

Potential Sources and Sinks of  
Manganese, Fluoride, Boron, Arsenic, and Molybdenum  
In Taconite Plant Process Waters

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Manganese, Fluoride, Boron, Arsenic, and Molybdenum  
In Taconite Plant Process Waters

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## EXECUTIVE SUMMARY

At current production levels, Inland Steel Mining Company (Inland), near Virginia, Minnesota, is expected to exceed the capacity of their tailings basin within five years. Consequently, Inland has submitted a plan to dispose of taconite tailings in an existing open mine pit. The Minnesota Department of Natural Resources (MN DNR), supported by a grant from the Iron Ore Cooperative Research Program, has been studying the potential water quality implications of underwater disposal of taconite tailings in existing mine pits. The primary objective of this study was to quantify the potential sources and sinks of five target elements (manganese, fluoride, molybdenum, arsenic, and boron) within a taconite processing plant.

In order to accomplish this objective, an overall mass balance between the process stream input waters and the effluent discharged to the tailings basin was determined. Process water chemistry was used to calculate relative mass changes between locations along the process line. Any location where there was a relative gain in mass for a given element was considered a source. A sink was any location where the relative mass of an element decreased. In order to investigate possible sources of the five target elements in taconite plant process waters, grab samples of process water were obtained from ten locations along a process line at Inland. This study dealt with compositional changes in process waters only, and did not address solid phase analysis of the tailings in the process stream.

Mass balances for the plant indicated that 13.5 T/yr fluoride and 0.59 T/yr manganese were released into solution during taconite processing. The overall fluoride contribution to the tailings basin was estimated at 0.2 ppm/yr. Fluoride levels in process waters were believed to be controlled by the solubility of the mineral fluorite ( $\text{CaF}_2$ ). The annual contribution of manganese to the tailings basin was estimated at approximately 10 ppb. However, dissolved manganese is not stable (i.e. precipitates as solid  $\text{MnO}_2$ ) in oxidized environments such as a tailings basin. Therefore, the actual contribution of manganese to the tailings basin is expected to be negligible. Plant mass balances for arsenic, boron, and molybdenum indicated that these elements were relatively conservative during taconite processing.

## 1. INTRODUCTION

Minnesota mining operations produce 40 million tons of taconite pellets annually. Taconite tailings are slurried with process waters and pumped to surface impoundments. The tailings settle to the basin floor, while much of the water is recycled for reuse in the plant. At current production levels, Inland Steel Mining Company (Inland), near Virginia, Minnesota, is expected to exceed the capacity of their tailings basin within five years. Consequently, Inland has submitted a plan to dispose of taconite tailings in the Minorca pit, an existing open mine pit. The Minnesota Pollution Control Agency will issue the required permit provided it can be shown that ground water supplies in the surrounding Biwabik Iron Formation will not be adversely impacted.

The Minnesota Department of Natural Resources (MN DNR) and the University of Minnesota (U of MN), supported by a grant from the Iron Ore Cooperative Research Program, have been studying the potential water quality implications of underwater disposal of taconite tailings in existing mine pits. As a result of extensive laboratory and field studies to determine the quality of water that results from intimate contact with tailings, five elements (manganese, fluoride, molybdenum, arsenic, and boron) have been identified as potentially problematic. At the time of this report, specific sources of these five elements have not been identified.

Elevated concentrations of these parameters may be a direct result of the dissolution of trace minerals in the tailings themselves. However, the sources of some elements may be somewhere within the processing plant. For example the grinding process, which decreases the particle size of the ore prior to magnetic separation, increases the surface area of the ore and tailings exposed to process waters, which may enhance dissolution. Furthermore, the inevitable breakdown of the grinding media may release elements, such as molybdenum, into process waters or tailings. The addition of processing reagents may create conditions that enhance the release of trace elements into the process stream, or may themselves be the source of some of these elements.

## 2. SCOPE

The primary objective of this study was to quantify the potential sources and sinks of manganese, fluoride, molybdenum, arsenic, and boron within a taconite processing plant. In order to accomplish this objective, an overall mass balance between the process stream input waters and the output water discharged to the tailings basin was determined. If there were a net gain or loss of mass for a particular element, then the concentrations of that element was tracked along the taconite process line. Since flow data at the locations where samples were taken were not available, the absolute change in mass for each element could not be quantified. However, the process water chemistry was used to calculate relative changes in mass between locations along the process line. Any location where there was a relative gain in mass for a given element was considered a source. A sink was any location where the relative mass change of an element decreased.

If the source of a problematic element can be traced back to the taconite processing plant, then the extent to which the element is problematic will be limited to the duration of plant operations. Once the plant discontinues production, there will be no further input to the tailings basin. Thus, the concentrations should decrease over time due to dilution from precipitation, surface runoff, and possibly ground water infiltration. However, if the plant is found to be a significant sink for a particular element, then the concentration in the tailings basin may be expected to increase after plant closure. In order to investigate possible sources of manganese, fluoride, molybdenum, arsenic, and boron in taconite plant process waters, grab samples of process water were obtained from ten locations along a process line at Inland Steel Mining Company's taconite processing operation.

