Detailed Analysis of Potential Environmental Impacts of Taconite Tailings Disposal in the Minorca Pit on Water Quality in the Missabe Mountain Pit

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# Detailed Analysis of Potential Environmental Impacts of Taconite Tailings Disposal in the Minorca Pit on Water Quality in the Missabe Mountain Pit

Final Report

Kim Lapakko Emmelyn Jakel

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#### EXECUTIVE SUMMARY

The Minnesota Department of Natural Resources and University of Minnesota conducted a joint study on the potential water quality impacts of disposing of taconite tailings in existing open mine pits. A brief summary of the results that apply to Ispat Inland Mining Company's proposal to dispose of tailings in the Minorca Pit appeared in a Supplemental Environmental Impact Statement (SEIS) produced by the MN DNR (MNDNR, 1999, 2000). This document provides a more detailed review of the results of the MN DNR/U of MN study, which focused on the levels of manganese, fluoride, molybdenum, arsenic and boron in waters closely associated with taconite tailings. These waters include those that are discharged with tailings from the taconite processing plant and those that are found within the pore spaces among tailings (i.e. tailings pore waters).

Operational water samples were collected from four taconite operations along the Mesabi Iron Range over a two and a half year period. Field and laboratory experiments were also conducted on taconite tailings and process waters from these operations. Finally, geochemical modeling was used to determine chemical reactions that control tailings pore water quality. Each of the four elements are discussed individually with regard to expected levels in flow leaving the Minorca Pit (source terms), transport through the aquifer (transport term), flow-weighted average concentrations expected in inputs to the Missabe Mountain Pit, and dilution and chemical reactions within the Missabe Mountain Pit.

Projected levels of manganese, fluoride, molybdenum, arsenic, and boron, which could evolve in the Missabe Mountain Pit as a result of taconite tailings disposal in the Minorca Pit, are discussed individually with regard to:

- 1) short and long-term levels expected in flow leaving the Minorca Pit (source terms),
- 2) transport through the Biwabik aquifer (transport term),
- 3) dilution of inputs to the Missabe Mountain Pit,
- 4) dilution by the volume of water stored within the Missabe Mountain Pit, and
- 5) chemical reactions within the Missabe Mountain Pit.

The projected source terms are largely based on chemical analyses of process waters discharged from Ispat Inland Mining Company's (Inland) taconite processing plant near Virginia, MN. In addition, laboratory and field experiments were conducted on Inland's process waters and tailings. Geochemical modeling was used to describe environmentally relevant chemical reactions associated with taconite tailings and the water which they contact.

Values for transport through the Biwabik aquifer included 100% transport for the most conservative estimate. Additional values were calculated using ground water concentrations from the Biwabik aquifer and geochemical modeling.

Dilution of inputs to the Missabe Mountain Pit was calculated based on water balances determined for the pit and the projected output from the Minorca Pit. Dilution by the volume

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#### 2. Site Description and Tailings Disposal Plan

Inland's taconite processing operation is located approximately two miles northeast of Virginia, MN (Figure 1). The Minorca Pit lies approximately 0.5 miles south of Inland's operation. At present, the water table in the Minorca Pit is at approximately 1400 feet mean sea level (M.S.L.), which may be as much as fifty feet lower than that of the adjacent ground water (Adams, 1998; MDH, 1998). Consequently, the pit acts as a hydrologic sink for surrounding ground water. Inland currently maintains the pit water level by pumping excess water to Sauntry Creek at an average rate of 1419 gpm (Indeco, 1999).

The proposed action would involve pumping coarse and fine tailings slurried with process water from the processing plant to the Minorca Pit. Tailings will settle to the pit floor, creating a clear water pool. Some of the water from this pool will continue to be used to augment stream flow in Sauntry Creek. Much of the water remaining in the clear pool will be pumped back to the plant for reuse.

After five years of tailings and process water deposition, the water level in the Minorca Pit is expected to reach 1450 feet M.S.L. (Table 1; Indeco, 1999). When water exceeds this level, it will flow from the Minorca Pit into the Biwabik aquifer. Both the clear water pool and tailings pore waters are expected to contribute to this flow. However, the primary source of outflow is assumed to be from the clear water pool until the tailings elevation reaches the lowest pit rim elevation (1470 feet M.S.L.). It is anticipated that once Inland begins to deposit tailings into the Minorca Pit, the tailings elevation will reach 1470 feet in approximately eight years (Indeco, 1999). Thus, the period during which Minorca Pit ground water outflow may be dominated by the clear water pool is assumed to be between years five and eight. After the tailings elevation reaches 1470 feet M.S.L., ground water outflow from the pit is assumed to be dominated by tailings pore water (i.e. all ground water output from the pit to surrounding ground water will be from tailings pore water). The pit is expected to reach its capacity ten years after disposal begins. At this time the surface will be prepared for vegetation.

The elevation at which ground water outflow from the Minorca Pit is anticipated is approximately 230 feet higher than the current water level in the Missabe Mountain Pit, which is used as the drinking water supply for the city of Virginia. Due to this gradient, flow from the Minorca Pit to the Missabe Mountain Pit is a distinct possibility. In order to provide the most conservative estimate of the potential water quality impacts of disposal of tailings in the Minorca Pit, it was assumed that ground water outflow from the Minorca Pit will eventually reach the Missabe Mountain Pit.

#### 3. Data Collection, Calculations, and Analytical Methods

The methods used during this study have been described in detail elsewhere (Berndt and Lapakko, 1997a, b; Berndt, 1998; Berndt et al., 1998, 1999; Jakel et al., 1998; Jakel and Lapakko, 1999a, b, c). However, they are summarized here in order to illustrate the approach used in this document. Out of more than 162 inorganic elements and organic compounds examined in waters associated with taconite tailings during the range-wide study (Berndt and Lapakko, 1997a), only four inorganic elements were identified as approaching or exceeding drinking water quality standards. These four elements were manganese, fluoride, molybdenum, and boron.

Two additional elements, arsenic and mercury, were also considered during this study. Arsenic has been reported to the MPCA at levels as high as 18 ug/L as part of the National Pollution Discharge Elimination System (NPDES) program. Although this value does not approach the existing drinking water quality standard of 50 ug/L, arsenic was included in this assessment because the US EPA is considering lowering the drinking water quality standard in January 2001.

Mercury emissions due to taconite processing have been of recent interest in Minnesota. Tailings and tailings pore waters from three of the participating operations were sampled specifically for mercury analysis. Mercury levels in the tailings pore waters were approximately three orders of magnitude lower (3 ng/L) than the drinking water quality standard (2 ug/L; Table A6.6). Additional mercury analyses were not conducted.

Five of the six elements (excluding mercury) will be referred to collectively as elements of concern, or ECs. It is important to note, however, that only three ECs (manganese, fluoride, and molybdenum) were found to approach or exceed drinking water quality standards at Inland's operation. Therefore, only these three ECs and arsenic were reviewed in the SEIS.

This document will provide a detailed discussion of the potential impacts of taconite tailings disposal in the Minorca Pit on EC concentrations in Missabe Mountain Pit waters. Each EC will be discussed individually with regard to expected levels in flow leaving the Minorca Pit (source terms), transport through the aquifer, flow-weighted average input concentrations to the Missabe Mountain Pit, and dilution and chemical reactions within the Missabe Mountain Pit (Figure 2).

#### 3.1. Minorca Pit Source Terms

Currently, the Minorca Pit acts as a sink for ground water, precipitation and runoff from the surrounding area, resulting in an average water level in the pit of approximately 1400 feet M.S.L. (MDH, 1998). As the Minorca Pit fills with tailings, the water level in the pit will rise. Once the water level within the pit reaches that of the surrounding ground water (1450 feet M.S.L.), water will flow out of the Minorca Pit as ground water (Adams, 1998). The range of expected EC concentrations in ground water exiting the Minorca Pit will be referred to as the "source

term." This term includes waters exiting the Minorca Pit from the clear water pool as well as tailings pore waters.

#### 3.1.1. Clear Water Pool Source Terms

#### 3.1.1.1. Approach

ECs are released into process waters during taconite processing. Consequently, concentrations of components which are not removed from solution by chemical precipitation or adsorption (e.g. Cl, Br) tend to increase as water recycles through the plant (Berndt and Lapakko, 1997a). If such increases occur, the degree to which they occur depends on the amount of dilutional water introduced to the process stream. At present, dilute make-up water from the Sauntry/Enterprise Pits is routinely added to the process stream as needed. However, precipitation onto and surface runoff into the existing tailings basin provide most of the dilutional water for the process stream.

During the first two years of tailings deposition in the Minorca Pit, the amount of dilutional water available will be less than that presently available in the tailings basin (Noramco, 1997; Indeco, 1999). Consequently, EC levels may increase during this time period. However, as the pit fills with tailings, the volume of water in the clear water pool, and therefore water available for recycling, decreases. In order to meet their process needs, Inland will have to supplement this flow with water from other sources. This supplemental flow will exceed that presently available in the tailings basin. As long as the source of the make-up water is dilute (e.g. the Enterprise or Sauntry Pits), EC levels in plant discharges should be maintained close to present levels. Therefore, plant discharge samples collected during the range-wide study represent the best available empirical estimate of the process water chemistry that will enter the Minorca Pit.

#### 3.1.1.2. Data collection

Operational field measurements of EC levels in waters closely associated with taconite tailings were collected over a two and a half year period (Appendix 2; Berndt and Lapakko, 1997a; Berndt et al., 1998, 1999; Lapakko et al., 1998). Ten water samples were collected at the point at which Inland discharges tailings and process water into the tailings basin. An additional eleven samples of clarified water were collected from the tailings basin reclaim barge, where water is pumped back to the plant for re-use.

#### 3.1.1.3. Calculation

Most of the process water entering the Minorca Pit will flow rapidly to the clear water pool, where it will be diluted by precipitation and ground water. In order to obtain a reasonable source term for the clear water pool, it was necessary to calculate the impact that process water inputs would have on EC levels over the ten year period of operation. Based on a preliminary tailings disposal plan (Indeco, 1999) and previous estimates of net precipitation and ground water flow (Noramco, 1997; Adams, 1998), two water balances were developed for the Minorca Pit clear

water pool (Table 2). For each water balance, changes in clear water pool chemistry were calculated assuming a well-mixed system and a plug-flow system. Values from each water balance were used to calculate changes in clear water pool chemistry assuming well-mixed (Table A2.2) and plug-flow (Table A2.3) approaches. Thus, four calculations provided a range of EC concentrations that can be expected in the clear water pool over the ten year operational time period. Although ground water outflow during this time period will be comprised of water from the clear water pool and tailings pore spaces, the clear water pool is assumed to dominate ground water outflow from the Minorca Pit between deposition years five and eight. EC concentrations calculated for that time period represent the clear water pool source term.

#### 3.1.2. Tailings Pore Water Source Term

#### 3.1.2.1. Approach

As the pit continues to fill with tailings and process water, conditions within the tailings mass will become less oxidizing. As the environment changes, chemical reactions between process water and tailings will change the composition of tailings pore waters within the Minorca Pit. Consequently, the quality of water observed in plant discharges and the clear water pool was not a good indication of source terms for the Minorca Pit. In order to determine appropriate source terms for each EC, it was necessary to examine the water chemistry resulting from tailings-water interactions in an environment isolated from the atmosphere. Tailings pore waters collected from Inland's tailings basin as well as field and laboratory experiments using tailings from Inland's operation (Appendix 2).

#### 3.1.2.2. Data collection

Water samples collected from a seep and two wells in the north dike of the tailings basin at Inland represented the closest operational simulation of tailings-water interaction expected in the Minorca Pit (Berndt and Lapakko, 1997 a; Berndt et al., 1998, 1999). An additional water sample was collected from a seep in the interior dike late in the study (Berndt et al., 1999).

Six operational field measurements of tailings pore water chemistry were also collected from the Snively Pit at US Steel-Minntac (Jakel et al., 1999a). The Snively Pit represents the only existing case of in-pit taconite tailings disposal in Minnesota. Some of the tailings generated by the Pilot Tac Operation were deposited in the Snively Pit from 1964 to 1972, with sporadic deposition until 1980. This situation provided data which will be used to represent the potential long-term impacts of in-pit taconite tailings disposal on ground water quality.

Tailings pore water quality was also measured in controlled field experiments. In-pit disposal of Laurentian taconite tailings was simulated using polyethylene plastic tanks (h = 10 ft., d = 4 ft.) embedded nine feet into an embankment at the MN DNR field experimental facility in Hibbing, MN (Berndt and Lapakko, 1997a; Jakel et al., 1998a; Jakel and Lapakko, 1999b). Two tanks were filled with tailings and process waters from Inland's operation and left open to the

atmosphere. Tailings pore water samples were collected from wells set approximately four feet into the tailings. Sixteen tailings pore water samples were collected over 116 weeks.

Laboratory experiments consisted of tailings from Laurentian ore and process waters collected directly from the tailings discharge pipe at Inland and transferred into two plastic columns (d = 2in, h = 15 ft.) fit with a sampling port at the base (Berndt and Lapakko, 1997a). The columns were secured in a vertical position and covered with an opaque plastic sheet to eliminate light. These columns simulated conditions that would be expected in the Minorca Pit as it is filled with tailings. Nine water samples were collected periodically over a period of seven months.

Once tailings and process waters have been deposited in a pit, process waters will eventually be replaced by precipitation and possibly ground water. In order to simulate these two events, process water in one column was replaced with deionized water to simulate rain water and the other was injected with ground water obtained from local wells drilled into the Biwabik aquifer (Berndt et al., 1998, 1999).

#### 3.1.2.3. Calculation

The range of concentrations measured in tailings pore waters during this study was used to represent tailings pore water compositions in the Minorca Pit if it is filled with tailings. The resultant water chemistry from these measurements and experiments were used as input for geochemical modeling software. Calculations using geochemical modeling software provided additional insight into the reactions controlling EC levels in tailings pore waters.

#### 3.2. Transport in the Biwabik Aquifer

3.2.1. Approach

As ground water flows out of the Minorca Pit, dissolved ECs may ultimately be transported to the Missabe Mountain Pit. The geology of the Biwabik Iron Formation is extremely complex with folded and fractured rocks, numerous fault zones, and abandoned mine pits. Each of these features affects the path of ground water flow within the Virginia Horn area.

Due to the complex hydrology, the flow time from the Minorca Pit to the Missabe Mountain Pit has not been quantified. However, some generalizations about ground water flow may be useful. These generalizations do not precisely quantify the length of time required for Minorca Pit waters to flow to the Missabe Mountain Pit, but rather roughly estimate the upper and lower bounds for the flow time.

#### 3.2.2. Data collection

Field measurements of water samples collected from eleven different wells in the Biwabik Formation aquifer were analyzed during this study (Table 8; Berndt et al., 1998, 1999). These measurements represented the best estimate of background EC levels in the Biwabik aquifer.

#### 3.2.3. Calculation

Initially, flow through bedrock in the Biwabik Iron Formation has been estimated at 0.7 to 1.8 feet/day (HDR, 1997). At this rate, ground water leaving the Minorca Pit and flowing through intact bedrock will reach the Missabe Mountain Pit (4650 feet away) in 7 to 18 years. However, if a direct connection exists via fractures in the bedrock, flow times between the two pits may be reduced to months, or even weeks.

These values do not represent a rigorous analysis of hydraulic conductivities and gradients in the area, which would be extremely difficult to develop due to the unknown frequency, dimensions, and location of fractures through which flow is transmitted. Therefore, to determine the highest possible impact of taconite tailings in the Minorca Pit on Missabe Mountain Pit water quality, it was assumed that the pits are hydrologically connected. Furthermore, it was assumed that all of the ground water exiting the Minorca Pit reported to the Missabe Mountain Pit immediately. This assumption has not been verified (MDH, 1998), however, it yields the most conservative analysis.

Although ground water from the Minorca Pit may not react as it flows through the aquifer, it is more likely that Minorca Pit waters will react with the host rock and water in the Biwabik aquifer. In order to gain additional insight into chemical controls on EC levels in tailings pore waters and the Biwabik aquifer, geochemical calculations were computed using the Geochemist's Workbench version 2.0 (Bethke, 1994). This model provided a useful tool for performing fluid speciation, mineral reaction, and surface adsorption calculations (Berndt and Lapakko, 1997 a, b; Berndt, 1998; Berndt et al., 1998, 1999). These calculations were used to predict the most likely EC levels in ground water flowing from the Minorca Pit to the Missabe Mountain Pit (Appendix 3).

3.3. Flow-Weighted Average Input Concentrations to the Missabe Mountain Pit

3.3.1. Approach

EC levels in the Missabe Mountain Pit are low, and meet the drinking water quality standards discussed in this document. Consequently, elevated EC levels in ground waters transported from the Minorca Pit to the Missabe Mountain Pit will tend to increase EC levels in Missabe Mountain Pit waters. The extent of this increase will depend on the concentration of the EC in ground water outflow from the Minorca Pit, the fraction of outflow reaching the Missabe Mountain Pit, dilution of this flow, the amount of unimpacted water entering the Missabe Mountain Pit from sources other than the Minorca Pit, and EC levels in these unimpacted waters. These factors were used to evaluate flow-weighted average input concentrations to the Missabe Mountain Pit. That is, a theoretical average concentration that would result if all inputs to the Missabe Mountain Pit were mixed together prior to entering the pit. This approach was similar to that used in the Health Risk Assessment conducted by the MDH (1998), which predicted EC concentrations in the net inflow to the Missabe Mountain Pit based, in part, on hydrologic balances for the Minorca and Missabe Mountain Pits.

#### 3.3.2. Calculation

At present, the Missabe Mountain Pit receives approximately 2135 gpm of unimpacted water from precipitation and local ground water (HDR, 1997). The Missabe Mountain Pit is expected to receive additional ground water input from Minorca Pit shortly after the water level in the Minorca Pit reaches 1450 feet M.S.L. The resultant flow rate was estimated for two hypothetical time periods (Adams, 1998). The first time period represented a temporary maximum outflow from the Minorca Pit as it is filled with tailings and process water and prior to reclamation. Based on the preliminary tailings disposal plan, the temporary maximum corresponds to depositional years five through ten (Indeco, 1999). During this time period, ground water outflow from the Minorca Pit was estimated at 701 to 839 gpm, or 33 to 39% of the total input to the Missabe Mountain Pit (Table 3, Appendix 4; Adams, 1998). This interpretation is considered to be the worst case scenario.

The second period begins after reclamation of the Minorca Pit. Once grasses have been established over the tailings surface, ground water flow from the Minorca Pit will decrease to 301 to 439 gpm, or 14 to 21% of the total input to the Missabe Mountain Pit (Table 3, Appendix 4; Adams, 1998). Forest vegetation further reduces ground water outflow to an estimated 136 to 274 gpm, or 6 to 13% of the total input to the Missabe Mountain Pit (Table 3, Appendix 4; Adams, 1998).

Further investigation of the Missabe Mountain Pit hydrologic balance led to the conclusion that ground water flow from the Minorca Pit should be in addition to the 2135 gpm total inflow to the Missabe Mountain Pit (Adams, 1999). In other words, current net precipitation and ground water inflow to the Missabe Mountain Pit will not be diminished by additional input from the Minorca Pit. In this case, ground water flow from the Minorca Pit will make up only 25 to 28% of the net input to the Missabe Mountain Pit during full development and 6 to 18% of the net input after the site has been reclaimed. Both interpretations will be considered in this document and in the SEIS.

3.4. Dilution and Geochemical Reaction in the Missabe Mountain Pit

3.4.1. Dilution

#### 3.4.1.1. Approach

Using the preliminary tailings deposition plan for the Minorca Pit (Indeco, 1999) along with the estimated contributions of ground water from the Minorca Pit (Adams, 1998, 1999) and a generalized water balance for the Missabe Mountain Pit (HDR, 1997; Wiskow, 1998), a multi-hypothetical approach was developed for determining the dilutional potential of water already present in the Missabe Mountain Pit. This multi-hypothetical approach took into consideration numerous variables including:

- 1. multiple source term magnitudes,
- 2. a shift from a clear water pool to a tailings pore water source term,
- 3. changes in ground water flow rates from the Minorca Pit over time, including the two reclamation conditions,
- 4. two different lengths of time to represent the "temporary maximum" ground water outflow from the Minorca Pit, and
- 5. two different interpretations of the Minorca Pit contribution to Missabe Mountain Pit net inputs.

#### 3.4.1.2. Calculation

This approach resulted in twelve separate calculations of EC concentrations changes in the Missabe Mountain Pit due to continuous dilution over a fifty year time period. In order to simplify the presentation, only the "worst case scenarios" are presented graphically. However, all twelve calculations can be found in Appendix 5.

In addition to the variables considered above, this approach was based on three important assumptions, each of which is intended to provide the most conservative analysis. First, it assumes that 100% of Minorca Pit outflow reports immediately to the Missabe Mountain Pit. As discussed in section 3.2, this assumption can neither be proved nor disproved.

Second, tailings deposition into the Minorca Pit is assumed to begin in 2004. This is approximately when Inland anticipates running out of room in their existing tailings basin. 2004 is also a convenient year because it implies that ground water outflow from the Minorca Pit would begin in 2009, the year that the water levels in the Missabe Mountain and Rouchleau Pits are expected to breach the earthen berm between them. This is important because the volume of the Missabe Mountain Pit below the berm has been calculated to be 5.6 billion gallons (Wiskow, 1998). Thus, 5.6 billion gallons can be used as the starting, dilutional, volume of water in the Missabe Mountain Pit at the time just before inflow from the Minorca Pit arrives. It is important to remember that the years selected here may not correspond to the final disposal plan, and therefore, must be treated as a hypothetical situation rather than fact.

Third, despite the fact that the water elevation in the Missabe Mountain and Rouchleau Pits will breach the berm separating them at some point during Inland's disposal plan, it was assumed that there would be little mixing of water between the two pits. Thus, an initial pit volume of 5.6 billion gallons was used rather than the total combined volume of 8 billion gallons (Wiskow, 1998). This is not entirely realistic, however, it reduces the amount of dilutional water available within the Missabe Mountain Pit. Consequently, it yields a conservative estimate of EC concentration changes due to inflow from the Minorca Pit.

#### 3.4.2. Geochemical Reactions

In addition to dilution, oxidizing conditions in the Missabe Mountain Pit may promote chemical reactions that further decrease EC levels. Therefore, geochemical controls on EC levels in the Missabe Mountain Pit were examined.

#### 3.4.2.1. Data collection

Water quality data were collected from the Missabe Mountain Pit and operational sites, as well as field and laboratory experiments, which simulated the reaction environment in the Missabe Mountain Pit. Water samples from five depths in the Missabe Mountain Pit were collected through the ice in March, 1999 (Table 10). Operational surface water measurements were collected from the plant discharge to the tailings basin and from the reclaim barge where clarified water is recycled back to the plant (Berndt and Lapakko, 1997a, b; Berndt et al., 1998, 1999). Tailings basin and Missabe Mountain Pit waters are similar in that they both receive dilutional water from precipitation and surface runoff. Furthermore, both waters are exposed to the atmosphere, and therefore, have similar chemical environments. Thus, it is believed that geochemical controls on EC levels in the tailings basin clear water pool will also control EC levels in the Missabe Mountain Pit.

Chemical controls operating in surface waters associated with taconite tailings were also examined in field and laboratory experiments. The field tank experiments were designed such that approximately 4.5 feet of surface water stood above the taconite tailings, exposed to the atmosphere (Berndt and Lapakko, 1997a; Jakel et al., 1998a; Jakel and Lapakko, 1999b). This situation simulated conditions in the tailings basin, and provided information regarding the persistence of ECs in these waters.

In order to better define the persistence of manganese in the Missabe Mountain Pit, batch experiments were conducted using waters obtained from monitoring well #6 at Inland and the Missabe Mountain Pit (Jakel and Lapakko, 1999c). Five separate dilutions were mixed in 2.5 gal buckets with a small hole punched in the lids to allow air transfer and stored at approximately 46 °F. These experiments were intended to simulate a situation where water with elevated EC levels mixed with water in the Missabe Mountain Pit. That is, they were used to examine potential chemical reactions in mixtures of water exiting a tailings impoundment under reducing conditions and water from the Missabe Mountain Pit.

#### 3.4.2.2. Calculation

Geochemical calculations conducted using the Geochemist's Workbench computer modeling software indicated that manganese is thermodynamically unstable in oxygenated waters such as the Missabe Mountain Pit. Consequently, dissolved manganese will oxidize to a solid manganese oxide phase.

#### 3.5. Chemical Analyses

Each water sample was analyzed for approximately 82 inorganic parameters including pH, alkalinity, temperature, and major and trace cations and anions. Temperature and pH (Beckman model 11 meter with Ross model 8165 combination electrode) were determined on site, while alkalinity titrations (APHA et al., 1995) were conducted at the MN DNR laboratory in Hibbing, MN. The levels of cations were analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer mode-SCIEX-Elan 5000) while anions were measured using ion chromatography (IC, Dionex Ion Chromatograph fitted with GP40 gradient pump, CD20 conductivity detector, and two AS4A anion exchange columns) at the U of MN. Mercury analyses were conducted by Frontier Geosciences, Seattle, WA.

#### 4. EC Summaries

Source terms, transport terms, and expected levels in the Missabe Mountain Pit for each of the four EC's are presented in the following discussion. Predicted EC levels in the Missabe Mountain Pit are also compared to primary and secondary drinking water quality standards. Finally, potential treatment issues for the Virginia Public Utility are considered

#### 4.1. Manganese

#### 4.1.1. Approach

If taconite tailings are disposed of in the Minorca Pit, manganese concentrations in waters associated with these tailings will become elevated relative to natural background levels. As the pit fills, water will flow from the Minorca Pit into the Biwabik Formation aquifer and, likely, to the Missabe Mountain Pit. The purpose of section 4.1 is to summarize results of the MN DNR-U of MN study on the ground water implications of taconite tailings disposal in the Minorca Pit with regard to manganese. Operational measurements, field and laboratory experiments, and geochemical modeling were used to; 1) determine the magnitude of manganese concentrations in outflow from the Minorca Pit (i.e. source term), 2) consider processes, including dilution and chemical reactions, that affect manganese levels during transport in the aquifer, 3) estimate average input concentrations to the Missabe Mountain Pit from all water sources, and 4) determine the extent to which dilution and other natural processes will decrease manganese levels within the Missabe Mountain Pit. A brief description of manganese geochemistry is presented as background prior to discussion of the processes affecting manganese release in the Minorca Pit, transport through the Biwabik aquifer, and fate in the Missabe Mountain Pit.

#### 4.1.2. Manganese Geochemistry

Manganese naturally occurs in several oxidation states, of which II, III, and IV are geochemically important. Manganese III and IV occur primarily as insoluble oxides (e.g. MnOOH,  $MnO_2$ ) and silicates. Manganese II is soluble, but also forms several stable minerals (e.g.  $MnCO_3$ , MnS). For the purposes of this document, we will focus on rhodochrosite ( $MnCO_3$ ) as the principle manganese II solid phase.

