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In-pit disposal of taconite tailings: geochemistry

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Progress Report: Through June 30, 1998

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Summary

Field, experimental, and theoretical studies have been conducted to help predict the fates of As, Mo, Mn, and F in taconite tailings deposited into abandoned open-pit mines on the Mesabi Range, NE Minnesota. Field data and calculations indicate that conditions and reactions occurring in tailings pore fluids are similar to those in Biwabik Iron Formation aquifers. Oxidation of siderite (FeCO₃) to iron oxide appears to be the primary reaction that consumes oxygen, lowers pH, and increases alkalinity of fluids reacting with minerals in tailings basins and also in the Biwabik Iron Formation aquifer. Computer simulations predict, in particular, that air-saturated deionized water (e.g., rainwater) reacting with siderite and ankerite produces Ca-Mg-HCO₃ waters with compositions nearly identical to those observed in Biwabik Iron Formation aquifers. A siderite oxidation model also predicts correctly observed increases in alkalinity and reductions in pH and Eh in process waters seeping through tailings in tailings basins. The conditions brought on by this reaction result in increased solubility of MnCO₃ and increased adsorption of As, Mo, and F.

Experiments and calculations were also conducted to evaluate mobilities of elements in tailings intruded, respectively, by either groundwater or input from precipitation events (e.g., surface runoff). While intrusion of tailings by groundwater leads to slight increases in the concentrations of As, Mo, Mn, and F relative to the initial groundwater, the amounts of these elements mobilized are small compared to concentrations initially present in process waters. Little reaction occurs between groundwaters intruded into tailings owing to the fact that no new oxygen is introduced (preventing further oxidation of siderite). Infiltration of tailings by local runoff derived from precipitation, on the other hand, introduces significant oxygen into the taconite tailings, and leads, therefore, to renewed oxidation of siderite, dissolution of carbonate minerals in the tailings may temporarily exceed values found in the pre-existing pore fluid, but the concentrations are still generally less than those in the initial process waters.

The overall amount of As, Mo, and F made available to the environment during mineral processing depends on the amounts of these elements that are converted into mobile components (soluble minerals, dissolved and adsorbed species). Fluoride in primary taconite ores, for example, is present in apatites and silicates (clays and amphiboles) which are generally insoluble or slow to react at low temperatures. Small fractions of these minerals that are not separated from the concentrate, however, may be heated to high temperatures during pelletization. F under these conditions is converted to highly volatile HF, which is freed from the mineral structure and recaptured and converted to F by plant scrubbers. Our results suggest that a significant fraction of this F is adsorbed onto the surfaces of minerals in tailings. This adsorbed F, while representing only a small fraction of the total F in tailings (e.g., 1% at Inland), can be remobilized later by water penetrating into the tailings.

Introduction

Taconite is a very hard, relatively low grade, silica rich iron-ore that forms the basis of the iron mining industry in NE Minnesota (Ojakangas and Matsch, 1982). The currently preferred taconite mining method in Minnesota involves grinding of the rock into a fine powder, magnetic separation of ore from non-ore minerals, agglomeration of the ore into pellets, and deposition of fine tailings and associated processing waters into large above-ground tailings basins. In some operations a flotation process is used to further remove silica from the separated ore prior to agglomeration.

Largely to avoid the need to construct and maintain tailings basins, mining companies in NE Minnesota are exploring the possible use of mine pits in the Biwabik Iron Formation for tailings disposal. Other possible benefits of in-pit disposal include elimination of the risk of tailings dam failure as well as reductions in dust generation, the area of land (including wetlands) disturbed by mining, and the amount of energy used for pumping tailings. Thus, laws preventing in-pit disposal of tailings have been modified recently making it possible for regulatory agencies to issue permits to fill pits with fine tailings, provided it can be shown that ground water supplies in the Biwabik Iron Formation will not be adversely impacted. The Biwabik Iron Formation is the only major bedrock aquifer in the region.

Tailings deposited in a pit may be exposed to water derived from a variety of sources, depending on local geographic and hydrologic factors. In active tailings basins, it is clear that the pore fluids within the deposited tailings are dominated by downward migration of process waters stored within the basins (Myette, 1991; Berndt and Lapakko, 1997 a,b). In a pit environment, however, it is likely that at some time during and after the pit-filling process, local groundwaters and/or surface runoff will displace processing waters within the pores of the tailings. Full evaluation of the potential impacts and merits of in-pit disposal of taconite tailings must consider, therefore, the potential consequences, if any, of reactions that may take place between tailings and water from a variety of sources.