At present, this study has only dealt with the composition changes in process waters, and did not include solid phase analysis of the tailings in the process stream. The solids flux and compositions may provide further insight into specific sources or sinks associated with the tailings themselves. If questions regarding specific sources and sinks within the processing plant still remain at the conclusion of this phase of study, another phase will be initiated to determine the mass changes in the tailings in the process stream. Furthermore, this document does not include an analysis of mass changes of specific elements in the tailings basin over time. While this information may be of interest, there is no known long term tailings basin water quality data for the elements of interest. Thus, the mass changes in the tailings basin over an extended period of time could not be calculated.

### 3. PREVIOUS WORK

An initial survey of Inland's taconite process waters was completed in August 1996 (Berndt and Lapakko, 1997a & b). Process water samples were taken from eight locations, labeled as follows: 1) Post grinding, 2) After hydroseparator, 3) Process water, 4) Plant thickener overflow, 5) Concentrate thickener, 6) Post fluxstone addition, 7) Scrubber water, and 8) Preconcentrate filtration.

The concentrations of manganese, fluoride, molybdenum, arsenic, and boron in seven of the eight process waters were relatively constant throughout the plant with a few notable exceptions. Scrubber water chemistry differed greatly from all other process waters in the plant. Manganese, fluoride, arsenic, and boron levels in the scrubber water ranged from approximately 4 to 39 times higher than in other process waters. Thus, the scrubber was a source of manganese, fluoride, arsenic, and boron in a taconite process stream. Water from the preconcentrate filtration, which contained recycled scrubber water, also tended to have elevated levels of these parameters, particularly fluoride and manganese, but not at the extremely high levels observed in the scrubber.

Molybdenum concentrations followed the opposite trend, decreasing in the scrubber water and increasing in the preconcentrate filtration relative to other locations in the plant. Thus, the scrubber may be a potential sink of molybdenum during taconite processing. Another exception to the generally constant concentrations observed in the process stream was at the post fluxstone addition. Both fluoride and manganese concentrations decreased by a factor of roughly five relative to other locations in the plant. However, the mechanism of this removal was not determined.

## 4. METHODS

### 4.1. Sampling Locations

Ten locations along the process stream were targeted for sampling (figure 1). Each location was chosen based upon accessibility and potential for identifying specific chemical inputs to the process stream. Since the primary source of process water is the tailings thickener overflow, a sample was obtained from this location. Other process water sources include the plant site settling basin, return water from the tailings basin, and water pumped to the plant from the Enterprise pit. Of these three, only the plant site settling basin was sampled during this study. Samples from the tailings basin have been collected quarterly as part of the MN DNR/U of MN study on the implication of in-pit disposal of taconite tailings (Lapakko et al., 1998; Berndt and Lapakko, 1997a, 1997b). An average of these analyses was used to represent the tailings basin contribution to the process stream. Similarly, the Enterprise pit water quality had been previously determined (HDR, 1997). Nine other samples were collected within the taconite plant at locations near potential sources such as the grinding plant, flotation cells, fluxstone plant, and the concentrator (table 1).

Once the process stream reaches the concentrate thickener, it no longer follows a linear flow path. In order to conceptually simplify the process stream, it was divided into three distinct "systems." Each system was described in terms of a central location, its inputs, and outputs. Samples were taken to represent all known inputs and outputs for each system. Since the flow path is convoluted, all three systems overlap, resulting in some redundancy. However, this redundancy should not present a problem.

The concentrate thickener was the center of the first system. The input stream to the concentrate thickener consisted of the flotation underflow, filtrate from the leaf filters, and water recycled from the scrubber. Outputs were the concentrate thickener overflow to the tailings thickener and the underflow to the slurry storage tank. Samples were taken from each of these five locations.

A second system centers on the slurry storage tank. Inputs to the slurry storage tank consisted of the taconite concentrate from the thickener underflow and the fluxstone slurry. A sample of the concentrate thickener underflow was easily obtained. However, the fluxstone contribution was more difficult to determine. The composition of the fluxstone slurry input is fairly complicated, because the "raw" water used during fluxstone grinding comes from three separate sources: the plant site settling basin, the tailings basin, and the Enterprise pit. Further complications arise because the percentage of each raw water source varies depending on plant water requirements at the time. Consequently, the composition of the raw water varies over time, possibly even within a few hours. The best estimate of the potential contributions from the raw water and the fluxstone was a sample obtained from the fluxstone ball mill discharge. The slurry storage tank had a single output to the leaf filters. Since it was impractical to obtain a sample from this line, a sample was taken directly from the storage tank. Overall, four samples were obtained to represent this system.

The third system centered on the leaf filters. A portion of the scrubber water is mixed with the concentrate prior to filtration. The sample from the slurry storage tank was used to represent the concentrate contribution, and scrubber water from Transfer A was obtained. A sample of the filtrate removed by the leaf filter represented the only process stream output, since the resulting concentrate contains less than nine percent water.

#### 4.2. Sample Handling and Analysis

Grab samples (250 mL) were obtained from ten locations along the process stream at Inland. Each sample was filtered at the plant using a 30 mL syringe and 0.2  $\mu\text{m}$  syringe filter. Major and trace chemical constituents were analyzed using ICP-MS and Ion Chromatography by Mike Berndt at the U of MN, Department of Geology.

