Mercury Chemistry and Mössbauer Spectroscopy of Iron Oxides During Taconite Processing on Minnesota's Iron Range

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ABSTRACT

The Minnesota Department of Natural Resources (DNR) has been studying the distribution and fate of mercury at four Minnesota taconite processing facilities. This paper details and interprets mercury concentration data and Mössbauer spectroscopic measurements made on solids generated in heating experiments and collected from taconite plants on Minnesota's Iron Range. During taconite processing, wet "greenballs" consisting predominantly of magnetite and possible other components (limestone flux, organic or bentonite binder, trace non-ore components) are conveyed into a furnace and converted to hematite by heating to 1200-1300ºC in the presence of air. Magnetite is first converted to magnetite/maghemite solid-solutions which attract and collect mercury released from greenball samples during conversion to hematite deeper in the furnace. The dual capture and release mechanisms can lead to high mercury concentrations in solids collected from the intermediate zones in the furnaces. Wet scrubbers sometimes capture large amounts of oxidized mercury released from induration, suggesting extensive transport of oxidized mercury takes place in process gases. A relationship such as:

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

is proposed to control this mercury oxidation rate during taconite induration. Future work is planned to verify the importance of this reaction and to determine if relatively simple, passive processes can be found to enhance mercury oxidation and capture during taconite induration.

INTRODUCTION

Taconite is a very hard, relatively low grade ore that forms the basis of the iron industry in Minnesota today. In 2005, six taconite companies were active, all of which mine on the Mesabi Iron Range. 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; Berndt et al., 2003).

During processing, magnetite is magnetically separated from other solids in the composite ore and the resulting concentrate is rolled with other minor components (fluxing agents, binders) into balls (“greenballs”). Mercury is released during induration, a process where the greenballs are hardened and converted to hematite by heating to high temperatures (1200 to 1300ºC) in air.

Mercury emissions from taconite are generated under conditions quite distinct from those in the much better studied coal-fired power plants (see Pavlish et al, 2003, for a review). For example, the primary source of mercury at coal-fired power plants is the fuel, while the primary source of mercury released during taconite processing on Minnesota’s Iron Range is typically the ore (Berndt, 2003). This is partly because relatively few companies use coal to fire their pellets, but even when coal is used, it takes only about 20 to 30 lbs of coal to fire one long ton of pellets. Unless the plant uses a low-mercury ore and/or high-mercury coal the amount of mercury released from the magnetite concentrate exceeds that derived from the coal.

Secondly, taconite processing gases remain more oxidizing than is typical for coal-fired power plants, which consume much of the oxygen in the combustion process (Zahl et al., 1995). Oxygen is an important component for reaction with mercury molecules during transport since oxidized mercury, Hg^{2+}, is much more soluble in scrubber waters than the volatiled reduced form, Hg^0. A more oxidizing flue gas may provide opportunities for taconite plants to control mercury through simple oxidation pathways.

Third, mercury released during taconite induration is exposed to large masses of potentially reactive iron oxide minerals. These minerals, although also present in smaller amounts in coal fired power plants, have been shown to promote oxidation and capture of Hg^0 from flue gases (Zygarlicke, 2003; Pavlish, 2003; Galbreath et al., 2005). The increased exposure of process gases to iron oxides during taconite processing may have a fundamental impact on mercury transport processes.

However, one important similarity between taconite processing and coal-fired power plants is that flue gases in both types of facilities can contain chloride, an important mercury oxidation agent, particularly in the presence of iron oxides (Pavlish et al, 2003; Galbreath et al., 2005). In the case of power plants, the fuel is the primary Cl source, but fluxing agents and pore fluids that accompany solids into induration furnaces are the primary source of Cl in taconite processing plants. The present study, was conducted specifically to evaluate how the presence of iron oxides and Cl in Minnesota’s processing plants affect mercury transport in induration furnaces.

METHODS

A major goal of this study was to provide fundamental information on relationships between magnetite oxidation, mercury concentration, and heating in taconite induration furnaces. Samples heated in experiments under various conditions were compared to samples collected in induration furnaces using Mössbauer spectroscopy to evaluate iron-oxide mineralogy and total digestion to analyze mercury.

Solids from bench-scale heating experiments were obtained from Blair Benner of the University of Minnesota-Coleraine Mineral Research Laboratory (CMRL) (Benner, 2005). Benner heated samples from taconite companies in N_2 gas and air for periods of time up to 20 minutes and then measured the remaining mercury. Temperatures ranged from 300 to 700ºC. Several of the samples obtained from Benner were analyzed for iron-oxide mineralogy using Mössbauer spectroscopy.

