0.217(1)	1993(8)
	1/28/2004	164(2)	1557(2)	0.145(1)	2422(2)
	Average	209	859	0.184	1540
	St. Dev.	180	668	0.109	826
Minntac Line 7	1/28/2004	223(2)	2489(2)	0.041(1)	1251(2)
	5/11/2004	291(2)	2723(2)	0.052(1)	1706(2)
	7/27/2004	305(2)	2564(2)	0.095(1)	2746(2)
	12/1/2004	234(2)	2830(2)	0.075(1)	2357(2)
	2/16/2005	*331(2)	2855(2)	0.058(1)	1987(2)
	5/20/2005	256(3)	1360(3)	0.100(3)	1613(3)
	8/15//2005	338(3)	3001(3)	0.065(1)	2407(4)
	Average	283	2546	0.070	2009
	St. Dev.	46	551	0.022	524
Evtac/ United	2/18/2003	64(1)	979(1)	0.916(3)	*6612(3)
	1/27/2004	273(3)	697(3)	0.903(1)	6571(3)
	5/11/2004	164(2)	594(2)	1.270(1)	7714(2)
	7/28/2004	112(2)	459(2)	2.260(1)	10491(2)
	11/29/2004	32(2)	322(2)	2.410(1)	7791(2)
	2/14/2005	1440(2)	848(2)	2.180(1)	19923(2)
	5/19/2005	962(3)	856(3)	1.210(4)	11829(3)
	8/17/2005	25(3)	534(3)	0.295(1)	1605(3)
	Average	456	602	1.604	9892
	St. Dev.	599	214	0.824	6043
Ispat/ Mittal	2/20/2003	1216(1)	617(1)	0.328(1)	3418(3)
	5/8/2003	852(2)	*2970(2)	0.142(1)	*5274(4)
	9/11/2003	1032(3)	2094(3)	0.175(1)	4697(3)
	1/27/2004	*1025(2)	*1563(2)	0.137(1)	3166(2)
	5/12/2004	3312(2)	*440(2)	0.095(1)	3730(2)
	11/30/2004	388(2)	1975(2)	0.118(1)	2719(2)
	2/15/2005	304(2)	4032(2)	0.170(1)	7157(2)
	5/19/2005	465(3)	2774(3)	0.123(3)	3865(3)
	8/17/2005	19(2)	8930(2)	0.078(1)	6865(4)
	Average	897	3630	0.117	4867
	St. Dev.	1360	3236	0.035	2009

Table 5.1.2 Data for plants that supplied solids for experiments discussed in this study.

	Indurator type, Fuel	$^{+}$*Additives*	*Scrubber System*	**"Blowdown" routing*
Hibtac	Straight-Grate, Nat. Gas	0.4 to 1% Flux, Na-Bentonite	Single-Pass	3400 gpm to concentrator
Minntac (L7 only)	Grate-Kiln, Coal, Nat. Gas.	8% Flux Na-Bentonite	Single-Pass	2950 gpm to concentrate thickener
United	Grate-Kiln, Petr. Coke/ Coal	Cellulose Binder	Recirculating	800 gpm to chip regrind
Mittal	Straight-Grate, Nat. Gas	10% Flux, Na-Bentonite	Recirculating	400 gpm to concentrate filter

$^{+}$Flux is a Ca-Mg limestone. *Blowdown rate is total scrubber water output per induration machine.

5.2 *Hibtac*

Hibtac operates a straight grate furnace and uses a single-pass scrubber system. This combination produces scrubber water containing low TSS and low total mercury Hg(T), but relatively high Hg(P). The average Hg(D) was 352 ng/l while average Hg(T) was 736 ng/l, meaning that nearly half of the mercury captured by wet scrubbers is dissolved and not initially bound to particulates. Scrubber water at this plant is sent directly to the concentrator, without removal of any suspended solids, and used for grinding coarse taconite ore. Two samples of process water collected from locations in the concentrator close to where the scrubber water and solids are mixed into the concentrator process stream contained only 4.3 and 4.7 ng/l Hg(D), a value only 3.0 ng/l greater than that of the procedural blanks (1.7 ng/l). Thus, it appears that extensive adsorption of Hg(D) occurs within the concentrator immediately upon mixing with the taconite ore. The challenge at this plant is to determine what fraction of the mercury captured by scrubbers is transported back to the induration furnaces and what fraction is routed to tailings basin.

Two series of experiments were conducted on Hibtac scrubber solids to evaluate mercury adsorption on magnetic and non-magnetic minerals (Table 5.2.1). In the first series mercury was allowed to adsorb from solution to scrubber solids overnight and the resulting solids were magnetically separated using the Davis Tube and analyzed for mercury. It was found that 92 % of the adsorbed mercury was associated with the nonmagnetic sample in HB-1-1 and 86% was adsorbed to non-magnetic sample in HB-1-2. The mass of minerals in the scrubber water was small because TSS was low but, based on the relative weights of the filter cake in HB-1-2, 73 % of the scrubber solid was composed of nonmagnetic minerals. Thus, for that sample, 86% of the mercury adsorbed to 73% of the solids.

A second series (HB-2) of experiments was performed to evaluate adsorption of mercury in mixtures of tailings and scrubber waters. In this case, 0, 5, or 10 mls (milliliters) of a suspension containing fine tailings from Hibtac was mixed with approximately 240-250 mls of freshly sampled scrubber water (HB-2-1 through HB-2-3, in Table 5.2.1). An additional experiment was performed using tailings and deionized water (HB-2-Tails). The purpose of adding a small amount of tailings to the mixture was to increase the mass of non-magnetic minerals compared to magnetic fraction and observe the relative distribution of mercury following adsorption from solution.

As was the case for experiment HB-1-1, TSS was very low, and so the mass of magnetic minerals in the scrubber solids was difficult to measure with accuracy (approximately 3 mg). Nevertheless, 95 to 96% of the mercury adsorbed to the non-magnetic samples in HB-2-1, HB-2-2, and HB-2-3. The percentage of mercury on non-magnetic minerals in these experiments was nearly the same with or without addition of tailings, indicating that addition of small amounts of tailings had little effect on mercury distribution among magnetic and non-magnetic fractions.

Because mass of mercury and mass of solids was measured in each of the experiments, Hg(P) concentrations could be computed for the magnetic and nonmagnetic fractions and compared to concentrations in bulk samples collected at the same time. Figure 5.2.1 shows Hg(P) for samples collected at the same time that experiments HB-1-1 and HB-1-2 were conducted. In this case three samples were collected and filtered immediately when these experiments were conducted. The bulk solids had an average of 3350 ng/g mercury. A fourth sample of scrubber water was collected at the same time but filtered when the magnetic separations was performed. As expected, the concentration for this bulk solid increased (to 4950 ng/g) due to adsorption of dissolved mercury onto the solids. Non-magnetic samples from the experiments had even higher mercury than this, or approximately 6000 ng/g, while magnetic samples had less, or only about 2500 ng/g.

A similar comparison for mercury concentration in bulk solids, and magnetic and non-magnetic fractions from the HB-2 series of experiments is shown in Figure 5.2.2. As was the case for the first series of experiments, Hg(P) for magnetic minerals was far less than for non-magnetic minerals. This again indicates mercury in scrubber waters preferentially adsorbs to non-magnetic minerals both in scrubber waters and scrubber water/tailings mixtures.