#### 4.3. Plant Mass Balance

Plant process waters originate from four different sources. By far, the largest contribution comes from the tailings thickener overflow which recycles clarified water back into the plant for reuse. Approximately 71,000 gallons per minute (gpm) of water is returned to the process water reservoir as tailings thickener overflow (HDR, 1997). The remaining process water comes from the tailings basin reclaim (2830 gpm), the plant site settling basin (1850 gpm), and the Enterprise pit (1580 gpm). Approximately 74,000 gpm of process water exits the plant to the tailings thickener. The remaining process water is lost to evaporation from the concentrated pellets. It is important to note that these flow values were based on average continuous flows from pumping records at Inland (HDR, 1997). These flow values were used in conjunction with process water chemistry to estimate the total mass input and output in process water from the plant.

#### 4.4. Relative Mass Change Calculations

Typically, quantification of dissolved species is achieved using the law of conservation of mass between inputs and outputs at a specific location. In this study, the flow volume at the ten locations was not measured, and therefore masses and mass balances could not be determined. However, relative mass changes along the process stream can be calculated using the process water chemistry. The mass of a dissolved species in solution is equal to the product of its concentration and the flow (equation 1),

$$M = C \times Q \quad (1)$$

where,  $M$  is the mass,  $C$  is the concentration, and  $Q$  is the flow. At any location along the process stream, the ratio of the output mass of a dissolved species to the input mass is equal to the ratio of the output and input concentrations (equation 2),

$$M_o/M_i = C_o/C_i \quad (2)$$

where the subscripts "o" and "i" denote output and input, respectively.

For conservative parameters (parameters which remain in solution), the sum of all input masses ( $M_1$  and  $M_2$ ) must equal the total output mass,  $M_o$  (equation 3),

$$M_1 + M_2 = M_o \quad (3)$$

Substituting C and Q into equation 3, we get equation 4:

$$M_o/(M_1+M_2) = C_oQ/(xC_1Q+yC_2Q) = C_o/(xC_1 + yC_2) \quad (4)$$

where x and y represent the fraction that each input contributed to the whole. Furthermore, the sum of each contribution must equal one, or 100% (equation 5),

$$x + y = 1 \quad (5)$$

Using the concentration of a conservative (non-reactive) element, such as bromide, for  $C_o$ ,  $C_1$ , and  $C_2$ , the values of x and y can be calculated. These values for x and y can then be used in equation 1 along with  $C_o$ ,  $C_1$ , and  $C_2$  of any dissolved constituent to determine the mass ratio, or relative mass change for that species. If the mixing of multiple inputs is the only factor affecting the mass change between two points, the mass ratio will equal one. If the mass ratio is greater than one, a source of that constituent was operating in the system. Similarly, if the mass ratio is less than one, the system acts as a sink.

This method was used to calculate the fractional contribution of each input to the concentrate thickener, slurry storage tank, and leaf filter. Both chloride and bromide were used as conservative elements to calculate the percent contribution from each of the three inputs to the concentrate thickener. Eighty seven percent of the input to the concentrate thickener (CT) came from the main process stream (i.e., the flotation cells; FL). Recycled scrubber water (S) accounted for 10% of the contribution, and 3% came from the leaf filters (LF). Thus, the mass ratio equation for the concentrate thickener is:

$$M_{CT}/(M_{FL}+M_S+M_{LF}) = C_{CT}/(0.87C_{FL}+0.10C_S+0.03C_{LF}) \quad (6)$$

Only one conservative element was required to calculate the fractional inputs to the slurry storage tank and the leaf filter. The fractional inputs were calculated using both chloride and bromide. The results differed by less than seven percent. Since bromide is more likely than chloride to behave as a conservative element in a taconite processing operation, the equations derived using bromide were considered more reliable. The fractional inputs to the slurry storage tank (SS) were 0.86 and 0.14 from the concentrate thickener and the fluxstone process line (F), respectively (equation 7). Almost all of the input to the leaf filter was from the slurry storage tank (99%), with only one percent contributed by the recycled scrubber water (equation 8).

$$M_{SS}/(M_{CT}+M_F) = C_{SS}/(0.86C_{CT}+0.14C_F) \quad (7)$$

$$M_{FP}/(M_{SS}+M_S) = C_{FP}/(0.99C_{SS}+0.01C_S) \quad (8)$$

These mass ratios were used to evaluate the apparent changes in concentration that were observed along the process stream.

## 5. RESULTS AND DISCUSSION

### 5.1. Comparison With Previous Results

Seven of the ten locations sampled in 1997 correspond to at least one of the seven locations sampled in 1996 (figure 1). Concentrations for each element were similar to those observed earlier at corresponding locations (figure 2). The observed differences were probably due to the recycling of process waters used in the plant. Frequent adjustments to processing variables (e.g. flow rate, flow volume, reagent use, etc.) to meet current plant requirements, may also affect the levels of certain elements in the process stream.

In general, the concentrations of most elements remained fairly constant throughout the process stream (figure 2). However, the fluxstone addition step appeared to have had a greater affect on molybdenum, fluoride, and boron levels than previously measured. Once again, the chemistry of the scrubber water varied dramatically from process waters at other locations in the plant (figure 3). As in the previous work, the scrubber acted as a source of nearly every analyzed element, with the notable exception of molybdenum.