The present study is an extension of an earlier study performed by Berndt and Lapakko (1997 a, b) who collected and analyzed many samples from active tailings basins and taconite processing plants and performed a series of experiments to evaluate the reactivity of taconite tailings with process waters. The study was instrumental in demonstrating that As, Mo, F, Mn, and B could be characterized as potentially problematic, but did not explicitly consider the possibility of water from other sources interacting with tailings.

This study was initiated by the Minnesota Department of Natural Resources, supported by a grant from the Iron Ore Cooperative Research Program, and executed jointly by the University of Minnesota and Department of Natural Resources. John Folman is acknowledged for his assistance in collecting and processing samples and for performance of all analysis carried out at the DNR laboratory in Hibbing (alkalinity titration, pH, Eh).

Objectives

Our main objectives are to evaluate chemical processes affecting mobility of elements in water potentially escaping from in-pit disposal sites and to determine their likely fate in water entering into the Biwabik Iron formation. Thus, the database for chemistry of water found in and near tailings basins has been extended by one year and has been expanded to include a range-wide suite of groundwater samples from Biwabik Iron Formation aquifers. These data were used to build the framework for a comprehensive geochemical interpretation on the chemical composition of waters interacting with minerals in the Biwabik Iron Formation. Experiments were also conducted to determine the effects, if any, of intrusion of groundwater or water derived from local precipitation into tailings. By combining field, experimental, and theoretical data, we hope to provide a sound foundation for predicting concentrations of elements in fluids leaving in pit disposal facilities and migrating through local groundwater environments.

Methods

The methods used in our study are effectively the same as those used by Berndt and Lapakko (1997) and are summarized below.

Chemical Analysis

Each water sample was analyzed for a large array of 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 were conducted at the Minnesota Department of Natural Resources (Mn DNR) laboratory in Hibbing. The concentrations of numerous 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 University of Minnesota. Tables 1 and 2 list a subset of inorganic species analyzed with approximate detection limits and the analytical technique used. Major cations were analyzed on water diluted by a factor of 10, while trace elements were analyzed directly on undiluted samples. Some elements (Fe, Mn, Sr and Ba) were analyzed at both dilutions to serve as a crosscheck on the analyses.

Tailings Basin Study

Over 80 water samples have now been collected from active tailings basins spanning the time period from June 1996, through April 1998. Sites visited in these studies include the tailings discharge pipe (where water is discharged from the processing plant into the tailings basin), the water return barge (where water is recycled from the tailings basin back to the processing plant), and seeps and wells in or near the tailings basin dike (after water from the tailings basin has reacted with tailings). One-liter grab samples were collected when possible, but samples from wells were collected using either a one-liter Teflon bailer or a battery operated pump. In these cases, a volume of water greater than or equal to three well volumes was collected and discarded before sample processing procedures were begun. In addition, water discharging into tailings basins from processing plants contains large amounts of suspended material that requires settling before the sample can be processed. Thus, the initial sample was collected using clean 20-liter pail, and a final sample used for analysis was collected from this container after the tailings had settled. All samples were filtered in the field immediately after sample collection and prior to performance of preservation procedures.

Three Minnesota taconite mining operations participated in the tailings basin portion of this study (Location maps are included in appendices I and II): National Steel Pellet Company near Keewatin (National), Inland Steel Mining Company near Virginia (Inland), and LTV Steel Mining Company near Hoyt Lakes (LTV). Each of these companies currently disposes tailings in above-ground tailings basins, but the processing methods vary. National uses nothing beyond magnetic separation to process their ore, Inland uses flotation to decrease SiO₂ in their pellets, while LTV uses flotation and softens their water. This is important because it permits assessment of possible relationships between taconite processing techniques and water quality.

National:

Plant discharge and intake (return from tailings basin) samples were collected on each visit to National's tailings basin. No seeps were available for sampling at National's tailings basin, however, two wells were found on the south side of the basin in October, 1997 (wells 12 and 14). Well 12 had a depth of approximately 15 feet, the bottom 5 of which was filled with water. Well 14 was 28 feet deep, the bottom 11-13 feet of which was filled with water. Both wells were located at road level, approximately 12-15' below the top of the tailings dike. Well 12 was believed to bottom out within the tailings dike, while well 14 was likely tapping water from glacial tills beneath the dike. More precise geologic information for this well will be collected.