These results imply that scrubber solids at Hibtac are mostly non-magnetic and that mercury is attracted more to non-magnetic minerals (hematite, silicates) than to magnetic minerals (magnetite, maghemite). This has important consequences for mercury cycling at Hibtac's processing plant. The data indicate that very little of the captured mercury is returned to the induration furnaces at this plant. This is because scrubber waters at Hibtac are sent to the concentrator where non-magnetic minerals containing the absorbed mercury are rejected by the magnetic separators. Approximately 90% or more of the captured mercury at this plant is routed to the tailings basin. Future efforts at this plant to oxidize and capture a larger percentage of the mercury from process gases should result in a corresponding decrease in mercury emissions because most of the captured mercury is already routed to tailings basins.

Table 5.2.1: Total mass and mercury distribution among magnetic and non-magnetic minerals for scrubber water-tailings mixtures at Hibtac. Bracketed numbers represent the actual masses of reactants and mercury on the filters following Davis Tube separation. Total water volume in each case was 250 mls. Unbracketed numbers represent the percentages of the total mass or of total mercury for the magnetic and non-magnetic fractions, respectively.

	Reactants	*Magnetic Solids*	*Nonmag. Solids*	*Hg in Magnetic Fraction*	*Hg in Nonmag. Fraction*
HB-1-1	Scrubber Water	(? mg)	(24 mg)	8 (12 ng)	92 (152 ng)
HB-1-2	Scrubber Water	27 (8 mg)	73 (22 mg)	14 (20 ng)	86 (128 ng)
HB-2-1	Scrubber Water + 0% Tailings	(3 mg)	(24 mg)	4 (8 ng)	96 (174 ng)
HB-2-2	Scrubber Water + 2% Tailings	8 (11 mg)	92 (116 mg)	4 (8 ng)	96 (221 ng)
HB-2-3	Scrubber Water + 4% Tailings	9 (18 mg)	91 (173 mg)	5 (10 ng)	95 (175 ng)
HB-2-tails	Tailings + DI Water	10 (14 mg)	90 (130 mg)	(<1 ng)	(7 ng)

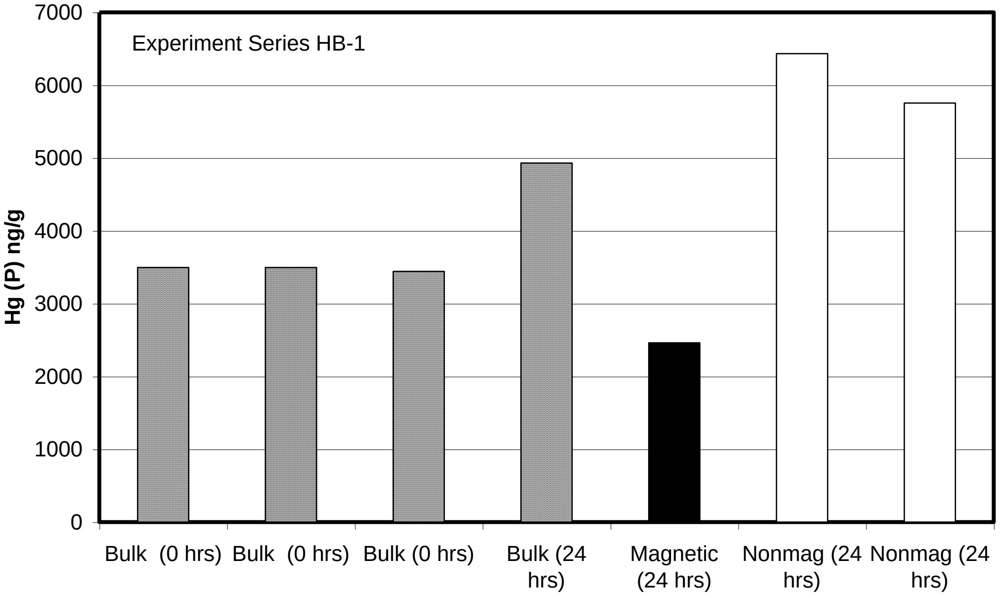

Figure 5.2.1 Hg(P) for solids from Hibtac in scrubber waters and in experiments involving scrubber waters. Bulk solids (hatched pattern) are composed of mixtures of magnetic (black pattern) and non-magnetic (white pattern) minerals, each of which have different mercury concentrations. Hg(P) for the bulk solid increased to close to 5000 ng/g, however, most of this mercury was adsorbed to non-magnetic minerals.

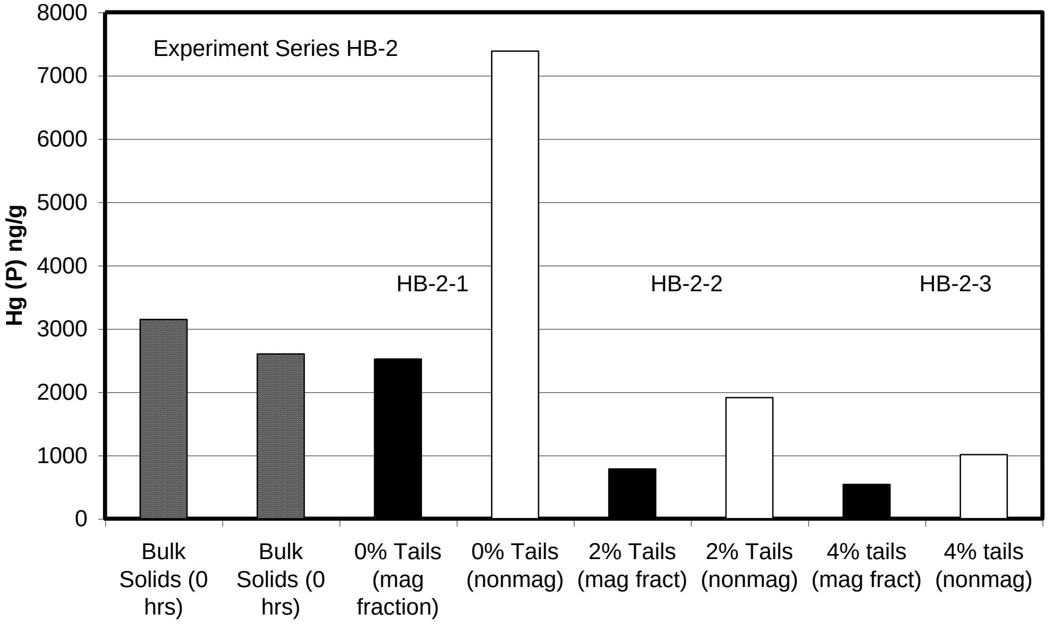

Figure 5.2.2 Hg(P) for solids from Hibtac in scrubber waters and in experiments involving mixtures of scrubber waters and fine tailings. Hg(P) for the nonmagnetic fraction was always greater than for the magnetic fraction, but the concentration in both decreased due to dilution effect from addition of tailings. Patterns are the same as described in Figure 5.2.1.

5.3 Minntac Line 7

Minntac sends their scrubber solids to a thickener where they are mixed with grate spill material that has passed through a grinding mill. Most of the scrubber water overflows the scrubber thickener. Sample analyses indicate that most of the mercury that was in the scrubber water adsorbs to the solids that exit through the scrubber-thickener underflow. These scrubber-thickener underflow solids eventually mix with the concentrate that is used to make greenballs. This means that most of the mercury captured in the scrubbers is recycled back to the greenballs. Thus, the percentage of captured mercury that is currently sent to the tailings basin at this plant appears to be small. Nevertheless, if mercury at this plant also adsorbs preferentially to the non-magnetic fraction as at Hibtac, then this plant could immediately cut stack emissions by sending their scrubber solids back to the concentrator rather than mixing them with the concentrate.