The low pH and elevated temperatures associated with the scrubber water may explain these observations. Previous geochemical modeling suggests that fluoride and manganese concentrations in water associated with tailings is controlled by the solubility of minerals such as fluorite ( $\text{CaF}_2$ ) and rhodochrosite ( $\text{MnCO}_3$ ) and manganese oxides ( $\text{MnO}_2$ ), respectively (Berndt and Lapakko, 1997 a, 1997b). Fluorite solubility is temperature sensitive, increasing at elevated temperatures. The solubility of rhodochrosite and manganese oxides are pH dependent, increasing at low pH. Thus, high fluoride and manganese levels observed in the scrubber water were probably the result of mineral dissolution under extreme conditions in the scrubber.

Low pH will also affect the ability of arsenic and molybdenum to adsorb onto iron oxide surfaces in the tailings. The ability of arsenic to adsorb onto iron oxides decreases at low pH, resulting in arsenic remobilization in the scrubber water. The opposite effect is true for molybdenum, which is less mobile in low pH waters. Berndt and Lapakko (1997a) concluded that if remediation measures were deemed necessary, the scrubber water would be a likely location. The results from this study provide further support for their conclusion.

## 5.2. Mass Balances for the Plant

The majority of the process water comes from the tailings thickener overflow, estimated at 70,801 gpm (HDR, 1997). The remaining process water comes from the tailings basin reclaim, plant site settling basin, and Enterprise Pit with flows of 2830, 1850, and 1580 gpm, respectively (HDR, 1997). An estimated 73,881 gpm of process water exits the plant to the tailings thickener, of which approximately 3080 gpm continues on to the tailings basin for disposal.

The chemical composition of each process water source varied widely. The highest levels of manganese, fluoride, boron, and molybdenum were found in the water recycled from the tailings thickener. Arsenic levels were highest in the plant site settling basin. The Enterprise Pit contained the lowest levels of all five elements, including manganese, arsenic, and molybdenum which were below detection. In terms of total mass input, the composition of the recycled tailings thickener water typically contributed more than 95% of the mass in the process water (table 2). The exception was for arsenic, of which only 64% of the input mass came from the tailings thickener.

The element with the largest total mass input to the plant was fluoride, with 1104 T entering the process stream annually (table 2). Arsenic input was the smallest at 0.33 T/yr. For each of the five elements of interest, the total mass input to the process stream was compared to the total mass output at the tailings thickener. This provided a measure of the net mass change for each element in the process stream due to taconite processing. Based on this calculation, taconite processing contributed 13.5 T/yr of fluoride and 0.59 T/yr of manganese to the process stream. The mass of molybdenum also increased slightly (0.01 T/yr) in process waters as water passed through the plant. The plant acted as net sink for boron and arsenic at -0.11 and -0.10 T/yr, respectively.

The impact that these masses would have on the composition of water in the tailings basin was determined by dividing the mass of each element leaving the tailings thickener as underflow by the volume of water in the tailings basin. Assuming that the volume is  $6.4 \times 10^8$  (Josephson, 1998), the annual fluoride contribution to the tailings basin was 0.2 ppm (table 2). Since fluoride concentrations in tailings basin waters average about 2.5 ppm, the magnitude of a 0.2 ppm/yr contribution from taconite processing represents an 9% annual increase. Using this same analysis for manganese, taconite processing contributed 10 ppb/yr to tailings basin waters. However, oxidizing conditions in the tailings basin will promote precipitation of  $\text{MnO}_2$ . Thus, the dissolved manganese contribution to the tailings basin is expected to be negligible. There was no net contribution of molybdenum. A net loss of 2 ppb/yr was calculated for both arsenic and boron (approximately 50% and 3%, respectively).

Of the 73,881 gpm of process water that exits the plant to the tailings thickener, approximately 3080 gpm continues down a discharge pipe to the tailings basin. As the tailings slurry proceeds along the discharge pipe, intimate contact between the tailings, water, and atmospheric oxygen may affect the masses of dissolved components. To estimate this mass change, average concentrations for each element were multiplied by the estimated flow (3080 gpm) and converted to units of tons per year (table 3). Based on this calculation, the actual fluoride, boron, arsenic, and molybdenum

contributions to the tailings basin increased, indicating that these elements were released from the tailings slurry during transport to the tailings basin. Manganese levels decreased, probably due to precipitation of  $MnO_2$ .

### 5.3. Quantification of Potential Sources and Sinks

Since flow data for the process stream within the plant were unavailable, the absolute mass changes between sampling locations could not be quantified. However, relative mass changes were determined using the method described in section 3.4. Relative mass changes were calculated at the rougher, flotation cells, concentrate thickener, slurry storage tank, and leaf filter (figure 3). Relative mass changes less than 20% were considered insignificant.

A sample taken from the **rougher underflow** was used to quantify the effect that grinding had on the composition of process waters. Relative mass changes were calculated for the rougher underflow relative to background process water. For the most part, the grinding process had little effect on the composition of process waters. Relative mass changes for manganese, fluoride, molybdenum, and boron did not exceed nine percent. However, arsenic decreased by 56% at the rougher underflow. This decrease was probably due to adsorption of arsenic to fresh iron oxide surfaces exposed during grinding of the ore.