Rhodochrosite is marginally soluble at neutral pH and dissolution is enhanced at low pH:

$$MnCO_3 + H^+ \rightarrow Mn^{2+} + HCO_3^-$$
(1)

As can be seen in reaction 1, rhodochrosite dissolution releases manganese II and alkalinity into solution. Under moderately reducing conditions (e.g. ground water), the dissolved form of manganese II is thermodynamically stable. Thus, dissolution of rhodochrosite under these conditions can lead to elevated levels of dissolved manganese. The extent to which manganese levels can become elevated will be a function of solution pH and alkalinity:

$$[Mn^{2+}] = K_{MnCO3} [H^+]/[HCO_3^-]$$

where,  $K_{MnCO3}$  represents the rhodochrosite solubility constant. Thus, a water with a high alkalinity will contain less dissolved manganese than a water with a lower alkalinity content at the same pH (Figure 5; Table A3.1).

(2)

When natural waters are oxygenated (e.g. pit lakes), dissolved manganese oxidizes to Mn III or Mn IV and forms insoluble manganese oxides. Several rate laws have been proposed for the inorganic oxidation of manganese in oxidized fresh waters (Stumm and Morgan, 1981; Eary and Schramke, 1990; Hoffman, 1990; Luther, 1990; Davison, 1993). In general, the rate equation can be expressed as:

$$-d[Mn(II)]/dt = k_0[Mn^{2+}] + k_1[Mn^{2+}][MnO_x]$$
(3)

where, the  $k_0[Mn^{2+}]$  term is usually considered negligible,  $k_1 = k[OH^-]^2 P_{O2}$ , and  $MnO_x$  represents a nonstoichiometric product that may be comprised of several manganese oxide minerals ( $\gamma$ -MnOOH,  $Mn_3O_4$ ,  $\delta$ -MnO<sub>2</sub>, and  $MnO_{1.3}$  to  $MnO_{1.9}$ ). Based on this rate law (equation 3), and the dependence of  $k_1$  on  $[OH^-]^2$ , manganese removal will accelerate at high pH (>9).

At the pH range of most pit lakes in northern Minnesota (6.5 - 8.5), manganese oxidation is a slow process (Stumm and Morgan, 1981; Langmuir, 1997). The half-life of dissolved manganese in natural waters, based on abiotic considerations alone, has been estimated at approximately three hundred years (Hamilton-Taylor and Davison, 1995). However, the activity of certain bacteria and fungi have been observed to catalyze manganese oxidation in natural waters, decreasing the half-life of dissolved manganese from one to one hundred days (Davison, 1993). Consequently, manganese levels in oxygenated pit lakes tend to be relatively low (Pierce and Tomcko, 1989).

### 4.1.3. Minorca Pit Manganese Source Term

Operational, field and laboratory measurements of manganese concentrations in waters closely associated with taconite tailings were collected over a two and a half year period (Berndt and Lapakko, 1997a, b; Berndt, 1998; Berndt et al., 1998, 1999). Operational measurements at Inland were taken from the tailings discharge pipe, clarified water in the tailings basin, a seep in the north dike of the tailings basin, and two wells outside the northeast edge of the tailings basin. A single measurement was obtained from a seep in the interior dike late in the study. Operational measurements of tailings pore waters were also made at the Snively Pit, US Steel-Minntac (USX, the only known case of in-pit disposal of taconite tailings in Minnesota), two wells at National Steel and Pellet Company (National), and one seep at LTV Steel Mining Company (LTV). Laboratory experiments were conducted on tailings initially saturated with process water and subjected to input from precipitation. Finally, geochemical computer models were used to define limits on manganese levels in tailings pore waters. These data will be used

in the following section to determine a range of manganese concentrations that could be expected to exit the Minorca Pit as ground water if the pit is filled with taconite tailings.

#### 4.1.3.1. Manganese Clear Water Pool Source Term

Between the fifth and eighth years of tailings deposition in the Minorca Pit, the clear water pool is assumed to determine the chemistry of water flowing out of the pit (see section 2). In reality, water may exit the pit from either the clear water pool or from the tailings pores. The clear water pool receives process water discharged from the plant in addition to precipitation, and during the initial stages of the operation, ground water. Elevated manganese concentrations in process waters may result in elevated manganese concentrations in water exiting the pit.

#### **Operational measurements**

Manganese concentrations in plant discharges ranged from 0.05 to 0.09 mg/L during this study (Table 7; Berndt et al., 1999). Assuming the maximum observed discharge concentration over an eight year period of tailings deposition, dilution within the clear water pool is expected to reduce manganese concentrations to 0.08 mg/L (Figure 3). However, dissolved manganese is unstable in an oxidizing environment such as that expected in the clear water pool. Manganese oxidation resulted in manganese concentrations typically less than 0.01 mg/L in the clear water pool of the existing tailings basin (Figure 4). This mechanism is also responsible for low levels of manganese found in abandoned open pits across the Mesabi iron range (Pierce and Tomcko, 1989).

#### **Experimental measurements**

The **field tank experiments** were designed such that approximately 4.5 feet of surface water stood above the taconite tailings, exposed to the atmosphere. This situation simulated conditions expected in the clear water pool above tailings in a pit, and provided information regarding the persistence of manganese in these waters. During the initial stages of the tank experiments, manganese concentrations in surface waters averaged 0.03 mg/L (Figure 4; Jakel et al., 1998a; Jakel and Lapakko, 1999b). This situation persisted for two to four months, at which time manganese concentrations decreased to less than 0.004 mg/L. Manganese concentrations remained at this low level for the duration of the experiment.

Similar results were observed in **laboratory batch experiments** on mixtures of water from a well at the north end of Inland's tailings basin and the Missabe Mountain Pit. Initial manganese concentrations in this experiment ranged from 0.1 mg/L to 3.7 mg/L (Jakel and Lapakko, 1999c). Manganese levels remained elevated in the dilution containing 3.7 mg/L manganese for thirty six weeks. This dilution continues to be sampled on a monthly basis. However, after seven to fourteen weeks, manganese levels in the mixtures that initially contained less than 2 mg/L manganese decreased to less than 0.05 mg/L (Figures 4 and 6). These levels remained low for the duration of the experiment. XRD and SEM analysis of the solids that precipitated out of these dilutions indicated the presence of an amorphous manganese-oxyhydroxide-silicate phase

(Berndt, 1999). These results provided empirical evidence that natural processes will reduce manganese concentrations from approximately 2 mg/L to low, part per billion, levels under oxygenated conditions.

#### 4.1.3.2. Manganese Tailings Pore Water Source Term

After approximately eight years of operation at the Minorca Pit, the elevation of deposited tailings is anticipated to reach the southern rim of the pit (see section 2). When this occurs, water will have to pass through tailings before exiting the pit as ground water. Since conditions within the tailings mass will be less oxidizing and because the pit water will have intimate contact with the tailings, the water chemistry observed in the clear water pool will no longer provide a good indication of source terms. The chemistry of tailings pore waters isolated from the atmosphere more closely simulates these long-term conditions, and the following data were collected under those conditions.

#### Source of manganese in taconite tailings pore waters

Carbonate minerals typically occur as complex mixtures of calcium, magnesium, iron, and manganese carbonates. Thus, it is probable that any carbonate phase found in nature will contain at least trace amounts of manganese, especially if iron is present.

Inland currently mines taconite from the Laurentian Pit, and tailings from this ore are proposed to be disposed of in the Minorca Pit. Tailings from Laurentian Pit ore contained two different iron-bearing carbonate minerals (siderite and ankerite) and possibly trace amounts of calcite (Table 4; Mattson, 1996). Manganese was associated with both carbonate species in the tailings. Elemental distributions indicated that approximately 23% of the manganese found in the tailings was associated with siderite and 4% with ankerite. Based on these values and chemical analyses (Tables 5 and 6), an approximate manganese carbonate content for both siderite and ankerite was calculated. Manganese carbonate was present in both minerals at levels that can be considered trace (i.e. approximately  $0.4 \text{ wt\% MnCO}_3$  in the tailings; Table A2.6). At this level, manganese release due to carbonate dissolution would be expected to be low.

Based on field and laboratory measurements of taconite tailings water quality, water in the pore spaces among tailings particles tend to be moderately reducing and slightly acidic (pH 6-7; Berndt and Lapakko, 1997a, b; Berndt, 1998; Berndt et al., 1998, 1999). Under these conditions, carbonate minerals present in the tailings can dissolve. The amount of manganese that can potentially be released depends on the composition of the carbonate phases present and pH and redox conditions of the solution.

Since carbonate dissolution is a pH-dependent process, any chemical process that generates acidity (i.e. decreases solution pH), promotes carbonate dissolution. Three important, acidity-generating processes must be considered in an in-pit disposal environment for taconite tailings. The first process involves oxidation of siderite. Sideritic iron oxidizes to form iron oxyhydroxides and releases acidity into solution:

$$FeCO_3 + 1/4O_2 + 5/2H_2O \rightarrow Fe(OH)_3 + HCO_3^- + H^+$$
 (4)

Another mechanism of acid generation is the oxidation of any organic matter intermixed with tailings. Oxidation of organic matter not only produces acidity but it also consumes oxygen:

$$\{CH_2O\} + O_2 \rightarrow H^+ + HCO_3^-$$
(5)

Finally, acid can be produced as a result of pyrite oxidation. Although taconite tailings across the Mesabi Range generally do contain pyrite, Inland's tailings contain approximately 0.01 wt% pyrite (0.006 wt% total sulfur; Table 4). At this low level, it is unlikely that pyrite oxidation could generate enough acidity to impact tailings pore water chemistry.

The acidity produced by reactions 4 and 5 will lead to dissolution of other carbonate minerals in the tailings. Ankerite is the most abundant carbonate mineral present in taconite tailings (Mattson, 1996). If siderite oxidation results in further dissolution of ankerite, excess calcium will be released into solution:

$$CaFe(CO_3)_2 + 1/4O_2 + 5/2H_2O \rightarrow Ca^{2+} + Fe(OH)_3 + 2HCO_3^{-}$$
 (6)

Alternatively, the acidity produced by reactions 4 and 5 can result in dissolution of manganese carbonate phases such as rhodochrosite:

$$MnCO_3 + H^+ \rightarrow Mn^{2+} + HCO_3^-$$
(7)

In general, calcium carbonates dissolve more readily than manganese carbonates. However, manganese carbonate dissolution will occur if calcium carbonates are absent or rendered inactive. Thus, manganese concentrations will become elevated in taconite tailings pore waters if calcium-bearing carbonates (e.g. ankerite) are not available.

#### **Operational measurements**

The highest manganese concentrations were observed in the two wells at Inland. Manganese concentrations in these waters ranged from 1.2 to 7.2 mg/L (Table 7; Berndt et al., 1999). Based on these operational measurements, a maximum manganese source term of approximately 7 mg/L would be reasonable. However, it is important to note that the water chemistry of these two wells was substantially different from other water sources at Inland, including the seeps, and similar water sources from National, LTV, and USX.

One of the major differences in water chemistry was the relatively high levels of manganese observed in well waters relative to the north and interior seeps. The average manganese concentration in the north seep was 3.2 mg/L compared to 4.6 mg/L for the wells (Table 7; Berndt et al., 1999). A single measurement taken from the interior dike seep had a manganese level of 0.08 mg/L (Berndt et al., 1999). Furthermore, manganese concentrations in these wells

were considerably higher than similar sites at National, LTV, and USX, where manganese concentrations averaged 0.03, 1.0, and 1.2 mg/L, respectively (Appendix 6; Berndt et al., 1999).

Elevated manganese levels in the wells at Inland may have been the result of conditions that were unique to the environment where the wells were drilled. It is important to note that the Laurentian tailings that are proposed to be disposed of in the Minorca Pit probably do not have the same carbonate composition as the tailings on the north side of the tailings basin where the wells are located. If the Laurentian tailings contain high levels of calcium carbonates relative to rhodochrosite, lower manganese levels would be expected (reaction 6). Furthermore, the tailings on the north side of the basin were deposited on top of an organic substrate. Oxidation of organic matter in intimate contact with tailings may have contributed to the elevated manganese levels observed in the wells (reaction 5). If conditions in the well were influenced by either of these conditions, then a manganese source term based on these data may be unrealistically high. Therefore, it is appropriate to regard a source term of 7 mg/L manganese levels in a pit disposal environment.

#### Laboratory column experiments

The laboratory columns simulated conditions that would be expected in the Minorca Pit as it is filled with tailings. Manganese concentrations in the water samples gradually increased over time (Berndt and Lapakko, 1997a). At the end of the seven month period, manganese concentrations in the two columns had reached 0.45 and 0.60 mg/L and probably had not yet reached a maximum concentration (Table 7).

Once tailings and process waters have been deposited in a pit, process waters will eventually be replaced by precipitation and possibly ground water. In order to simulate these two events, the columns were drained of the process water and refilled. One column was refilled with deionized water to simulate rain water and the other was injected with ground water obtained from local wells drilled into the Biwabik aquifer (Berndt et al., 1998, 1999). During a twenty seven week period, manganese concentrations in the rain water column were reasonably constant, averaging 0.30 mg/L (Table 7). Manganese concentrations in the ground water column increased sharply from 0.42 mg/L in the initial ground water to 0.86 mg/L after the first week of the experiment. However, these concentrations gradually decreased over the subsequent twenty nine weeks to a relatively constant level of 0.2 mg/L (Table 7). Based on the results of these column experiments, manganese to approximately 0.2 - 0.3 mg/L as process waters are replaced by precipitation and/or ground water.

#### **Field tank experiments**

Manganese concentrations in the tailings pore waters from both field tanks averaged 0.08 mg/L throughout the 116-week experiment (Table 7; Jakel and Lapakko, 1999b).

#### Geochemical modeling results

Manganese levels in taconite tailings pore waters are believed to be controlled by the solubility of a manganese carbonate phase (Berndt and Lapakko, 1997a; Berndt, 1998; Berndt et al., 1998, 1999). Rhodochrosite solubility is a function of the solution pH and alkalinity (equation 2). Based strictly on rhodochrosite dissolution, it was demonstrated that manganese concentrations in the range of 5-10 mg/L can be achieved in waters at 5-10 °C and an alkalinity of 150 to 200 mg CaCO<sub>3</sub>/L (Figure 5; Berndt, 1998). This model was used to predict the chemistry of tailings pore waters that might be expected as tailings basin waters seep through taconite tailings (Berndt et al., 1998). Carbonates in the taconite tailings were represented by stoichiometric amounts of siderite, dolomite, and rhodochrosite in the simulations. However, when dolomite was removed from the assemblage, the high manganese and iron concentrations observed in the wells at Inland could be simulated (Berndt et al., 1998).

#### 4.1.3.3. Summary of Manganese Source Term Ranges

Manganese is released by dissolution of manganese-bearing minerals present in the tailings. Based on the data collected during the range-wide study, a manganese source term range of 0.01 mg/L to 7 mg/L was selected for the Minorca Pit (Table 7). Manganese concentrations in oxygenated waters, which are representative of the **clear water pool** in the Minorca Pit, were at the lower end of this range. The oxygenated waters sampled include existing tailings basin surface waters, oxygenated waters in field tank and laboratory batch experiments, and water from abandoned open pits, including the Missabe Mountain Pit. These low levels are due to the unstable nature of dissolved manganese in oxygenated waters, resulting in oxidation of manganese to  $MnO_2$ . Since water contained in the Minorca Pit clear water pool will be well oxygenated, manganese levels in the waters exiting the Minorca Pit through the clear water pool are expected to be approximately 0.01 mg/L.

Manganese levels in **tailings pore waters** during the range-wide study ranged from 0.05 mg/L to 7 mg/L. The 0.05 mg/L value was representative of manganese concentrations observed in waters associated with tailings from the Laurentian Pit (e.g. tank experiments). It is likely that the tailings that Inland has proposed to dispose of in the Minorca Pit will be compositionally similar to these tailings. However, the ore body composition may vary, and therefore, there is no guarantee that manganese concentrations will remain as low as 0.05 mg/L.

Based on the rain and ground water column experiments, long-term release is expected to be in the range of 0.2 - 0.3 mg/L. These values are within the range of manganese concentrations found in the Biwabik aquifer (0.0 - 0.7 mg/L, average 0.2 mg/L; Berndt et al., 1998). This situation would occur after the process water trapped within tailings pore spaces has been replaced by either rain or ground water. This process is expected to take decades.

The upper end of this range, 7 mg/L, was defined by the maximum manganese concentration observed in the wells on the north dike of Inland's tailings basin. This value may have been

elevated by factors not anticipated to be influential in the Minorca Pit (e.g. incorporation of organic matter or other acid generating material with the tailings). As mentioned above, geochemical modeling indicates that this value is reasonable for the conditions found in the tailings basin dike.

#### 4.1.4. Manganese Transport Through the Biwabik Aquifer

The most conservative estimate of manganese concentrations in Minorca Pit ground water transported through the Biwabik aquifer assumes no dilution or removal due to chemical reactions. Based on this assumption, the manganese transport term will equal the Minorca Pit source term. That is, the manganese transport term will range from 0.01 mg/L to 7 mg/L. It is likely that ground water outflow from the Minorca Pit will be diluted by other ground water sources in the aquifer. The extent of this dilution cannot be quantified, but is considered in the flow-weighted average concentration for the total input to the Missabe Mountain Pit.

Geochemical calculations based on the observed water chemistry in an environment isolated from the atmosphere indicated that manganese levels could not exceed 1 mg/L in the Biwabik aquifer (Figure 5; Table A3.1). Water samples taken from eleven different wells in the Biwabik aquifer contained relatively high alkalinity, averaging 186 mg CaCO<sub>3</sub>/L (Table 8; Berndt et al., 1998). These high alkalinity levels suggested that manganese levels are controlled by the solubility of a manganese carbonate phase (e.g. rhodochrosite). This is consistent with the observed range of manganese concentrations (0.00 - 0.69 mg/L) in Biwabik Formation wells sampled during this study (Table 8; Berndt et al., 1998).

# 4.1.5. Flow-Weighted Manganese Concentrations in Missabe Mountain Pit Inputs

Based on the measurements described in section 4.1.3, manganese concentrations in the Minorca Pit can be expected to be in the range of 0.01 to 7 mg/L (see section 4.1.3). In order to provide the most conservative estimates, it will be assumed that any manganese released in the Minorca Pit will ultimately reach the Missabe Mountain Pit. However, it is not unlikely that manganese levels will be controlled at the rhodochrosite solubility limit during transport in the Biwabik aquifer. In this situation, elevated manganese concentrations in Minorca Pit ground waters entering the Missabe Mountain Pit could not exceed 1 mg/L (see section 4.1.4).

Water from the Minorca Pit, direct precipitation, and other ground water sources contribute to the total water input to the Missabe Mountain Pit. It is estimated that the Minorca Pit will contribute a temporary maximum of 28 to 39 percent of the total inflow (Adams, 1998, 1999). This is a temporary maximum because, the volume of water collected in the Minorca Pit will decrease after the site has been reclaimed.

At this temporary maximum, flow-weighted average input concentrations in waters entering the Missabe Mountain Pit would range from 0.1 mg/L to 2.8 mg/L (Table 9), assuming concentrations in the dilutional water were similar to that of the Biwabik Iron Formation ground

water (i.e. approximately 0.18 mg/L; Berndt et al., 1998). It is important to note that this calculation does not consider dilution by water stored in the Missabe Mountain Pit, which will be calculated in the following section (section 4.1.6). Current manganese levels in the Missabe Mountain Pit are around 0.003 mg/L (Table 10).

Reclamation of the Minorca Pit disposal site will most likely consist of establishing a selfsustaining, diverse cover of vegetation over the tailings surface. Vegetation increases evapotranspiration, and consequently, will reduce infiltration of surface waters into the tailings. Thus, after the site has been reclaimed, flow from the Minorca Pit to the Missabe Mountain Pit will decrease. If the site is reclaimed with grasses, Minorca Pit input flow will be reduced to 18 to 21 percent of the total input flow to the Missabe Mountain Pit (Adams, 1998, 1999). This would increase dilution, and flow-weighted input manganese concentrations would be reduced to less than 1.6 mg/L (Table 9). If forest vegetation (i.e. trees) is established over the tailings surface, the Minorca Pit input would be reduced to approximately 13% of the Missabe Mountain Pit input. Flow-weighted manganese concentrations in Missabe Mountain Pit inputs would then be expected to be less than 1.1 mg/L (Table 9).

4.1.6. Dilution and Geochemical Reaction in the Missabe Mountain Pit

4.1.6.1. Decrease of Dissolved Manganese Levels Due to Dilution

Using the maximum manganese source term for depositional years five to ten, the flow-weighted average input manganese concentration for inputs to the Missabe Mountain Pit was determined to be 2.8 mg/L (see paragraph 3, section 4.1.5). Since this input occurs for a relatively short period of time, the water stored in the Missabe Mountain Pit will dilute the flow-weighted average input manganese concentration to 1.7 mg/L (Table A5.3).

This calculation was based on the worst case scenario, where source and transport terms were assumed to be 7 mg/L. Flow-weighted average input concentrations to the Missabe Mountain Pit were determined for three time periods; active operations in the Minorca Pit, short-term reclamation of the Minorca (grasses), and long-term reclamation goals (established forest vegetation). Dilution by the water stored within the Missabe Mountain Pit was estimated for a fifty year period beginning when tailings are first deposited in the Minorca Pit. Based on these calculations, manganese concentrations in the Missabe Mountain Pit are expected to reach a maximum concentration of 1.7 mg/L just prior to closure of the Minorca Pit (Table A5.3). Subsequent to closure and successful reclamation of the Minorca Pit, diluted manganese levels in the Missabe Mountain Pit are expected to gradually decrease over time.

#### 4.1.6.2. Removal Due to Natural Processes

In addition to dilution, manganese concentrations in the Missabe Mountain Pit will also be reduced by chemical and/or biological oxidation and subsequent precipitation. The kinetics of the inorganic reaction appear to be quite slow (Langmuir, 1997). However, manganese oxidation is extremely sensitive to microbial catalysis (Davison, 1993; Ehrlich, 1996). Operational, field

and laboratory measurements of manganese concentration changes in oxygenated waters associated with taconite tailings were consistent with manganese oxidation predictions (Figure 4).

#### **Operational measurements**

Previous water quality measurements of mine pit lakes in northeastern Minnesota imply that manganese concentrations will be maintained at a low level if the pit waters have a dissolved oxygen content greater than 8 mg/L (Pierce and Tomcko, 1989). Excluding the three pits that exhibited some oxygen depletion, manganese concentrations in pit lakes were less than 0.13 mg/L, averaging 0.04 mg/L (Table A5.4).

The Missabe Mountain Pit has been classified as a moderately oligotrophic lake, meaning that the water is deep, clear, and contains very few nutrients (MDH, 1998). Measurements taken in May, 1992 indicated that even at a depth of approximately 120 feet, these waters still contain moderate amounts of dissolved oxygen. These measurements were repeated by the MN DNR in March, 1999 when dissolved oxygen levels were expected to be low. At a depth of 150 feet, the dissolved oxygen concentration was 5.7 mg/L, or 47% of saturation, and contained less than 0.006 mg/L manganese (Table 10). Therefore, it is reasonable to expect that at least the upper 150 feet of water in the Missabe Mountain Pit is adequately oxygenated to promote manganese oxidation and precipitation.

Manganese concentrations in plant process waters discharged to the tailings basin at Inland averaged 0.06 mg/L (Table 7; Berndt et al., 1999). In the tailings basin, these waters are diluted with precipitation and surface runoff from the surrounding watershed. Based on the average concentrations of chloride and bromide in discharge and tailings basin waters, dilution would be expected to decrease manganese concentrations by one third, or to 0.04 mg/L. However, manganese concentrations in the clarified water that is pumped back to the plant for re-use averaged 0.004 mg/L during this study (Figure 4; Berndt et al., 1999). This implies that natural processes (e.g. manganese oxidation) were active in the tailings basin.

#### **Experimental measurements**

During the initial stages of the **field tank experiments**, manganese concentrations in surface waters averaged 0.03 mg/L (Jakel et al., 1998a; Jakel and Lapakko, 1999b). This situation persisted for two to four months, at which time manganese concentrations decreased to less than 0.004 mg/L (Figure 4). Manganese concentrations remained at this low level for the duration of the experiment. These results provided empirical evidence that natural processes will reduce manganese concentrations to low, part per billion, levels.

In order to better define an appropriate reaction time for manganese oxidation, **laboratory batch experiments** were conducted on mixtures of water from the Missabe Mountain Pit and one of the wells at Inland (Jakel and Lapakko, 1999c). These experiments were intended to simulate

a situation where water with an elevated manganese concentration mixed with water in the Missabe Mountain Pit. Preliminary results indicated that manganese removal occurred at a rate of approximately 2.6 mg Mn/L/yr until roughly 30% of the dissolved manganese was removed from the system. At this time, oxidation rates accelerated to 7 - 19 mg Mn/L/yr (Figure 6). Manganese concentrations in the Missabe Mountain Pit are expected to reach a temporary maximum of approximately 1.7 mg/L. Based on these oxidation rates, manganese levels in the Missabe Mountain Pit would be expected to decrease below 0.05 mg/L in approximately nineteen weeks. At present, this is the best available estimation of required reaction time from the MN DNR/U of MN study.

The actual reaction time available, or residence time, in the Missabe Mountain Pit can be estimated based the water consumption by the city of Virginia and the pit volume. These values are approximately 0.6 billion gallons per year and 3.3 billion gallons, respectively (Wiskow, 1998). Dividing the pit volume by the annual consumption yields a residence time of 5.5 years  $(3.3 \times 10^9 \text{ gallons}/0.6 \times 10^9 \text{ gallons}/\text{year} = 5.5 \text{ years})$ . However, the volume of water in the Missabe Mountain Pit is increasing and is expected to reach 8 billion gallons by the year 2009 (Wiskow, 1998). Assuming the same consumption rate, the residence time will increase to 13.3 years. This is about forty times the duration required for manganese removal predicted by the MN DNR tank experiments and thirty six times the duration estimated by the batch experiments.

In summary, it is believed that manganese oxidation will reduce concentrations in the Missabe Mountain Pit to low, part per billion, levels as long as pit waters remain oxygenated. If dissolved oxygen were to become depleted in the Missabe Mountain Pit, manganese levels could become elevated.