Inland:

Plant discharge and intake (return from tailings basin) samples were collected on each visit to Inland's tailings basin. In addition, a single seep was sampled on the NW side of Inland Steel's tailings basin during our initial visit in June, 1996. This seep was inactive during later visits. Water was also collected from a seep found on the north side of the tailings basin on our fourth through eighth visits. Two monitoring wells were installed by Inland Steel at the north edge of their tailings basin dike on Aug. 22, 1996. The first (MW-5) was drilled to the basement rock (Giants Range Granite) and screened between approximately 7 to 9 feet. The second (MW-6) was bored nearby to a depth of approximately 5 feet and screened for the interval between 3 and 5 feet below the surface. Both wells were sampled on all subsequent visits, weather permitting.

LTV:

A rapidly flowing seep was found on the southwest side of LTV's tailings basin during all of visits. Plant discharge and intake (return from tailings basin) samples were also collected on each visit.

USX/Snively pit tailings disposal site

Several samples were also collected from the tailings basin at USX early in our previous study, but later efforts were focused on obtaining water samples from the Snively Pit tailings disposal site. Tailings were deposited by USX within the Snively Pit from 1964 to 1980, providing us with an ideal opportunity to study the long-term effects of in-pit tailings disposal on groundwater chemistry. Until recently, the only activity in the pit was the pumping of mine-water from the nearby East Pit into the Snively Pit. Most of this water flowed directly back out of the Snively through porous road bed material on the west end of the pit, but some of this water may also have percolated into the tailings. The groundwater level in the Snively pit was found to be approximately 60 feet below the surface of the tailings owing to dewatering operations in the nearby East Pit. This made it necessary for us to drill a well deep into the tailings (89 feet) in order to obtain a representative sample of the pore fluids from this site. After completion of the well in October, 1996, samples were collected periodically, thereafter, beginning in November, 1996. A sample of the water being discharged into the pit was also collected on each visit for comparison purposes. Groundwater levels dropped recently owing to de-watering and active mining operation taking place around the Snively.

Biwabik Iron Formation ground waters

A large amount of data on the composition of water in the Biwabik Iron Formation are presented by Cotter et al (1965), but these data were inadequate for our purposes owing to the age of the dataset and because the chemical analysis for trace elements was incomplete. Thus, a total of eleven water samples were collected from city wells along the iron range in early May, 1998. These data not only provided us with range-wide information on the background levels of As, Mo, Mn, B, and F of pore waters currently existing in Biwabik Iron Formation aquifers, but also permitted assessment of chemical reactions potentially affecting chemical transport of these elements through the Biwabik Iron Formation. Field measurements (temperature, pH, conductivity, Eh) and samples were taken at each site with the pump running and water treatment processes deactivated (e.g., raw water samples). Samples were filtered on site and analyzed using the same procedures used for samples from tailings basins (see above). Cities participating in this part of the study included Calumet, Nashwauk, Keewatin, Hibbing, Buhl, Kinney, and Mountain Iron.

Laboratory study

Column Experiments

A series of experiments was conducted in our earlier study to evaluate chemistry of mineral processing waters reacting with tailings in an environment isolated from the atmosphere. The results from those experiments were presented by Berndt and Lapakko (1997 a,b) and will not be repeated here. However, the tailings and experimental apparatus used in those experiments were re-used in our current experiments (see below), so we briefly review the experimental apparatus and procedures here. Columns used in experiments were constructed of 2-inch inner diameter plastic tubing, 15 feet in length, and fitted with a sampling port at the base. The tubing was secured in vertical orientation and covered with an opaque plastic sheet to eliminate penetration of light. An amount of fluid equal to approximately one pore volume was passed through the column over a time period of 57 weeks. Samples were collected periodically throughout the year and analyzed for all of the same inorganic components measured in the field portion of the study.

During tailings deposition in a pit, it is likely that pore fluids (process waters) in tailings will at some time be replaced either by groundwater, seeping in from the pitwalls after the pit is filled, or by rainwater which may penetrate the tailings from above. One of the major purposes of this portion of our study was to determine if trace metals adsorbed on the surfaces of iron-oxides during interaction of tailings with process waters could be remobilized when the pore fluid was replaced by groundwater or surface runoff. Thus, it was important to use tailings that had aged previously in an environment closed from the atmosphere (rather than fresh tailings), such that trace components initially present in process waters were already adsorbed onto the tailings. The tailings used in the column experiments during our previous study were ideal for this purpose since they were relatively well characterized and had been exposed to process waters for a period of 1 year. During this one year time period, the bulk of the As and Mo existing in process waters at the beginning of the experiment was adsorbed onto the tailings. F was also partially taken up by the tailings, while significant Mn was released to the fluid.