Once the ore has been crushed to the grinding set point, the process stream flows to the **flotation cells** to separate residual silica from the concentrate. Separation is enhanced by the addition of several reagents which may affect the composition of process waters. To quantify the relative mass changes that occurred at the flotation cells, waters leaving the flotation cells, both as overflow (tailings) and underflow (concentrate) were compared to the input process water represented by the rougher underflow. While fluoride and molybdenum levels were conserved, large relative mass changes were observed for manganese, boron, and arsenic at the flotation cell. Both manganese and boron levels decreased slightly, 38 and 19%, respectively. Arsenic levels almost tripled compared to the water leaving the rougher. The exact mechanism affecting manganese, boron, and arsenic levels in process waters at the flotation cells is not known. Specific flotation reagents were not investigated as part of this study, although chemical reagents used during flotation may have some effect.

The **concentrate thickener** has multiple inputs and outputs (see section 3.1). Relative mass changes occurring at the concentrate thickener were quantified by comparing the average output from 1) the overflow to the tailings thickener and 2) the concentrate underflow to the combined inputs from the flotation underflow, leaf filters, and the scrubber (equation 6). Manganese, fluoride, and boron levels were conserved in the concentrate thickener process waters. Arsenic in the process waters leaving the concentrate thickener was 63% lower than the combined arsenic input. This loss is most likely due to adsorption of arsenic onto iron oxide minerals in the concentrate and/or tailings. In contrast, the mass of molybdenum increased by 34% relative to the concentrate thickener inputs. Molybdenum mobility is highly pH dependent, increasing as pH increases. The pH of the process stream at the tailings discharge has been reported in the range of 8.2 to 8.6 (Berndt and Lapakko,

1997a). Assuming a similar pH for other locations along the process stream, molybdenum release from the solids into the process stream could be expected.

Prior to pelletization, the concentrated taconite is slurried with fluxstone and stored in a large tank. A water sample from the **slurry storage tank** was used to quantify the relative mass changes induced by the fluxstone addition (equation 7). Fluoride, boron, and calcium levels decreased (44, 42, and 38%, respectively) after the fluxstone addition. Fluoride removal is believed to be controlled by precipitation of the mineral fluorite. Process stream waters were supersaturated with respect to fluorite. However fluorite precipitation appeared to be slow relative to the residence time of water in the process stream. Although boron was removed from the slurry storage tank water, the mechanism of boron removal was uncertain. Slow adsorption to iron oxides may explain the loss. However, additional investigation is required. The relative mass of molybdenum doubled in the process stream after the fluxstone addition. This increase was most likely due to desorption of molybdenum at the relatively high pH of the slurry.

**Vacuum filtration**, is the last step prior to pelletization. Leaf filters remove most of the remaining water from the concentrate slurry. A small amount of hot water from the scrubber is added to the process stream to improve filtration. The concentration changes of most of the elements (manganese, arsenic, molybdenum, and boron) in the leaf filter water reflected the high inputs of the scrubber water. However, the relative mass increase for fluoride was 97% in the filtrate, far more than would be expected from the scrubber water contribution alone.

## 6. SUMMARY AND CONCLUSIONS

Mass balances for the plant indicated that 13.5 T/yr fluoride and 0.59 T/yr manganese were released into solution during taconite processing. Fluoride removal was observed in the taconite concentrate-fluxstone slurry storage tank. However, the subsequent release from the leaf filters and the scrubber into the process stream was much larger than the removal in the slurry storage tank. The overall fluoride contribution to the tailings basin was estimated at 0.2 ppm/yr.

Fluoride levels in process waters were believed to be controlled by the solubility of the mineral fluorite. Process waters throughout the plant were supersaturated with respect to fluorite. Furthermore, fluorite solids have been observed on the leaf filter bags (Engresser, 1997), and possibly in the lines that recycle scrubber water (Berndt, 1997). The extremely high fluoride levels in the scrubber water may be explained by increased fluorite solubility at elevated temperatures.

The annual contribution of manganese to the tailings basin was estimated to be approximately 10 ppb. However, dissolved manganese is not stable in oxidized environments such as a tailings basin. Therefore, the actual contribution of manganese to the tailings basin is expected to be negligible.

Plant mass balances for arsenic, boron, and molybdenum indicated that these elements are relatively conservative during taconite processing. Apparently, the sources of each element balanced were balanced by sinks of similar magnitude.

## 7. FUTURE WORK

The exact source and mechanism of fluoride release into the process stream is still uncertain. Since the plant mass balance indicated that fluoride concentrations increased during taconite processing, future work should focus primarily on this element. Improved quantification of mass changes may assist in the identification of specific fluoride sources. True mass balances at specific locations along the process stream could be achieved with estimated flow rates at each of the sampling locations, if this information becomes available. Currently, fluoride levels in process stream waters are believed to be controlled by a solid phase, most likely fluorite. Analysis of solid phases may also provide insight into possible mineral sources of fluoride. Measuring the pH, alkalinity, and temperature of process stream waters may improve our understanding of the solid phases that appear to control fluoride levels during taconite processing.

Manganese levels also increased during taconite processing. However, manganese will be removed from tailings basin waters due to the formation of manganese oxide minerals. Thus, manganese levels are of lesser concern.

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Table 1. Taconite plant locations sampled in this study were chosen based upon accessibility and their potential for identifying specific chemical inputs to the process stream.