Samples were also collected from beneath the grates in active induration furnaces at four taconite processing facilities. An important distinction between taconite operations is that some use “grate-kiln” furnaces (Fig. 1) while others operate “straight-grates” (Fig. 2). Grate-Kiln facilities dry and heat pellets on a grate, but final firing is done in a rotating kiln. Drying, heating, and firing procedures are all performed on the grate in a straight-grate facility, however, a “hearth layer” consisting of pre-fired pellets is added beneath fresh greenball samples to protect the grate from the intense heat used in the firing zones. This fundamental difference in plant design, when superimposed with other less distinct differences in plant operation procedures makes every plant on the Iron Range unique. Samples in this study were collected from two straight grates and two grate kilns. Samples were sieved (<100-mesh) to remove chips and large grains and then analyzed for total mercury at Cebam, Inc., in Seattle, Washington. Most samples were also analyzed for iron-oxide mineralogy using Mössbauer spectroscopy. In each case, information on temperature was collected for the zones where dust was sampled.

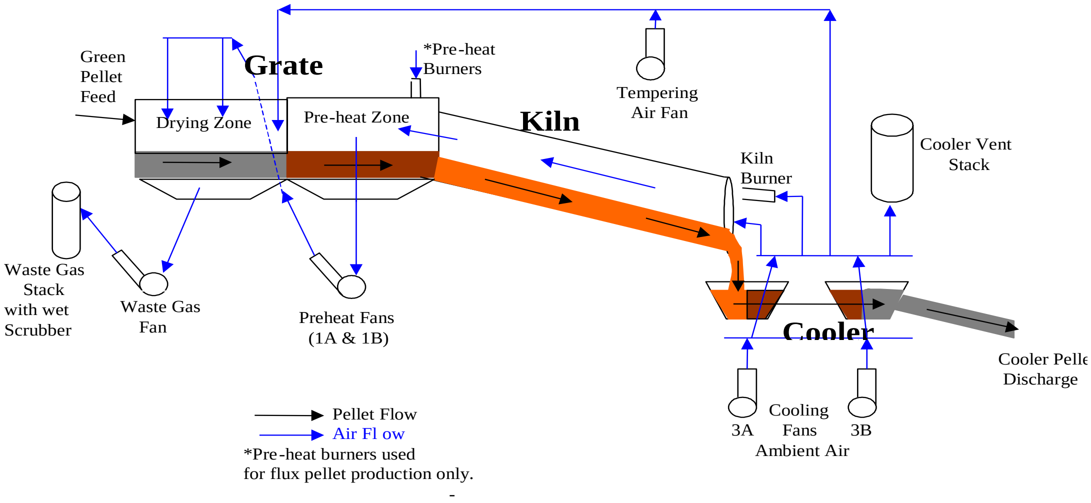

Figure 1. Diagram of a grate-kiln taconite pellet induration process. Fresh, wet pellets (termed green balls) fed into the system are systematically dried, heated, and hardened into pellets as they pass from the drying zone to the rotating kiln. Drying and heating is accomplished using gases, that are generated by cooling of the hot pellets and burning of fresh fuels in the kiln. The gases interact with pellets in the kiln, and are passed through pellet beds in the drying and pre-heat zones. The gases carry mercury and dust to the wet scrubbers. The preheat burner near the center of the diagram is used only for fluxed pellet production.

Fresh greenball and scrubber water samples were also collected from these plants and analyzed for mercury. Water samples were filtered at the plant, reacted with BrCl overnight, and then analyzed using $SnCl_2$ reduction, gold trap collection, and CVAFS detection (modified EPA 1631). The filters containing the scrubber solids were dried at 104ºC for analysis, weighed, and digested in hot acid (HCl/HNO_3, 3/1), and the mercury analyzed also using $SnCl_2$ reduction and gold trap collection, followed by CVAFS detection (modified EPA 1631). Greenball samples were disaggregated into powder, digested in hot acid prior to analysis for mercury. All mercury analyses for samples collected at the taconite companies where analyzed by Cebam Analytical, Inc., Seattle, Washington. 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.