Experiments at this plant were conducted during three separate visits as shown in Table 5.3.1. For MN-1-1, MN-2-1, MN-2-2, and MN-3-4, scrubber water was reacted with suspended solids overnight prior to performing a Davis-Tube separation. Unlike Hibtac, scrubber solids at Minntac were predominantly magnetic. Approximately 75 to 94% of the scrubber solids in these experiments were magnetic. As was the case at Hibtac, however, the mercury appeared to adsorb preferentially to non-magnetic minerals suspended in the scrubber water. In fact, 90 to 94% of the mercury was associated with the non-magnetic minerals, even though the mass of non-magnetic minerals was small compared to the mass of magnetic minerals.

Results from experiments involving scrubber waters and tailings mixtures at Minntac were conducted using approximately 50 mls of tailings slurry and 200 mls of scrubber water or, in one case, deionized water. The tailings/solids mixtures resulted in addition of a large mass of magnetic minerals as well as non-magnetic minerals, such that the relative mass of magnetic and non magnetic fractions was approximately the same for all of the experiments. In all of the experiments with tailings, 96 to 98 % of the mercury was found on the non-magnetic solids.

Figures 5.3.1 and 5.3.2 show the relative concentrations for mercury on the magnetic and nonmagnetic fractions as compared to that of the bulk solids collected at the same time as the experiments were begun. Results from MN-1-1 are shown in Figure 5.3.1 where the scrubber water had initial Hg(P) concentration close to 2000 ng/g. The results indicate that the non-magnetic fraction had a mercury concentration approaching 10,000 ng/g, while the magnetic fraction had a relatively low concentration of approximately 220 ng/g.

A similar comparison for experiments MN-2-1 and MN-2-2 is shown in Figure 5.3.2. The scrubber water solids in the these experiments had an average Hg(P) of 3000 ng/g. Results reveal that the non-magnetic fraction had between 40,000 and 50,000 ng/g mercury, while the magnetic fraction only averaged 210 ng/g mercury. Results for MN-3-4 (not shown in a figure) were similar to this.

In the experiments with tailings (Series MN-3 experiments in Table 5.3.1), the mercury concentrations in magnetic and non-magnetic fractions were dominated by their respective concentrations in the primary tailings (Figure 5.3.3). Interestingly, the mercury concentration in the magnetic fraction in all three experiments was essentially identical to that of the starting tailings, while that in the non-magnetic fraction was uniformly elevated, owing to sequestration of most of the mercury from the scrubber water.

The results of these experiments imply that Minntac could potentially cut mercury emissions by sending their scrubber solids back to the concentrator grinding mills rather than mixing them with concentrate and sending them to the agglomerator. Recycled mercury to Line 7 would be decreased by 90 to 94% if scrubber water solids were routed to the concentrator. In addition, the magnetic fraction of these solids, or approximately 75 to 94% of the suspended solids for this line, would be recovered in the concentration process.

Table 5.3.1 Mass and mercury distribution among magnetic and non-magnetic minerals for scrubber water-tailings mixtures at Minntac. Bracketed numbers represent the actual masses of reactants and mercury on the filters following Davis Tube separations. Total water volume in each case was 250 mls. Unbracketed numbers represent the percentages of the total mass or of total mercury for the magnetic and non-magnetic fractions, respectively.

	Reactants	*Magnetic Solids*	*Nonmag. Solids*	*Hg in Magnetic Fraction*	*Hg in Nonmag. Fraction*
MN-1-1	Scrubber Water	74 (56 mg)	26 (20 mg)	6 (12 ng)	94 (181 ng)
MN-2-1	Scrubber Water	94 (94 mg)	6 (7 mg)	7 (19 ng)	93 (262 ng)
MN-2-2	Scrubber Water	94 (80 mg)	6 (5 mg)	6 (17 ng)	94 (283 ng)
MN-3-Tails	Tailings + DI water	5 (1.364 g)	95 (26.74 g)	4 (32 ng)	96 (789 ng)
MN-3-1	Tailings + Scrubber Water	4 (0.919 g)	96 (19.84 g)	2 (20 ng)	98 (879 ng)
MN-3-2	Tailings + Scrubber Water	5 (1.079 g)	95 (22.6 g)	3 (27 ng)	97 (815 ng)
MN-3-3	Tailings + Scrubber Water	4 (0.846 g)	96 (19.3 g)	4 (22 ng)	96 (540 ng)
MN-3-4	Scrubber Water	90 (59 mg)	10 (7 mg)	10 (18 ng)	90 (172 ng)

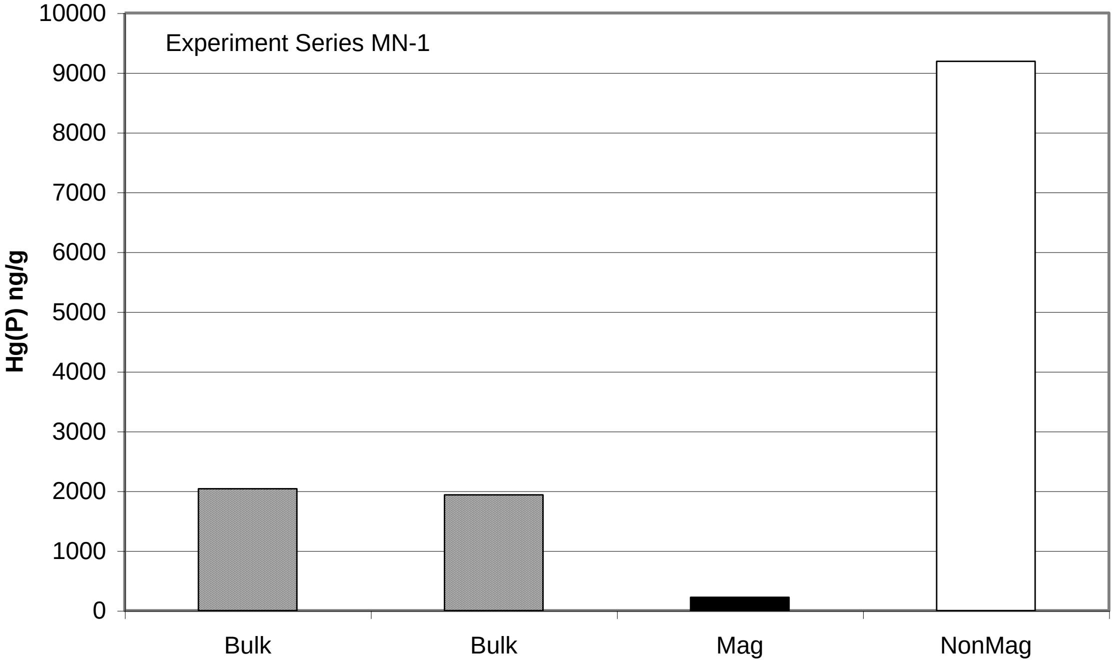

Figure 5.3.1 Hg(P) for solids from MN-1 experiments for Minntac as described in Table 5.3.1. Bulk solids (hatched pattern) are composed of mixtures of magnetic (black pattern) and non-magnetic (white pattern) minerals, each of which have different mercury concentrations. The nonmagnetic fraction was greatly enriched in Hg relative to the bulk solid and magnetic fraction.