Location	Targeted Process
Tailings Thickener Overflow	supplies approximately 96% of the process water
Rougher Underflow	effects of grinding on element release
Flotation Overflow	effect of flotation reagents on tailings stream
Flotation Underflow	effect of flotation reagents on concentrate stream
Concentrate Thickener Overflow	effect of concentrating ore, and one of the concentrate thickener "system" outputs
Concentrate Thickener Underflow	effect of concentrating ore, one of the concentrate thickener "system" outputs, and one of the slurry storage tank inputs
Fluxstone Ball Mill Effluent	contribution from the fluxstone grinding process line, and one of the slurry storage tank inputs
Slurry Storage Tank	process stream changes that may be kinetically controlled, and one of the leaf filter inputs
Filtrate from Leaf Filters	effect of removing water from the concentrate
Scrubber	inputs to concentrate thickener and leaf filters

Table 2. Input and output masses for Inland's taconite processing plant.

	Mn (T/yr)	F (T/yr)	Mo (T/yr)	As (T/yr)	B (T/yr)
Enterprise Pit	0	1.80	0	0	0.07
Plant Site Settling Basin	0	16.84	0.20	0.09	0.32
Tailings Basin Reclaim	0.01	14.41	0.15	0.02	0.33
Tailings Thickener Overflow	13.88	1071	8.13	0.21	13.73
<b>Total Plant Input</b>	<b>13.89</b>	<b>1104</b>	<b>8.47</b>	<b>0.33</b>	<b>14.45</b>
<b>Plant Output to Tails Thickener</b>	<b>14.49</b>	<b>1117</b>	<b>8.48</b>	<b>0.22</b>	<b>14.33</b>
<b>Mass Change (in T/yr)</b>	<b>0.59</b>	<b>13.52</b>	<b>0.01</b>	<b>-0.10</b>	<b>-0.11</b>
<b>Annual Contribution (ppb)<sup>1</sup></b>	<b>10</b>	<b>233</b>	<b>0</b>	<b>-2</b>	<b>-2</b>

<sup>1</sup>Based upon an estimated tailings basin volume of 640,200,000 gallons (Josephson, 1998).

Table 3. Dissolved fluoride, boron, arsenic, and molybdenum masses were estimated to increase in the tailings slurry water during transport to the tailings basin.

Tailings Discharge Pipe	Mn (ppb)	F (ppm)	B (ppb)	As (ppb)	Mo (ppb)
Concentration	64.8	4.2	122	3	78
Mass (T/yr)	0.38	24.5	0.71	0.02	0.45
Contribution to tailings basin (ppb/yr)	6	0.4	12	0	8