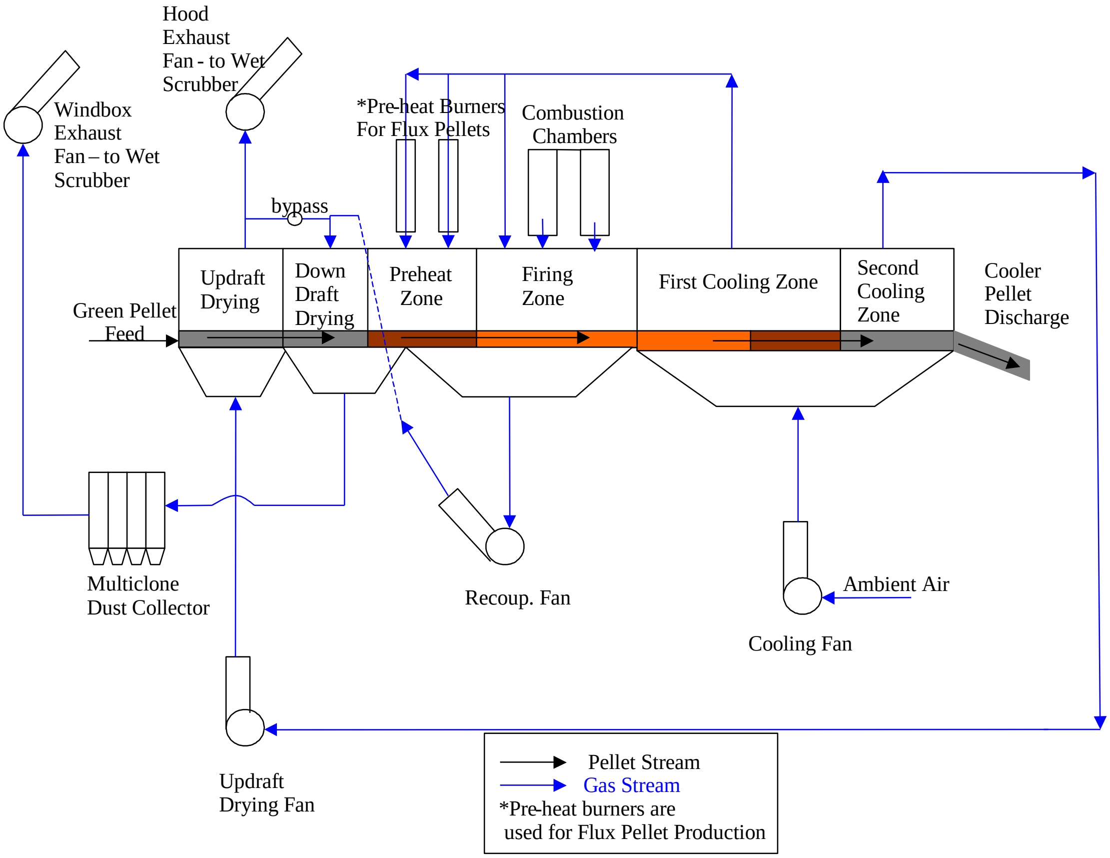

Figure 2. Diagram of a straight-grate taconite induration furnace. Fresh pellets are carried on a grate through a furnace and cooled by fresh air passed through the pellet bed. The air used for cooling the hot pellets and the gases generated in the firing zone are used for drying and heating the pellets.

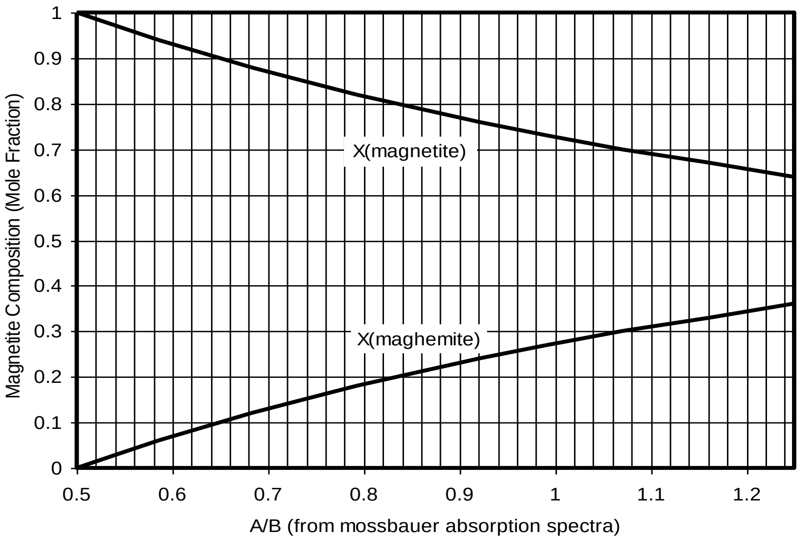

Figure 3: Ideal relationship between A/B from Mössbauer spectroscopic measurements, and magnetite/maghemite solid solution composition.

Mössbauer Spectroscopy

Mössbauer spectroscopy is a sensitive technique for measuring the atomic environments of iron atoms in a compound. The technique works by measuring absorption of gamma radiation of very specific wavelengths, generated by an oscillating radioactive source material (^{57}Co). The oscillation causes a Doppler shift of the emitted gamma radiation, while a detector records absorption as a function of gamma wave frequency. Thus, results are typically presented in terms of absorption versus velocity of the radioactive source. The details of the technique are not important for this discussion, but it is important to realize that the method permits clear distinction and quantification of the relative amounts of iron that are found in the crystal lattices of magnetite and various oxidation products. Mössbauer spectroscopic measurements were made at the University of Minnesota (Minneapolis), Institute for Rock Magnetism.