# 4.1.7. Comparison of Predicted Concentrations to Drinking Water Quality Standards

The MDH has set a site-specific, health-based standard of 1.3 mg/L for the Missabe Mountain Pit (MDH, 1998). At maximum ground water input from the Minorca Pit to the Missabe Mountain Pit, flow-weighted average manganese concentrations in the net input to the Missabe Mountain Pit are expected to be in the range of 0.1 - 2.8 mg/L (Table 9), which exceeds the health-based standard. After the reclamation of the Minorca Pit, the impact that Minorca Pit waters have on manganese concentrations in the Missabe Mountain Pit are expected to diminish. Depending on the type of vegetation established over the Minorca Pit tailings, long-term manganese input concentrations to the Missabe Mountain Pit will decrease to less than 1.1 mg/L (Table 9), which does not present a human health risk (MDH, 1998).

Although this projection meets the health-based drinking water quality standard, a secondary standard of 0.05 mg/L manganese exists for drinking waters. The secondary standard is an aesthetic standard and is not related to health risks. However, the Virginia Public Utility must meet this standard for drinking water supplied to the city of Virginia. If dilution is the only process reducing manganese concentrations in ground water flowing out of the Minorca Pit, the secondary standard will be exceeded. Based on data from the Missabe Mountain Pit, the tailings

basin, and field and laboratory experiments, oxidizing conditions in the Missabe Mountain Pit will result in manganese oxidation and removal of dissolved manganese to below acceptable levels. Nonetheless, any exceedence of the secondary standard poses treatment issues for the Virginia Public Utility.

#### 4.1.8. Treatment Methods Used at the Virginia Public Utility

One potential concern is the occurrence of an unoxidized zone near the bottom of the Missabe Mountain Pit, where Virginia draws its water supply from. In such a zone elevated manganese concentrations could persist. If mixing occurred (e.g. spring or fall turnover) this manganese would be distributed throughout the water column. This would tend to increase concentrations at the intake for Virginia's water supply and may present future water treatment issues.

Currently, the Virginia public utility uses a system designed to physically separate particulate matter from the water supply (Wiskow, 1998). Fluoride, chloride, and an aluminum-polymer coagulant are added to the water prior to entering a sedimentation basin where much of the particulate matter settles out. Water is then pumped through pressure sand filters to remove any remaining particulate matter from their water supply. At present, the public utility is testing a membrane filtration system on a pilot-scale for possible future use. They are also considering a gravity filtration system. A membrane filtration system is expected to be able to remove manganese as long as the input concentration is below 0.05 mg/L (Wiskow, 1998). Chemical oxidation in the flocculators and sedimentation basin may improve manganese removal. However, it may also have a detrimental affect on the membrane filters because they are not chemically resistant.

#### 4.2. Fluoride

#### 4.2.1. Approach

If taconite tailings are disposed of in the Minorca Pit, fluoride concentrations in waters associated with these tailings will become elevated relative to natural background levels. As the pit fills, water will flow from the Minorca Pit into the Biwabik Formation aquifer and, likely, to the Missabe Mountain Pit. The purpose of section 4.2 is to summarize results of the MN DNR-U of MN study on the ground water implications of taconite tailings disposal in the Minorca Pit with regard to fluoride. Operational measurements, field and laboratory experiments, and geochemical modeling were used to; 1) determine the magnitude of fluoride concentrations in outflow from the Minorca Pit (i.e. source term), 2) consider processes, including dilution and chemical reactions, that affect fluoride levels during transport in the aquifer, 3) estimate average input concentrations to the Missabe Mountain Pit. A brief description of fluoride mobilization due to taconite processing is presented as background prior to discussion of the processes affecting fluoride release in the Minorca Pit, transport through the Biwabik aquifer, and fate in the Missabe Mountain Pit.

#### 4.2.2. Source of Fluoride in Water Associated with Taconite Tailings

Fluoride is believed to be mobilized during taconite processing, specifically during induration (Berndt and Lapakko, 1997a; Engesser, 1998; Jakel et al., 1998b, 1999d). In general, fluoride in unprocessed ore is immobile because it is bound in relatively insoluble minerals. Mattson (1996) reported that fluoride in the Biwabik Iron Formation is associated with apatite and some of the higher metamorphic grade silicates (e.g. hornblende, cummingtonite, grunerite) found in the eastern end of the Mesabi iron range. Mineralogical and chemical analyses of taconite tailings collected from Inland contained approximately 0.2 wt.% apatite (Table 4; Berndt and Lapakko, 1997a) and 240 ppm fluoride (Table 6; Berndt and Lapakko, 1997a). Using a general composition for "pure" fluorapatite, 0.2 wt.% would account for approximately one third (74 ppm) of the fluoride present in the tailings sample. No other major fluoride-bearing minerals were identified in tailings from Inland's operation. This is consistent with the low fluoride levels commonly found in the Biwabik Formation aquifer (Table 8; Berndt et al., 1998).

During mineral processing, most of the fluoride-bearing minerals are separated from the ore and disposed along with tailings into the tailings basin. If all of the fluoride-bearing minerals were treated in this fashion, the concentration of fluoride in mineral processing streams and tailings basins would be expected to be low. However, because no ore separation process is 100% efficient, a small fraction of the fluoride-bearing minerals are streamed along with the concentrate into the induration plant.

Materials are heated to extremely high temperatures during induration. Fluoride in apatite and silicates can be converted quickly to volatile HF in the presence of water vapor (Zhu and Sverjensky, 1991). Gasses containing dust and HF that are derived during heating and drying of the pellets are swept into scrubber stacks, where the dust is collected and HF is redissolved into the water. Fluoride levels in the resulting scrubber waters have been measured at nearly 100 mg/L during this study (Berndt and Lapakko, 1997a; Jakel et al., 1998b; Jakel and Lapakko, 1999d).

Most of the scrubber water is routed to the concentrate thickener and leaf filters, although they are mixed back into the process stream throughout the plant (Josephson, 1998). As these waters mix, fluorite ( $CaF_2$ ) precipitates out of solution. If fluorite precipitates in the concentrate, it will be incorporated in the taconite pellets and released by the mechanism described above during induration. Alternatively, fluorite crystals have also been observed on leaf filter bags to such a degree that the filter bags become fouled and must be replaced (Engesser, 1998), removing fluoride from the process stream permanently. The relative proportions of fluorite precipitated in the concentrate versus on leaf filter bags has not been quantified. However, it is believed that the majority of the fluoride released during induration cycles between the concentrate and scrubber waters.

Any fluoride in scrubber waters that does not precipitate as fluorite will eventually be discharged to the tailings basin. Fluoride is discharged to the tailings basin in solution and adsorbed to the

tailings, in addition to occurring in the relatively insoluble minerals originally present in the rock. Additional adsorption (or desorption) of fluoride may occur in the tailings basin.

Small-scale column experiments were conducted in order to determine the amount of labile fluoride present on taconite tailings (Berndt et al., 1998). Fresh tailings and process water were slurried and transferred into 40-cm columns. After the tailings had settled, the process water used to slurry the tailings was decanted from the top of the columns and replaced with deionized water. Flow rates were calculated to permit residence times of two and three days. The amount of labile fluoride on the tailings was approximately twice that in the original process water. This led to the conclusion that the tailings contained approximately 2 ppm leachable fluoride. This constitutes less than 1% of the 240 ppm fluoride found in Inland's tailings (Table 6). In the event that the Minorca Pit is filled with tailings, this same process will contribute elevated fluoride levels in the taconite tailings pore waters in the pit.

#### 4.2.3. Expected Fluoride Source Term for the Minorca Pit

Operational, field, and laboratory measurements of fluoride concentrations in waters closely associated with taconite tailings were collected over a two and a half year period (Berndt and Lapakko, 1997a, b; Berndt, 1998; Berndt et al., 1998, 1999). Operational measurements at Inland were taken from the tailings discharge pipe, clarified water in the tailings basin, a seep in the north dike of the tailings basin, and two wells outside the northeast edge of the tailings basin. A single measurement was obtained from a seep in the interior dike late in the study. Operational measurements were also made at the Snively Pit, US Steel-Minntac (USX, the only known case of in-pit disposal of taconite tailings in Minnesota), two wells at National Steel and Pellet Company (National), and one seep at LTV Steel Mining Company (LTV). Laboratory experiments were conducted on tailings initially saturated with process water and subjected to input from precipitation. Finally, geochemical calculations were used to define limits on fluoride levels in tailings pore waters. These data will be used in the following section to determine a range of fluoride concentrations that could be expected to exit the Minorca Pit as ground water if the pit is filled with taconite tailings.

#### 4.2.3.1. Fluoride Clear Water Pool Source Term

Between the fifth and eighth years of tailings deposition in the Minorca Pit, the clear water pool is assumed to determine the chemistry of water flowing out of the pit (see section 2). In reality, water may exit the pit from either the clear water pool or from the tailings pores. The clear water pool receives process water discharged from the plant in addition to precipitation, and during the initial stages of the operation, ground water. Elevated fluoride concentrations in process waters will result in elevated fluoride concentrations in water exiting the Minorca Pit.

#### **Operational measurements**

Fluoride concentrations in plant discharges ranged from 2.3 to 7.6 mg/L during this study (Table 11; Berndt et al., 1999). Assuming the maximum observed discharge concentration over an eight year period of tailings deposition, dilution within the clear water pool is expected to reduce fluoride concentrations to 6.2 mg/L (Figure 7). This value is somewhat higher than those observed in the clear water pool of the existing tailings basin (1.3 - 3.5 mg/L; Berndt et al., 1999). This is because the gradual loss of ground water inputs and decreasing volume of the clear water pool in the Minorca Pit results in less dilution than currently observed in the tailings basin (see section 3.1.1).

#### **Experimental measurements**

The **field tank experiments** were designed such that approximately 4.5 feet of surface water stood above the taconite tailings, exposed to the atmosphere. This situation simulated conditions expected in the clear water pool above tailings in a pit, and provided information regarding the persistence of fluoride in these waters. Fluoride concentrations fluctuated within a fairly constant range throughout the tank experiments, averaging 4.2 mg/L (Table 11; Jakel et al., 1998a; Jakel and Lapakko, 1999b). Fluctuations were largely due to seasonal events (i.e. precipitation, freeze/thaw cycles). However, a slight decrease in fluoride concentrations was observed after seventy two weeks. The reason for this increase is unclear at present.

#### 4.2.3.2. Fluoride Tailings Pore Water Source Term

After approximately eight years of tailings deposition in the Minorca Pit, the elevation of deposited tailings is anticipated to reach the southern rim of the pit (see section 2). When this occurs, water will have to pass through tailings before exiting the pit as ground water. Since conditions within the tailings mass will be less oxidizing, and because the pit water will have intimate contact with the tailings, the water chemistry in the clear water pool will no longer provide a good indication of source terms. The chemistry of tailings pore waters isolated from the atmosphere more closely simulates these long-term conditions, and the following data were collected under those conditions.

#### **Operational measurements**

Fluoride concentrations in the two wells and the seep located in the north dike of the tailings basin ranged from 0.6 to 3.6 mg/L (Table 11; Berndt et al., 1999). Fluoride levels in tailings pore waters at Inland were slightly lower than those observed in the seep at LTV, which averaged 3.9 mg/L (Table A6.2). However, they were significantly higher than fluoride levels measured in similar waters from National and USX which averaged 0.4 mg/L and 0.2 mg/L, respectively (Table A6.2). The single sample obtained from the seep in the interior dike contained 4.6 mg/L fluoride, which was slightly lower than fluoride levels in plant discharges to the tailings basin on that day (5.3 mg/L; Berndt et al., 1999).

#### Laboratory column experiments

The laboratory columns simulated conditions that would be expected in the Minorca Pit as it is filled with tailings. Initial fluoride concentrations of 3.7 mg/L and 3.5 mg/L reflected fluoride concentrations in the plant discharges when the tailings were collected (Berndt and Lapakko, 1997a). Therefore, these samples were not considered representative of fluoride levels in a pit disposal environment. Fluoride levels in the remaining samples were relatively constant over the seven month experiment, averaging 3.0 mg/L (Table 11).

Once tailings and process waters have been deposited in a pit, process waters will eventually be replaced by precipitation and possibly ground water. In order to simulate these two events, the columns were drained of the process water and refilled. One column was refilled with deionized water to simulate rain water and the other was injected with ground water obtained from local wells drilled into the Biwabik aquifer (Berndt et al., 1998, 1999). During a twenty seven week period, fluoride concentrations in the rain water column averaged 3.2 mg/L (Table 11). Fluoride concentrations in the rain water column gradually increased from 1.2 mg/L to 2.2 mg/L (Table 11). It is unclear whether or not this column had reached an equilibrium condition. Therefore, 2.2 mg/L fluoride may not reflect the maximum fluoride level that could be attained in the ground water column experiment.

#### **Field tank experiments**

During the first sixteen to twenty one weeks of the tank experiments, fluoride concentrations varied from 5.1 mg/L to 9.0 mg/L (Jakel et al., 1998a; Jakel and Lapakko, 1999b). These initial fluoride levels reflected the high fluoride levels typically observed in plant discharges. Tailings pore waters appeared to have reached an equilibrium condition with respect to fluoride after this initial equilibration period. This equilibrium condition has persisted for approximately two years and has been characterized by fluoride levels in the range of 3.6 to 5.9 mg/L in the tailings pore waters (Table 11).

4.2.3.3. Geochemical Controls on Fluoride Levels in the Minorca Pit

Two geochemical controls on fluoride levels in waters associated with taconite tailings have been identified during this study. Solubility limits of the mineral fluorite,  $CaF_2$ , were initially believed to control fluoride levels (Berndt and Lapakko, 1997a; Berndt, 1998). However, the behavior of fluoride in waters associated with taconite tailings has been particularly difficult to quantify, since thermodynamic solubility constants available to "predict" fluorite saturation vary widely (Brown and Roberson, 1977; Hem, 1985; Johnson et al., 1991; Wolery, 1992). In addition to these, an empirical solubility constant was developed by Berndt et al. (1999) based on the relatively low calcium and high fluoride levels measured at LTV's taconite operation. Since this empirical solubility constant was derived from waters associated with taconite tailings, it was considered to be the most relevant to Inland's situation.

Subsequent to these measurements, small-scale laboratory column experiments led to the conclusion that fluoride removal also occurs by an adsorption mechanism (Berndt et al., 1998, 1999). In terms of fluoride mobility, the concentration of fluoride was initially similar to that of the process water filling the pores. Only after two full pore volumes of fluid had passed through the column did the concentration of fluoride begin to decrease. Even then, fluoride concentrations decreased quite gradually, depending on the amount of fluid passed through the column. The fact that the concentration of fluoride in these experiments depended solely on the amount of fluid that passed through the column implies that an adsorption/desorption process controls fluoride mobility in Inland's tailings rather than a mineral dissolution process. This behavior was also modeled using geochemical modeling software (Berndt et al., 1999). The potential effect of both of these mechanisms will be discussed in this section.

#### **Clear water pool**

Operational measurements of fluoride levels in process waters and tailings basin waters at Inland suggested net fluoride removal from tailings basin waters (Jakel and Lapakko, 1999d). However, they did not provide insight into the removal mechanism. Fluoride concentrations in tailings basin waters generally fall below the solubility limit suggested by Berndt et al. (1999), implying that these waters are undersaturated with respect to the mineral fluorite. Therefore, it is assumed that fluoride removal from similar surface waters is controlled by an adsorption mechanism.

Fluoride removal did not occur in surface waters of the field tank experiments for approximately seventy weeks (Jakel and Lapakko, 1999b). However subsequent to seventy weeks, some fluoride removal appeared to occur. Elevated fluoride concentrations in these waters generally corresponded to elevated calcium concentrations. Furthermore, fluoride concentrations were not consistent with fluorite solubility limits suggested by Berndt et al. (1999) or any other source. Therefore, fluorite solubility was probably not controlling fluoride levels. It is assumed that an adsorption mechanism is responsible for fluoride removal in surface waters of the taconite tailings tanks.

#### Tailings pore water

In general, fluoride levels were lower in tailings pore waters that contained relatively high levels of calcium (Berndt and Lapakko, 1997a, b; Berndt, 1998; Berndt et al., 1998, 1999). This suggested that fluoride levels were controlled by fluorite solubility. Furthermore, many of the operational, field, and laboratory measurements of pore water chemistry related to Inland's tailings can be described by the fluorite saturation curve defined by the Brown and Roberson (1977) experiments (Figure A6.2). However, when compared to the solubility limits defined by waters associated with LTV's tailings (Berndt et al., 1999), Inland tailings pore waters were undersaturated with respect to the mineral fluorite.

The results of the small-scale column experiments were also used to quantify the amount of labile (i.e. adsorbed) fluoride on taconite tailings (Berndt et al., 1998). These results indicated

that approximately 2 ppm of fluoride was adsorbed onto tailings surfaces. This represents less than 1% of the 240 ppm fluoride measured in tailings from Inland (Berndt et al., 1997). Some of the remaining fluoride is believed to be associated with apatite minerals present in the tailings. Based on our analyses, taconite tailings contain no more than 74 ppm fluoride as apatite (Tables 4 and 6). Thus, 164 ppm of the fluoride in these tailings is unaccounted for (240 ppm total - 2 ppm adsorbed - 74 ppm as apatite). It is assumed that this fluoride is distributed as a trace element in low metamorphic grade silicate minerals present in the tailings. These minerals are talc, stilpnomelene, and minnesotaite, and comprise 11%, 11%, and 3%, respectively, of the Inland tailings. If the average fluoride content of these three minerals is 656 ppm (164/0.25) they would account for the remaining 164 ppm of fluoride in the tailings.

Based on these findings, it seems reasonable to assume that most of the labile fluoride present in the tailings pore water is controlled by an adsorption/desorption mechanism. This is also consistent with operational measurements of fluoride levels in tailings pore waters and laboratory experiments using tailings and process waters from taconite operations across the range (see "Fluoride" section, page 24, of Berndt et al., 1999).

#### 4.2.3.4. Summary of Fluoride Source Term Ranges

Fluoride is released from soluble fluoride phases produced as a result of the induration and scrubbing processes during taconite processing (Berndt and Lapakko, 1997a; Berndt et al., 1998, 1999; Jakel and Lapakko, 1999d). Based on the data collected during the range-wide study, a fluoride source term range of 1 to 6 mg/L was selected (Table 11). Analyses of plant discharges and calculation of dilution in the Minorca Pit clear water pool led to a **clear water pool source term** of 6 mg/L. Since fluoride is released during taconite processing, fluoride levels in plant discharges will increase if plant process waters are not supplemented with make-up water from dilute sources (e.g. Sauntry and Enterprise Pits). However, the preliminary tailings disposal plan (Indeco, 1999) indicates that substantial amounts of make-up water will be required after the first two years of tailings deposition in the Minorca Pit.

Fluoride levels in **pore waters** associated with Inland's tailings during the range-wide study ranged from 1 mg/L to 6 mg/L. Unlike the other three ECs, the range of fluoride concentrations in tailings pore waters appeared to be normally distributed. Therefore, it is appropriate to use an average concentration as a refined source term. Based on sixty two tailings pore water samples collected from field and laboratory experiments, as well as measurements taken at Inland's tailings basin, the average fluoride concentration in tailings pore waters was 3.2 mg/L with a standard deviation of 1.2. This value represents the most likely tailings pore water source term for fluoride in the Minorca Pit. The upper end of the range of observed fluoride concentrations (6 mg/L) was typical of tailings pore analyses from field tank experiments. This value will be considered the worst case scenario in this assessment.

#### 4.2.4. Fluoride Transport Through the Biwabik Aquifer

The most conservative estimate of fluoride levels in Minorca Pit ground water transported through the Biwabik aquifer assumes no dilution or removal due to chemical reactions. Based on this assumption, the fluoride transport term will equal the Minorca Pit source term. That is, the fluoride transport term will range from 1 to 6 mg/L. It is likely that ground water outflow from the Minorca Pit will be diluted by other ground water sources in the aquifer. The extent of this dilution cannot be quantified, but is considered in the fluor-weighted average concentration for the total input to the Missabe Mountain Pit.

During another phase of this study, water samples taken from eleven different wells in the Biwabik aquifer were analyzed (Berndt et al., 1998). These waters contained low levels of fluoride and relatively high levels of calcium, averaging 0.3 mg/L, 45 mg/L, respectively (Table 8). If tailings pore waters containing 6 mg/L fluoride (i.e. the upper end of the source term range) were to flow out of the Minorca Pit into the aquifer, fluoride levels would not be expected to exceed the fluorite (CaF<sub>2</sub>) solubility limit. The maximum fluoride concentration that would be expected at fluorite saturation would be determined by calcium levels in the aquifer. Calcium levels in the Biwabik well samples ranged from 33 to 70 mg/L (Berndt et al., 1998). At these calcium levels and using the empirical solubility constant determined by Berndt et al. (1999), fluoride concentrations in the aquifer could not exceed 4.3 to 6.2 mg/L (Figure 8).

#### 4.2.5. Flow-Weighted Fluoride Concentrations in Missabe Mountain Pit Inputs

Based on the measurements described in section 4.2.3, fluoride concentrations in the Minorca Pit can be expected to be in the range of 1 to 6 mg/L. In order to provide the most conservative estimates, it will be assumed that any fluoride released from the Minorca Pit will ultimately reach the Missabe Mountain Pit. However, it is not unlikely that fluoride levels will be controlled at the fluorite solubility limit during transport in the Biwabik aquifer. In this situation, elevated fluoride concentrations in Minorca Pit ground waters entering the Missabe Mountain Pit would be in the range of 4 to 6 mg/L (see section 4.2.4).

Water from the Minorca Pit, direct precipitation, and other ground water sources contribute to the total water input to the Missabe Mountain Pit. It is estimated that the Minorca Pit will contribute a temporary maximum of 28 to 39 percent of the total inflow (Adams, 1998, 1999). This is a temporary maximum because the volume of water collected in the Minorca Pit will decrease after the site has been reclaimed.

At the temporary maximum, flow-weighted average fluoride concentrations in waters entering the Missabe Mountain Pit would range from 0.5 to 2.5 mg/L (Table 12), assuming concentrations in the dilutional water were similar to that of the Biwabik Iron Formation ground water (i.e. approximately 0.28 mg/L; Berndt et al., 1998). It is important to note that this calculation does not consider dilution by water stored in the Missabe Mountain Pit, which will be calculated in the following section (section 4.2.6). Current fluoride levels in the Missabe Mountain Pit are around 0.21 mg/L (Table 10).
Reclamation of the Minorca Pit disposal site will most likely consist of establishing a selfsustaining, diverse cover of vegetation over the tailings surface. Vegetation increases evapotranspiration, and consequently, will reduce infiltration of surface waters into the tailings. Thus, after the site has been reclaimed, flow from the Minorca Pit to the Missabe Mountain Pit will decrease. If the site is reclaimed with grasses, Minorca Pit input flow will be reduced to 18 to 21 percent of the total input flow to the Missabe Mountain Pit (Adams, 1998, 1999). This would increase dilution, and flow-weighted average input fluoride concentrations would be reduced to less than 1.5 mg/L (Table 12). If forest vegetation (i.e. trees) is established over the tailings surface, the Minorca Pit input would be reduced to approximately 13 percent of the Missabe Mountain Pit input (Adams, 1998, 1999). Flow-weighted fluoride concentrations to the Missabe Mountain Pit would then be expected to be less than 1.0 mg/L (Table 12).

#### 4.2.6. Dilution and Geochemical Reaction in the Missabe Mountain Pit

Using the maximum fluoride source term for depositional years five to ten, the flow-weighted average input fluoride concentration for inputs to the Missabe Mountain Pit was determined to be 2.5 mg/L (see paragraph 3, section 4.2.5). Since this input occurs for a relatively short period of time, the water stored in the Missabe Mountain Pit will dilute the flow-weighted average input fluoride concentration to 1.6 mg/L (Figure 9; Table A5.5).

This calculation was based on the worst case scenario, where source and transport terms were assumed to be 6 mg/L. Flow-weighted average input concentrations to the Missabe Mountain Pit were determined from three time periods; active operations in the Minorca Pit, short-term reclamation of the Minorca (grasses), and long-term reclamation goals (established forest vegetation). Dilution by the water stored within the Missabe Mountain Pit was estimated for a fifty year period beginning when tailings are first deposited in the Minorca Pit. Based on these calculations, fluoride concentrations in the Missabe Mountain Pit are expected to reach a maximum concentration of 1.6 mg/L just prior to closure of the Minorca Pit (Figure 9; Table A5.5). Subsequent to closure and successful reclamation of the Minorca Pit, diluted fluoride levels in the Missabe Mountain Pit are expected to affect fluoride levels in the Missabe Mountain Pit.

# 4.2.7. Comparison of Predicted Concentrations to Drinking Water Quality Standards

At maximum ground water input from the Minorca Pit, average fluoride concentrations in the Missabe Mountain Pit are expected to be as high as 1.6 mg/L (Figure 9; Table A5.5). This value meets the both the primary drinking water quality standard of 4 mg/L, and the non-health based secondary standard at 2 mg/L.

#### 4.2.8. Treatment Methods Used at the Virginia Public Utility

Currently, the Virginia public utility adds fluoride to the water supply for the city of Virginia (Wiskow, 1998). Fluoride levels in water entering the public utility are monitored on a monthly

basis. If fluoride levels were to increase in the Missabe Mountain Pit due to disposal of taconite tailings in the Minorca Pit, additional fluoride in the water supply may not be necessary. However, if fluoride levels in the Missabe Mountain Pit were to increase rapidly, water entering the utility may require more frequent monitoring intervals.

#### 4.3. Molybdenum

#### 4.3.1. Approach

If taconite tailings are disposed of in the Minorca Pit, molybdenum concentrations in waters associated with these tailings will become elevated relative to natural background levels. As the pit fills, water will flow from the Minorca pit into the Biwabik Formation aquifer and, likely, to the Missabe Mountain Pit. The purpose of section 4.3 is to summarize results of the MN DNR-U of MN study on the ground water implications of in-pit disposal of taconite tailings with regard to molybdenum. Operational measurements, field and laboratory experiments, and geochemical modeling were used to 1) determine the magnitude of molybdenum concentrations in outflow from the Minorca Pit (i.e. source term), 2) consider processes, including dilution and chemical reactions, that affect molybdenum levels during transport in the aquifer, 3) estimate average input concentrations to the Missabe Mountain Pit from all water sources, and 4) determine the extent to which dilution might decrease molybdenum levels within the Missabe Mountain Pit. A brief description of molybdenum mobilization due to taconite processing is presented as background prior to discussion of the processes affecting molybdenum release in the Minorca Pit, transport through the Biwabik aquifer, and fate in the Missabe Mountain Pit.

#### 4.3.2. Source of Molybdenum in Water Associated with Taconite Tailings

Molybdenum is mobilized during taconite processing. Lubricants used throughout the taconite process stream contain molybdenum in the form of molybdenite ( $MoS_2$ ), and therefore, represent one potential source. The grinding media (i.e. balls and rods) used to reduce the particle size of the ore represent another potential source of molybdenum. The inevitable physical breakdown and corrosion of the grinding media is the most likely mechanism of molybdenum release in this case, although this has not been verified.