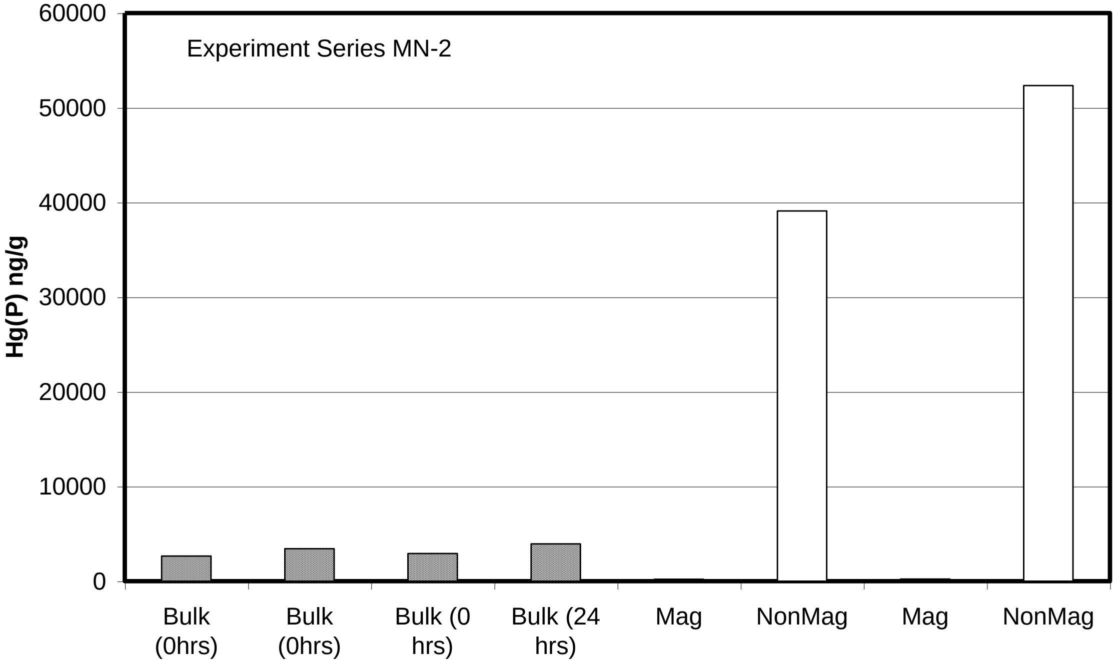

Figure 5.3.2 Hg(P) for solids from MN-2 experiments in Table 5.3.1. Patterns have same meaning as in Fig. 5.3.1. The nonmagnetic fraction was once again greatly enriched in Hg relative to the bulk solid and magnetic fraction, reaching 50000 ng/g.

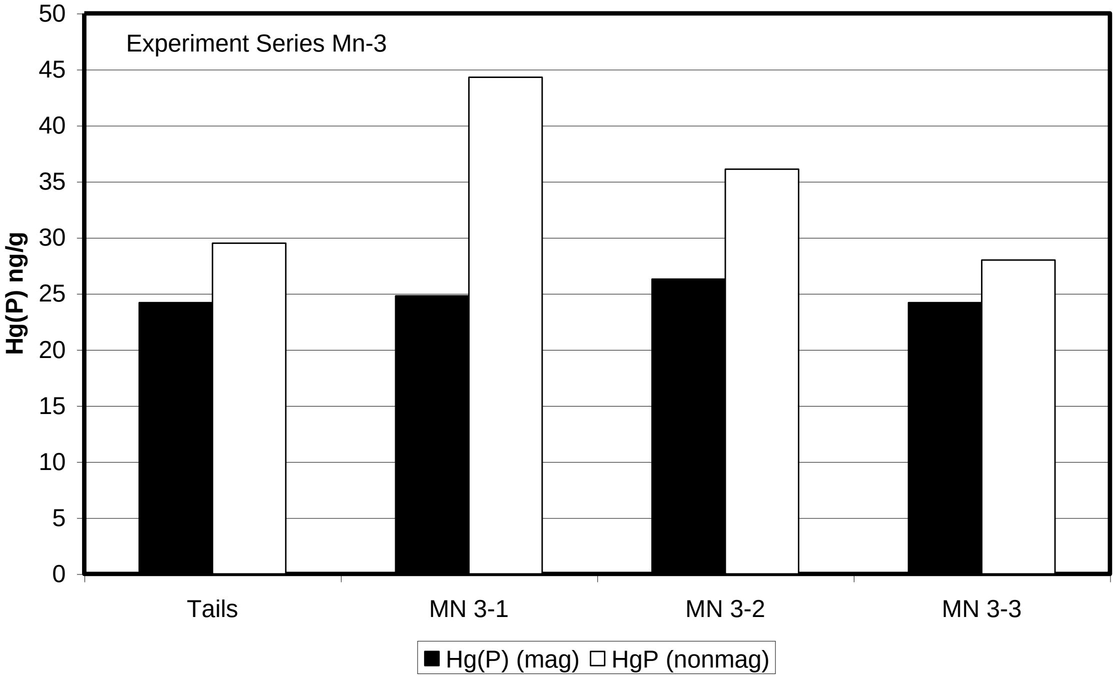

Figure 5.3.3 Hg(P) for solids from MN-3 experiments in Table 5.3.1. Patterns have same meaning as in Fig. 5.3.1. The scale is greatly changed from previous two figures. Adding scrubber water to tailings had little impact on the mercury concentration in the magnetic fraction in the tailings, but increased significantly the mercury concentration in the non-magnetic fraction.

5.4 United Taconite

United Taconite sends their scrubber waters and solids to a chip regrind mill where it is mixed with other solids, reground, and mixed with concentrate from the plant. Because only a very small fraction of the mercury captured at United Taconite is initially dissolved in the water, it was expected that most of the captured mercury at this plant would be recycled back to the induration furnace with the scrubber solids.

However, two samples of the water returning to the concentrator from the agglomerator were collected in one of our visits to the taconite plant. These samples contained lower Hg(D) (= 12 ng/l), Hg(P) (= 117 ng/g), TSS (=0.497 wt%) and Hg(T) (= 589 ng/l) than scrubber water samples, but the concentrations were much higher than expected for a stream containing overflow from a concentrate thickener. It appears that, at least on the day this site was sampled, significant mercury was being sent from the pellet plant back to the concentrator. This stream will be studied in greater detail in future studies. As was the case at Hibtac, the fate of the mercury sent to the concentrator depends on how the element partitions between magnetic and non-magnetic minerals.

Experiments at this plant were conducted during three separate visits as shown in Table 5.4.1. For UN-1-1, UN-2-1, UN-2-2, and UN-3-4, scrubber water was reacted with suspended solids overnight prior to performing a Davis Tube magnetic separation of the solids. The average magnetic and non-magnetic fractions were nearly equal but significant variation was observed: the magnetic fraction ranged from as low as 42 percent of the total mass up to 68 percent. The tendency for mercury to adsorb to non-magnetic minerals was not as strong as was observed at Minntac. Only 76 to 88% of the mercury partitioned onto the non-magnetic minerals in scrubber water at U-Tac while 90 to 94 % of the mercury partitioned into the non-magnetic fraction at Minntac, despite the fact that the scrubber solids from Minntac had a lower non-magnetic fraction than those from U-Tac.