Groundwater Injection Experiments

Groundwater used in experiments was collected from Keewatin which had been studied previously by Jim Walsh at the Minnesota Department of Health (Walsh, 1997). The starting composition of this water was essentially the same as that of well #2, with near neutral pH, slightly reduced as is typical of groundwaters in the region (Cotter *et al.*, 1965). Because groundwater composition changes rapidly when exposed to air (due to CO_2 degassing and O_2 entrainment) a special procedure was used to prevent these effects. The groundwater was collected using a special apparatus designed to permit continuous purging of the solution with a 1% CO_2 and 99% N_2 gas mixture. This procedure effectively kept unwanted oxygen from entering the fluid and maintained CO_2 levels at values typical for groundwater (Drever, 1997). The groundwater was injected into the columns from the base port such that it would displace the existing pore fluids from below and eliminate possible entrainment of oxygen and loss of CO_2 during the transfer process.

Because the columns are quite large (15 feet), sufficient sample could be injected into the columns to provide adequate fluid for full evaluation of groundwater/tailings interaction for the entire period of our study (several months). Because of the low permeability of tailings, however, the injection process was very slow and required several weeks to complete. The fluid was purged with the CO_2/N_2 mixture throughout the entire injection process to further prevent entrainment of O_2 and loss of CO_2 during this period.

Rainwater Experiments

Rainwater is also a potential reactant during in-pit disposal, particularly after the pit has been filled with tailings. In contrast to the groundwater penetration scenario, it is important that the water introduced during rainwater experiments is introduced into the tailings in a fully oxygenated state (saturated with air). This was accomplished simply by replacing the water existing above the tailings/water interface at the top of the columns with deionized water, and opening the sampling valve at the base of the column to permit the water to flow downward through the columns. As fluid is removed at the base of the column, it is displaced at the top of the column by oxygenated "rainwater". The first eight weeks of the experiments were characterized by flow of deionized water through the columns until a total of 4 liters of water had been collected at the base (flow rate equals approximately 500 mls/week). Since the pore volume for each of the columns is approximately 1.5 to 2 liters, this amount of flow should have been more than adequate to displace all of the pore fluid existing in the column. After this, the fluid was allowed to equilibrate with minerals in the column for a period of 15 weeks. The flow rate was then increased again to 500 mls/week to evaluate the effects, if any of large amounts of dilute water flowing through the tailings.

Small Scale Fluoride Leach Study

Tailings have on the order of 200 ppm fluoride, but the majority of this fluoride is probably contained in silicate minerals (clays and/or amphiboles) and/or in the mineral fluorapatite (Zhu and Sverjensky, 1991) none of which are easily altered at low temperatures. A series of separate experiments was designed, therefore, to characterize the amount of easily extractable F in tailings. The experimental procedure in this case was to fill a small column with tailings and then to flow water through the column, continuously monitoring F concentration until little or no more F could be leached. Columns used for this purpose were constructed of glass and measured approximately 40 cm in height and had an internal volume of 22.5 mls. A slurried mixture of freshly collected tailings and process waters were then used to fill the columns. After allowing the tailings to settle out of solution, the remaining pore fluid was decanted from the top of the column and replaced by deionized water. Flow was initiated and allowed to continue freely for a period of two weeks with samples collected daily for the first week and every two to three days, thereafter.

Computer Modeling

Fluid speciation, mineral saturation, and reaction path calculations were performed using "The Geochemist's Workbench, vs. 2.0" (Bethke, 1994). Thermodynamic data used in this program are predominantly from Johnson et al. (1992) and Dzomback and Morel (1990). The data was expanded to include modeling of MoO_4^- and F⁻ adsorption effects using adsorption constants estimated by Dzomback and Morel (1990) who derived them using correlation algorithms. Calculations were performed on an SGI work-station at the University of Minnesota.

Tailings from each of the mining companies participating in this study were analyzed in our previous study (Berndt and Lapakko, 1997 a,b). The chief carbonate minerals in taconite tailings are ankerite and siderite, which account for the bulk of the carbonate minerals found in tailings rangewide. Carbonate minerals react rapidly with fluids tending to neutralize acid and precluding, therefore, extreme acidic conditions (e.g., pH < 6.5) from being found in taconite tailings pore fluids. The relative amounts of siderite and ankerite in any particular ore horizon may vary considerably, as siderite is generally primary, and ankerite is secondary (Morey, personal communication).