Considerable importance in this study was placed on the relative distribution of iron on A and B sites of magnetite grains. As magnetite oxidizes it forms a solid solution between magnetite and maghemite. The oxygen is added by increasing the proportion of oxidized iron in A versus B sites and accommodating this change with the introduction of site vacancies in the B site. Mössbauer spectroscopy not only evaluates mineralogy of iron oxides (e.g., magnetite, maghemite or γ-Fe_2O_3, and hematite or α-Fe_2O_3), but determines the relative distribution of iron atoms in magnetite that are located on A or B sites. Thus, the relative absorption by iron in A and B sites (A/B) reflects magnetite composition (Coey, 1971; Papamarinopoulus et al., 1982; see Fig. 3).

Table 1: Mercury concentration and mineralogy of samples from greenball heating experiments.

Temperature (ºC)	*Gas*	*Time (min)*	*Hg (ng/g)*	*Mineralogy*[*]	*Magnetite A/B*
Start			7.62	100 % mt	0.72
			7.59		
300 (572ºF)	Air	20	6.42		
	N_2	20	2.69		
400 (752ºF)	Air	20	2.89	89% mt, 11 % hm	0.98
	N_2	20	0.75		
500 (932ºF)	Air	20	3.70	77% mt, 23% hm	1.26
	N_2	20	0.92	89% mt, 11% hm?	0.59
600 (1112ºF)	Air	20	2.17		
	N_2	20	0.48		
700 (1292ºF)	Air	20	2.07		

[*] mt = magnetite solid-solution, hm=hematite

RESULTS

Results from one set of Benner's (2005) heating experiments are presented in Table 1. Benner (2005) found that most of the mercury in taconite is released at temperatures below 400ºC, especially during heating in N_2. However, a larger fraction of the mercury is retained if heating takes place in air, rather than N_2, even to temperatures as high as 700ºC.

The starting sample was composed of magnetite that was slightly oxidized even before heating, as indicated by A/B = 0.72 (as opposed to 0.50 for stoichiometric magnetite, see Fig. 3). Heating this material in N_2 for 20 minutes at 500ºC resulted in a decrease in the amount of magnetite and a shift in magnetite composition (to A/B = 0.59). Some of the magnetite was replaced by a mineral that appeared to be a mixture of maghemite and hematite. One possibility is that the initial magnetite simply unmixed into near-stoichiometric magnetite and Fe_2O_3, releasing its mercury in the process. It appears that mineralogic changes and mercury release occur rapidly for magnetite, even in the absence of O_2. Mössbauer results for samples heated in air at 400 and 500ºC revealed systematic mineralogic changes, as well. 11% of the magnetite was replaced by hematite at 400ºC while 23% was replaced by hematite during heating at 500ºC. Moreover, the magnetite that remained became systematically more oxidized, with A/B increasing from 0.72 in the starting material, to 0.98 at 400 and 1.26 at 500ºC, representing approximately 27 and 36 percent maghemite component, respectively.

Pertinent data on location, temperature, mercury concentration, and iron-oxide mineralogy for dust samples collected from grates at taconite plants are presented in Table 2. Mercury concentrations were surprisingly elevated in some samples. For example, concentrations of mercury reached as high as 464 ng/g in the preheat zone at one company (Fig. 4), which compares to only 11 ng/g in the starting material. Mercury concentrations were also elevated in the preheat zones at all of the companies, suggesting

Table 2 Locations, temperatures, mercury concentrations, mineralogy and magnetite composition (A/B) of samples collected from taconite plants during this study.

Plant	*Location*[**]	*Overbed T (ºF)*	*Underbed Tº(F)*	*Hg ng/g*	*Mineralogy* %mt / %hm / %mh*	*Magnetite A/B*
Straight. Grate #1	Greenball			11	96 / 0 / 4	0.57
	UDD WB2.5	342	490	18		
	UDD WB6.5	342	490	32	50 / 50 / 0	0.61
	DDD WB8	573	340	19	94 / 6 / 0	0.62
	PH WB12	897	195	94	90 / 10 / 0	0.64
	PH WB14	1248	202	464	94 / 6 / 0	0.65
	PH WB16	1402	253	127		
	FZ WB18	2300	350	22	88 / 12 / 0	0.69
Grate Kiln #1	Greenball			12	100 / 0 / 0	0.61
	DD1	654	199	91	91 / 9 / 0	0.65
	DD2	1049	246	57		
	DD2	1443	493	66	91 / 9 / 0	0.63
	PH WB1	2076	544	15		
	PH WB3	2076	890	2.7	36 / 64 / 0	0.56
	PH WB5	2076	1215	0.7		
Grate Kiln #2	Greenball			14	100 / 0 / 0	0.59
	DDD	525	384	24		
				24		
				21		
				24	37 / 63 / 0	0.48
	PH	1852	1291	1.7		
				1.6	35 / 65 / 0	0.59
				1.6		
				2.2		
Straight Grate #2	Greenball			10		
	DDD WB9	720	250	7	92 / 8 / 0	0.64
	DDD WB 11	720	250	10	87 / 13 / 0	0.61
	PH WB 13	1854	250	60	91 / 9 / 0	0.60
	PH WB17	2257	700	58	92 / 8 / 0	0.61
	FZ WB 19	2332	725	26	74 / 26 / 0	0.61
	FZ WB 21	2313	730	10	63 / 37 / 0	0.75