Results from experiments involving scrubber waters and tailings mixtures at United Taconite were conducted by mixing approximately 50 mls of tailings slurry, and 200 ml of freshly collected scrubber water. While magnetic minerals were present in the tailings, the mixture had a net increase in the non-magnetic fraction up to 86 to 87% of the total solids. In the experiments with tailings, 86 to 90 % of the mercury was found on the non-magnetic fraction. Tailings with no addition of scrubber water had 94% of the mercury on the non-magnetic fraction while scrubber water with no addition of tailings for the experiments had only 76 % of the mercury on the non-magnetic fraction.

Figures 5.4.1 and 5.4.2 show the relative concentrations for mercury on the magnetic and nonmagnetic fractions as compared to that of the bulk solids collected at the same time the experiments were performed. Results from test UN-1-1 are shown in Figure 5.4.1. The scrubber water in this test had an initial Hg(P) of approximately 800 ng/g. The Hg(P) of the magnetic fraction was about 300 ng/g and the Hg(P) for the nonmagnetic fraction was more than 1300 ng/g. Experiments UN-2-1 and UN-2-2 are shown (Figure 5.4.2). The solids suspended in the scrubber water for these tests initially had Hg(P) averaging 530 ng/g which is intermediate to the 130 and 710 ng/g values for Hg(P) of the magnetic and nonmagnetic fractions, respectively. For UN-3-4 (not shown in a figure), where the scrubber water had an initial Hg(P) of 460 ng/g, the magnetic fraction had only 182 ng/g mercury, while the non-magnetic fraction contained approximately 1240 ng/g mercury. Thus, as was the case for Hibtac and Minntac, mercury partitions to the non/magnetic fraction of scrubber solids.

In the experiments with tailings (Series UN-3 experiments in Table 5.4.1), the mercury concentrations in magnetic and non-magnetic fractions were dominated by their respective concentrations in the primary tailings (Figure 5.4.3), but the concentration of mercury in both the magnetic and non-magnetic fractions increased relative to tailings. This was expected because the magnetic fraction for solids suspended in the scrubber water at U-Tac had a relatively large fraction of the mercury (24%) when the experiments were performed, and the magnetite in tailings had very little mercury. The concentration of mercury in the magnetic fraction represents a mixture of mercury from the two sources of magnetite – scrubber solids magnetite and tailing magnetite.

Comparing these results with those from Minntac suggests a possible mechanism exists at United Taconite that promotes some adsorption onto the magnetic fraction in scrubber solids. One possibility is that the adsorption of mercury is related to the presence of more oxidized coatings on magnetite grains at Utac than at Minntac. Scrubber solids at U-Tac have a larger non-magnetic fraction than scrubber solids at Minntac. Because the chief non-magnetic mineral in scrubber solids is likely magnetite that has been converted to hematite, a larger non-magnetic component indicates greater oxidation of the solids. However, it is important to note that magnetite grains only partially converted to hematite will be sufficiently magnetic to partition into the magnetic fraction of solids separated with a Davis Tube.

Another possibility is adsorption of the mercury to silicate gangue minerals associated with the magnetic minerals in the magnetic fraction. Minntac and Mittal use flotation, a process that removes additional silica from concentrate not removed by magnetic separation. United Taconite does not use flotation and, therefore, the mineral gauge concentration associated with magnetic minerals in the concentrate will be higher than at Minntac or Mittal.

Minntac and Mittal Steel also produce fluxed pellets, which introduces carbonate minerals into the agglomeration and induration processes. Fluxed pellets are manufactured by adding 8-10% limestone (dolomite and calcite) to the concentrate prior to producing greenballs for induration. These carbonate minerals potentially affect solution pH in the scrubber waters, although the pH of tailings/scrubber water mixtures in concentrators at taconite plants is typically high (8 to 9).

Table 5.4.1 Mass and mercury distribution among magnetic and non-magnetic minerals for scrubber water-tailings mixtures at U-Tac. Bracketed numbers represent the actual masses of reactants and mercury on the filters following Davis Tube separations. Total water volume in each case was 250 mls. Unbracketed numbers represent the percentages of the total mass or of total mercury for the magnetic and non-magnetic fractions, respectively.

	Reactants	*Magnetic Solids*	*Nonmag. Solids*	*Hg in Magnetic Fraction*	*Hg in Nonmag. Fraction*
UN-1-1	Scrubber Water	51	49	20	80
		(826 mg)	(801 mg)	(257 ng)	(1051 ng)
UN-2-1	Scrubber Water	42	58	12	88
		(286 mg)	(397 mg)	(38 ng)	(287 ng)
UN-2-2	Scrubber Water	48	52	15	85
		(511 mg)	(550 mg)	(66 ng)	(386 ng)
UN-3-Tails	Tailings + DI water	4	96	6	94
		(865 mg)	(19.35 g)	(22 ng)	(323 ng)
UN-3-1	Tailings + Scrubber Water	14	86	12	88
		(1.542 g)	(9.15 g)	(106 ng)	(808 ng)
UN-3-2	Tailings + Scrubber Water	13	87	10	90
		(1.706 g)	(11.71 g)	(100 ng)	(876 ng)
UN-3-3	Tailings + Scrubber Water	13	87	14	86
		(2.136 g)	(13.77 g)	(137 ng)	(843 ng)
UN-3-4	Scrubber Water	68	32	24	76
		(1.305 g)	(624 mg)	(238 ng)	(772 ng)

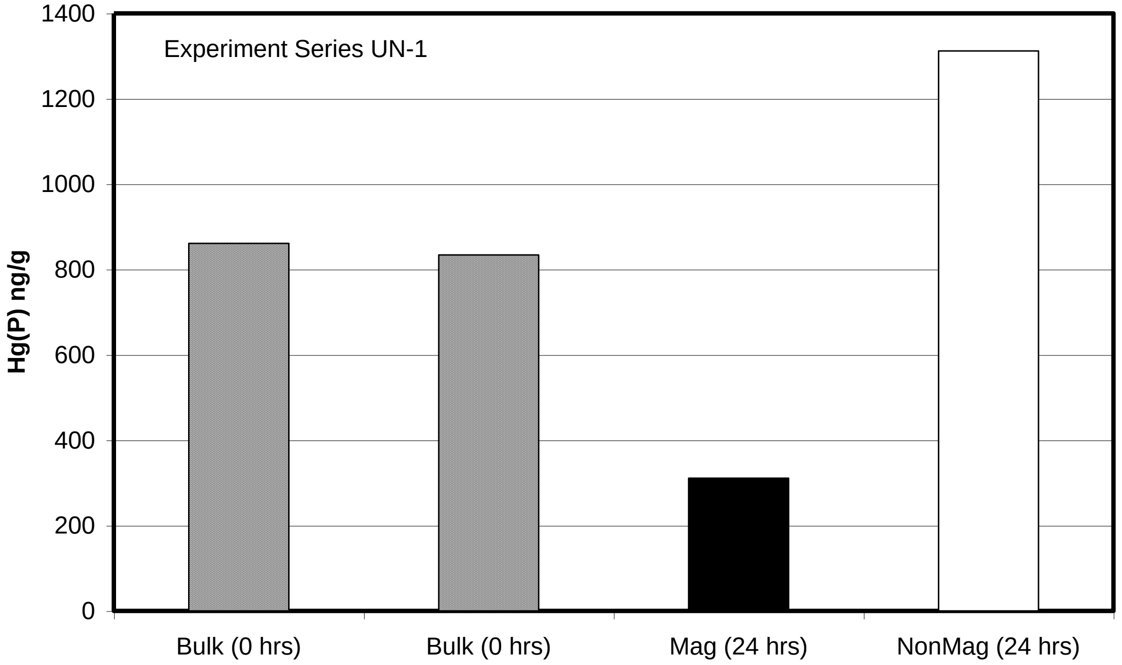

Figure 5.4.1 Hg(P) for solids from UN-1 experiments in Table 5.4.1. Bulk solids (hatched pattern) are composed of mixtures of magnetic (black pattern) and non-magnetic (white pattern) minerals, each of which have different mercury concentrations. As was observed for Hibtac and Minntac, Hg(P) was enhanced in nonmagnetic minerals compared to the bulk solid or to magnetic minerals.