Based on the molybdenum content (0.02 - 0.035%) and attrition rate (2.35 T/yr) of the grinding media used at Inland (Josephson, 1998), it was calculated that roughly 2.5 to 4.4 T/yr molybdenum could be released during taconite processing (Table A2.7; Jakel and Lapakko, 1999d). Attrition of the grinding media is the result of physical breakdown and corrosion (Johnson, 1998; Josephson, 1998). Whereas corrosion releases molybdenum into solution, that is not necessarily the case with physical breakdown. Thus, this estimate is probably artificially high. It is important to note that these molybdenum sources are operational, and will not persist after plant operations cease.

#### 4.3.3. Expected Molybdenum Source Term for the Minorca Pit

Operational, field, and laboratory measurements of molybdenum concentrations in waters closely associated with taconite tailings were collected over a two and a half year period (Berndt and Lapakko, 1997a, b; Berndt, 1998; Berndt et al., 1998, 1999). Operational measurements at Inland were taken from the tailings discharge pipe, clarified water in the tailings basin, a seep in the north dike of the tailings basin, and two wells outside the northeast edge of the tailings basin. A single measurement was obtained from a seep in the interior dike late in the study. Operational measurements were also made at the Snively Pit, US Steel-Minntac (USX, the only known case of in-pit disposal of taconite tailings in Minnesota), two wells at National Steel and Pellet Company (National), and one seep at LTV Steel Mining Company (LTV). Laboratory experiments were conducted on tailings initially saturated with process water and subjected to input from precipitation. Finally, geochemical computer models were used to define limits on molybdenum levels in tailings pore waters. These data will be used in the following section to determine a range of molybdenum concentrations that could be expected to exit the Minorca Pit as ground water if the pit is filled with tailings.

#### 4.3.3.1. Molybdenum Clear Water Pool Source Term

Between the fifth and eighth years of tailings deposition in the Minorca Pit, the clear water pool is assumed to determine the chemistry of water flowing out of the pit (see section 2). In reality, water may exit the pit from either the clear water pool or from the tailings pores. The clear water pool receives process water discharged from the plant in addition to precipitation and, during the initial stages of the operation, ground water. Elevated molybdenum concentrations in process waters will result in elevated molybdenum concentrations in water exiting the pit.

#### **Operational measurements**

Molybdenum concentrations in plant discharges ranged from 68 to 157 ug/L during this study (Table 13; Berndt et al., 1999). Assuming the maximum observed discharge concentration over an eight year period of tailings deposition, dilution within the clear water pool is expected to reduce molybdenum concentrations to 130 ug/L (Figure 10). This value is higher than those observed in the clear water pool of the existing tailings basin (16 - 49 ug/L; Berndt et al., 1999). This is because the gradual loss of ground water inputs and decreasing volume of the clear water pool in the Minorca Pit result in less dilution than currently observed in the tailings basin (see section 3.1.1).

#### **Experimental measurements**

The **field tank experiments** were designed such that approximately 4.5 feet of surface water stood above the taconite tailings, exposed to the atmosphere. This situation simulated conditions expected in the clear water pool above tailings in a pit, and provided information regarding the persistence of molybdenum in these waters. Molybdenum concentrations fluctuated due to

seasonal events (i.e. precipitation, freeze/thaw cycles), averaging 67 ug/L (Jakel and Lapakko, 1999b). A slight decrease in molybdenum levels over 116 weeks may have been the result of adsorption of molybdenum to iron oxides.

#### 4.3.3.2. Molybdenum Tailings Pore Water Source Term

After approximately eight years of operation at the Minorca Pit, the elevation of deposited tailings is anticipated to reach the southern rim of the pit (see section 2). When this occurs, water will have to pass through tailings before exiting the pit as ground water. Since conditions within the tailings mass will be less oxidizing and because the pit water will have intimate contact with the tailings, the water chemistry observed in the clear water pool will no longer provide a good indication of source terms. The chemistry of tailings pore waters isolated from the atmosphere more closely simulates these long-term conditions, and the following data were collected under those conditions.

#### **Operational measurements**

Molybdenum concentrations in the two wells and the seep located in the north dike of the tailings basin ranged from 1.5 to 14 ug/L (Table 13; Berndt et al., 1999). Molybdenum levels in tailings pore waters at Inland were similar to those observed in the wells at National and lower than those observed in the seep at LTV, which averaged 10 ug/L and 31 ug/L, respectively (Table A6.3). However, they were significantly higher than molybdenum levels measured in similar waters from USX which averaged 0.6 ug/L (Table 13). The single sample obtained from the seep in the interior dike contained 42 ug/L molybdenum (Berndt et al., 1999).

#### Laboratory column experiments

The laboratory columns simulated conditions that would be expected in the Minorca Pit as it is filled with tailings. Initial molybdenum concentrations of 100 ug/L and 94 ug/L reflected molybdenum concentrations in the plant discharges when the tailings were collected (Berndt and Lapakko, 1997a). However, these levels concentrations decreased throughout the experiment, ultimately reaching 25 ug/L and 15 ug/L, respectively (Table 13).

Once tailings and process waters have been deposited in a pit, process waters will eventually be replaced by precipitation and possibly ground water. In order to simulate these two events, the columns were drained of the process water and refilled. One column was refilled with deionized water to simulate rain water and the other was injected with ground water obtained from local wells drilled into the Biwabik aquifer (Berndt et al., 1998, 1999). During a twenty three week period, molybdenum concentrations in the rain water column decreased from 14 ug/L to 9 ug/L (Berndt et al., 1998, 1999). However, they suddenly increased to 19 ug/L at week twenty seven (Table 13). Molybdenum concentrations in the ground water column gradually increased from 3.6 ug/L to 10 ug/L (Table 13).

#### Field tank experiments

Molybdenum concentrations remained relatively constant in tailings pore waters throughout the 116 week experiment, averaging 24 ug/L (Table 13; Jakel and Lapakko, 1999b).

#### **Geochemical modeling results**

Geochemical calculations indicate that molybdenum adsorbs to iron oxide minerals. This is a pH-dependent process, where dissolved molybdenum in the form of molybdate ( $MoO_4^{2^-}$ ) adsorbs more strongly as pH decreases. Tailings-ground water interaction in an environment isolated from the atmosphere results in slightly lower fluid pH than oxidized waters contacting taconite tailings. The lower fluid pH favors molybdenum adsorption (Berndt and Lapakko, 1997a; Berndt, 1998). Thus, it is believed that molybdenum removal in tailings pore waters is due to an adsorption mechanism.

#### 4.3.3.3. Summary of Molybdenum Source Term Ranges

The only mechanisms of molybdenum release that have been identified at present are the breakdown of lubricants containing  $MoS_2$  and corrosion of grinding media used during taconite processing. Based on the data collected during the MN DNR/U of MN study, a molybdenum source term range of 1 to 130 ug/L was selected (Table 13). The upper end of this range was calculated based on dilution of process water discharged from the plant in the Minorca Pit clear water pool. This represents a short-term, **clear water pool source term** that is appropriate to use between the fifth and eighth years of operation at the Minorca Pit.

Molybdenum levels in **tailings pore waters** during the range-wide study ranged from 1 ug/L to 45 ug/L. The upper end of this range represented analyses of tailings pore waters from the field and laboratory experiments (i.e. process water columns). The lower end of this range was defined by tailings pore waters from wells and seeps around Inland's tailings basin. Since the molybdenum release is the result of operational processes, the source term is expected to decrease to extremely low levels (as seen in the Snively Pit) after site closure.

4.3.4. Molybdenum Transport Through the Biwabik Aquifer

The most conservative estimate of molybdenum levels in Minorca Pit ground water transported through the Biwabik aquifer assumes no dilution or removal due to chemical reactions. Based on this assumption, the molybdenum transport term will equal the Minorca Pit source term. That is, the molybdenum transport term will range from 1 ug/L to 130 ug/L. It is likely that ground water outflow from the Minorca Pit will be diluted by other ground water sources in the aquifer. The extent of this dilution cannot be quantified, but is considered in the flow-weighted average concentration for the total input to the Missabe Mountain Pit.

If Minorca Pit ground waters do mix with ground water already present in the aquifer, geochemical processes can be expected to control molybdenum concentrations during transport. Geochemical calculations indicated that molybdenum is attenuated by iron oxides in the aquifer depending on the pH of water in the aquifer (Figure A3.1; Berndt, 1998; Berndt et al., 1998, 1999). Based on measurements from wells in the Biwabik Formation, the pH of these waters ranges from 6.7 to 8.1 (Table 8). In this pH range, molybdenum levels in the aquifer are expected to decrease during transport through the aquifer, although the extent to which this will occur cannot be quantified. In general, molybdenum adsorption to iron oxides will occur during the period of maximum flow from the Minorca Pit (e.g. prior to reclamation of the site). This is also the time period in which dilution will have the least impact on molybdenum levels entering the Missabe Mountain Pit.

#### 4.3.5. Flow-Weighted Molybdenum Concentrations in Missabe Mountain Pit Inputs

Based on the measurements described in section 4.3.3, molybdenum concentrations in the Minorca Pit can be expected to range from 1 ug/L to 130 ug/L. In order to provide the most conservative estimates, it will be assumed that any molybdenum released in the Minorca Pit will ultimately reach the Missabe Mountain Pit. Thus, inputs to the Missabe Mountain Pit from the Minorca Pit will be assumed to contain 1 - 130 ug/L molybdenum.

Water from the Minorca Pit, direct precipitation, and other ground water sources contribute to the total water input to the Missabe Mountain Pit. It is estimated that the Minorca Pit will contribute a temporary maximum of 28 to 39 percent of the total inflow (Adams, 1998, 1999). This is a temporary maximum because the volume of water collected in the Minorca Pit will decrease after the site has been reclaimed.

At this temporary maximum, flow-weighted average molybdenum input concentrations to the Missabe Mountain Pit would range from 0.5 to 51 ug/L (Table 14), assuming concentrations in the dilutional water were similar to that of the Biwabik Iron Formation ground water (i.e. approximately 0.2 ug/L; Berndt et al., 1998). It is important to note that this calculation does not consider dilution by water stored in the Missabe Mountain Pit, which will be calculated in the following section (section 4.3.6). Current molybdenum levels in the Missabe Mountain Pit are less than 1 ug/L (Table 10).

Reclamation of the Minorca Pit disposal site will most likely consist of establishing a selfsustaining, diverse cover of vegetation over the tailings surface. Vegetation increases evapotranspiration, and consequently, will reduce infiltration of surface waters into the tailings. Thus, after the site has been reclaimed flow from the Minorca Pit to the Missabe Mountain Pit will decrease. If the site is reclaimed with grasses, Minorca Pit inputs are expected to be reduced to 18 to 21 percent of the total input flow to the Missabe Mountain Pit (Adams, 1998, 1999). This would increase dilution, and flow-weighted average input molybdenum concentrations would be reduced to less than 28 ug/L (Table 14). If forest vegetation (i.e. trees) is established over the tailings surface, the Minorca Pit input would be reduced to approximately 13 percent of the Missabe Mountain Pit input (Adams, 1998, 1999). Flow-weighted average molybdenum concentrations in Missabe Mountain Pit inputs would then be expected to decrease to less than 18 ug/L (Table 14). No chemical controls are expected to influence molybdenum levels in the Missabe Mountain Pit.

#### 4.3.6. Dilution and Geochemical Reaction in the Missabe Mountain Pit

Using the maximum molybdenum source term for depositional years five to ten, the flowweighted average input molybdenum concentration for inputs to the Missabe Mountain Pit was determined to be 51 ug/L (see paragraph 3, section 4.3.5). Since this input occurs for a relatively short period of time, the water stored in the Missabe Mountain Pit will dilute the flow-weighted average input molybdenum concentration to 25 ug/L (Figure 11).

This calculation was based on the worst case scenario, using maximum source and transport terms. Flow-weighted average input concentrations were determined for three time periods; active operations in the Minorca Pit (source and transport term = 130 ug/L), short-term reclamation of the Minorca with grasses (source and transport term = 45 ug/L), and long-term reclamation with forest vegetation (source and transport term = 45 ug/L). Dilution by the water stored within the Missabe Mountain Pit was estimated for a fifty year period beginning when tailings are first deposited in the Minorca Pit. Based on these calculations, molybdenum concentration of the Minorca Pit, molybdenum levels in the Missabe Mountain Pit are expected to reach a maximum concentration of 25 ug/L just prior to closure of the Minorca Pit (Figure 11). Subsequent to closure and successful reclamation of the Minorca Pit, molybdenum levels in the Missabe Mountain Pit are expected to are expected to affect molybdenum levels in the Missabe Mountain Pit.

# 4.3.7. Comparison of Predicted Concentrations to Drinking Water Quality Standards

At maximum ground water input from the Minorca Pit, average molybdenum concentrations in waters entering the Missabe Mountain Pit are expected to be as high as 51 ug/L (Table 14). This value exceeds the drinking water quality standard at 30 ug/L.

This condition is expected to occur during an assumed six year period of maximum ground water outflow from the Minorca Pit. During this time period, dilution by the volume of water stored in the Missabe Mountain Pit will be sufficient to dilute molybdenum concentrations in the net inflow to less than 25 ug/L (Figure 11). Long-term molybdenum concentrations in the Missabe Mountain Pit are expected to decrease gradually, reaching approximately 15 ug/L in fifty years. Thus, even at maximum ground water input from the Minorca Pit, molybdenum levels in the Missabe Mountain Pit are expected to be lower than the primary drinking water standard of 30 ug/L. Consequently, no treatment issues at the Virginia Public Utility are expected to arise.

#### 4.4. Arsenic

#### 4.4.1. Approach

If taconite tailings are disposed of in the Minorca Pit, arsenic concentrations in the tailings pore waters will become elevated relative to natural background levels. As the pit fills, water will flow from the Minorca Pit into the Biwabik Formation aquifer and, likely, to the Missabe Mountain Pit. The purpose of section 4.4 is to summarize results of the MN DNR-U of MN study on the ground water implications of taconite tailings disposal in the Minorca Pit with regard to arsenic. Operational measurements, field and laboratory experiments, and geochemical modeling were used to; 1) determine the magnitude of arsenic concentrations in outflow from the Minorca Pit (i.e. source term), 2) consider processes, including dilution and chemical reactions, that affect arsenic levels during transport in the aquifer, 3) estimate average input concentrations to the Missabe Mountain Pit from all water sources, and 4) determine the extent to which dilution and other natural processes might decrease arsenic levels within the Missabe Mountain Pit.

4.4.2. Source of Arsenic in Waters Associated with Taconite Tailings

Arsenic is believed to be released due to oxidation of trace amounts of pyrite present in taconite tailings (Berndt et al., 1999). Thus, it is possible that arsenic release from taconite tailings will continue after closure of the Minorca Pit if the tailings remain exposed to the atmosphere. However, standard reclamation practices should reduce the extent of pyrite oxidation within the tailings, and therefore, long-term arsenic release from the tailings.

#### 4.4.3. Arsenic Source Terms for the Minorca Pit

Operational, field and laboratory measurements of arsenic concentrations in waters closely associated with taconite tailings were collected over a two and a half year period (Berndt and Lapakko, 1997a, b; Berndt, 1998; Berndt et al., 1998, 1999). Operational measurements at Inland were taken from the tailings discharge pipe, clarified water in the tailings basin, a seep in the north dike of the tailings basin, and two wells outside the northeast edge of the tailings basin. A single measurement was obtained from a seep in the interior dike late in the study. Operational measurements were also made at the Snively Pit, US Steel-Minntac (USX, the only known case of in-pit disposal of taconite tailings in Minnesota), two wells at National Steel and Pellet Company (National), and one seep at LTV Steel Mining Company (LTV). Laboratory experiments were conducted on tailings initially saturated with process water and subjected to input from precipitation. Finally, geochemical computer models were used to define limits on arsenic levels in tailings pore waters. These data will be used in the following section to determine a range of arsenic concentrations that could be expected to exit the Minorca Pit as ground water if the pit is filled with tailings.

#### 4.4.3.1. Arsenic Clear Water Pool Source Term

Between the fifth and eighth years of tailings deposition in the Minorca Pit, the clear water pool is assumed to determine the chemistry of water flowing out of the pit (see section 2). In reality, water may exit the pit from either the clear water pool or from the tailings pores. The clear water pool receives process water discharged from the plant in addition to precipitation, and during the initial stages of the operation, ground water. Elevated arsenic concentrations in process waters will result in elevated arsenic concentrations in water exiting the pit.

#### **Operational measurements**

Arsenic concentrations in plant discharges ranged from 1.9 to 5.5 ug/L during this study (Table 15; Berndt et al., 1999). Assuming the maximum observed discharge concentration over an eight year period of tailings deposition, dilution within the clear water pool is expected to reduce arsenic concentrations to 4.5 ug/L (Figure 12). Arsenic concentrations in the clear water pool of the tailings basin (3.1 - 7.4 ug/L) are generally higher than those observed in process waters discharged from the plant. Similar observations were made for process and tailings basin waters at LTV (Berndt et al., 1999). Arsenic is believed to be associated with trace amounts of sulfide minerals present in taconite tailings. Oxidation of these sulfides within the tailings basin results in arsenic release into the clear water pool. The magnitude of arsenic release in the tailings basin was estimated at 0.03 T/yr (Jakel and Lapakko, 1999d). Consequently, relative to plant discharge values, arsenic concentrations in the existing tailings basin more accurately approximated those in the Minorca Pit clear water pool.

#### **Experimental measurements**

The field tank experiments were designed such that approximately 4.5 feet of surface water stood above the taconite tailings, exposed to the atmosphere. This situation simulated conditions in the tailings basin, and provided information regarding arsenic release in these waters. During the first thirty eight weeks of the experiment, arsenic concentrations remained constant, averaging 2 ug/L (Jakel and Lapakko, 1999b). Subsequently, arsenic concentrations increased, reaching maximum concentrations of 12 to 14 ug/L, where they remained for the duration of the experiment.

#### 4.4.3.2. Arsenic Tailings Pore Water Source Term

After approximately eight years of operation at the Minorca Pit, the elevation of deposited tailings is anticipated to reach the southern rim of the pit (see section 2). When this occurs, water will have to pass through the tailings before exiting the pit as ground water. Since conditions within the tailings mass will be less oxidizing and because the pit water will have intimate contact with the tailings, the water chemistry observed in the clear water pool will no longer provide a good indication of source terms. The chemistry of tailings pore waters isolated from the atmosphere more closely simulates these long-term conditions, and the following data were collected under those conditions.

#### **Operational measurements**

Arsenic concentrations in the two wells and the seep located in the north dike of the tailings basin ranged from 0.2 to 5.6 ug/L, excluding statistical outliers (Table 15; Berndt et al., 1999). Arsenic levels in tailings pore waters at Inland were generally similar to those observed in the wells at National and USX, and the seep at LTV (Table A6.4). The single sample obtained from the seep in the interior dike contained 2.8 ug/L arsenic (Berndt et al., 1999).

#### Laboratory column experiments

The laboratory columns simulated conditions that would be expected in the Minorca Pit as it is filled with tailings. Arsenic concentrations in the water samples gradually decreased from 8.3 and 6.1 ug/L to 3.8 ug/L and 2.1 ug/L, respectively (Table 15; Berndt and Lapakko, 1997a).

Once tailings and process waters have been deposited in a pit, process waters will eventually be replaced by precipitation and possibly ground water. In order to simulate these two events, the columns were drained of the process water and refilled. One column was refilled with deionized water to simulate rain water and the other was injected with ground water obtained from local wells drilled into the Biwabik aquifer. During a twenty seven week period, arsenic concentrations in the rain water column averaged 4.9 ug/L (Table 15). Arsenic concentrations in the ground water column averaged 2.5 ug/L for thirty weeks (Table 15).

#### Field tank experiments

Arsenic levels in these waters were low throughout the 116-week experiment, ranging from 0.6 ug/L to 4.2 ug/L (Table 15; Jakel and Lapakko, 1999b).

#### **Geochemical modeling results**

Geochemical calculations indicate that arsenic adsorbs to iron oxide minerals (Berndt and Lapakko, 1997a; Berndt, 1998; Berndt et al., 1998, 1999). This is a pH-dependent process, where arsenic in the form of  $As(OH)_4^-$  adsorbs to positively charged surface sites on iron oxides. Arsenic desorbs as  $As(OH)_3$  under moderately reducing conditions and neutral pH. However, these conditions have not been observed in tailings pore waters during this study. Thus, it is believed that arsenic removal in tailings pore waters is due to an adsorption mechanism.

#### 4.4.3.3. Summary of Arsenic Source Term Ranges

Arsenic is believed to be released by the oxidation of trace amounts of pyrite present in the tailings. Based on analyses of Inland's plant discharges and tailings pore waters, an arsenic source term range of 0.1 to 7 ug/L was selected (Table 15). The lowest arsenic levels were found in the north seep at Inland. These values are actually lower than those measured in the Biwabik aquifer (Berndt et al., 1998) and the Missabe Mountain Pit (Table 10). The upper end of this

range was defined by a calculated value for the **clear water pool** and a few high values observed in the wells at Inland and the rain water column experiments. Despite this wide range of values, the majority of **tailings pore waters** sampled during this study contained 2 - 4 ug/L arsenic.

#### 4.4.4. Arsenic Transport Through the Biwabik Aquifer

The most conservative estimate of arsenic levels in Minorca Pit ground water transported through the Biwabik aquifer assumes no dilution or removal due to chemical reactions. Based on this assumption, the arsenic transport term will equal the Minorca Pit source term. That is, the arsenic transport term will range from 0.1 ug/L to 7 ug/L. It is likely that ground water outflow from the Minorca Pit will be diluted by other ground water sources in the aquifer. The extent of this dilution cannot be quantified, but is considered in the flow-weighted average concentration for the total input to the Missabe Mountain Pit.

If Minorca Pit ground waters do mix with ground water already present in the aquifer, geochemical processes can be expected to control arsenic levels during transport. Geochemical calculations indicated that arsenic will be attenuated by iron oxides in the aquifer 2 to 13 times more than the nonreactive elements chloride and bromide (Berndt, 1998). Elevated arsenic levels in the aquifer may decrease during transport through the aquifer (Figure A3.1), although the extent to which this will occur cannot be quantified. In general, arsenic adsorption to iron oxides will occur during the period of maximum flow from the Minorca Pit (e.g. prior to reclamation of the site). This is also the time period in which dilution will have the least impact on arsenic levels entering the Missabe Mountain Pit.

#### 4.4.5. Flow-Weighted Arsenic Concentrations in Missabe Mountain Pit Inputs

Based on the measurements described in section 4.4.3, arsenic concentrations in the Minorca Pit can be expected to be in the range of 0.1 ug/L to 7 ug/L. In order to provide the most conservative estimates, it will be assume that any arsenic released in the Minorca Pit will ultimately reach the Missabe Mountain Pit. Thus, inputs to the Missabe Mountain Pit from the Minorca Pit are assumed to contain 0.1 - 7 ug/L arsenic.

Water from the Minorca Pit, direct precipitation, and other ground water sources contribute to the total water input to the Missabe Mountain Pit. It is estimated that the Minorca Pit will contribute a temporary maximum of 28 to 39 percent of the net inflow (Adams, 1998, 1999). This is a temporary maximum because the volume of water collected in the Minorca Pit will decrease after the site has been reclaimed.

At this temporary maximum, flow-weighted average input concentrations to the Missabe Mountain Pit would range from 0.4 to 3.0 ug/L arsenic (Table 16), assuming concentrations in the dilutional water were similar to that of the Biwabik Iron Formation ground water (i.e. approximately 0.5 ug/L; Berndt et al., 1998). It is important to note that this calculation does not consider dilution by water stored in the Missabe Mountain Pit, which will be calculated in

the following section (section 4.4.6). Current arsenic levels in the Missabe Mountain Pit are approximately 0.7 ug/L (Table 10).

Reclamation of the Minorca Pit disposal site will most likely consist of establishing a selfsustaining, diverse cover of vegetation over the tailings surface. Vegetation increases evapotranspiration, and consequently, will reduce infiltration of surface waters into the tailings. Thus, after the site has been reclaimed, flow from the Minorca Pit to the Missabe Mountain Pit will decrease. If the site is reclaimed with grasses, Minorca Pit inputs are expected to be reduced to 18 to 21 percent of the total flow to the Missabe Mountain Pit (Adams, 1998, 1999). This would increase dilution, and flow-weighted input arsenic concentrations would be reduced to less than 1.9 ug/L arsenic (Table 16). If forest vegetation (i.e. trees) is established over the tailings surface, the Minorca Pit input would be reduced to approximately 13 percent of the Missabe Mountain Pit input (Adams, 1998, 1999). Flow-weighted average arsenic concentrations in Missabe Mountain Pit inputs would then be expected to be less than 1.3 ug/L (Table 16).

4.4.6. Dilution and Geochemical Reaction in the Missabe Mountain Pit

Using the maximum arsenic source term for depositional years five to ten, the flow-weighted average input arsenic concentration for inputs to the Missabe Mountain Pit was determined to be 3.0 ug/L (see paragraph 3, section 4.4.5). Since this input occurs for a relatively short period of time, the water stored in the Missabe Mountain Pit will dilute the flow-weighted input arsenic concentration to 2.2 ug/L or lower (Figure 13). Assuming the worst case scenario, arsenic levels in the Missabe Mountain Pit will reach 2.2 ug/L just prior to closure of the Minorca Pit, and will decrease subsequent to successful reclamation of the site. Geochemical calculations indicate that arsenic will tend to co-precipitate with iron oxides (Berndt, 1998). Thus, arsenic levels in the Missabe Mountain Pit may also be reduced by chemical and/or biological oxidation and subsequent precipitation of iron oxides, further reducing arsenic levels in the Missabe Mountain Pit.

# 4.4.7. Comparison of Predicted Concentrations to Drinking Water Quality Standards

Even at maximum ground water input from the Minorca Pit, arsenic levels in the Missabe Mountain Pit are expected to be considerably lower than the primary drinking water standard of 50 ug/L. However, the US EPA is expected to lower this standard by the year 2001. Arsenic levels in the Missabe Mountain Pit are anticipated to meet the future drinking water quality standard if it is reduced to the range of 5 - 10 ug/L. Therefore, no treatment issues at the Virginia Public Utility are expected to arise.

#### 4.5. Boron

#### 4.5.1. Approach

If taconite tailings are disposed of in the Minorca Pit, boron concentrations in waters associated with these tailings will become elevated relative to natural background levels. As the pit fills, water will flow from the Minorca Pit into the Biwabik Formation aquifer and, likely, to the Missabe Mountain Pit. The purpose of section 4.5 is to summarize results of the MN DNR-U of MN study on the ground water implications of in-pit disposal of taconite tailings with regard to boron. Operational measurements, field and laboratory experiments, and geochemical modeling were used to 1) determine the magnitude of boron concentrations in outflow from the Minorca Pit (i.e. source term), 2) consider processes, including dilution and chemical reactions, that affect boron levels during transport in the aquifer, 3) estimate average input concentrations to the Missabe Mountain Pit from all water sources, and 4) determine the extent to which dilution might decrease boron levels within the Missabe Mountain Pit.