Silicate minerals in tailings are typically dominated by quartz, stilpnomelane, minnesotaite, and talc. Silicates are generally much slower to react with aqueous fluids than are carbonate minerals, however, they can have a significant impact on solution chemistry if reaction times are long. Stilpnomelane has exchange sites which can affect the relative concentrations of exchangeable cations such as Ca, Mg, Na, and K. The other major reactants commonly found in taconite tailings are the non-magnetic iron oxides (hematite and goethite). The presence of these minerals in tailings has an important influence on the mobility of Mo and As which are present as oxyanions $(As(OH)_4, MoO_4)$. Negatively charged species such as these tend to adsorb to iron-oxides under neutral to acid pH conditions.

The carbonate minerals in tailings are complex solid solutions of Fe, Mn, Mg, and Ca carbonates which are not easily modeled using computer applications. In addition, the silicate minerals minnesotaite, talc, and stilpnomelane are complex solid solutions as they exist in the taconite tailings environment. Carbonate reactions were modeled in our simulations using stoichiometric siderite (FeCO₃), dolomite $(CaMg(CO_3)_2)$, and rhodochrosite (MnCO₃). Reaction of fluid with stilpnomelane and silicates was not considered explicitly, although such minerals provide important functions by controlling the concentrations of Si, Na, and K (cation exchange). The current version of Geochemist's Workbench does not permit modeling of cation exchange reactions. Our primary aim in this case was to identify chemical processes affecting redox and pH which affect strongly the adsorption and desorption of anions, and solubility of MnCO₃. Developing a means to assess pH and redox also gives us a means to assess mobilities of Mo, F, As, and Mn in a variety of geochemical settings.

Results and Discussion

The chemical composition of water in tailings basins can be found in appendix III, while the chemical composition of waters sampled from the Biwabik Iron Formation are presented in appendix IV. Averaged major element chemistries of water in and near tailings basins and of water within the Biwabik Iron formation are provided in Table 3 and presented in Figure 1.

A number of trends can be seen in the major element chemistry for waters plotted in Figure 1. First, virtually all waters in tailings basins have higher concentrations of Cl, SO_4 , HCO₃, Mg, and Na, than water typically found in Biwabik Iron Formation aquifers. This is not surprising since the grinding and oxidation of iron ore leads to significant dissolution of minerals. The second trend that can be clearly seen in Figure 1 and Table 3 is that the waters discharged into tailings basins have higher concentrations of nearly all elements than the fluids that are stored within the basin. This suggests to us that the water within the basin is diluted by rain or melting snow during storage within the basin. Since most of the water discharged to the basin is recycled back to the plant and re-used in the processing step, the concentrations of elements within the basins reflects the relative amounts of water recycled and replenished (water precipitating in the basin and/or pumped in from other areas).

The final general trend that can be seen in Figure 1 is that the concentrations of many of the major elements found in basin waters; HCO_3 , Ca, and Mg, in particular, increase again during seepage of the water through the tailings pile (compare "basin" and "reacted" waters). It is important to understand the mechanisms responsible for these changes in major element chemistry before we can fully evaluate factors affecting concentrations of trace elements of concern: Mo, As, F, and Mn.

Carbonic acid generation during siderite oxidation

Carbonic acid (H_2CO_3) is probably the most common form of acid in natural waters, and is responsible for most of the weathering that occurs in nature. Berndt et al. (1997a,b) suggested that carbonic acid generation in tailings might be analogous to a similar process known to take place in soils, whereby organic carbon is oxidized to H_2CO_3 during bacterial respiration (e.g., Stumm and Morgan, 1996; Drever, 1997; Langmuir, 1997). Production of carbonic acid in this manner consumes O_2 , decreases solution pH, and promotes dissolution of other nearby carbonate and silicate minerals. Since all of these effects are observed during tailings/water interaction, it is possible that this process is participating in the chemical alteration of tailings in taconite basins.