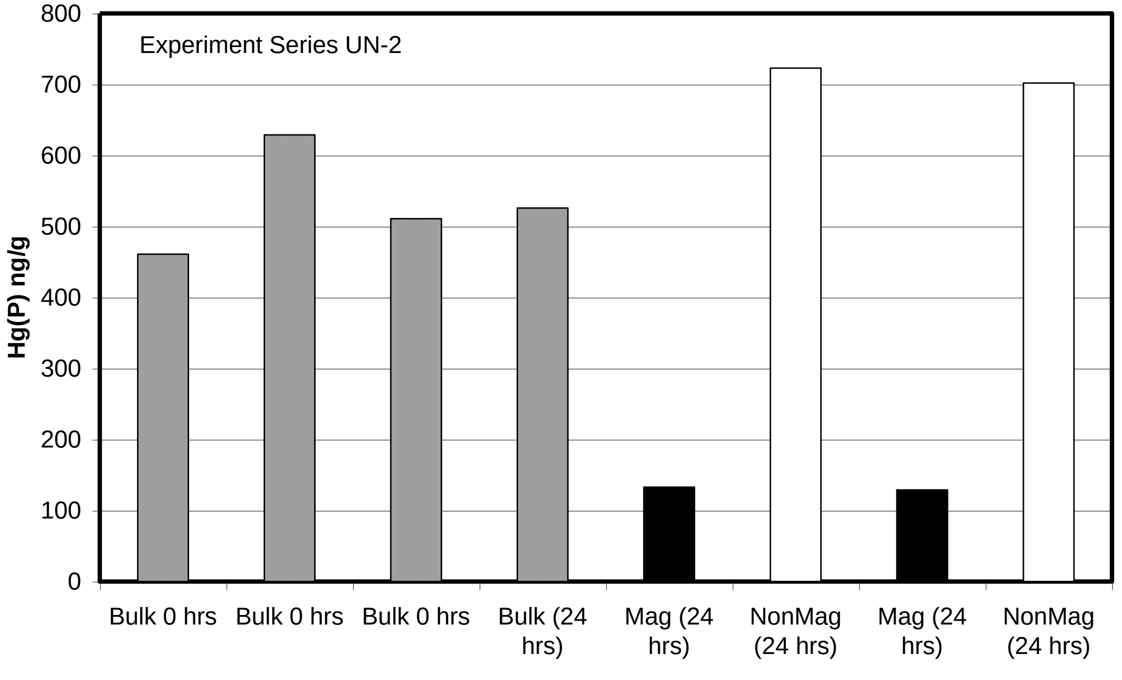

Figure 5.4.2 Hg(P) for solids from UN-2 experiments in Table 5.4.1. Distribution is similar to that shown in Figure 5.4.1, although concentrations for bulk, magnetic, and nonmagnetic fractions are lower.

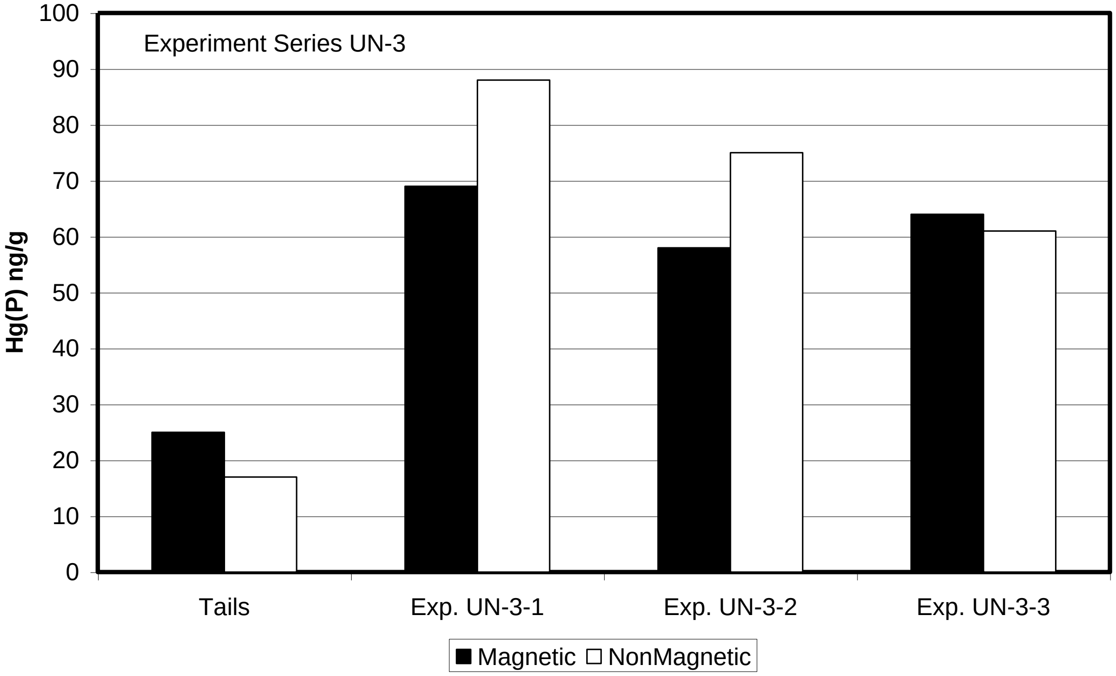

Figure 5.4.3 Hg(P) for solids from UN-3 experiments described in Table 5.4.1. Adding scrubber waters to tailings increased the mercury concentrations in both the magnetic and non-magnetic phase. Solid black pattern represents mercury concentration in the magnetic fraction while white pattern represents the mercury concentration in the corresponding non-magnetic fraction.

5.5 Mittal

Mittal Steel uses a recirculating scrubber and has a relatively low blow-down rate. This means that the average residence time for mercury in the scrubber system is long compared to other systems and thus provides an opportunity for Hg capture and adsorption to occur, potentially leading to very high, but quite variable Hg(D) and Hg(P) values. This company sends their scrubber solids and waters to the concentrate filter and little mercury remains dissolved in the water following the process. Thus, most of the captured mercury at this plant also appears to recycle back to the induration furnace and probably only a small fraction is directed to the tailings basin.