[*] mt=magnetite, hm=hematite, mh=%maghemite

[**] UDD=Updraft drying, WB=windbox, DDD=Downdraft drying, PH=preheat, FZ=Firing Zone.

a general process whereby mercury released from greenball in some parts of the furnace (high temperature) reabsorbs to greenballs and process dust at lower temperatures. The total amount of mercury collected in dust from each zone likely depends on plant-specific variations in heating rate, gas routing, and mercury concentration in the primary minerals.

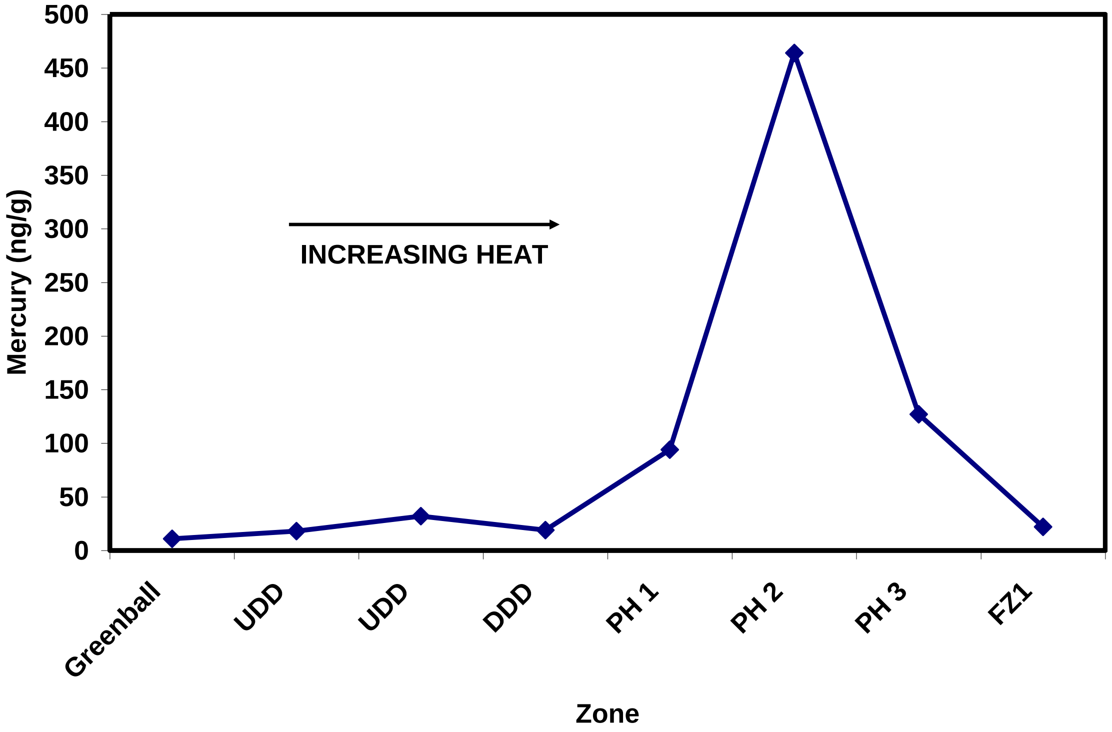

Figure 4. Mercury concentrations in dust samples collected from Straight-Grate #1. Concentrations increased to 464 ng/g in the preheat zone and then decreased again as the firing zone was approached.

The specific temperature range for mercury release and adsorption in taconite plants is not easy to evaluate due to the intense thermal gradients that exist in induration furnaces. Temperatures across the pellet bed can differ by well over 500ºC (see Table 2). Samples collected from some locations contain abundant hematite suggesting at least a fraction of the collected material was exposed to very high temperatures, perhaps in the firing zone. In straight grates, hematite can also come from the hearth layer. Even when hematite is present, however, all of the samples contain a significant magnetite component, and the A/B ratios for this magnetite were only slightly shifted compared to the starting greenball samples. A/B for the magnetite component for samples whose mercury concentrations are plotted in Fig. 4 increased gradually from 0.57 in the starting sample to 0.69 for the sample from the firing zone. The change in A/B at other plants was less systematic, but still much less than observed in the heating experiments.