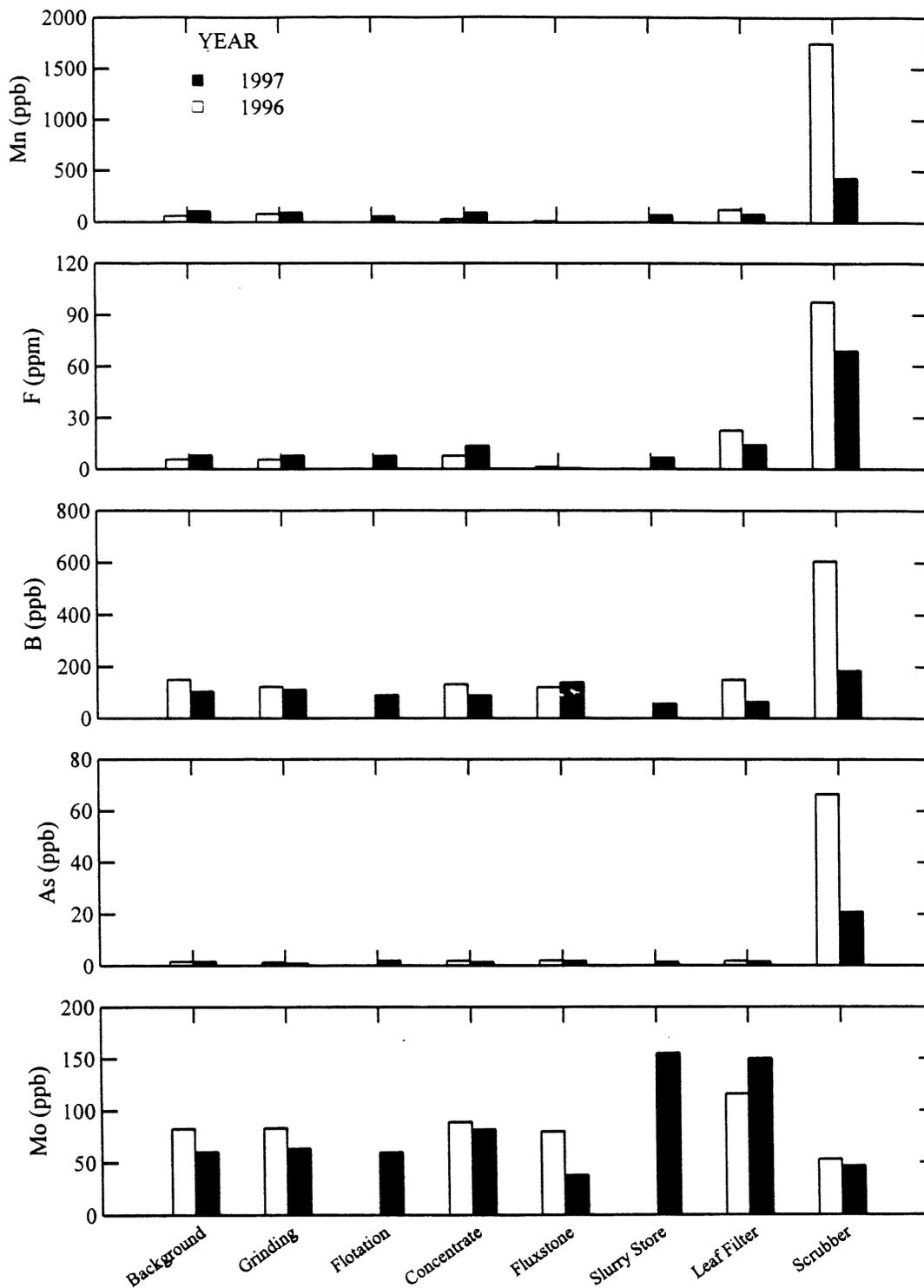


Figure 2. Concentrations of the five target elements remained relatively constant between 1996 and 1997. Samples were not taken from the flotation cells or slurry storage tank in 1996.

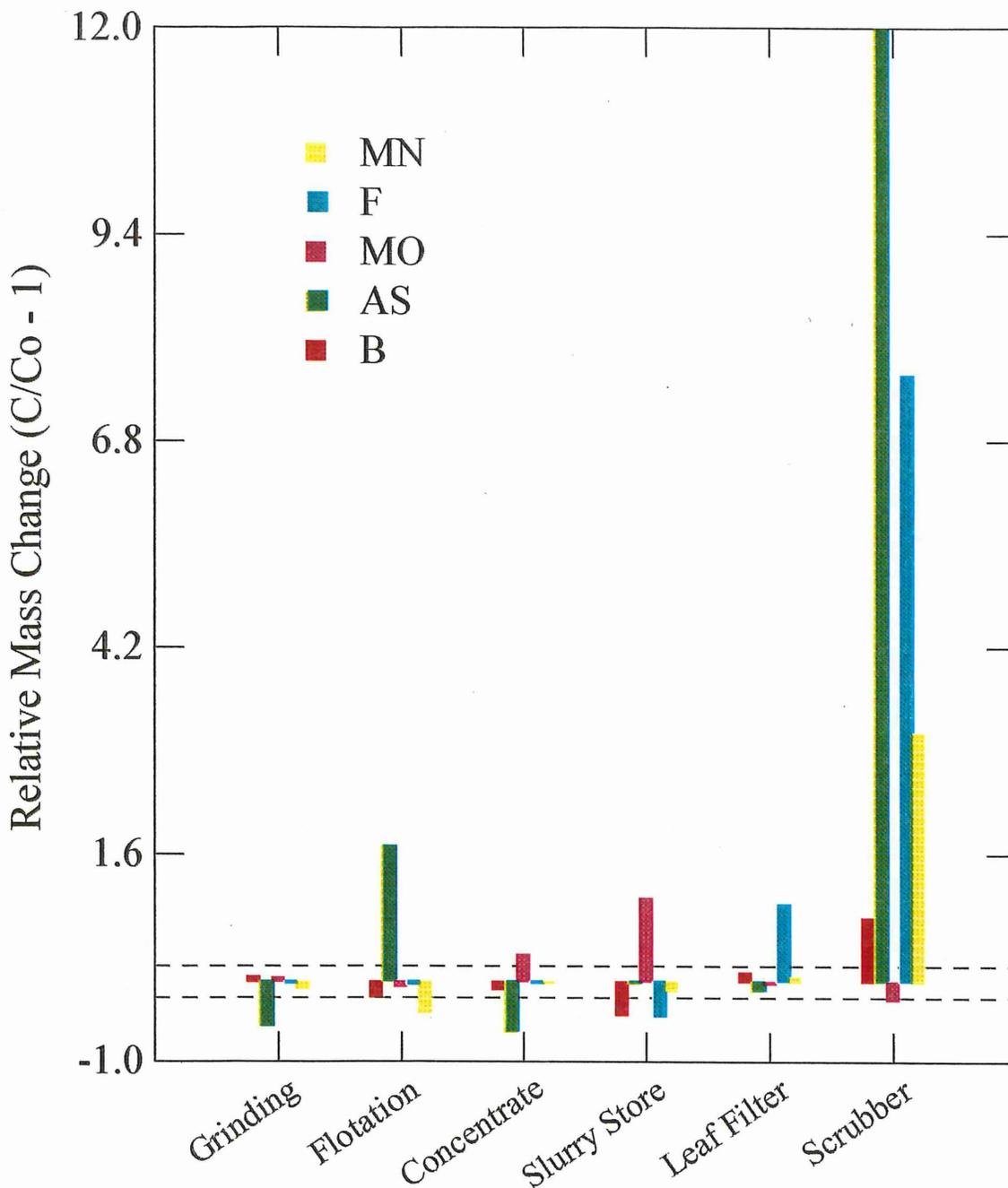


Figure 3. Relative mass changes smaller than 20% (between the dashed lines) indicated no significant input or removal at that location. The scrubber acted as a source of every target element except molybdenum. The slurry storage tank was a sink for fluoride and boron and a source of molybdenum.

Appendix 1

Water quality data

Table A1. Water quality data from ten locations within Inland Steel's taconite process plant.