Experiments at this plant were conducted during three separate visits as shown in Table 5.5.1. For ML-1-1, ML-2-1, ML-2-2, and ML-3-4, scrubber water was reacted with suspended solids overnight prior to performing a Davis Tube magnetic separation of the solids. The non-magnetic minerals dominate the scrubber solids at this plant comprising 54 to 73% of the total solids. Moreover, the experiments clearly indicated that mercury adsorbed overwhelmingly to the nonmagnetic minerals (94 to 96% of the total mercury was adsorbed to non-magnetic minerals). Thus, although this plant produces scrubber solids that are even more oxidized than scrubber solids at United Taconite, the mercury avoids adsorption to magnetic minerals in a manner similar to that found at Minntac and Hibtac. When tailings/scrubber water mixtures were used in experiments (See ML-3-1, ML-3-2, and ML-3-3), the fraction of mercury on the non-magnetic minerals dominated that on the magnetic minerals, as well. In particular, 92 to

96 % of the mercury was associated with the non-magnetic minerals in tailings and tailings/scrubber water mixtures.

Figures 5.5.1 and 5.5.2 provide a comparison of Hg(P) in magnetic and non-magnetic components and bulk solids suspended in scrubber waters. For ML-1-1 (Figure 5.5.1), H(P) for the bulk scrubber water was initially close to 4000 ng/g, but Hg(P) concentrations in the magnetic and nonmagnetic fractions were only 100 and 2770 ng/g, respectively. The low values suggest either that mercury was dissolved from solids during the experiments or that the sample used in the experiments was non-representative of the scrubber water. For ML-2-1 and ML-2-2 (Figure 5.5.2), the Hg(P) of the bulk solution was 8930 ng/l and this value increased to 9200 ng/l during reaction overnight. However, mercury in the samples that underwent magnetic separation averaged only 1090 and 8780 ng/g Hg(P) for the magnetic and nonmagnetic fractions, respectively. The solids in all three of these experiments had lower mercury concentrations than the bulk solution, which suggests that mercury dissolved during the experiments. This loss of mercury did not appear to occur in experiments with scrubber solids from other companies, nor was it noticed in the scrubber solids in experiment ML-3-3 (not shown), where the bulk solid had 1975 ng/g Hg(T), the magnetic fraction contained 260 ng/g, and the non-magnetic fraction concentration was slightly greater than 2411 ng/g.

One possibility to account for the loss of mercury from scrubber solids is that it is the result of an equilibration process whereby solids containing very high mercury concentrations begin to release mercury into the water used in the experiments. It may not be coincidence that the two samples in our study where mercury appeared to be lost involved solids that had the highest concentrations of mercury.

Mercury concentrations for tailings experiments (ML-3 series of experiments in Table 5.5.1 and also shown in Figure 5.5.3) indicate that the mercury concentration in both the magnetic and non-magnetic fractions increased. This was expected based on the relatively low concentration for mercury in both magnetic and non-magnetic fractions of the tailings as compared to the concentrations in the respective fractions for the scrubber solids.

Table 5.5.1 Mass and mercury distribution among magnetic and non-magnetic minerals for scrubber water-tailings mixtures at Mittal Steel. Bracketed numbers represent the actual masses of reactants and mercury on the filters following Davis Tube separations. Total water volume in each case was 250 mls. Unbracketed numbers represent the percentages of the total mass or of total mercury for the magnetic and non-magnetic fractions, respectively.

	Reactants	*Magnetic Solids*	*Nonmag. Solids*	*Hg in Magnetic Fraction*	*Hg in Nonmag. Fraction*
ML-1-1	Scrubber Water	46	54	3	97
		(78 mg)	(91 mg)	(8 ng)	(252 ng)
ML-2-1	Scrubber Water	27	73	5	95
		(28 mg)	(73 mg)	(30 ng)	(636 ng)
ML-2-2	Scrubber Water	34	66	6	94
		(38 mg)	(76 mg)	(42 ng)	(671 ng)
ML-3-Tails	Tailings + DI water	4	96	6	94
		(404 mg)	(11.10 g)	(9 ng)	(137 ng)
ML-3-1	Tailings + Scrubber Water	5	95	8	92
		(385 mg)	(8.16 g)	(18 ng)	(208 ng)
ML-3-2	Tailings + Scrubber Water	5	95	7	93
		(343 mg)	(6.62 g)	(19 ng)	(253 ng)
ML-3-3	Tailings + Scrubber Water	5	95	4	96
		(522 mg)	(11.01 g)	(17 ng)	(370 ng)
ML-3-4	Scrubber Water	33	67	5	95
		(66 mg)	(138 mg)	(17 ng)	(332 ng)

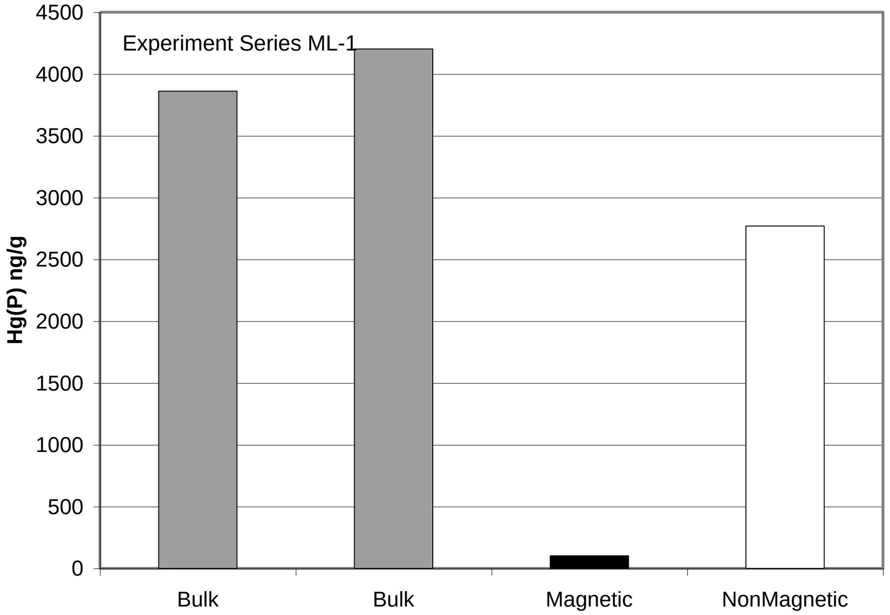

Figure 5.5.1 Hg(P) for magnetic and nonmagnetic minerals in scrubber solids at Mittal for ML-1 experiments described in Table 5.5.1. Patterns are same as in previous figures. Both non-magnetic and magnetic phases had low Hg(P) compared to bulk solids suggesting some redissolution of adsorbed Hg.