Greenball and scrubber water mercury concentrations (Table 3) varied widely across the range and at each plant during a two year sampling study. However, mercury concentrations were generally high at all plants, especially in the filtered solids. This indicates significant mercury oxidation takes place in induration furnaces. It appears that the oxidized mercury atoms are transported both attached to dust particles and as molecular volatile species such as $HgCl_{2(g)}$ since both particulate and dissolved mercury concentrations are elevated. Mass balance estimates indicate that over 40% of the

Table 3 Mercury concentrations and TSS for greenball and scrubber water samples. Hg(D) = Dissolved mercury, Hg(P) = concentration of mercury for dried filtrate, Hg(T) = total mercury concentration including dissolved and particulate fractions.

Plant	*Date*	*Greenball Hg (ng/g)*	*Hg(D) (ng/l)*	*Hg(P) (ng/g)*	*TSS (wt%)*	*Hg(T) (ng/l)*
Straight	Average	18.6	325	2528	0.019	671
Grate #1	St. Dev.	5.7	164	2525	0.011	314
Grate	Average	11.3	273	2470	0.070	1943
Kiln #1	St. Dev.	3.2	42	563	0.024	541
Grate	Average	16.6	542	616	1.866	11550
Kiln #2	St. Dev.	5.1	626	236	0.578	5004
Straight	Average	8.4	1117	2305	0.126	4368
Grate #2	St. Dev.	1.3	1465	1504	0.031	1929

released mercury was captured in wet scrubbers some days at some plants. In other cases, capture efficiencies were less than 10%. Understanding the mechanisms and processes leading to the wide variation in mercury speciation (in scrubber water) and capture efficiencies during taconite processing is needed for design of cost-effective mercury technologies for these plants.

DISCUSSION

Results from this study have shown that mercury transport during taconite processing involves a relatively complex series of reactions, whereby some of the mercury released at high temperatures in the furnaces is recaptured by magnetite and/or magnetite/maghemite solid-solutions. To simplify understanding of the release and capture process, four independent reactions (Table 4) can be used to represent processes most likely to impact mercury release during taconite induration. Reactions 1 and 2 represent conversion of magnetite to either magnetite/maghemite solid-solutions or hematite, while Reactions 3 and 4 represent release of mercury in reduced and oxidized forms, respectively. Each of the reactions in Table 4 proceeds from left to right upon heating of magnetite in taconite induration furnaces, and the challenge is to determine specific processes affecting the relative rates of each.

Magnetite oxidation to maghemite is important because it controls the composition of dust that may or may not react with, and ultimately help trap, reduced mercury ($Hg^0_{(g)}$) in process gases. Zygarlicke (2003), for example, demonstrated that maghemite participates in reactions with gaseous mercury, while magnetite and hematite do not. Maghemite forms when oxygen is added to magnetite without modification of the spinel-type crystal lattice. Formation of this mineral has long been considered to take place at intermediate temperatures in taconite induration furnaces (Papanatassiou, 1970), however, its abundance as a mineral phase, and its importance with respect to mercury transport during taconite processing, was previously unknown. Data in the present study provide an indication of time needed for magnetite to convert to magnetite/maghemite solid-solutions, but perhaps more importantly, demonstrate that mercury reacts not just with maghemite, but also with magnetite/maghemite solid-solutions that may be close in composition to magnetite.

Reaction 1 in Table 4 does not appear to take place on a scale where it is easily observable in bulk dust samples from grates. We note, however, that the process may take place on a small scale during pellet induration. While A/B values did tend to increases slightly during induration, the amount was not nearly as much as in experiments. This behavior can be understood, perhaps, by considering in more detail the steps needed for magnetite oxidation to maghemite to take place (Columbo et al., 1965; O'Reilly, 1984; Zhou et al., 2004). First, oxygen must be adsorbed to the surface of the grain. This takes place by reaction of oxygen with electrons from the Fe^{+2} component in magnetite to form Fe^{+3} and O^{-2} ions. This has the effect of extending the mineral lattice. Fe^{+3}/Fe^{+2} ratio at the mineral surface increases as a result of this interaction, and a cation site vacancy develops in the vicinity of the added oxygen. Ionic and electronic diffusion then occur to reduce the chemical gradients, and given time, the grain may become homogeneous.