Location	Tailings Thickener Overflow	Rougher Underflow	Flotation Overflow	Flotation Underflow	Concentrate Thickener Overflow	Concentrate Thickener Underflow	Fluxstone Slurry	Slurry Storage Tank	Leaf Filter Filtrate	Scrubber Transfer A
<b>majors (ppm)</b>										
Al	0.003	0.002	0.001	0.002	0.002	0.002	0.012	0.003	0.003	0.130
Si	5.77	5.36	5.61	6.22	5.48	5.31	6.08	2.88	2.67	11.49
P	0.030	<0.010	0.011	0.011	<0.008	<0.009	<0.008	0.013	0.014	0.040
Fe	<0.01	<0.01	<0.01	<0.02	<0.02	<0.01	<0.02	<0.02	<0.02	3.59
Mn	0.11	0.09	0.06	0.06	0.09	0.09	0.00	0.08	0.09	0.48
Sr	0.16	0.16	0.16	0.15	0.18	0.18	0.39	0.21	0.26	0.21
Ba	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01
Ca	30.0	29.1	29.9	28.9	33.8	33.9	33.1	21.0	21.9	49.9
Mg	43.0	41.1	42.0	42.1	43.2	43.6	72.4	43.7	43.4	52.7
Na	47.6	46.4	45.4	44.3	40.0	39.7	47.8	34.3	36.7	54.7
K	7.9	7.7	7.9	8.5	7.6	7.4	16.1	3.1	3.6	10.3
F	8.0	7.8	7.6	7.3	13.6	13.3	0.4	6.5	14.1	68.9
Cl	70.6	70.2	68.8	67.5	79.7	78.4	189.9	90.2	95.9	171.4
NO <sub>2</sub> -N	0.05	0.05	0.05	0.04	0.05	0.05	0.02	0.01	0.07	0.11
Br	0.54	0.53	0.53	0.51	0.61	0.59	2.01	0.79	0.79	1.29
NO <sub>3</sub> -N	1.86	1.86	1.74	1.65	1.30	1.25	0.81	0.81	0.74	2.39
SO <sub>4</sub>	59.1	59.0	58.8	58.0	64.4	65.5	65.3	57.4	61.4	116.7
<b>trace (ppb)</b>										
Li	22.4	22.0	21.6	24.3	19.9	20.9	27.8	12.4	13.4	28.0
B	102.5	109.4	91.3	85.4	87.7	87.4	138.4	55.2	63.1	184.2
Sc	1.41	1.30	1.54	1.58	1.43	1.28	1.64	0.75	0.69	2.81
Ti	2.33	3.56	4.12	0.13	3.01	2.97	3.19	2.15	1.98	6.04
V	0.47	0.44	0.23	0.23	0.54	0.36	1.11	0.31	0.52	7.70
Cr	0.49	1.08	1.18	1.10	0.60	1.08	1.20	0.81	0.45	10.96
Mn	103.6	94.0	58.8	58.5	95.5	95.0	0.6	72.7	80.1	426.5
Fe	10.88	12.71	7.35	11.30	8.84	10.55	9.50	17.08	5.45	3521
Co	0.14	0.13	0.09	0.08	0.10	0.08	0.13	0.10	0.09	0.70
Ni	1.05	1.17	0.47	0.78	1.13	1.39	0.92	1.31	1.40	14.48
Cu	0.27	0.38	0.42	0.39	0.91	0.65	0.55	0.36	0.84	158.90
Zn	26.4	26.3	26.8	29.3	27.6	30.2	27.1	33.4	31.2	149.7
Ge	0.11	0.15	0.15	0.15	0.22	0.19	0.26	0.15	0.16	1.94
As	1.59	0.70	1.85	1.93	1.47	1.28	1.85	1.41	1.42	20.66
Se	0.00	0.00	2.19	0.00	0.00	0.00	2.33	0.00	0.00	29.24
Br	507.8	513.0	576.2	539.9	609.6	602.6	2138.0	826.9	876.0	1365.0
Rb	5.81	5.98	6.52	7.00	6.44	6.03	10.86	2.32	2.71	13.39
Sr	168.9	165.1	169.7	165.8	178.9	175.2	390.2	230.1	260.6	212.8
Y	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01
Mo	60.6	63.4	64.1	55.6	79.2	84.6	37.8	155.1	150.0	46.5
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Cd	0.02	0.02	0.04	0.04	0.05	0.04	0.03	0.10	0.14	0.44
Sn	0.28	0.06	0.25	0.12	0.25	0.04	0.00	0.00	0.33	0.78
Sb	0.05	0.07	0.07	0.07	0.07	0.08	0.18	0.05	0.04	0.08
Te	0.01	0.02	0.02	0.00	0.00	0.01	0.01	0.00	0.00	0.04
Cs	0.89	0.91	1.00	1.06	1.08	0.90	0.05	0.30	0.37	5.74
Ba	4.92	4.81	3.53	3.75	5.93	5.03	5.75	7.42	10.86	12.78
W	0.70	0.56	0.44	0.30	0.23	0.14	0.47	0.13	0.30	0.52
Pb	0.01	0.00	0.02	0.00	0.03	0.03	0.04	0.01	0.04	55.07
U	0.08	0.11	0.07	0.06	0.05	0.08	0.01	0.00	0.00	0.12