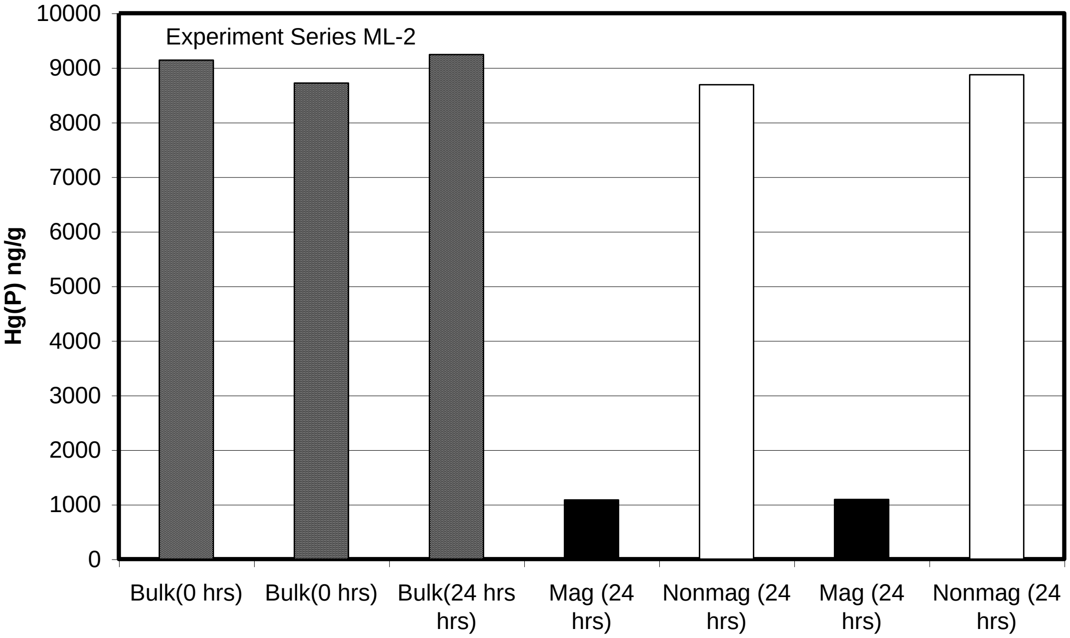

Figure 5.5.2 Hg(P) magnetic and nonmagnetic minerals in scrubber solids at Mittal Steel for ML-2 experiments in Table 5.5.1.

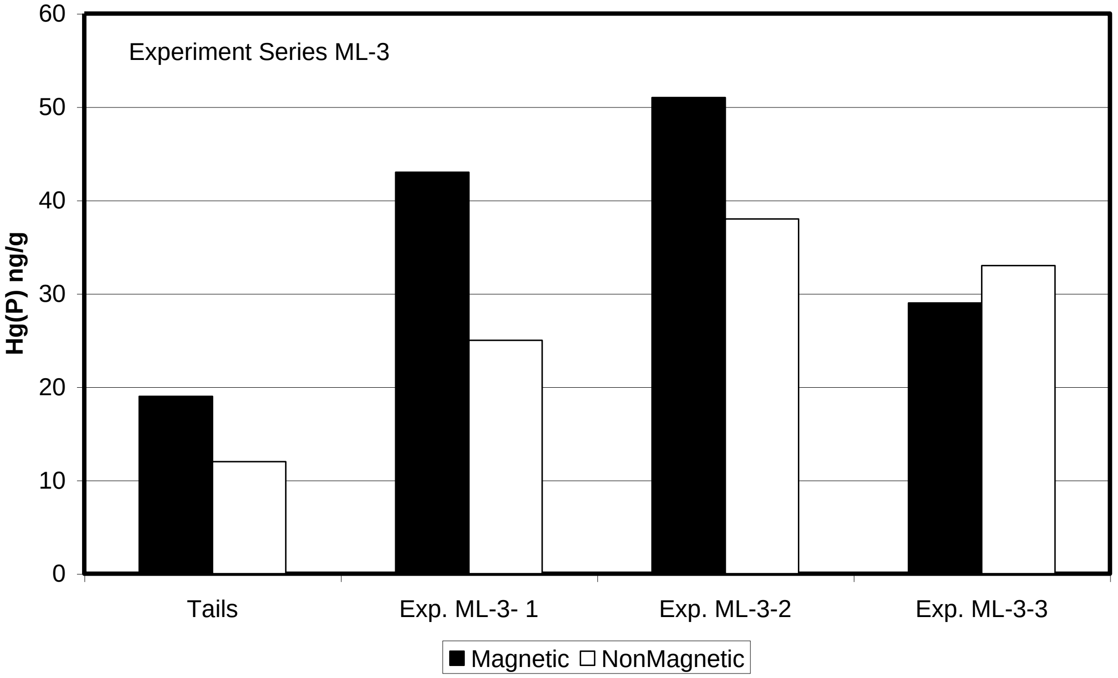

Figure 5.5.3 Hg(P) following addition of scrubber water to tailings at Mittal Steel. The concentration of mercury increased for both magnetic and non-magnetic fractions, however, the total concentration for either fraction remained relatively low.

6 Conclusions

Wholesale recycling of scrubber-solids back to the induration furnace results in recovery of iron-oxide units from the dust, but also results in recycling and release of a large fraction of the captured mercury. One alternative to this practice would be to route all of the scrubber solids to tailings basins or similar disposal sites, but this practice would result in loss of previously processed product. Another alternative involves sending scrubber solids back to the concentrator to permit retrieval of the magnetic components of the scrubber solids while disposing of the non-magnetic components to tailings basins. Projected mercury rejection and iron recovery efficiencies for this process is plant specific (Table 6.1) and depends on the mineralogy and chemistry of scrubber waters and suspended solids:

(1) Magnetic separation of scrubber solids in the concentrator is already practiced at Hibtac. Results from this study suggest this company is eliminating approximately 90-95% of the captured mercury from its process lines. If a means can be found to increase oxidation and capture of mercury from process gases during induration, this company appears to be well poised to reject the additional mercury without further change to its mineral processing lines.

(2) Magnetic separation of scrubber solids would have the greatest impact on decreasing mercury emissions at Minntac. This company has a single pass scrubber that captures dust with a high magnetic content, and with very high levels of mercury in the small non-magnetic fraction. 90 to 94% of the recycled mercury would be rejected if

Minntac routed the scrubber solids to the grinding mills in the concentrator, and 75 to 94% of the iron units associated with the dust could be recovered. However, it is unknown at this time what implications such routing would have on pellet quality and production rates.

(3) Magnetic separation of scrubber dust does not appear to be as efficient for United Taconite as at Minntac. United Taconite already appears to route most of the captured mercury back to the concentrator; however, not enough samples were obtained to quantify this. If U-Tac routed all of the scrubber solids to the grinding mills in the concentrator, then approximately 75 to 88% of the mercury in the scrubber dust would be rejected with the tailings. The company would lose about half of the iron units associated with the scrubber dust.

(4) Magnetic separation of scrubber dust at Mittal Steel would be highly effective in preventing recycling of captured mercury to the induration furnaces. Mercury concentrations on solids can reach high levels owing to use of a recirculating scrubber at this plant. Mixing tailings with the scrubber waters disperses the mercury onto a larger mass of non-magnetic solids. If Mittal sent their scrubber solids to the concentrator grinding mills, it would prevent recycling of 94 to 97% of mercury contained on the scrubber dust, but they would also lose more than half of the iron units associated with the dust.

Future planned research will compare the feasibility of magnetic separation to reject mercury in taconite plants as opposed to other mineral processing techniques such as rejection of scrubber fines (Benner, 2001) or full disposal of scrubber solids (currently practiced at Keetac).

Table 6.1 Summary of data for scrubber solid recycling at taconite plants.

Plant	*Estimated Mercury Capture Efficiency*[*]	*Current Hg Rejection Rate*	*Mercury Rejection Rate for Magnetic Separation*	*Iron Recovery Rate for Magnetic Separation*
Hibtac	0.11 ± 0.06	86-96%	86-96%	10-27%
Minntac 7	0.33 ± 0.13	Near 0%	90-94%	74-94%
United	0.27 ± 0.08	Unknown	76-85%	42-68%
Mittal	0.14 ± 0.06	Near 0%	94-97%	27-46%

[*] From Berndt and Engesser (2005)

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