If time is insufficient for diffusion to take place, then only the outer boundaries of the grains can convert to maghemite. Oxidation of magnetite grains, thus, occurs from the outside in, such that full oxidation of the interior portions is diffusion limited and can only take place as fast as diffusion permits. The outer surface mineralogy and rate of mineral growth is complex, depending on temperature, humidity, oxygen availability, and nucleation effects, as well as crystal orientation (Zhou et al., 2004). Based on results from experiments and under-grate samples, conversion of magnetite to magnetite/maghemite solid-solutions can take place on relatively short time scales at 400 and 500ºC. However, time scales for induration furnaces are even shorter than those used in experiments, so only the outer-most surfaces of magnetite grains have time to convert to magnetite/maghemite solid-solutions. Since only the outer surface of the grains contacts mercury in the process gases, surface conversion of magnetite to maghemite may be all that is needed. Experimental data (Benner, 2005) indicate the process (Reaction 1) begins at temperatures less than 400 ºC and will likely continue until eclipsed by conversion to hematite. To understand mercury transport in taconite induration furnaces, therefore, it is important to determine where magnetite and magnetite/maghemite solid-solutions convert to hematite (Reaction 2).

Ultimately, nearly all of the magnetite in greenballs is converted to hematite by exposure to air at temperatures of 1200 to 1300ºC later in the induration process. Hematite is not known as a significant oxidant for $Hg^0_{(g)}$ at power plants (Zygarlicke, 2003). Thus, conversion of magnetite to hematite may limit mercury oxidation and capture during induration, and the mineralogic conversion process likely signals the final release of mercury to process gases during taconite induration.

For greenball samples heated in air, it took 20 minutes of exposure at 400 and 500ºC to convert 11 and 23% of the solids, respectively, to hematite. Reaction times are lower, but temperatures are higher during induration. Hematite formation begins to dominate the oxidation process in the preheat zones in grate-kiln furnaces and in the firing zone at straight grate furnaces. In all four grates sampled, mercury decreases in dust coincide with hematite increases, consistent with the idea that hematite generation effectively releases all of the mercury from magnetite/hematite solid-solutions. It is somewhat paradoxical in terms of predicting mercury release when at least a fraction of the mercury released from hematite formation will be adsorbed to solids and transported directly back to the part of the furnace where it had just been released.

This leads to consideration of the conversion of mercury from its oxidized immobile form, $HgO_{(ss)}$, to its reduced and volatile form, $Hg^0_{(g)}$ (Reaction 3). The subscript "*(ss)*" in $HgO_{(ss)}$ is used to indicate Hg in magnetite/maghemite solid-solutions, however, the nature and form of this component is not well known. In primary greenball samples Hg may be dispersed throughout the grain or combined with other trace components such as sulfur. However, the high concentration of mercury observed for dust samples composed exclusively of slightly oxidized magnetite in preheat zones (Fig. 4) leaves little doubt that the element exists as a surface adsorbate once it is recaptured by minerals in the furnace.

The precise manner in which mercury evolves from the surface of magnetite/maghemite solid-solutions may provide an important constraint on the form of mercury in the resulting process gas, and can impact the behavior of mercury in wet scrubber systems. Reaction 3 is a hypothetical mechanism for producing $Hg^0_{(g)}$, the form of mercury to be avoided, if possible, because it is not captured by wet scrubbers unless subsequent chemical reactions promote oxidation in the process gas phase. Reaction 4,

Table 4: Primary chemical reactions that constrain mercury release, transport, and capture in taconite induration furnaces.

Number	*Chemical reaction*	*Importance for Hg transport*
(1)	$\underset{\text{Magnetite}}{2Fe_3O_{4(ss)}} + ½\ O_2(g) = \underset{\text{Maghemite}}{3Fe_2O_{3(ss)}}$	Maghemite interacts with mercury in flue gases, while magnetite does not. The minerals have the same structure and form a solid solution but little is known about how mercury reacts with magnetite solid solutions.
(2)	$\underset{\text{Magnetite}}{2Fe_3O_4} + ½\ O_2(g) = \underset{\text{Hematite}}{3Fe_2O_3}$	Mercury is released when magnetite is converted to hematite in induration furnaces. Hematite does not interact with mercury in flue gases.
(3)	$HgO_{(ss)} = Hg^0_{(g)} + 1/2O_{2(g)}$	$Hg^0_{(g)}$ is insoluble in water and cannot be caught by wet scrubbers. $HgO_{(ss)}$ represents mercury associated with magnetite and magnetite/maghemite solid-solutions.
(4)	$HgO_{(ss)} + 2HCl_{(g)} = HgCl_{2(g)} + H_2O_{(g)}$	$HgCl_{2(g)}$ is soluble in water and the Hg^{2+} base atom can adsorb to solids. This species is more easily captured by wet scrubbers than $Hg^0_{(g)}$.

however, represents a hypothetical mechanism for generating $HgCl_2^0{}_{(g)}$, a molecule containing mercury in oxidized form which is easily captured by wet scrubber system and which can adsorb to solids. The relative overall rates of Reactions like 3 and 4 will dictate the relative amounts of mercury released in taconite induration furnaces that can be captured either as particulate or dissolved mercury or which will be released to the atmosphere ($Hg^0{}_{(g)}$).