#### 4.5.2. Source of Boron in Waters Associated with Taconite Tailings

Boron is mobilized during taconite processing. Diamond drilling lubricants represent one potential source of boron (Inland, 1999). Boron is also mobilized during induration (Berndt and Lapakko, 1997a; Jakel et al., 1998b; Jakel and Lapakko, 1999d). However, the mechanism of boron release has not been identified in either case.

#### 4.5.3. Minorca Pit Boron Source Term

Operational, field, and laboratory measurements of boron concentrations in waters closely associated with taconite tailings were collected over a two and a half year period (Berndt and Lapakko, 1997a, b; Berndt, 1998; Berndt et al., 1998, 1999). Operational measurements at Inland were taken from the tailings discharge pipe, clarified water in the tailings basin, a seep in the north dike of the tailings basin, and two wells outside the northeast edge of the tailings basin. A single measurement was obtained from a seep in the interior dike late in the study. Operational measurements were also made at the Snively Pit, US Steel-Minntac (USX, the only known case of in-pit disposal of taconite tailings in Minnesota), two wells at National Steel and Pellet Company (National), and one seep at LTV Steel Mining Company (LTV). Laboratory experiments were conducted on tailings initially saturated with process water and subjected to input from precipitation. Finally, geochemical computer models were used to define limits on boron levels in tailings pore waters. These data will be used in the following section to determine the concentration of boron that could be expected to exit the Minorca Pit as ground water if the pit is filled with tailings.

#### 4.5.3.1. Boron Clear Water Pool Source Term

Between the fifth and eighth years of tailings deposition in the Minorca Pit, the clear water pool is assumed to determine the chemistry of water flowing out of the pit (see section 2). In reality, water may exit the pit from either the clear water pool or from the tailings pores. The clear water pool receives process water discharged from the plant in addition to precipitation, and during the initial stages of the operation, ground water. Elevated boron concentrations in process waters will result in elevated boron concentrations in water exiting the pit.

#### **Operational measurements**

Boron concentrations in plant discharges ranged from 66 to 212 ug/L during this study (Table 17; Berndt et al., 1999). Assuming the maximum observed discharge concentration over an eight year period of tailings deposition, dilution within the clear water pool is expected to reduce boron concentrations to 171 ug/L (Figure 14). This value is higher than those observed in the clear water pool of the existing tailings basin (27 - 100 ug/L; Berndt et al., 1999). This is because the gradual loss of ground water inputs and decreasing volume of the clear water pool in the Minorca Pit result in less dilution than currently observed in the tailings basin (see section 3.1.1).

#### **Experimental measurements**

The **field tank experiments** were designed such that approximately 4.5 feet of surface water stood above the taconite tailings, exposed to the atmosphere. This situation simulated conditions expected in the clear water pool above tailings in a pit, and provided information regarding the persistence of boron in these waters. Boron concentrations fluctuated within a fairly constant range throughout the tank experiments, averaging 115 ug/L (Jakel and Lapakko, 1999b). Fluctuations were largely due to seasonal events (i.e. precipitation, freeze/thaw cycles).

#### 4.5.3.2. Boron Tailings Pore Water Source Term

After approximately eight years of operation at the Minorca Pit, the elevation of deposited tailings is anticipated to reach the southern rim of the pit (see section 2). When this occurs, water will have to pass through the tailings before exiting the pit as ground water. Since conditions within the tailings mass will be less oxidizing and because the pit water will have intimate contact with the tailings, the water chemistry observed in the clear water pool will no longer provide a good indication of source terms. The chemistry of tailings pore waters isolated from the atmosphere more closely simulates these long-term conditions, and the following data were collected under those conditions.

#### **Operational measurements**

Boron concentrations in the two wells and the seep located in the north dike of the tailings basin ranged from 27 to 77 ug/L (Table 17; Berndt et al., 1999). Boron levels in tailings pore waters

at Inland were similar to those observed in the wells at National and USX, which averaged 41 ug/L and 32 ug/L, respectively (Table A6.5). These values were significantly lower than boron levels measured in the seep at LTV, which averaged 457 ug/L (Table A6.5). The single sample obtained from the seep in the interior dike contained 113 ug/L boron (Berndt et al., 1999). In general, the highest boron levels at Inland were observed in plant discharges to the tailings basin, which ranged from 66 - 212 ug/L (Table 17).

#### Laboratory column experiments

The laboratory columns simulated conditions that would be expected in the Minorca Pit as it is filled with tailings. Boron concentrations in these waters ranged from 135 - 290 ug/L and averaged 213 ug/L (Table 17; Berndt and Lapakko, 1997a).

Once tailings and process waters have been deposited in a pit, process waters will eventually be replaced by precipitation and possibly ground water. In order to simulate these two events, the columns were drained of the process water and refilled. One column was refilled with deionized water to simulate rain water and the other was injected with ground water obtained from local wells drilled into the Biwabik aquifer. During a twenty seven week period, boron concentrations in the rain water column generally decreased from 281 ug/L to 57 ug/L (Table 17; Berndt et al., 1998, 1999). Boron concentrations in the ground water column gradually increased from 72 ug/L to 256 ug/L (Table 17).

#### **Field tank experiments**

Boron concentrations remained relatively constant in tailings pore waters throughout the 116week experiment, averaging 97 ug/L (Table 17; Jakel and Lapakko, 1999b).

4.5.3.3. Summary of Boron Source Term Ranges

Based on analyses of Inland tailings pore waters, a boron source term range of 30 to 300 ug/L was selected (Table 17). The upper end of this range was typical of tailings pore analyses from laboratory column experiments. In general, boron levels in controlled experiments were higher than operational field observations. The lower end of this range represented analyses of tailings pore waters from wells and seeps around Inland's tailings basin and the well at USX. Since the boron release is the result of operational processes, the source term is expected to decrease to extremely low levels (as seen in the Snively Pit) after closure.

4.5.4. Boron Transport Through the Biwabik Aquifer

The most conservative estimate of boron levels in Minorca Pit ground water transported through the Biwabik aquifer assumes no dilution or removal due to chemical reactions. Based on this assumption, the boron transport term will equal the Minorca Pit source term. That is, the boron transport term will range from 30 ug/L to 300 ug/L. It is likely that ground water outflow from the Minorca Pit will be diluted by other ground water sources in the aquifer. The extent of this dilution cannot be quantified, but is considered in the flow-weighted average concentration for the total input to the Missabe Mountain Pit. No chemical controls are expected to influence boron levels during transport in the aquifer.

#### 4.5.5. Flow-Weighted Boron Levels in Missabe Mountain Pit Inputs

Based on the measurements described in section 4.5.4, boron concentrations in the Minorca Pit can be expected to range from 30 ug/L to 300 ug/L. In order to provide the most conservative estimates, it will be assume that any boron released in the Minorca Pit will ultimately reach the Missabe Mountain Pit. Thus, inputs to the Missabe Mountain Pit from the Minorca Pit will be assumed to contain 30 - 300 ug/L boron.

Water from the Minorca Pit, direct precipitation, and other ground water sources contribute to the total water input to the Missabe Mountain Pit. It is estimated that the Minorca Pit will contribute a temporary maximum of 28 to 39 percent of the total inflow (Adams, 1998, 1999). This is a temporary maximum because the volume of water collected in the Minorca Pit will decrease after the site has been reclaimed.

At this temporary maximum, flow-weighted average input concentrations would range from 40 to 145 ug/L boron (Table 18), assuming concentrations in the dilutional water were similar to that of the Biwabik Iron Formation ground water (i.e. approximately 46 ug/L; Berndt et al., 1998). It is important to note that this calculation does not consider dilution by water stored in the Missabe Mountain Pit. Current boron levels in the Missabe Mountain Pit are less than 20 ug/L (Table 10).

Reclamation of the Minorca Pit disposal site will most likely consist of establishing a selfsustaining, diverse cover of vegetation over the tailings surface. Vegetation increases evapotranspiration, and consequently, will reduce infiltration of surface waters into the tailings. Thus, after the site has been reclaimed, flow from the Minorca Pit to the Missabe Mountain Pit will decrease. If the site is reclaimed with grasses, Minorca Pit inputs are expected to be reduced to 18 to 21 percent of the total flow to the Missabe Mountain Pit (Adams, 1998, 1999). This would increase dilution, and flow-weighted input concentrations would be reduced to less than 99 ug/L boron (Table 18). If forest vegetation (i.e. trees) is established over the tailings surface, the Minorca Pit input would be reduced to approximately 13 percent of the total flow to the Missabe Mountain Pit input (Adams, 1998, 1999). Flow-weighted average boron concentrations in Missabe Mountain Pit inputs would then be expected to be less than 79 ug/L (Table 18). No chemical controls are expected to influence boron levels in the Missabe Mountain Pit.

# 4.5.6. Comparison of Predicted Concentrations to Drinking Water Quality Standards

Even at maximum ground water input from the Minorca Pit, boron levels in the Missabe Mountain Pit are expected to be lower than the primary drinking water standard of 600 ug/L. Consequently, no treatment issues at the Virginia Public Utility are expected to arise.

#### 5. Conclusions

#### 5.1. Worst Case Scenario

Outflow from the Minorca Pit will have EC levels which are elevated relative to those presently in the Missabe Mountain Pit and Biwabik aquifer. Minorca Pit flow which enters the Missabe Mountain Pit will elevate EC levels in the Missabe Mountain Pit above those presently observed. However, based on evaluation of the worst case scenario, dilution and geochemical controls are expected to maintain EC levels in the Missabe Mountain Pit below existing health-based and drinking water quality standards.

Manganese levels in Missabe Mountain Pit input waters are expected to meet the health-based standard set by the MDH (1998) and the secondary drinking water quality standard due to chemical reactions in the pit. Oxidizing conditions in the Missabe Mountain Pit are expected to promote manganese removal which will reduce manganese concentrations to levels presently found in the pit.

Fluoride and molybdenum levels are not expected to exceed the drinking water quality standards in the Missabe Mountain Pit. No geochemical controls are expected to reduce these levels during transport in the Biwabik aquifer. However, dilution of Minorca Pit inputs to the Missabe Mountain Pit is expected to be sufficient to reduce fluoride and molybdenum concentrations to levels lower than the drinking water quality standards but higher than those presently found in the Missabe Mountain Pit.

Dilution is also expected to maintain arsenic concentrations in the Missabe Mountain Pit to levels lower than the drinking water quality standards but higher than those presently found in the Missabe Mountain Pit. Arsenic concentrations in the Missabe Mountain Pit may be reduced further by co-precipitating with iron oxyhydroxides.

5.2. Mitigating Factors to the Worst Case Scenario

The above assessment was based on the worst case scenarios for each EC. However, several mitigating factors exist that would tend to decrease EC levels actually observed in the Missabe Mountain Pit:

1. Clear water pool source terms were determined assuming the maximum EC levels measured in plant discharges to the tailings basin during the MN DNR/U of MN study. However, discharge concentrations will decrease after several years of tailings deposition in the Minorca Pit because process waters needs will have to be met with make-up water from other sources (presumably the Sauntry or Enterprise Pits). This is a particularly important consideration in assessing fluoride and molybdenum concentrations in the clear water pool.

- 2. During the time period when the clear water pool dominates outflow from the Minorca Pit (years 5 8), our calculations assumed that the clear water pool represented 100% of the outflow. It is more likely that ground water outflow during that time period will be a mixture of water from the clear water pool and tailings pore waters. In most cases, EC levels in ground water outflow would be lower than predicted by the clear water pool alone. For example, the molybdenum levels in the clear water pool (130 ug/L source term) would be diluted by tailings pore waters (45 ug/L source term), resulting in molybdenum levels in ground water outflow that fall somewhere between these two values. The opposite effect would be expected for the manganese, since the source term for the clear water pool (<0.01 mg/L) is lower than the source term for the tailings pore waters (7 mg/L).
- 3. The manganese tailings pore water source term (7 mg/L) was based on the maximum measured concentration in wells along the existing tailings basin. In the absence of acid generating materials (e.g. organic matter) in the tailings mass, manganese concentrations in tailings pore waters are expected to be less than 1 mg/L.
- 4. Minorca Pit ground waters were assumed to flow through the Biwabik aquifer to the Missabe Mountain Pit with no interaction with existing ground water or host rock. However, it is likely that manganese, molybdenum, and arsenic will be attenuated to some degree in the aquifer. Based on geochemical calculations, manganese levels in the aquifer are unlikely to exceed 1 mg/L. Attenuation of molybdenum and arsenic could not be quantified, but qualitatively, these concentrations will decrease due to adsorption to iron oxides present in the host rock.
- 5. A value of 39% was used to represent the Minorca Pit contribution to the flow-weighted average EC concentrations in the net inputs to the Missabe Mountain Pit. This value was decreased to 28% after additional interpretation (Adams, 1999), which would decrease the impact that outflow from the Minorca Pit would have on water quality in the Missabe Mountain Pit.
- 6. Dilution within the Missabe Mountain Pit did not include the volume of water in the Rouchleau Pit nor precipitation and ground water inputs to that pit. Depending on the timing of tailings disposal in the Minorca Pit, it is likely that the water level in these two pits will have risen above the berm currently separating them. Therefore, the volume of dilutional water available will be larger than that used to assess the worst case scenario. In the best case scenario, assuming complete mixing of the Rouchleau and Missabe Mountain Pits, the dilution water available within these two pits would increase approximately 40%.
- 7. The water balance used to calculate flow-weighted average EC concentrations did not distinguish between precipitation and ground water. Therefore, it was assumed that all inputs, other than flow from the Minorca Pit, had EC levels similar to those measured in

the Biwabik aquifer. This assumption overestimates EC levels in the net inputs to the Missabe Mountain Pit, since precipitation does not contain ECs.

#### 5.3. Recommendations

- 1. Water quality of plant discharges into the Minorca Pit should be monitored. If EC levels in these waters become elevated, Inland will need to make adjustments to maintain concentrations in the Minorca Pit at acceptable levels. This will be particularly important for molybdenum in the clear water pool. Whereas rigorous analysis of acceptable discharge levels has not been conducted, the values used in this study resulted in Missabe Mountain Pit concentrations which met drinking water quality standards. Therefore, they represent one option for acceptable plant discharge levels.
- 2. Tailings pore water quality in the Minorca Pit should be monitored in order to ensure accuracy of the predicted source terms. Conditions in the Minorca Pit are not fully represented by those encountered in Inland's tailings basin or controlled experiments. Natural mineralogical variations in tailings composition or unforeseen changes in taconite processing methods could result in elevated levels of the four EC's or other elements in the Minorca Pit. Variables such as these could not be accounted for in this analysis.
- 3. Conditions in the Missabe Mountain Pit should be monitored to ensure that oxidizing conditions are maintained as the water level in this pit rises. If pit waters become reducing, manganese removal by natural processes will be compromised.
- 4. Monitoring of incoming water to the water treatment plant should continue and may require an increased sampling frequency. This will be particularly important for fluoride, since fluoridation adjustments will be necessary if fluoride levels in the Missabe Mountain Pit increase.

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## Ispat Inland Steel's Proposed Tailings Disposal Site



Figure 1. Map of the area near Virginia, Minnesota including Ispat Inland Mining Company's taconite processing plant and the Minorca and Missabe Mountain Pits.





In order to evaluate potential impacts on water quality in the Missabe Mountain Pit, a direct connection with the Minorca Pit was assumed. EC concentrations were evaluated at four points along this flow path; 1) water exiting the Minorca Pit, 2) transport through the aquifer, 3) flow-weighted average inputs to the Missabe Mountain Pit, and 4) within the Missabe Mountain Pit.



Figure 3. The results of four calculations suggested that manganese concentrations in the Minorca Pit clear water pool will be approximately 0.07 - 0.08 mg/L between the fifth and tenth years of tailings deposition. This decrease was due to dilution in the Minorca Pit, and did not consider chemical reactions (i.e. oxidation) in the clear water pool.

### Manganese Levels Observed in Oxygenated Environments



Figure 4. Manganese levels in the Minorca Pit clear water pool and the Missabe Mountain Pit are expected to be less than 0.01 mg/L (dashed line). Low levels of dissolved manganese are observed in surface waters associated with taconite tailings and in mine pits in northern Minnesota due to chemical oxidation of dissolved manganese, and subsequent precipitation of solid manganese oxide, MnO<sub>2</sub>. A few elevated manganese levels were observed in tailings basins during extended periods of ice cover (e.g. winter).



Figure 5. Maximum manganese levels in the Biwabik aquifer are controlled by the solubility of rhodochrosite,  $MnCO_3$ . Water in the Biwabik aquifer typically has  $pCO_2$  values between 0.001 and 0.01 and alkalinities between 0.3 and 0.5 mM (150 and 250 mg/L as CaCO<sub>3</sub>). Based on these ranges, manganese levels cannot exceed 1 mg/L.



Figure 6. For mixtures of tailings pore and Missabe Mountain Pit waters with initial manganese concentrations less than 2 mg/L, manganese concentrations decreased to less than 0.01 mg/L in fourteen weeks (Jakel and Lapakko, 1999c).



Figure 7. Assuming 7.6 mg/L fluoride in plant discharges, fluoride concentrations in the Minorca Pit clear water pool are expected to reach 6 mg/L approximately five years after tailings deposition begins. The decrease from 7.6 mg/L to 6 mg/L is due to dilution alone.

## Fluorite Solubility Control on Fluoride Levels



Figure 8. Maximum fluoride levels in the Biwabik Formation aquifer are likely to be controlled by the solubility of the mineral fluorite (CaF<sub>2</sub>; Berndt et al., 1999). Within the range of observed calcium concentrations in the Biwabik aquifer (vertical dashed lines), fluoride levels are expected to range from 4.3 to 6.2 mg/L.

Predicted Fluoride Levels in the Missabe Mountain Pit Due to Elevated Input Levels from the Minorca Pit



### Range of Estimates

- Minimum
- × Refined Estimate
- Maximum
- Figure 9. Although no geochemical controls are expected for fluoride in the Missabe Mountain Pit, dilution by the volume of water stored within the pit will be sufficient to reduce fluoride levels below the primary and secondary drinking water quality standards (4 mg/L and 2 mg/L, respectively).



Figure 10. Assuming 160 ug/L molybdenum discharged from Inland's plant, molybdenum concentrations in the Minorca Pit clear water pool may increase to 130 ug/L within five years of the onset of tailings deposition. The decrease from 160 ug/L to 130 ug/L will be due to dilution alone.

Predicted Molybdenum Levels in the Missabe Mountain Pit Due to Elevated Input Levels from the Minorca Pit



### Range of Estimates

- Minimum
- × Refined Estimate
- Maximum
- Figure 11. Although no geochemical controls are expected for molybdenum in the Missabe Mountain Pit, dilution by the volume of water stored within the pit will be sufficient to reduce fluoride levels below the drinking water quality standard (30 ug/L).



Dilution of Inland Plant Discharges

Figure 12. Arsenic concentrations in the Minorca Pit clear water pool are not expected to exceed 5 ug/L during the time period in which tailings are deposited in the Minorca Pit.

Predicted Arsenic Levels in the Missabe Mountain Pit Due to Elevated Input Levels from the Minorca Pit



### Range of Estimates

- Minimum
- × Refined Estimate
- Maximum
- Figure 13. Even at maximum input from the Minorca Pit, arsenic levels in the Missabe Mountain Pit are expected to be well below the current drinking water quality standard of 50 ug/L.


Figure 14. Boron levels in the Minorca Pit clear water pool are not expected to exceed 175 ug/L during the time period in which tailings are deposited in the Minorca Pit.

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Table 1.Based on the preliminary tailings disposal schedule for the Minorca Pit (Indeco,<br/>1999), the local ground water gradient is expected to reverse after approximately<br/>five years of tailings and process water deposition (i.e. once the clear water pool<br/>elevation reaches 1450 feet).

Years of Deposition	Cumulative Tailings Deposition (ac-ft)	Operating Pool Water Volume (ac-ft)	Max. Pool Water Volume (ac-ft)	Max. Pool Elevation (feet M.S.L.)
· 3	8400	1160	1160	1432
5	14000	1150	1150	1450
8	22400	2000	1500	1478
10	28000	500	600	1478

	Flow Rate Estimates (gpm)				
	Indeco (1999)/ Noramco (1997)	Adams (1998)			
INPUTS:					
Process water discharged to the clear water pool	1904 <sup>1</sup>	1904 <sup>1</sup>			
Net precipitation	440	663			
Ground water inflow	979	338 - 0 <sup>2</sup>			
OUTFLOW:					
Sauntry Creek	1419	1419			
Ground water outflow	0 - 839 <sup>3</sup>	0 - 839 <sup>3</sup>			
Plant reclaim	calculated by difference	calculated by difference			

Table 2.	Two water balances were used to calculate dilution of process waters in the
	Minorca Pit clear water pool.

<sup>1</sup> Calculated by subtracting the volume of process water assumed to remain in the tailings pore spaces. Data from Indeco (1999). <sup>2</sup> Ground water inputs to the pit will gradually decrease as the water level rises to approximately 1450 feet M.S.L. (Adams, 1998). <sup>3</sup> Ground water outflow will gradually increase as the pit fills with tailings (Adams, 1998).

Table 3.	Summary of hydrologic data used by Adams (1998) to determine the potential
	contribution of Minorca Pit waters to the Missabe Mountain Pit.

Component	Flow Rate (gpm)	Notes
Average annual net inflow	2135	assuming no input from the Minorca Pit
	701-839	"full development"
Minorca contribution	301-439	"reclamation-grasses"
	136-274	"reclamation-trees"

Table 4.Mineralogy of tailings from ore mined from the Laurentian Pit. Modal analysis<br/>(wt%) and mineral identifications are based on microscopy, heavy mineral<br/>separation, and SEM analysis (Mattson, 1996).

Mineral	Weight %
Magnetite	1
Hematite	17
Goethite	1 .
Mn-oxides	nd
Calcite	nd
Siderite	7
Ankerite	4
Quartz	44
Stilpnomelene	11
Minnesotaite	3
Talc	11
Cummingtonite	nd
Fe-Hornblende	nd
Greenalite	tr
Chlorite	tr
Apatite	0.2
Pyrite	0.01

tr = possible trace

Major Elements	Weight %
Al <sub>2</sub> O <sub>3</sub>	0.75
CaO	1.64
Cr <sub>2</sub> O <sub>3</sub>	<0.01
Fe <sub>2</sub> O <sub>3</sub>	28.72
K <sub>2</sub> O	0.19
MgO	3.96
MnO	0.85
Na <sub>2</sub> O	0.07
P <sub>2</sub> O <sub>5</sub>	0.08
SiO <sub>2</sub>	56.9
TiO <sub>2</sub>	0.01
LOI	4.96
Total	98.13%
$CO_2$	3.11%

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Table 5.Major element composition of taconite tailings from ore mined from the<br/>Laurentian Pit (Mattson, 1996).

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Trace Element	ppm
F	240
Ag .	<0.2
As	18
В	<20
Ва	20
Be	<0.5
Bi	4
Cd	<0.5
Со	15
Cr	8
Cu	7
Hg	0.035
Мо	<1
Ni	3
Pb	<2
Rb	4
Sb	<0.2
Se	<0.2
Sr	41
V	11
W	40
Zn	10

Table 6.Trace element composition of tailings from ore mined from the Laurentian Pit<br/>(Mattson, 1996). Hg analyses conducted by Frontier Geosciences.

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# Table 7.Summary of manganese source terms based on operational, field, and laboratory<br/>water chemistry measurements.

Clear Water Pool:

Data Source	N	Average [Mn] (mg/L)	Range (mg/L)
Tailings basin	11	0.01	0.001 - 0.076
Tank experiments	20	0.004	0.001 - 0.021
Mn oxidation experiments	4	0.002	0.004 - 0.009
Pierce and Tomcko, 1989	8	na	<0.01 - 22.5
Recommended Clear Pool Source Term			< 0.01

Tailings Pore Water:

Data Source	N	Average [Mn] (mg/L)	Range (mg/L)
Tailings discharge pipe	10	0.06	0.05 - 0.09
North seep at Inland	7	3.2	1.7 - 4.1
North wells at Inland	15	4.6	1.2 - 7.2
Snively Pit (USX)	6	1.3	1.0 - 1.9
Tank experiments	32	0.08	0.05 - 0.12
Process water columns	6	$0.6^{1}$	0.45 - 0.70
Rain water columns	6	0.3	0.26 - 0.34
Ground water columns	5	$0.2^{2}$	0.16 - 0.21
Recommended Pore Water Source Term			0.05 - 7

na = not applicable

<sup>1</sup> Mn levels appeared to be increasing at the end of the experiment, therefore the average from the last three data points of both columns was used here.
 <sup>2</sup> Represents an average of the last five samples (weeks 12 to 30), when Mn levels stabilized.

Paramete r	Calumet #2	Calumet #3	Nashwauk #3	Nashwauk #4	Keewatin #1	Keewatin #2	Scranton	Buhl #1	Buhl #2	Kinney #2	Mt Iron #2	Avg.	Range
 T (°C)	9	8	7	7	8	8	7	7.4	7.9	7	7.5	8	7-9
рН	7.96	8.14	6.89	7.22	7.57	7.27	7.29	6.73	6.95	7.25	7.31	7.33	6.7-8.1
Major Eler	nents (mg/L)												
Mn	0.05	0.09	0.08	0.06	0.69	0.28	0.00	0.00	0.31	0.33	0.11	0.18	0-0.7
Ca	32.7	34.3	47.6	34.7	47.7	69.6	47.7	45.8	47.3	41.3	45.3	44.9	33-70
Mg	15.0	16.0	20.2	19.1	17.3	28.5	36.1	25.2	25.5	20.6	24.5	22.5	15-36
Na	7.1	7.2	7.2	4.7	7.7	8.5	11.2	8.8	9.6	6.7	12.0	8.2	5-12
ı K	2.4	2.7	2.1	2.1	1.1	1.6	1.9	2.1	2.0	0.5	1.1	1.8	0.5-2.7
F	0.23	0.20	0.78	0.49	0.24	0.17	0.23	0.14	0.20	0.17	0.26	0.28	0.1-0.8
Cl	2.3	6.4	2.3	1.7	1.5	8.3	15.0	3.7	7.6	1.8	11.4	5.6	1.5-15
SO₄	7.8	16.8	13.3	9.5	10.5	106	80.1	41.9	35.0	22.3	35.6	34.4	8-106
HCO <sub>3</sub>	161	154	207	167	206	199	198	195	211	158	191	186	154-211
Trace Elem	nents (ug/L)												
В	106	106	27.0	15.4	46.9	68.9	18.7	28.1	16.6	31.1	44.9	46.3	15-106
As	0.7	0.7	0.4	0.3	0.3	0.2	0.2	0.1	0.2	1.9	0.5	0.5	0.1-1.9
Мо	0.72	0.66	0.13	0.05	0.16	0.26	0.13	0.01	0.04	0.28	0.18	0.24	0.01-0.7

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Table 8.Biwabik Iron Formation ground water chemistry based on analyses of eleven different wells across the Mesabi iron<br/>range. These wells were sampled on a single occasion in May, 1998.

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Source Term Situation Predicted Net Input Input from Minorca Pit Concentration (mg/L) 7 Operational maximum 39% 2.8 7 Operational maximum 28% 2.5 7 Standard reclamation 21% 1.6 7 18% Standard reclamation 1.4 7 Established forest vegetation 13% 1.1 7 12% Established forest vegetation 1.0 1 39% 0.5 Operational maximum 1 Operational maximum 28% 0.4 1 Standard reclamation 21% 0.3 1 Standard reclamation 18% 0.3 0.3 1 Established forest vegetation 13% 0.3 1 Established forest vegetation 12% 0.05 39% 0.1 Operational maximum 0.05 Operational maximum 28% 0.1 0.05 Standard reclamation 21% 0.2 0.2 0.05 Standard reclamation 18% 0.2 0.05 Established forest vegetation 13% 0.05 12% 0.2 Established forest vegetation 0.01 39% 0.1 Operational maximum 0.01 0.1 Operational maximum 28% 0.01 Standard reclamation 21% 0.1 0.01 Standard reclamation 18% 0.1 0.01 Established forest vegetation 13% 0.2 0.01 Established forest vegetation 12% 0.2

Table 9. Flow-weighted average manganese concentrations in the net inflow to the Missabe Mountain Pit will not meet drinking water quality standards, assuming the maximum tailings pore water source term from the Minorca Pit and an aquifer ground water contribution of 0.18 mg/L.

Depth (feet)	Temperature (°C)	DO (mg/L)	Alkalinity (mg/L as CaCO <sub>3</sub> )	Mn	F (mg/L)	Мо	As	В
0	1	9.3	220	5.6	0.23	0.12	0.5	18
50	4	8.6	220	0.2	0.21	0.00	0.3	19
100	4	8.1	220	2.8	0.21	0.88	1.1	11
150	4	5.7	220	0.4	0.21	0.28	0.6	5.3
200	4	nd	220	5.7	0.21	0.84	1.1	6.8
Average			220	3.0	0.21	0.42	0.7	12

Table 10.EC levels in the Missabe Mountain Pit.Concentrations are in units of ug/L<br/>unless otherwise noted.

nd = not determined

Summary of fluoride source terms based on operational, field, and laboratory Table 11. water chemistry measurements.

Data Source	N	Average	Range
	14	[F] (mg/L)	(mg/L)
Tailings discharge pipe	10	4.6	2.3 - 7.6 <sup>1</sup>
North seep at Inland	8	2.3	1.2 - 3.0
North wells at Inland	15	2.5	0.6 - 3.6
Snively Pit (USX)	6	0.2	0.16 - 0.31
Tank experiments	22	$4.2^{2}$	3.6 - 5.9
Process water columns	6	$3.0^{3}$	2.8 - 3.0
Rain water columns	6	3.2	1.7 - 4.1
Ground water columns	3	$2.2^{4}$	2.1 - 2.3
Recommended Source Term			<u>1 - 6<sup>1</sup></u>

na = not applicable

<sup>1</sup> Clear water pool contribution expected to be no more than 6 mg/L.
<sup>2</sup> Fluoride levels stabilized after the first sixteen weeks of the experiment.
<sup>3</sup> Fluoride levels appeared to be decreasing at the end of the experiment, therefore, the average of the last three samples from both columns was used here.
<sup>4</sup> Fluoride levels appeared to be increasing at the end of the experiment, therefore, the fluoride levels appeared to be increasing at the end of the experiment, therefore, the fluoride levels appeared to be increasing at the end of the experiment, therefore, the fluoride levels appeared to be increasing at the end of the experiment, therefore, the fluoride levels appeared to be increasing at the end of the experiment, therefore, the fluoride levels appeared to be increasing at the end of the experiment, therefore, the fluoride levels appeared to be increasing at the end of the experiment, therefore, the fluoride levels appeared to be increasing at the end of the experiment.

average of the last three samples (weeks 20, 25, and 30) was used here.

Source Term	Situation	Input from Minorca Pit	Predicted Net Input Concentration (mg/L)
6	Operational maximum	39%	2.5
6	Operational maximum	28%	1.9
6	Standard reclamation	21%	1.5
6	Standard reclamation	18%	1.3
. 6	Established forest vegetation	13%	1.0
6	Established forest vegetation	12%	1.0
4	Operational maximum	39%	1.7
4	Operational maximum	28%	1.3
4	Standard reclamation	21%	1.1
4	Standard reclamation	18%	0.9
4	Established forest vegetation	13%	0.8
4	Established forest vegetation	12%	0.7
3	Operational maximum	39%	1.3
3	Operational maximum	28%	1.0
3	Standard reclamation	21%	0.9
3	Standard reclamation	18%	0.7
3	Established forest vegetation	13%	0.6
3	Established forest vegetation	12%	0.6
1	Operational maximum	39%	0.6
1	Operational maximum	28%	0.5
1	Standard reclamation	21%	0.4
1	Standard reclamation	18%	0.4
1	Established forest vegetation	13%	0.4
1	Established forest vegetation	12%	0.4

Table 12.Flow-weighted average fluoride concentrations in net inputs to the Missabe<br/>Mountain Pit, assuming an aquifer ground water contribution of 0.28 mg/L.

Table 13.Summary of molybdenum source terms based on operational, field, and<br/>laboratory water chemistry measurements.

Data Source	N	Average [Mo] (ug/L)	Range (ug/L)
Tailings discharge pipe	10	110	68 - 157 <sup>1</sup>
North seep at Inland	8	7.1	1.5 - 13.7
North wells at Inland	15	6.4	3.0 - 8.4
Snively Pit (USX)	6	0.6	0.1 - 1.5
Tank experiments	32	24	13 - 45
Process water columns	6	$24^{2}$	15 - 34
Rain water column	6	11 <sup>3</sup>	7.1 - 19
Ground water column	3	9.4 <sup>4</sup>	8.7 - 9.9
Recommended Source Term			<u>1 - 130<sup>1</sup></u>

na = not applicable

<sup>1</sup> Clear water pool contribution expected to be no more than 130 ug/L.

 $^{2}$  Mo levels decreased throughout the experiment, therefore, the average of the last three samples from the two columns were used here.

<sup>3</sup> Mo concentrations appeared to be increasing at the end of the experiment, however, all six values were used.

<sup>4</sup> Mo concentrations appeared to be increasing at the end of the experiment, therefore, an average of the last three samples (weeks 20, 25, and 30) was used here.

Source Term	Situation	Input from Minorca Pit	Predicted Net Input Concentration (ug/L)
130	Operational maximum	39%	51
130	Operational maximum	28%	37
130	Standard reclamation	21%	28
130	Standard reclamation	18%	24
· 130	Established forest vegetation	13%	17
130	Established forest vegetation	12%	16
75	Operational maximum	39%	29
75	Operational maximum	28%	21
75	Standard reclamation	21%	16
. 75	Standard reclamation	18%	14
75	Established forest vegetation	13%	10
75	Established forest vegetation	12%	9
45	Operational maximum	39%	18
45	Operational maximum	28%	13
45	Standard reclamation	21%	10
45	Standard reclamation	18%	8
45	Established forest vegetation	13%	6
45	Established forest vegetation	12%	6
15	Operational maximum	39%	6
15	Operational maximum	28%	4
15	Standard reclamation	21%	3
15	Standard reclamation	18%	3
15	Established forest vegetation	13%	2
15	Established forest vegetation	12%	2

Table 14.Flow-weighted average molybdenum concentration in net inputs to the Missabe<br/>Mountain Pit, assuming an aquifer ground water contribution of 0.4 ug/L.

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Data Source	N	Average [As] (ug/L)	Range (ug/L)
Tailings discharge pipe	10	3.6	1.9 - 5.5
North seep at Inland	8	1.1	0.2 - 2.1
North wells at Inland	15	4.1	1.5 - 5.6 <sup>2</sup>
Snively Pit (USX)	6	1.2	0.1 - 4.8
Tank experiments	32	2.4	0.6 - 4.2
Process water columns	10	3.7 <sup>1</sup>	2.1 - 5.4
Rain water columns	6	4.9	2.6 - 7.2
Ground water columns	8	2.5	1.2 - 3.7
Recommended Source Term	na		0.1 - 7

Summary of arsenic source terms based on operational, field, and laboratory Table 15. water chemistry measurements.

na = not applicable<sup>1</sup> Arsenic concentrations stabilized after six to ten weeks. <sup>2</sup> Excluding statistical outliers (Systat V8).

Source Term	Situation	Input from Minorca Pit	Predicted Net Input Concentration (ug/L)
7	Operational maximum	39%	3.0
7	Operational maximum	28%	2.3
7	Standard reclamation	21%	1.9
7	Standard reclamation	18%	1.7
. 7	Established forest vegetation	13%	1.3
7 \	Established forest vegetation	12%	1.3
3	Operational maximum	39%	1.5
3	Operational maximum	28%	1.2
3	Standard reclamation	21%	1.0
3	Standard reclamation	18%	1.0
3	Established forest vegetation	13%	0.8
3	Established forest vegetation	12%	0.8
0.1	Operational maximum	39%	0.4
0.1	Operational maximum	28%	0.4
0.1	Standard reclamation	21%	0.4
0.1	Standard reclamation	° 18%	0.4
0.1	Established forest vegetation	13%	0.5
0.1	Established forest vegetation	12%	0.5

Table 16.Flow-weighted average arsenic concentration in net inputs to the Missabe<br/>Mountain Pit, assuming an aquifer ground water contribution of 0.5 ug/L.

Data Source	N	Average [B]	Range
	19	(ug/L)	(ug/L)
Tailings discharge pipe	10	121	66 - 212
North seep at Inland	8	52	34 - 76
North wells at Inland	15	47	27 - 77
Snively Pit (USX)	6	32	14 - 45
Tank experiments	32	97	52 - 169
Process water columns	18	213	135 - 290
Rain water column	6	145	57 - 281
Ground water column	1	na	$256^{1}$
Recommended Source Term	na		30 - 300

Summary of boron source terms based on operational, field, and laboratory water Table 17. chemistry measurements.

na = not applicable <sup>1</sup> B concentrations appeared to be increasing at a rapid rate at the end of the experiment, therefore, only the last sample (week 30) is included here.

Table 18.	Flow-weighted	average	boron	concentration	in	net	inputs	to	the Missabe
	Mountain Pit, as	ssuming a	n aquif	fer ground wate	r co	ontril	oution o	of 40	5 ug/L.

Source Term	Situation	Input from Minorca Pit	Predicted Net Input Concentration (ug/L)
300	Operational maximum	39%	145
300	Operational maximum	28%	112
300	Standard reclamation	. 21%	99
300	Standard reclamation	18%	92
300	Established forest vegetation	13%	79
300	Established forest vegetation	12%	76
30	Operational maximum	39%	40
30	Operational maximum	28%	42
30	Standard reclamation	21%	43
30	Standard reclamation	18%	43
30	Established forest vegetation	13%	44
30	Established forest vegetation		44

## Appendix 1

## Summary of Data Collected

- Table A1.1.
   Identification of the Five Elements of Concern
- Table A1.2.
   Summary of operational field measurement made during this study.
- Table A1.3.
   Summary of field and laboratory water quality samples collected during this study.

Table A1.1.The five elements of concern were identified as elements that approached or<br/>exceeded drinking water quality standards in water samples collected from at<br/>least one of the participating taconite operations. Arsenic was included because<br/>the US EPA is expected to lower the drinking water standard in 2001.

Element of Concern	National	US Steel- Minntac	Inland	LTV
Mn	Х	х	х	x
F			х	х
As			,	
Мо	х		х	х
B				X

Taconite Operation	Sample Location	Number of Samples	Notes
	Plant Discharge	11	
	Tailings Basin	11	
National	Well #12	6	not sampled until 10/97
	Well #14	3	only sampled between 10/97 and 4/98
	Plant Discharge	10	operation closed 4/97
	Tailings Basin	11	
Inland	Well #5 "Deep Well"	7	not installed prior to initial visit, frozen on three occasions
	Well #6 "Shallow Well"	9	not installed prior to initial visit, frozen on one occasion
	North Seep	8	not sampled 9/96, frozen on two occasions
	Interior Dike Seep	1	this seep was not identified until the end of this study
	Plant Discharge	11	
LTV	Tailings Basin	11	
	Seep	11	
	Snively Pit Well #1	6	
USX	East Pit Sump #2	6	
	East Pit Sump #10	1	

 Table A1.2.
 Summary of operational water quality samples collected during this study.

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Taconite Operation	Exp	periment	Number of Samples	Notes
		Process Water	18	samples from two separate columns
National	Columns	Rain Water	9	one column from process water expt.
		Ground Water	10	one column from process water expt.
·		Process Water	18	samples from two separate columns
	Columna	Rain Water	9	one column from process water expt.
	Columns	Ground Water	10	one column from process water expt.
		Small-scale	18	Inland tailings only
Inland	Tanks	Surface Water	26	two separate tank experiments
		Pore Water	32	two separate tank experiments
	Batch	Well #6 and Missabe Mountain Pit Waters	65+	manganese only, still in progress
		Process Water	18	samples from two separate columns
	Columns	Rain Water	9	one column from process water expt.
LTV		Ground Water	10	one column from process water expt.
		Surface Water	32	two separate tank experiments
	Tanks	Pore Water	31	two separate tank experiments

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Table A1.3.Summary water quality samples collected from field and laboratory experiments<br/>during this study.

## Appendix 2

## Data and Calculations Used in to Evaluate

## EC Source Terms in the Minorca Pit

Table A2.1.	Summary of operational measurements and field and laboratory experiments used
	to determine Minorca Pit source terms.
Table A2.2.	Method #1 used to calculate EC levels in the Minorca Pit clear water pool
	assuming complete mixing.
Table A2.3.	Method #2 used to calculate EC levels in the Minorca Pit clear water pool
	assuming a plug-flow system.
Table A2.4.	Calculated water balance for the Minorca Pit clear water pool, based on a ten year
	preliminary tailings deposition plan developed by Indeco (1999).
Table A2.5.	Estimation of EC concentrations in the Minorca Pit clear water pool.
Table A2.6.	Estimation of MnCO <sub>3</sub> content in Inland's tailings.
Table A2.7.	Estimation of molybdenum release from grinding media to process waters.

Taconite Operation	Sample Type		Sample Location	Number of Samples <sup>1</sup>
			Plant Discharges	10
			Tailings Basin Clear Water Pool	11
	OnemailMa		Well #5 "Deep Well"	7
	Operational Measurement		Well #6 "Shallow Well"	9
Inland			North Seep	8
munu			Interior Dike Seep	1
	Experimental	Columns	Process Water	18
			Rain Water	9
			Ground Water	10
			Small-scale	18
		Tanks	Pore Water	32
USX	Operational Me	asurement	Snively Pit Well #1	6

Table A2.1.Summary of operational measurements and field and laboratory experiments used<br/>to determine Minorca Pit source terms.

<sup>1</sup> Concentrations of some elements had not reached an equilibrium value at the end of some experiments, therefore many of these samples were discarded as source terms. See individual elements for details.

Table A2.2.Method used to calculate EC levels in the Minorca Pit clear water pool during<br/>tailings deposition into the pit. This method assumes complete mixing of stored<br/>and input waters prior to removal of any water for any given time period.

#### Step 1: General Equation

$$M_{net} = M_{stored} + \sum M_{input} - \sum M_{output}$$
(A2.2.1)

where,

"Net" refers to the mass present in the Minorca Pit at the end of a time period;

"Stored" refers to the mass present in the Minorca Pit at the beginning of a time period; "Input" refers to waters entering the Minorca Pit; and

"Output" refers to waters exiting the Minorca Pit.

#### Step 2: Adapt Equation A2.2.1 to the Minorca Pit situation

$$M_{mp,t+1} = M_{mp,t} + M_{discharge} + M_{netp} + M_{gw,in} - M_{reclaim} - M_{sc} - M_{gw,out}$$
(A2.2.2)

where, M = mass and the subscripts indicate:

mp,t+1 = Minorca Pit at the end of a time period,

mp,t = Minorca Pit at the beginning of a time period,

discharge = waters discharged from the taconite processing plant,

netp = net precipitation

gw,in = ground water flow into the pit,

reclaim = clear pool water reclaimed for re-use in the plant,

sc = water pumped from the clear pool to Sauntry Creek, and

gw,out = ground water flow out of the pit.

#### Step 3: Convert mass equation (A2.2.2) into terms of concentration (C) and volume (V)

$$C_{mp,t+1} V_{mp,t+1} = C_{mp,t} V_{mp,t} + C_{discharge} V_{discharge} + C_{netp} V_{netp} + C_{gw,in} V_{gw,in} - C_{reclaim} V_{reclaim} - C_{sc} V_{sc} - C_{gw,out} V_{gw,out}$$
(A2.2.3)

#### Step 4: Assume pure water for precipitation/evaporation (i.e. $C_{netp} = 0$ )

$$C_{mp,t+1} V_{mp,t+1} = C_{mp,t} V_{mp,t} + C_{discharge} V_{discharge} + C_{gw,in} V_{gw,in} - C_{reclaim} V_{reclaim} - C_{sc} V_{sc} - C_{gw,out} V_{gw,out}$$
(A2.2.4)

#### Step 5: Since the system is well-mixed (i.e. $C_{output} = C_{reclaim} = C_{sc} = C_{gw,out} = C_{mp,t+1}$ ), Equation A2.2.4 can be rewritten as

$$C_{mp,t+1} V_{mp,t+1} = C_{mp,t} V_{mp,t} + C_{discharge} V_{discharge} + C_{gw,in} V_{gw,in} - C_{mp,t+1} V_{reclaim} - C_{mp,t+1} V_{sc} - C_{mp,t+1} V_{gw,out}$$
(A2.2.5)

Step 6: Collecting all of the  $C_{mp,t+1}$  terms on the left side, and dividing, we get

 $C_{mp,t+1} = (C_{mp,t}V_{mp,t} + C_{discharge}V_{discharge} + C_{gw,in}V_{gw,in})/(V_{mp,t+1} + V_{reclaim} + V_{sc} + V_{gw,out})$ (A2.2.6)

• Equation A2.2.6 can be used to calculate the impact that elevated concentrations in the water discharged from the plant has on the chemistry of the clear water pool. This calculation was completed for ten-one year time periods, or over the ten year period of tailings disposal in the Minorca Pit. The source of the values used for each of the above terms are summarized in the tables below.

Concentration Terms	Data Source	Notes
$C_{mp,t}$	HDR Engineering, 1997	for $t = 0$ (before deposition begins)
$C_{discharge}$	Berndt and Lapakko, 1997a; Berndt et al., 1998, 1999	
C <sub>gw,in</sub>	Berndt et al., 1998	Biwabik aquifer wells
Volume Terms	Data Source	Notes
$V_{mp,t}$	HDR Engineering, 1997	assumes water elevation of 1400'
$V_{discharge}$	Noramco, 1997	assumes 65% of the discharged water reaches the clear water pool
$V_{gw,in}$	Adams, 1998; Indeco, 1999	assumed maximum ground water inflow at year zero, decreasing (linear) to zero at year five
$V_{mp,t+1}$	Indeco, 1999	reported values for deposition years 3, 5, 8, and 10
	MN DNR calculation	interpolated for deposition years 1, 2, 4, 6, 7, and 9
$V_{reclaim}$	MN DNR calculation	calculated by difference
V <sub>sc</sub>	Indeco, 1999	maintained at 1419 gpm
V <sub>gw,out</sub>	Adams, 1998	assumed no net ground water flow at year five, increasing (linear) to maximum outflow for years 8 through 10

Table A2.3. Method used to calculate EC levels in the Minorca Pit clear water pool during tailings deposition into the pit. This method assumes plug flow of stored water exiting the pit followed by a plug of mixed input waters moving through the pit during any given time period.

#### Step 1: Calculate the mass stored in the clear water pool volume

$$M_{\text{stored}} = C_{\text{stored}} V_{\text{stored}}$$
(A2.3.1)

#### Step 2: Calculate the average input concentration

$$C_{avg,in} = \sum M_{in} / \sum V_{in}$$
(A2.3.2)

This value will also be the concentration of water stored in the pit for the next time period. That is  $C_{avg,in,t=0} = C_{stored,t=1}$ .

# Step 3: Calculate the volume of water that exits the pit at the average input concentration

$$V_{avg.out} = V_{out.total} - V_{stored}$$
(A2.3.3)

## Step 4: Calculate the mass that exits the pit in the volume of water exiting at the average input concentration

$$\mathbf{M}_{\text{avg,out}} = \mathbf{C}_{\text{avg,in}} \, \mathbf{V}_{\text{avg,out}} \tag{A2.3.4}$$

#### **Step 5:** Calculate the total mass exiting the pit

$$\mathbf{M}_{\text{total,out}} = \mathbf{M}_{\text{avg,out}} + \mathbf{M}_{\text{stored}}$$
(A2.3.5)

Step 6: Calculate the average concentration of all outputs, including the initial plug of stored water exiting the pit and the subsequent plug of averaged input water exiting the pit

$$C_{avg,out} = M_{total,out} / \sum V_{out}$$
(A2.3.6)

				· · ·							
						DEPOSIT	ION YEAR				
		1	2	3	4.	5	6	7	8	9	10
NET STORAGE	Minorca Pit	890	910	900	0	0	180	180	180	470	460
INPUTS	Plant Discharges	1900	1900	1900	1900	1900	1900	1900	1900	1900	1900
	Net Precip.	440 - 660	440 - 660	440 - 660	440 - 660	440 - 660	440 - 660	440 - 660	440 - 660	440 - 660	440 - 660
	Ground Water	270-780	200-590	140-390	70-200	0	0	0	0	0	0
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OUTPUTS .	Sauntry Creek	1400	1400	1400	1400	1400	1400	1400	1400	1400	1400
	Ground Water	0	0	0	0	0	280	560	840	840	840
	Plant Reclaim	2320- 2610	2270- 2440	2200- 2230	1140- 1230	940-1160	400-1060	560-780	280-510	570-790	560-780

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Table A2.4.Estimated water balance for the Minorca Pit clear water pool, based on a ten year preliminary tailings deposition plan<br/>developed by Indeco (1999). Flow rates are reported in gpm.

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Table A2.5.EC concentrations in the Minorca Pit clear water pool between the fifth and eighth years of tailings deposition are expected<br/>to be elevated. This is the time period during which the clear water pool is expected to dominate the chemistry of ground<br/>waters exiting the Minorca Pit. Four calculations were conducted using maximum observed EC concentrations in plant<br/>discharges, two hypothetical systems, and two estimated water balances for the Minorca Pit.

Element of Concern	Discharge	Assumed System	Source of Hydrologic Data	Concentration Between
	Concentration			Deposition Years 5 and 8
Mn (mg/L)	0.1	well-mixed	Indeco, 1999	0.08
- -			Adams, 1998	0.07
		plug flow	Indeco, 1999	0.08
			Adams, 1998	0.07
F (mg/L)	7.6	well-mixed	Indeco, 1999	6.2
			Adams, 1998	5.6
		plug flow	Indeco, 1999	6.2
			Adams, 1998	5.6
Mo (ug/L)	160	well-mixed	Indeco, 1999	130
			Adams, 1998	119
		plug flow	Indeco, 1999	130
· .			Adams, 1998 .	119
As (ug/L)	5.5	well-mixed	Indeco, 1999	4.5
			Adams, 1998	4.1
		plug flow	Indeco, 1999	4.5
			Adams, 1998	4.1
B (ug/L)	210	well-mixed	Indeco, 1999	171
			Adams, 1998	156
		plug flow	Indeco, 1999	171
			Adams, 1998	156

Table A2.6. Estimation of  $MnCO_3$  content in Inland's tailings based on chemical and mineralogical analyses by Mattson (1996).

Data from Mattson (1996):

Carbonates	Weight %	Fe Distribution (wt%)	Mn Distribution (wt%)
Siderite	7	12	23
Ankerite	4	2	4

 $Fe_2O_3 = 28.72 \text{ wt\%}$ MnO = 0.85 wt%

Calculate weight % of Fe and Mn:

 $(28.72g \text{ Fe}_2\text{O}_3/100g \text{ rock})(1\text{mol Fe}_2\text{O}_3/160g \text{ Fe}_2\text{O}_3)(2\text{mol Fe}/1\text{mol Fe}_2\text{O}_3)(1\text{mol Fe}/56g \text{ Fe}) = 20.10 \text{ wt\% Fe}$ (0.85g MnO/100g rock)(1mol MnO/71g MnO)(1mol Mn/1mol MnO)(55g Mn/1mol Mn) = 0.66 wt% Mn

#### SIDERITE

Calculate weight % of Fe and Mn associated with siderite:

 $(20.10g \text{ Fe}/100g \text{ rock})(0.12g \text{ Fe}_{sid}/1g \text{ Fe}) = 2.41 \text{ wt\%}$  Fe associated with siderite

 $(0.66g \text{ Mn}/100g \text{ rock})(0.23g \text{ Mn}_{sid}/1g \text{ Mn}) = 0.15 \text{ wt}\% \text{ Mn}$  associated with siderite

Calculate molar ratio of Fe and Mn in siderite:

 $(2.41g \text{ Fe}_{sid}/100g \text{ rock})(1\text{ mol Fe}/56g \text{ Fe})(100g \text{ rock}/7g \text{ sid})(116g \text{ sid}/1\text{ mol sid}) = 0.71 \text{ mol Fe}/\text{mol siderite}$ 

 $(0.15g \text{ Mn}_{\text{sid}}/100g \text{ rock})(1\text{mol Mn}/55g \text{ Mn})(100g \text{ rock}/7g \text{ sid})(116g \text{ sid}/1\text{mol sid}) = 0.045\text{mol Mn}/\text{mol siderite}$ 

Approximate molecular formula of siderite in Inland's tailings:

Fe<sub>0.71</sub>(Ca,Mg)<sub>0.24</sub> Mn<sub>0.05</sub> CO<sub>3</sub>

Estimate MnCO<sub>3</sub> in siderite:

 $(0.05 \text{mol MnCO}_3/\text{mol sid})(115 \text{g MnCO}_3/\text{mol MnCO}_3)(1 \text{mol sid}/116 \text{g sid})(7 \text{g sid}/100 \text{g rock}) = 0.35 \text{ wt}\%$  as MnCO<sub>3</sub>

#### ANKERITE

Calculate weight % of Fe and Mn associated with ankerite:

 $(20.10g \text{ Fe}/100g \text{ rock})(0.02g \text{ Fe}_{ank}/1g \text{ Fe}) = 0.40 \text{ wt\%}$  Fe associated with ankerite

(0.66g Mn/100g rock)(0.04g Mn\_{ank}/1g Mn) = 0.03 wt\% Mn associated with ankerite

Calculate molar ratio of Fe and Mn in ankerite:

 $(0.40g \text{ Fe}_{ank}/100g \text{ rock})(1 \text{ mol Fe}/56g \text{ Fe})(100g \text{ rock}/4g \text{ ank})(216g \text{ ank}/1 \text{ mol ank}) = 0.39 \text{ mol Fe}/\text{mol ankerite}$ 

 $(0.03g Mn_{ank}/100g rock)(1mol Mn/55g Mn)(100g rock/4g ank)(216g ank/1mol ank) = 0.03mol Mn/mol ankerite$ 

Approximate molecular formula of ankerite in Inland's tailings:

 $(Ca, Mg)_{1.58} Fe_{0.39} Mn_{0.03} (CO_3)_2$ 

Estimate MnCO<sub>3</sub> in ankerite:

 $(0.03 \text{mol } MnCO_3/\text{mol } ank)(115 \text{g } MnCO_3/\text{mol } MnCO_3)(1 \text{mol } ank/216 \text{g } ank)(4 \text{g } ank/100 \text{g } \text{rock}) \\ = 0.06 \text{ wt } \% \text{ as } MnCO_3 \\$ 

Carbonate	MnCO <sub>3</sub> (wt% of rock)
Siderite	0.35
Ankerite	0.06
Total	0.41

#### TOTAL ESTIMATED MnCO3 IN INLAND'S TAILINGS

Estimation of molybdenum release from grinding media to process waters. Table A2.7.