While it is unlikely that the iron-oxide mineralogy would be strongly affected by the presence or absence of small amounts of $HCl_{(g)}$ in process gases, there is good reason to expect HCl to favor Reaction 4 over Reaction 3 under conditions of relatively modest HCl concentrations. Galbreath and Zygarlicke (2000), for example, showed that the dominant transformation pathways for mercury in flue gases in coal fired power plants was by heterogeneous chlorination reactions taking place at mineral surfaces on fly-ash. The reaction products were a combination of particle-bound mercury and $HgCl_{2(g)}$. Results from mercury oxidation experiments involving gas reactions with fly ash have suggested a direct role for Fe-oxides, in particular (Ghiorshi, 1999; Lee *et al.*, 2001). Subsequently, Galbreath et al. (2005) performed experiments to confirm that reactions between $Hg^0{}_{(g),}$ HCl, and maghemite lead to a high degree of oxidation of mercury in flue gases.

The high mercury concentrations in many of the under-grate samples support reactivity of iron oxides with mercury during taconite processing, and the relatively high concentration of mercury in scrubber waters provides evidence that the mercury finally released from induration is sometimes highly oxidized (e.g., 40%). The predominant source of Cl is thought to be the pore fluid from processing waters and lime stone flux material which upon heating to 1200 to 1300ºC in the firing zone, is expected to be volatilized as $HCl^0{}_{(g)}$. Air containing the $HCl^0{}_{(g)}$ travels into the preheat and drying zones where it may react with the mercury bearing iron oxides.

Mass balance results suggest taconite processing gases contain 1 to 10 ppmv Cl, values that are relatively low compared to those needed for homogenous gas phase HCl oxidations to occur (e.g., Widmer *et al.*,1998). Thus, it is unlikely that homogenous gas reactions with HCl promote oxidation during taconite induration. However, Edwards et al. (2001) showed that the predominant Cl species for mercury oxidation in homogenous reactions were trace molecular species such as $Cl^0{}_{(g)}$ and $Cl_2^0{}_{(g)}$ which oxidize $Hg^0{}_{(g)}$ orders of magnitude more rapidly than HCl. It is unknown whether such metastable species exist in taconite processing gases. Alternatively, the heterogenous reactions between HCl and iron oxides that come into contact with the processing gases can account for the oxidized mercury in scrubber waters (Ghiorshi, 1999; Lee *et al*, 2001; Zygarlicke, 2003; Galbreath et al, 2005). Certainly, there is abundant opportunity for processing gases containing $Hg^0{}_{(g)}$ and HCl to come into contact with iron oxides.

Capture efficiencies range between 9 and 40%, with the highest recovery values found for plants that use grate-kilns. While a simple difference in the grate type might be partially responsible for the difference in capture rates, it is also possible that the trend is related to differences in residence times and concentration of reactive components (e.g., HCl and/or iron oxides). An overall reaction describing heterogeneous oxidation of mercury by magnetite/maghemite solid-solutions and HCl can be written:

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

Future studies are planned to measure gas chemistry directly in taconite induration furnaces as well as to test whether Cl injection has a direct impact on mercury oxidation and capture by wet scrubbers.

It should be mentioned, however, that just increasing the capture rate for mercury in induration furnaces will be insufficient to reduce mercury in taconite stack emissions. Currently, three out of the four plants studied here simply recycle most of the captured mercury back to the induration plants. Several potential means to ensure the majority of captured mercury is routed to tailings basins, rather than back to the induration plant, are being investigated.

CONCLUSIONS

Experiments were performed and samples were collected from beneath grates and wet scrubbers in four induration furnaces to identify the primary processes affecting mercury release and capture for the taconite industry. Magnetite/maghemite solid-solutions formed during heating of the fresh magnetite-dominated greenballs in air and correspondingly, mercury release rates were greatly reduced compared to when the greenballs were heated in N_2. These results agreed with observations from under-grate samples from taconite induration furnaces which revealed considerable uptake of mercury at moderate temperatures. In general, therefore, it appears that mercury release during induration begins at approximately 450ºC and continues to unspecified higher temperatures, as the magnetite converts to hematite, which appears to exclude and not react with mercury.

Subsequent to release, mercury can readsorb to magnetite/hematite solid-solutions but the overall rate of capture by wet scrubbers appears to depend both on the availability of $HCl^0_{(g)}$ and particulate phases, most likely magnetite/maghemite solid-solutions, consistent with a reaction such as:

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

Despite the considerable uncertainty that exists in computation of mass fluxes for mercury, chloride, and particulates in taconite induration furnaces, the relationships observed in this study provide evidence that relatively simple procedures involving injection of Cl and/or maghemite/magnetite may provide a relatively cheap and simple means to control mercury emissions during induration at taconite processing facilities.

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