Estimates from Ron Visness (formerly MN DNR): Mo content of the grinding media = 0.02%Grinding media attrition rate =  $3 \text{ lb/T}_{ore}$ 

Data from Dave Johnson, US Steel-Minntac:

Mo content of the grinding media = 0.01 - 0.05%Grinding media attrition rate =  $0.5 \text{ lb/T}_{ore}$ Ore feed =  $49 \times 10^6 \text{ T/yr}$ 

Mo Content (%)	Attrition Rate (lb/T)	Mo Release (T/yr)
0.01	0.5	1.2
0.05	0.5	6.1

Data from Gus Josephson, Ispat Inland:

Mo content of the grinding media = 0.02 - 0.035%Grinding media attrition rate =  $2.35 \text{ lb/T}_{ore}$ 

#### Data from Inland, Annual Report to the MN DNR, 1997

Tailings discharged in  $1997 = 7.3 \times 10^6 \text{ T/yr}$ assuming 2.2  $T_{tails}$  for every 1  $T_{pellets}$ , 3.3 x 10<sup>6</sup>  $T_{pellets}$  produced in 1997 total ore processed = 7.3 + 3.3 = 10.6 million  $T_{ore}$ 

Mo Content (%)	Attrition Rate (lb/T)	Mo Release (T/yr)
0.02	2.35	2.5
0.035	2.35	4.4

## Appendix 3

## Data and Calculations Used to Evaluate Refined EC Transport Terms Between the Minorca and Missabe Mountain Pits

Table A3.1. Supporting data for estimates of maximum manganese levels in the Biwabik aquifer based on the solubility of rhodochrosite, MnCO<sub>3</sub>.
Figure A3.1. Adsorption model depicting behavior of fluoride, molybdenum, and arsenic in the presence of iron oxide minerals.

Table A3.1.Supporting data for Figure A3.1.Biwabik Formation waters typically have a<br/> $pCO_2 = 0.01$  atm and an alkalinity = 3mM.

$$MnCO_3 + CO_2(g) + H_2O = Mn^{++} + 2HCO_3^{--}$$

where,  $CO_2$  and  $H_2O$  represent the acid source,  $H^+$ , in reaction 1.

T (°C)	Log K	Alkalinity (M)	pCO <sub>2</sub>	Mn (M)	Mn (mg/L)
0	-7.63	0.003	0.01	2.62e-05	1.44
8	-7.76	0.003	0.1	1.92e-04	10.55
8	-7.76	0.003	0.05	9.60e-05	5.28
8	-7.76	0.003	0.025	4.80e-05	2.64
8	-7.76	0.003	0.0125	2.40e-05	1.32
8	-7.76	0.003	0.00625	1.20e-05	0.66
8	-7.76	0.003	0.003125	6.00e-06	0.33
8	-7.76	0.003	0.0015625	3.00e-06	0.16
8	-7.76	0.003	0.00078125	1.50e-06	0.08
8	-7.76	0.003	0.0001	1.92e-07	0.01
8	-7.76	0.004	0.1	1.08e-04	5.94
8	-7.76	0.004	0.05	5.40e-05	2.97
8	-7.76	0.004	0.025	2.70e-05	1.48
8	-7.76	0.004	0.0125	1.35e-05	0.74
8	-7.76	0.004	0.00625	6.75e-06	0.37
8	-7.76	0.004	0.003125	3.38e-06	0.19
8	-7.76	0.004	0.0015625	1.69e-06	0.09
8	-7.76	0.004	0.00078125	8.44e-07	0.05
8	-7.76	0.004	0.0001	1.08e-07	0.01
			٩		
8	-7.76	0.005	0.1	6.92e-05	3.80
8	-7.76	0.005	0.05	3.46e-05	1.90
8	-7.76	0.005	0.025	1.73e-05	0.95
8	-7.76	0.005	0.0125	8.64e-06	0.47
8	-7.76	0.005	0.00625	4.32e-06	0.24
8	-7.76	0.005	0.003125	2.16e-06	0.12
8	-7.76	0.005	0.0015625	1.08e-06	0.06
8	-7.76	0.005	0.00078125	5.40e-07	0.03
8	-7.76	0.005	0.0001	6.92e-08	0.00



Figure A3.1 Geochemical adsorption model depicting behavior of adsorbing species in average tailings basin water reacting with minnesotaite, siderite, cristobalite, rhodochrosite, and 60 m<sup>2</sup> of hematite per liter of solution (Berndt, 1998). The reduction in pH favors adsorption of arsenic and molybdenum.

## Appendix 4

Data and Calculations Used in to Evaluate Flow-weighted Average Input Concentration Terms to the Missabe Mountain Pit

Table A4.1.Summary of hydrologic data sources used by Adams (1998)

Table A4.1.Summary of hydrologic data sources used by Adams (1998) to determine the potential contribution of Minorca Pit waters<br/>to the Missabe Mountain Pit.

Pit	Component	Flow Rate (gpm)	Source	Notes
,		570-700	monthly pumping records for winter 1989-90	pit was pumped dry "pit empty", no precipitation input
	ground water inflow	400-450	Theim Equilibrium Equation	"pit empty", experimental application to mine pits
		338	water level records from 11/15/97 to 12/18/97	present water level = 1400 ft M.S.L., no precipitation input
		335-600	avg. annual net inflow - ground water inflow	
Minorca	net precip- derived inflow	619-782	elevation maps (1996), Baker (1979), Antonson	"pit empty"
		544-692	(199?), Perry and Brooks (1993)	"present"
	avg. annual net inflow	1019-1232	calculated value	"pit empty"
		882-1030	calculated value	"present"
,		701-839		"full development"
	ground water outflow	301-439	USGS (1991), elevation maps (1996), Noramco (1997)	"reclamation-grasses"
		136-274		"reclamation-trees"
	avg. annual net inflow	2135	HDR Engineering (1997)	assuming no input from the Minorca Pit
Missabe Mountain		701-839		"full development"
	Minorca inflow	301-439	USGS (1991), elevation maps (1996), Noramco (1997)	"reclamation-grasses"
		136-274	· · · · · · · · · · · · · · · · · · ·	"reclamation-trees"
## Appendix 5

## Data and Calculations Used to Evaluate Dilution

### Within the Missabe Mountain Pit

Table A5.1.	Summary of operational measurements and field and laboratory experiments used to determine EC concentrations in the Missabe Mountain Pit.
Table A5.2.	Method used to calculate EC levels in the Missabe Mountain Pit after receiving impacted waters from the Minorca pit.
Table A5.3.	Summary of approaches used to estimate maximum impact on manganese levels in the Missabe Mountain Pit.
Table A5.4.	Manganese concentrations in the Missabe Mountain Pit, are expected to be less than 0.01 mg/L.
Table A5.5.	Summary of approaches used to estimate maximum impact on fluoride levels in the Missabe Mountain Pit.
Table A5.6.	Summary of approaches used to estimate maximum impact on molybdenum levels in the Missabe Mountain Pit.
Table A5.7.	Summary of approaches used to estimate maximum impact on arsenic levels in the Missabe Mountain Pit.
Table A5.8.	Summary of approaches used to estimate maximum impact on boron levels in the Missabe Mountain Pit.
Table A5.9.	Summary of EC concentrations along the flow path from the Minorca Pit to the Missabe Mountain Pit.

Table A5.1.Summary of operational measurements and field and laboratory experiments used<br/>to determine EC concentrations in the Missabe Mountain Pit.

Operation	Sample Type	Sample Location	Number of Samples	Notes
Virginia Public Utility	Operational	Missabe Mountain Pit	5	taken at 50' intervals to 200'
	Operational	Plant Discharge	10	operation closed during 4/97
Inland		Tailings Basin	11	
	Field	Tank Experiments	26	surface waters
	Laboratory	Batch Experiments	65+	manganese only, still in progress

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Table A5.2. Method used to calculate EC levels in the Missabe Mountain Pit after receiving impacted waters from the Minorca pit. This method assumes complete mixing of stored and input waters prior to removal of any water for any given time period.

#### Step 1: General Equation

$$M_{net} = M_{stored} + \sum M_{input} - \sum M_{output}$$
(A5.2.1)

where,

"Net" refers to the mass present in the Minorca Pit at the end of a time period; "Stored" refers to the mass present in the Minorca Pit at the beginning of a time period; "Input" refers to waters entering the Minorca Pit; and "Output" refers to waters exiting the Minorca Pit.

### Step 2: Adapt Equation A5.2.1 to the Missabe Mountain Pit situation

$$M_{mmnt+1} = M_{mnt} + M_{mn} + M_{hetn} + M_{hiwabik} - M_{virginia}$$
(A5.2.2)

where, M = mass and the subscripts indicate:

mmp,t+1 = Missabe Mountain Pit at the end of a time period, mmp,t = Missabe Mountain Pit at the beginning of a time period, mp = ground water from the Minorca Pit, netp = net precipitation biwabik = ground water from the Biwabik aquifer, and virginia = water pumped from the pit for use by the city of Virginia.

#### Step 3: Convert mass equation (A5.2.2) into terms of concentration (C) and volume (V)

$$C_{mmp,t+1}V_{mmp,t+1} = C_{mmp,t}V_{mmp,t} + C_{mp,t}V_{mp,t} + C_{netp}V_{netp} + C_{biwabik}V_{biwabik} - C_{virginia}V_{drgmar}^{A5} 2.3)$$

#### Step 4: Assume pure water for precipitation/evaporation (i.e. $C_{netp} = 0$ )

$$C_{mmp,t+1}V_{mmp,t+1} = C_{mmp,t}V_{mmp,t} + C_{mp,t}V_{mp,t} + C_{biwabik}V_{biwabik} - C_{virginia}V_{virginia}$$
(A5.2.4)

# Step 5: Since the system is well-mixed (i.e. $C_{virginia} = C_{mmp,t+1}$ ), Equation A5.2.4 can be rewritten as

$$C_{mmp,t+1} V_{mmp,t+1} = C_{mmp,t} V_{mmp,t} + C_{mp,t} V_{mp,t} + C_{biwabik} V_{biwabik} - C_{mmp,t+1} V_{virginia}$$
(A5.2.5)

#### Step 6: Collecting all of the C<sub>mmp,t+1</sub> terms on the left side, and dividing, we get

$$C_{mp,t+1} = (C_{mmp,t}V_{mmp,t} + C_{mp,t}V_{mp,t} + C_{biwabik}V_{biwabik})/(V_{mmp,t+1} + V_{virginia})$$
(A5.2.6)

		NO	OUTFLOW FR	OM MINORCA PIT		
	Operations within the Mino	orca Pit		Missabe Mt Pit Cor	centration Estimates (m	g/L)
Depositional Time Period (Years)	from Minorca (deposition year)	Reclamation Conditions	Minorca Source Term	Minorca Contribution to Missabe Net Input	Max. Net Input Conc.	Max. Estimated Conc. in Missabe During This Time Period
0-4	5-10	none	7	0%	0.003 (background)	0.0
0-4	5-10	none	7	0%	0.0	0.0
0-4	5-10	none	1	0%	0.0	0.0
0-4	5-10	none	1	0%	0.0	0.0
0-4	5-10	none	0.05	0%	0.0	0.0
0-4	5-10	none	0.05	0%	0.0	0.0
0-4	8-10	none	7	0%	0.0	0.0
0-4	8-10	none	7	0%	0.0	0.0
0-4	8-10	none	1	0%	0.0	0.0
0-4	8-10	none		0%	0.0	0.0
0-4	8-10	none	0.05	0%	0.0	0.0
	0-10	none	0.05	0.0		0.0
		MINORCA OUTF	LOW DOMINA	ATED BY CLEAR WATER	POOL	
5-8	5-10	none	7.	39%	2.8	1.4
5-8	5-10	none		28%	2.5	1.2
5-8 5-9	5-10	none		39% 29 <i>m</i>	0.5	0.2
2-8 5 9	5-10	none	0.05	28%	0.4	0.2
5-8 5 9	5-10	none	0.05	39% 28 <i>m</i>	0.1	0.1
58	5-10	none	0.03	28%	0.1	0.1
5-8	8-10	none	7 .	29%	2.0	0.8
5-8	8-10	none	í í	30%	0.5	0.7
5-8	8-10	none	l î	28%	0.4	0.2
5-8	8-10	none	0.05	39%	0.1	0.1
5-8	8-10	none	0.05	28%	0.1	0.1
		MINORCA OUTFL	OW DOMINA	TED BY TAILINGS PORE	WATER	
8-10	5-10	none	7	39%	2.8	1.7
8-10	5-10	none	7	28%	2.5	1.4
8-10	5-10	none		39%	0.5	0.3
8-10	5-10	none	0.05	28%	0.4	0.3
8-10	5.10	none	0.05	39% 28%	0.1	0.1
11-40	5-10	arassy vegetation	7	28%	16	1.7
11-40	5-10	grassy vegetation	7	18%	1.0	1.7
11-40	5-10	grassy vegetation	l í	° 21%	0.3	0.3
11-40	5-10	grassy vegetation	i	18%	0.3	0.3
11-40	5-10	grassy vegetation	0.05	21%	0.2	0.1
11-40	5-10	grassy vegetation	0.05	18%	0.2	0.1
41-50+	5-10	forest vegetation	7	13%	1.1	1.6
41-50+	5-10	forest vegetation	7	12%	1.0	1.4
41-50+	5-10	forest vegetation	1	13%	0.3	0.3
41-50+	5-10	forest vegetation	1	12%	0.3	0.3
41-50+	5-10	forest vegetation	0.05	13%	0.2	0.2
41-50+	5-10	forest vegetation	0.05	12%	0.2	0.2
8-10	8-10	none		39%	2.8	1.3
8-10	8-10	none		28%	2.5	1.1
8-1U 8-10	0-1U 8.10	none		37% 78%	0.5	0.2
8-10	8-10	none	0.05	20%	0.4	0.2
8-10	8-10	none	0.05	28%	0.1	0.1
11-40	8-10	grassy vegetation	7	21%	1.6	1.6
11-40	8-10	grassy vegetation	7	18%	1.4	1.3
11-40	8-10	grassy vegetation	1	21%	0.3	0.3
11-40	8-10	grassy vegetation	1	18%	0.3	0.3
11-40	8-10	grassy vegetation	0.05	21%	0.2	0.1
11-40	8-10	grassy vegetation	0.05	18%	0.2	0.1
41-50+	8-10	forest vegetation	7	13%	· 1.1	1.6
41-50+	8-10	forest vegetation	7	12%	1.0	1.3
41-50+	8-10	forest vegetation	1	13%	0.3	0.3
41-50+	8-10	torest vegetation		12%	0.3	0.3
41-50+	8-10	torest vegetation	0.05	13%	0.2	0.2
41-50+	8-10	torest vegetation	0.05	12%	0.2	0.2

Table A5.3.Summary of approaches (i.e. equation A5.2.6) used to estimate maximum impact<br/>on manganese levels in the Missabe Mountain Pit. Concentrations in mg/L.

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Table A5.4.	Based on operational measurements in taconite tailings basins, laboratory and
	field experiments, and analyses of pit waters, manganese concentrations in the
	Missabe Mountain Pit, are expected to be less than 0.01 mg/L.

Data Source	Condition	Designator	Duration of Elevated Mn (months)	Mn (mg/L)
Taconite	Tailings basin clear pools	National	na	0.03
Operations		Inland	na	0.01
		LTV	, na	0.03
Tank	Surface water above taconite	Tank 3	2 - 9.5	0.00
Experiments	tailings and exposed to the atmosphere	Tank 4	4 - 9.5	0.01
Mn Oxidation Experiments	Tailings pore water mixed with oxidized pit water and exposed to the atmosphere	100% pore water	nd	3.2
		50% pore water	3.5	0.01
		24% pore water	1.75	0.01
		12.5% pore water	1.75	0.00
		2.5% pore water	1.75	0.01
Pierce and	Field measurements in existing pit lakes	Embarrass Pit	na	0.01
Tomcko, 1989		Forsyth Pit	na	22.5 <sup>1</sup>
		Gilbert Pit	na	<0.01
		Kinney Pit	na	0.25
		Miners Pit	na	4.3
		St. James Pit	na	0.02
		Stubler Pit	na	0.13
		Tioga Pit	na	<0.01

"nd" = not determined "na" = not applicable <sup>1</sup> the surface area of this pit is significantly smaller than the Missabe Mountain Pit, therefore it was not considered representative of conditions in the Missabe Mountain Pit.

Table A5.5.	Summary of approaches (i.e. equation A5.2.6) used to estimate maximum impact
	on fluoride levels in the Missabe Mountain Pit. Concentrations in mg/L.

		<u>NO (</u>	OUTFLOW FR	OM MINORCA PIT		
Depositional	Derations within the Mino	rca Pit		Missabe Mt Pit Cor	icentration Estimates (m	g/L) Max Estimated Cona in
Time Period	from Minorca	Reclamation	Minorca	Minorca Contribution to	Max. Net Input Conc.	Missabe During This
(Years)	(deposition year)	Concitotis	Source Term			Time Period
0-4	5-10	none	6	0%	0.3 (background)	0.3
0-4	5-10	none	6	0%	0.3	0.3
0-4	5-10	none	3	0%	0.3	0.3
0-4	5-10	none	3	0%	0.3	0.3
0-4	5-10	none	1	0%	0.3	0.3
0-4	8-10	none	6	0%	0.3	0.3
0-4	8-10	none	6	0%	0.3	0.3
0-4	8-10	none	3	0%	0.3	0.3
0-4	8-10	none	3	0%	0.3	0.3
0-4	8-10	none	1	0%	0.3	0.3
0-4	8-10	none	1	0%	0.3	0.3
		MINORCA OUTF	LOW DOMIN	ATED BY CLEAR WATER	POOL	
5-8	5-10	none	6	39%	2.5	1.3
5-8	5-10	none	6	28%	1.9	1.2
5-8	5-10	none	3	39%	1.3	0.8
5-8	5-10	none	3	28%	1.0	0.7
5-8	5-10	none		39%	0.6	0.4
5-8 5-8	5-10	none	6	28%	0.5	0.4
5-8	8-10	none	6	28%	19	0.8
5-8	8-10	none	3	39%	1.3	0.5
5-8	8-10	none	3	28%	1.0	0.5
5-8	8-10	none	1	39%	0.6	0.3
5-8	8-10	none	1	28%	0.5	0.3
		MINORCA OUTFU		TED BY TAILINGS PORE	WATER	
8-10	5-10	none	6	39%	2.5	1.6
8-10	5-10	none	6	28%	1.9	1.3
8-10	5-10	none	3	39%	1.3	0.9
8-10	5-10	none	3	28%	1.0	0.8
8-10	5-10	none	1	39%	0.6	0.4
8-10	5-10	none	1	28%	0.5	0.4
11-40	5-10	grassy vegetation	6	21%	1.5	1.6
11-40	5-10	grassy vegetation	6	18%	1.3	1.3
11-40	5-10	grassy vegetation		21%	0.9	0.9
11-40	5 10	grassy vegetation	5	1070	0.7	0.8
11-40	5-10	grassy vegetation		18%	0.4	0.4
41-50+	5-10	forest vegetation	6	13%	1.0	1.5
41-50+	5-10	forest vegetation	6	12%	1.0	1.3
41-50+	5-10	forest vegetation	3	13%	0.6	0.9
41-50+	5-10	forest vegetation	3	12%	0.6	0.8
41-50+	5-10	forest vegetation	1	13%	0.4	0.4
41-50+	5-10	forest vegetation	1	12%	0.4	0.4
8-10	8-10	none	6	39%	2.5	1.2
8-10	8-10	none	6	28%	1.9	1.1
8-10	8-10	none		39% 20 <i>0</i> 2	1.3	0.7
8-10	8-10	none		28%	1.0	0.0
8-10	8-10	none		28%	0.5	0.4
11-40	8-10	grassy vegetation	6	21%	1.5	1.5
11-40	8-10	grassy vegetation	6	18%	1.3	1.3
11-40	8-10	grassy vegetation	3	21%	0.9	0.8
11-40	8-10	grassy vegetation	3	18%	0.7	0.7
11-40	8-10	grassy vegetation	1	21%	0.4	0.4
11-40	8-10	grassy vegetation	1	18%	0.4	0.4
41-50+	8-10	forest vegetation	6	13%	1.0	1.4
41-50+	8-10	torest vegetation	6	12%	1.0	1.2
41-50+	8-10	forest vegetation		13%	0.6	0.8
41-30+	0-1U 8 10	forest vegetation		1270	0.0	0.7
41-50+	8-10	forest vegetation	li	12%	0.4	0.4

Table A5.6.	Summary of approaches (i.e. equation A5.2.6) used to estimate maximum impact
	on molybdenum levels in the Missabe Mountain Pit. Concentrations in ug/L.

NO C Operations within the Minorca Pit			OUTFLOW FR	<u>OM MINORCA PIT</u> Missabe Mt Pit Co	ncentration Estimates (up	
Depositional	Period of Max. Outflow	Designation	Minora	Minorea Contribution to		Max. Estimated Conc. in
Time Period (Years)	from Minorca (deposition year)	Conditions	Source Term	Minorca Contribution to Missabe Net Input	Max. Net Input Conc.	Missabe During This Time Period
0-4	5-10	none	130	0%	0.4 (background)	0.4
0-4	5-10	none	130	0%	0.4	0.4
0-4	5-10	none	45	0%	0.4	0.4
0-4	5-10	none	45	0%	0.4	0.4
0-4	5-10	none	15	0%	0.4	0.4
0-4	5-10	none	15	0%	0.4	04
0.4	8 10	none	130	0%	0.4	0.4
0-4	8-10	none	130	0%	0.4	0.4
0-4	8-10	none	130	0%	0.4	0.4
0-4	8-10	none	45	0%	0.4	. 0.4
0-4	8-10	none	.45	0%	0.4	0.4
0-4	8-10	none	15	0%	0.4	0.4
0-4	8-10	none	15	0%	0.4	0.4
		MINORCA OUTF	LOW DOMINA	TED BY CLEAR WATER	POOL	
5-8	5-10	none	130	39%	51	25
5-8	5-10	none	130	28%	37	21
5-8	5-10	none	45	39%	18	9
5.9	5-10	none	45	2804	12	7
5-0	5-10	none	15	2070	- 13 E	2
5-8	5-10	none	15	39%	0	٤
5-8	5-10	none	15	28%	4	3
5-8	8-10	none	130	39%	51	13
5-8	8-10	none	130	28%	37	12
5-8	8-10	none	45	39%	18	5
5-8	8-10	none	45	28%	13	4
5-8	8-10	none	15	39%	6	2
5-8	8-10	none	15	28%	4	2
0.10	5.10	MINORCA OUTFL	JW DOMINAI	TED BY TAILINGS PORE	WATER	25
8-10	5-10	none	130	39%	51	25
8-10	5-10	none	130	28%	37	21
8-10	5-10	none	45	39%	18	11
8-10	5-10	none	45	28%	13	9
8-10	5-10	none	15	39%	6	4
8-10	5-10	none	15	28%	4	3
11-40	5-10	grassy vegetation	130	21%	28	22
11 40	5-10	grassy vegetation	120	1904	20	19
11-40	5-10	grassy vegetation	150	1070	24 10	10
11-40	5-10	grassy vegetation	45	21%	10	11
11-40	5-10	grassy vegetation	45	18%	8	9
11-40	5-10	grassy vegetation	15	21%	3	4
11-40	5-10	grassy vegetation	15	18%	3	3
41-50+	5-10	forest vegetation	130	13%	17	11
41-50+	5-10	forest vegetation	130	12%	16	9
41-50+	5_10	forest vegetation	45	130%	6	. 10
41 50.	5 10	forest vegetation	15	1000	6	0 10
41-30+	5-10	forest vegetation	43	12%	0	ŏ
41-50+	5-10	torest vegetation	15	13%	2	3
41-50+	5-10	torest vegetation	15	12%	2	3
8-10	8-10	none	130	39%	51	14
8-10	8-10	none	130	28%	37	12
8-10	8-10	none	45	39%	18	8
8-10	8-10	none	45	28%	13	7
8_10	8-10 8-10	none	15	30%	6	2
0-10	0-10	none	15	5770 7977	4	5
8-10	8-10	none	15	28%	4	2
11-40	8-10	grassy vegetation	130	21%	28	14
	8-10	grassy vegetation	130	18%	24	12
11-40	0.10	grassy vegetation	45	21%	10	10
11-40 11-40	8-10	=	1 10	1907	8	8
11-40 11-40 11-40	8-10 8-10	grassy vegetation	1 45	1070		
11-40 11-40 11-40	8-10 8-10 8-10	grassy vegetation	45	21%	2	3
11-40 11-40 11-40 11-40	8-10 8-10 8-10	grassy vegetation grassy vegetation	45	21%	3	3
11-40 11-40 11-40 11-40 11-40	8-10 8-10 8-10 8-10	grassy vegetation grassy vegetation grassy vegetation	45 15 15	21% 18%	3 3	3 3
11-40 11-40 11-40 11-40 11-40 41-50+	8-10 8-10 8-10 8-10 8-10	grassy vegetation grassy vegetation grassy vegetation forest vegetation	45 15 15 130	21% 18% 13%	3 3 17	3 3 10
11-40 11-40 11-40 11-40 41-50+ 41-50+	8-10 8-10 8-10 8-10 8-10 8-10	grassy vegetation grassy vegetation grassy vegetation forest vegetation forest vegetation	45 15 130 130	21% 18% 13% 12%	3 3 17 16	3 3 10 9
11-40 11-40 11-40 11-40 11-40 41-50+ 41-50+ 41-50+	8-10 8-10 8-10 8-10 8-10 8-10 8-10	grassy vegetation grassy vegetation grassy vegetation forest vegetation forest vegetation forest vegetation	45 15 15 130 130 .45	21% 18% 13% 12% 13%	3 3 17 16 6	3 3 10 9 9
11-40 11-40 11-40 11-40 41-50+ 41-50+ 41-50+ 41-50+	8-10 8-10 8-10 8-10 8-10 8-10 8-10 8-10	grassy vegetation grassy vegetation grassy vegetation forest vegetation forest vegetation forest vegetation forest vegetation	45 15 15 130 130 .45 45	21% 18% 13% 12% 13%	3 3 17 16 6 6	3 3 10 9 9 8
$11-40 \\ 11-40 \\ 11-40 \\ 11-40 \\ 11-40 \\ 41-50+ \\ 41-50+ \\ 41-50+ \\ 41-50+ \\ 41-50+ $	8-10 8-10 8-10 8-10 8-10 8-10 8-10 8-10	grassy vegetation grassy vegetation grassy vegetation forest vegetation forest vegetation forest vegetation forest vegetation	45 15 15 130 130 .45 45 15	18% 21% 13% 12% 13% 12%	3 3 17 16 6 6 2	3 3 10 9 9 8 3

Table A5.7.	Summary of approaches (i.e. equation A5.2.6) used to estimate maximum impact
	on arsenic levels in the Missabe Mountain Pit. Concentrations in ug/L.

		NO (	DUTFLOW FR	OM MINORCA PIT		
(	Operations within the l	Minorca Pit		Missabe Mt Pit Con	ncentration Estimates (ug	;/L)
Depositional	Period of Max.		Minorca	Minorca Contribution to		Max. Estimated Conc. in
Time Period	Outflow from Minor	caReclamation Conditions	Source Term	Missabe Net Input	Max. Net Input Conc.	Missabe During This
(Years)	(deposition year)					Time Period
0-4	5-10	none	7	0%	0.7 (background)	0.7
0-4	5-10	none	7	0%	0.7	0.7
0-4	5-10	none	3	0%	0.7	0.7
0-4	5-10	none	3	0%	0.7	0.7
0-4	5-10	none	0.1	0%	0.7	0.7
0-4	5-10	none	0.1	0%	0.7	0.7
0-4	8-10	none	7	0%	0.7	0.7
0-4	8-10	none	7	0%	0.7	0.7
0-4	8-10	none	3	0%	0.7	0.7
0-4	8-10	none	3	0%	0.7	0.7
0-4	8-10	none	0.1	0%	0.7	0.7
0-4	8-10	none	0.1	0%	0.7	0.7
					POOL	
5 9	5 10	MINORCA OUTF		ATED BY CLEAR WATER	POOL	1 0
2-0 2 2	5 10 -	none	, ,	5770 780L	5.U 2 2	1.0
5-0	5 10	none	2	2070	2.5	1.0
5-0	5-10	none	5	3970 3970	1.5	1.1
50	5-10	none		20%	1.2	1.0
2-8	5-10	none	0.1	39%	0.4	0.6
5-8	5-10	none	0.1	28%	0.4	0.6
5-8	8-10	none		39%	3.0	1.3
5-8	8-10	none		28%	2.3	1.2
5-8	8-10	none	3	39%	1.5	0.9
5-8	8-10	none	3	28%	1.2	0.8
5-8	8-10	none	0.1	39%	0.4	0.7
	8-10	none	0.1	28%	0.4	0.7
		MINORCA OUTER		TED BY TAILINGS POPE	WATED	
8-10	5-10	MINORCA OUTIL		30%	30	2.1
8-10	5-10	none	7	28%	23	1.8
8-10	5-10	none	3	30%	1.5	1.0
8-10	5-10	none	3	28%	1.5	1.2
8-10	5-10	none		30%	0.4	0.5
8-10	5-10	none	0.1	280	0.4	0.5
11-40	5-10	arassy vegetation	7	21%	10	2.1
11-40	5-10	grassy vegetation	7	18%	1.7	18
11-40	5-10	grassy vegetation	3	21%	1.7	1.0
11-40	5 10	grassy vegetation	3	18%	1.0	1.2
11-40	5 10	grassy vegetation		210%	1.0	0.5
11-40	5 10	grassy vegetation	0.1	190%	0.4	0.5
41.50+	5.10	forest vegetation	7	13%	13	1.0
41-50+	5-10	forest vegetation	7	12%	1.5	1.5
41-50+	5-10	forest vegetation	3	13%	0.8	1.0
41-50-	5_10	forest vegetation	2	12%	0.8	0.9
41-50-	. 5-10 5-10	forest vegetation	01	13%	0.5	04
41-50+	5-10	forest vegetation	0.1	12%	0.5	04
8_10	8_10	pone	7	30%	3.0	17
8-10	8-10	pone	7	28%	2.3	15
8-10	8_10	none	1 3	30%	1.5	1.0
8-10	8_10	none	2	2970 2806	1.5	0.0
8_10	8_10	none		30%	04	0.6
8-10	8-10	none	0.1	28%	0.4	0.6
11_40	8_10	arassy vegetation	7	20.00	10	10
11_40	8_10	grassy vegetation	1 7	180%	1.7	1.7
11-40	8_10	grassy vegetation	1	210%	10	10
11-40	8-10 8-10	grassy vegetation	1	180%	10	0.0
11-40	8-10	grassy vegetation		210%	0.4	0.5
11-40	8-10 8-10	grassy vegetation	0.1	180%	0.4	0.5
41-50-	8-10	forest vegetation	7	130%	13	1 8
41-50+	8-10 8-10	forest vegetation	1 7	170%	1.3	1.6
41-50-	8-10 8-10	forest vegetation	1 1	1200	0.8	10
41-50+	8-10	forest vegetation		12%	0.8	0.9
41-50+	8-10	forest vegetation	1 01	13%	0.5	0.4
41-50+	8-10	forest vegetation	0.1	12%	0.5	0.4

Table A5.8.	Summary of approaches (i.e. equation A5.2.6) used to estimate maximum impact							
	on boron levels in the Missabe Mountain Pit. Concentrations in ug/L.							

Time Period (Years)	Outflow from Minore (deposition year)	aReclamation Conditions	Minorca Source Term	Minorca Contribution to Missabe Net Input	Max. Net Input Conc.	Max. Estimated Conc. in Missabe During This Time Period
0-4	5-10	none	300	0%	12 (background)	12
0-4	5-10	none	300	0%	12	12
0-4	5-10	none	30	0%	12	12
0-4	5-10	none	30	0%	12	12
0-4	8-10	none	300	0%	12	12
0-4	8-10	none	300	0%	12	12
0-4	8-10	none	30	0%	12	12
0-4	8-10	none	30	0%	12	12
		MINORCA OUTF	LOW DOMINA	TED BY CLEAR WATER	POOL	
5-8	5-10	none	300	39%	145	76
5-8	5-10	none	300	28%	112	71
5-8	5-10	none	30	39%	40	25
5-8	5-10	none	30	28%	42	28
5-8	8-10	none	300	39%	145	54
5-8	8-10	none	300	28%	112	53
5-8	8-10	none	30	39%	40	27
5-8	8-10	none	30	28%	42	28
				TED BY TAILINGS PORE	WATER	
8-10	5-10	DODE	300	30%	145	97
8-10	5-10	none	300	28%	112	83
8-10	5-10	none	30	39%	40	29
8-10	5-10	none	30	28%	42	32
11-40	5-10	grassy vegetation	300	21%	99	99
11-40	5-10	grassy vegetation	300	18%	92	89
11-40	5-10	grassy vegetation	30	21%	43	41
11-40	5-10	grassy vegetation	30	18%	43	42
41-50+	5-10	forest vegetation	300	13%	79	98
41-50+	5-10	forest vegetation	300	12%	76	89
41-50+	5-10	forest vegetation	30	13%	44	41
41-50+	5-10	forest vegetation	30	12%	44	42
8-10	8-10	none	300	39%	145	75
8-10	8-10	none	300	28%	112	71
8-10	8-10	none	30	. 39%	40	30
8-10	8-10	none	30	28%	42	32
11-40	8-10	grassy vegetation	300	21%	99	97
11-40	8-10	grassy vegetation	300	18%	92	88
11-40	8-10	grassy vegetation	30	21%	43	41
11-40	8-10	grassy vegetation	30	18%	43	42
41-50+	8-10	forest vegetation	300	13%	79	96
41-50+	8-10	forest vegetation	300	12%	76	87
41-50+	8-10	forest vegetation	30	13%	44	42
	~			100		10

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Table A5.9.	Summary of the source terms, transport terms, expected levels in the Missabe Mountain Pit, and drinking water quality
	standards for the five EC's. Units in ug/L unless otherwise noted

Terms	Conditions	Criteria	Mn	F (mg/L)	Mo (ug/L)	As	В
Minorca Pit Source	Clear Water Pool	Deposition Year 5-8	0.01	6	130	4.5	171
Term <sup>1,2</sup>	Tailings Pore Water	Deposition Year 8+	0.05 - 7	1 - 6	1 - 45 <sup>3</sup>	0.1 - 7	30 - 300
Biwabik Aquifer	No Removal or Dilution		0.01 - 7	1 - 6	1 - 130	0.1 - 7	30 - 300
Transport Term	Chemical Controls		14	4-65	na	36	na
		Temporary Maximum	0.02 - 1.7	0.3 - 1.6	1.4 - 25	0.5 - 2.1	29 - 92
Missabe Mountain Pit	Dilution <sup>7,8</sup>	Reclamation w/ Grasses	0.1 - 1.7	0.4 - 1.6	3.4 - 22	0.5 - 2.1	41 - 99
Concentrations		Reclamation w/ Trees	0.2 - 1.6	0.4 - 1.5	3.0 - 11	0.4 - 1.9	41 - 98
	Chemical Controls		<0.019	na	na	1 <sup>10</sup>	na
		Health-based value	1.311	na	na	na	na
Drinking Water Quality Standards		Primary	0.1	4	30	50	600
		Secondary	0.0512	213	na	<1014	na

<sup>1</sup> A monitoring well should be installed in the Minorca Pit tailings in order to monitor fluctuations in the levels of the five EC's over time.

<sup>2</sup> Source terms for F and Mo will decrease over time, particularly after successful reclamation of the Minorca Pit.

<sup>3</sup> Mo source terms appeared to be dependent on the levels found in plant discharges, which vary over time.

<sup>4</sup> Assumes chemical control by rhodochrosite solubility in the aquifer, calculation in Table A3.1.

<sup>5</sup> Assumes chemical control by fluorite solubility (Berndt et al., 1999) in the aquifer based on measured calcium concentrations.

<sup>6</sup> This value was based on visual inspection of the distribution of arsenic levels in tailings pore waters during this study. It is intended to illustrate arsenic removal due to adsorption to iron oxides in the Formation.

<sup>7</sup> These values were calculated assuming a dilution water composition based on that observed in the Biwabik aquifer wells (Table 8).

<sup>8</sup> Dilution factors of 6% - 39% depend upon implementation of successful reclamation at the Minorca Pit upon closure.

<sup>9</sup> This value assumes oxidizing conditions in the Missabe Mountain Pit will promote precipitation of manganese oxides. Based on measurements in the tailings basin and manganese oxidation experiments.

<sup>10</sup> This value assumes oxidizing conditions in the Missabe Mountain Pit will promote co-precipitation of arsenic with iron oxides. Based on measurements from the manganese oxidation experiments.

<sup>11</sup> This is a site-specific, health-based standard developed by the Minnesota Department of Health (1998).

<sup>12</sup> This is an aesthetic standard that the Virginia Public Utility must meet for the city water supply.

<sup>13</sup> The secondary fluoride standard is not an enforceable standard.

<sup>14</sup> The US EPA is considering lowering the primary arsenic standard to less than 10 ug/L in the future.

"na" = not applicable

Table A6.1.Statistical summary of manganese concentrations observed in waters associated<br/>with taconite tailings from four taconite operations. Samples were collected as<br/>part of the MN DNR and U of MN study on the water quality implications of in-<br/>pit disposal of taconite tailings.

Manganese Concer	ntrations (mg/L)	National	USX- Minntac	Inland	LTV
Tailings	Average	0.06	nd	0.06	0.03
Discharge Pipe	Standard Deviation	0.04	nd	0.01	0.01
	Range	0.01-0.13	nd	0.05-0.09	0.02-0.05
	N	11	nd	10	11
Tailings Basin	Average	0.03	nd	0.01	0.03
Reclaim Barge	Standard Deviation	0.04	nd	0.02	0.03
	Range	0.002-0.12	nd	0.001-0.08	0.001-0.08
	N	11	nd	11	11
Seep	Average	nd	nd	2.8	1.0
	Standard Deviation	nd	nd	1.3	0.20
	Range	nd	nd	0-4.1	0.7-1.4
	N	nd	nd	8	11
Wells	Average	0.03	1.3	4.6	nd
	Standard Deviation	0.03	0.36	1.5	nd
	Range	0.005-0.10	1.0-1.9	1.2-7.2	nd
	N	9	6	16	nd
Sump	Average	nd	3.11	nd	nd
	Standard Deviation	nd	2.8	nd	nd
	Range	nd	1.4-8.6	nd	nd
	Ν	nd	6	nd	nd

Primary drinking water quality standard: 1.3 mg/l (MDH, 1998)

Secondary water quality standard: 0.05 mg/l (US EPA, MCL)

Table A6.2.Statistical summary of fluoride concentrations observed in waters associated with<br/>taconite tailings from four taconite operations. Samples were collected as part<br/>of the MN DNR and U of MN study on the water quality implications of in-pit<br/>disposal of taconite tailings.

Fluoride Concent	rations (mg/L)	National	USX- Minntac	Inland	LTV
Tailings	Average	0.98	nd	4.57	9.8
Discharge Pipe	Standard Deviation	0.16	nd	1.61	1.1
	Range	1.10 - 1.55	nd	2.30 - 7.62	7.5 - 10.9
	N	11	nd	10	. 11
Tailings Basin	Average	0.98	nd	2.74	8.5
Reclaim Barge	Standard Deviation	0.11	nd	0.60	0.9
	Range	0.85 - 1.14	nd	1.31 - 3.46	7.5 - 9.7
	. <b>N</b>	11	nd	11	11
Seep	Average	nd	nd	2.26	3.9
	Standard Deviation	nd	nd	0.59	0.9
	Range	nd	nd	1.18 - 3.02	1.8 - 4.8
	Ν	nd	nd	8	11
Wells	Average	0.58	0.24	2.52	nd
	Standard Deviation	0.05	0.06	1.02	nd
	Range	0.51 - 0.65	0.16 - 0.31	0.56 - 3.64	nd
	N	6	6	16	nd
Sump	Average	nd	0.20	nd	nd
	Standard Deviation	nd	0.04	nd	nd
	Range	nd	0.16 - 0.25	nd	nd
	N	nd	6	nd	nd

Primary drinking water quality standard: 4 mg/L (MDH, 1998)

Unenforceable secondary water quality standard: 2 mg/L (Berndt and Lapakko, 1997; Wiskow, 1998)

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In-Pit Disposal Project Fluorite Saturation Limits

Figure A6.2. In general, elevated fluoride levels in tailings pore waters were only observed when calcium levels were low. This implied that fluoride levels in tailings pore waters are controlled by the solubility of the mineral fluorite, CaF<sub>2</sub> (black solid lines, Brown and Roberson, 1977; Berndt et al., 1999). Each symbol represents the average fluoride and calcium composition of each water type. (Inl = Inland, Nat = National, gw = ground water, pw = process water, rw = rain water, col = column experiment) Table A6.3.Statistical summary of molybdenum concentrations observed in waters associated<br/>with taconite tailings from four taconite operations. Samples were collected as<br/>part of the MN DNR and U of MN study on the water quality implications of in-<br/>pit disposal of taconite tailings.

Molybdenum Conce	entrations (ug/L)	National	USX- Minntac	Inland	LTV
Tailings	Average	58.1	nd	110	340
Discharge Pipe	Standard Deviation	14.7	nd	38	41
	Range	36.8 - 76.2	nd	68 - 157	282 - 434
	N	11	nd	10	11
Tailings Basin	Average	41	nd	35	279
Reclaim Barge	Standard Deviation	6.0	nd	10	33
	Range	27 - 47	nd	16 - 49	215 - 323
	Ν	11	nd	11	11
Seep	Average	nd	nd	7.1	86
	Standard Deviation	nd	nd	4.5	31
	Range	nd	nd	1.5 - 13.7	15 - 129
	N	nd	nd	8	11
Wells	Average	10.3	0.6	6.4	nd
	Standard Deviation	2.0	0.5	1.6	nd
	Range	8.1 - 13.6	0.1 - 1.5	3.0 - 8.4	nd
	Ņ	6	6	15	nd
Sump	Average	nd	2.2	nd	nd
	Standard Deviation	nd	1.8	nd	nd
	Range	nd	0.2 - 5.3	nd	nd
	N	nd	6	nd	nd

Primary drinking water quality standard: 30 ug/L (MDH, 1998)

Table A6.4.Statistical summary of arsenic concentrations observed in waters associated with<br/>taconite tailings from four taconite operations. Samples were collected as part<br/>of the MN DNR and U of MN study on the water quality implications of in-pit<br/>disposal of taconite tailings.

Arsenic Concent	rations (ug/L)	National	USX- Minntac	Inland	LTV
Tailings	Average	2.13	nd	3.6	4.0
Discharge Pipe	Standard Deviation	0.83	nd	1.3	1.6
	Range	0.60 - 3.20	nd	1.9 - 5.5	1.5 - 6.4
	N	11	nd	10	11
Tailings Basin	Average	1.6	nd	5.1	11.1
Reclaim Barge	Standard Deviation	0.6	nd	1.4	5.7
	Range	0.7 - 2.5	nd	3.1 - 7.4	5.9 - 21.9
	N	11	nd	11	11
Seep	Average	nd	nd	1.1	4.8
	Standard Deviation	nd	nd	0.7	1.2
	Range	nd	nd	0.5 - 2.1	2.2 - 6.1
	N	nd	nd	8	11
Wells	Average	0.44	1.2	4.1	nd
	Standard Deviation	0.15	1.8	1.8	nd
	Range	0.14 - 0.51	0.1 - 4.8	1.5 - 8.1	nd
	N	6	6	15	nd
Sump	Average	nd	2.1	nd	nd
	Standard Deviation	nd	2.3	nd	nd
	Range	nd	0.4 - 6.6	nd	nd
	<u>N</u>	nd	66	. nd	nd

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Primary drinking water quality standard: 50 ug/L (MDH, 1998)

May be reduced to 2 - 10 ug/L in the future.

Table A6.5.Statistical summary of boron concentrations observed in waters associated with<br/>taconite tailings from four taconite operations. Samples were collected as part<br/>of the MN DNR and U of MN study on the water quality implications of in-pit<br/>disposal of taconite tailings.

Boron Concentr	rations (ug/L)	National	USX- Minntac	Inland	LTV
Tailings	Average	73	nd	121	349
Discharge Pipe	Standard Deviation	18	nd	48	95
	Range	53 - 104	nd	66 - 212	204 - 501
	N	11	nd	10	11
Tailings Basin	Average	53	nd	70	334
Reclaim Barge	Standard Deviation	13	nd	20	75
	Range	32 - 74	nd	27 - 100	226 - 453
	N	11	nd	11	11
Seep	Average	nd	nd	52	457
	Standard Deviation	nd	nd	17	59
	Range	nd	nd	34 - 76	338 - 527
	N	nd	nd	8	11
Wells	Average	41	32	47	nd
·	Standard Deviation	11	13	14	nd
	Range	28 - 55	14 - 45	27 - 77	nd
	Ν	6	6	. 15	nd
Sump	Average	nd	30	nd	nd
	Standard Deviation	nd	13	nd	nd
	Range	nd	5.9 - 42	nd	nd
	<u>N</u>	nd	6	nd	nd

Primary drinking water quality standard: 600 ug/L (MDH, 1998)

Table A6.6.Summary of mercury concentrations observed in waters associated with taconite<br/>tailings from four taconite operations. Samples were collected as part of the MN<br/>DNR and U of MN study on the water quality implications of in-pit disposal of<br/>taconite tailings. Mercury analyses were conducted by Frontier Geosciences.

Mercury Concentrations (ng/L unless otherwise noted)		National	USX- Minntac	Inland	LTV
Taconite Tailings	Average	18.3	46.6	35.4	7.0
(ng/g)	Standard Deviation	1.7	na	na	na
	Range	17.1 - 19.5	na	na	na
	N	2	1	1	1
Seep	Average	nd	nd	2.99	2.44
	Standard Deviation	nd	nd	na	na
	Range	nd	nd	na	na
	N	nd	nd	1	1
Wells	Average	2.69	2.46	2.85	nd
	Standard Deviation	na	na	0.02	nd
	Range	na	na	2.83 - 2.86	nd
	N	1	1	2	nd

Drinking water quality standard: 2000 ng/L (US EPA)

A7.1. Copy of the memo sent to reviewers requesting comments on this document.

# **Office Memorandum**

DATE: January 27, 2000

- TO: John Adams
   Hillary Carpenter, MDH
   Jim Walsh, MDH
   Dick Clark, MPCA
   John Engesser, NRRI
- FROM: Emmelyn Jakel Kim Lapakko
- PHONE: 651/296-0908

SUBJECT: Ispat Inland Mining Company - In Pit Tailings Disposal Project Summary of the geochemical study

> As most of you are aware, the DNR has prepared a Supplemental Environmental Impact Statement (SEIS) for Ispat Inland Mining Company's (Inland) proposal to deposit taconite tailings into the Minorca Pit, near Virginia, Minnesota. As part of this process, the Division of Lands and Minerals and University of Minnesota studied the potential water quality implications of in pit disposal of taconite tailings. Results from this study that were directly related to Inland's proposal have been summarized in two reports: a brief summary that appears as an appendix in the SEIS and a more detailed version that documents specific results and the rationale used in our evaluation.

> Enclosed you will find a copy of the more detailed version of the geochemical study entitled, "Detailed Analysis of Potential Environmental Impacts of Taconite Tailings Disposal in the Minorca Pit on Water Quality in the Missabe Mountain Pit." At this time, we are requesting comments on this document. We would like to include your comments and our responses as an addendum to the report. Most of you have been involved with the project, so I am asking for a fairly quick response. Please return any comments to me by March 15, 2000 (e-mail: <u>lyn.jakel@dnr.state.mn.us;</u> fax: 651-296-5939; phone: 651-296-0908). Give me a call if you have any questions.

Thank you.

Enclosure (1)

A7.2. Comments received from reviewers

Dick Clark, PCA Feb. 8, 2000

1. Page 7, section 3.2.3.

Flow is dependent on the local gradient as well as the hydraulic conductivity. This calculation appears to use hydraulic conductivity only. Is the 0.7 - 1.8 ft/day a K-value? If so, it is at unit gradient (used to compare different materials). Check this with John Adams, it may require some clarification in the text.

- 2. General comment on the use of the word "expected" throughout the document. He correlates that with the phrase "most likely." He would have used something like, "could be as high as," or "a maximum value of"...
- 3. He will pass it by some of their water quality standards people to see if they would be interested/able to review it. They tend to be surface water people, but may be interested anyway.
- 4. He would like a copy of the final document when it is completed.

From:	"JIM WALSH" <james.walsh@sunny.health.state.mn.us></james.walsh@sunny.health.state.mn.us>
To:	"Lyn Jakel" <lyn.jakel@dnr.state.mn.us></lyn.jakel@dnr.state.mn.us>
Date:	3/13/00 9:46AM
Subject:	Re: request for comments

Hi Lyn,

In general I thought the report looked good. A few specific comments:

1) The second sentence on page 42 doesn't make sense to me. Should the word " longer" be replaced with "more"?

2) The source of boron in the tailings water is not identified whereas you speculate on the sources of the other EC's. I think this should be clarified.

3) Item 3 on page 50 mentions that manganese removal by natural processes would be compromised if reducing conditions become prevalent. Couldn't the same be said for arsenic?

Thanks for the opportunity to comment.

Jim

James Walsh MDH/Environmental Health P.O. Box 64975 St. Paul, MN 55164-0975 Phone: (651) 215-0806 Fax: (651) 215-0978 james.walsh@health.state.mn.us John Engesser, NRRI: On page 15 you give 2 examples of reactions that decrease the pH of water.

Another reaction that increases hydronium ion concentration in tailing water is the oxidation of sulfide minerals (pyrite). You do mention the oxidation of pyrite when discussing the dissolution of arsenic on page 39. However, I think it also adds to the dissolution of carbonates (manganese

carbonate). The oxidation of sulfide to sulfuric acid is probably not as prevalent in the Minorca tailing basin as it is in some of the other taconite tailing basins, but probably should be mentioned.

There is no analytical value for the amount of sulfur in the tailings in Tables 5 or 6. In Table 4 you indicate the tailings are 0.01% pyrite, however, a total sulfur value would be an indication of the effect that sulfide oxidation has on the tailing water chemistry. The amount of total sulfur contained in taconite tailings is usually between 0.02 and 0.20 percent.

Response: The maximum amount of acid produced due to pyrite oxidation would consume approximately 0.5 % of the carbonate minerals present in the tailings ( $3.7 \times 10^{-4}$  moles of acid generated x  $100\% \div 7.1 \times 10^{-2}$  moles of acid consumed). Consequently, pyrite oxidation is not expected to generate enough acid to explain the water chemistry observed in Inland's tailings pore waters.

Parameter	Chemical Analysis <sup>1</sup> (wt %)	Maximum Amount of Acid Generated <sup>2</sup> /Consumed <sup>3</sup> (moles)
Total S	0.006	3.7 x 10 <sup>-4</sup>
CO <sub>2</sub>	3.11	• 7.1 x 10 <sup>-2</sup>

<sup>1</sup>Based on analyses conducted by Lerch Bros.

<sup>2</sup>Assumes two moles of acid produced for every mole of sulfur oxidized. <sup>3</sup>Assumes near-neutral pH, and therefore, one mole of acid consumed for every mole of carbonate mineral.