On the other hand, an alternative means to account for generation of carbonic acid during tailings alteration was suggested by Berndt (1998) who noted that oxidation of siderite to iron oxide (represented here by $Fe(OH)_3$) produces just such an effect:

$$FeCO_3 + 0.25 O_{2ag} + 2.5 H_2O = H_2CO_3 + Fe(OH)_3.$$
 (1)

While only 1 mmol of H_2CO_3 is produced for each mmol of O_2 reduced by organic carbon (e.g. $CH_2O + O_2 = H_2CO_3$), 4 mmolal of H_2CO_3 are produced for each mmolal of O_2 reduced during siderite oxidation! Thus, this reaction has a much greater potential of affecting water chemistry in tailings basin than does simple oxidation of organic matter. More specifically, this reaction, in combination with dissolution reactions involving Ca-Mg carbonate, can induce large increases in the concentrations of Ca, Mg, and dissolved HCO_3 by a reaction such as:

$$CaMg(CO_3)_2 + 2H_2CO_3 = Ca^{++} + Mg^{++} + 4 HCO_3^{-}$$
 (2)

Reactions 1 and 2 can be combined and the overall reaction and written:

$$4FeCO_3 + O_2 + 10H_2O + 2CaMg(CO_3)_2 = 4Fe(OH)_3 + 2Ca^{++} + 2Mg^{++} + 8HCO_3^{--}$$
 (3)

We can see by this reaction, that consumption of 1 mmole of dissolved oxygen results in the generation of 8 mmoles of HCO_3^- , and 2 mmoles each of Ca^{++} and Mg^{++} .

There is good reason to favor carbonic acid generation by oxidation of siderite rather than oxidation of organic compounds in the case of taconite tailings reaction. In particular, there is little organic carbon present in tailings, but there is abundant siderite. Siderite has been shown to react quickly in other tailings environments (Ptacek and Blowes, 1993). In addition, oxidation of organic carbon in a closed environment typically leads to highly reducing conditions (Bass-Becking et al, 1960), well below those typically encountered in our study of water chemistry on the iron range. Siderite oxidation, on the other hand, only leads to mildly reducing conditions (Berndt, 1998). Because the process that controls redox, also controls the mobility of redox-sensitive elements such as As and Mn, the identification of the dominant reducing mechanism is key to predicting trace element mobilities in a wide range of environments that might be encountered during in-pit disposal.

Finally, and perhaps most importantly, is that fact that reaction 3, when combined with realistic measurements of temperature and O_2 solubility, can predicts closely the chemical composition of groundwaters currently existing within the Biwabik Iron Formation (Figures 2 and 3). For example, if we consider that water in the Biwabik Iron Formation was derived from local rainwater and snow melt, then its oxygen content at the time it infiltrates the water basin can be computed by assuming saturation with respect to air (Figure 2). We then react this water with a combination of carbonate minerals representing siderite (FeCO₃) and ankerite ((Ca,Mg,Fe,Mn)CO₃ which are common minerals in the Biwabik Iron Formation (Morey, 1992; Berndt and Lapakko, 1997a). Because ankerite is a complex solid solution for which thermodynamic data were not available, its alteration behavior was represented by dolomite [(Ca,Mg)CO₃]. Carbonate minerals are known to equilibrate with fluids much more rapidly than silicate minerals (Drever, 1997). Finally, we assume that the reaction runs to completion, such that the resulting fluid is in equilibrium with all of the minerals placed in the system.

The results of the simulation, shown in Figure 3, reveal that the computed composition of air-saturated water equilibrating with siderite and ankerite is remarkably similar to that of water presently found in the Biwabik Iron Formation. Both contain approximately 3 mmolal of alkalinity balanced largely by near equal amounts of dissolved Ca and Mg, and only small amounts of dissolved Fe or Mn. The only significant variant between natural samples and the computer simulation is that some groundwaters have significant amounts of SO₄, due likely to localized oxidation of minor sulfide minerals (e.g., pyrite). Sulfate is enriched in process waters at some operations, most likely due to a similar process (Lapakko and Jagunich, 1991). Although water in the Biwabik Iron Formation was recharged from the surface through glacial sediments and regional outcrops, the strong correlation between the field measurements and computer simulations suggests to us that most water in the Biwabik Iron Formation aquifer is derived from local precipitation that has reacted with siderite and ankerite. However, it is unknown what proportion of the chemical reactions take place within soils and glacial sediments or within the Biwabik Iron Formation itself.

Since minerals in tailings basins were, ultimately, derived from the Biwabik Iron Formation, it might be expected that waters reacting in tailings environments would experience many of the same reactions as waters found within the Biwabik Iron Formation. Several important differences exist, however, between waters reacting in the Biwabik Iron Formation and water in tailings basins. In particular, water penetrating into the pores of tailings in tailings basins has already been reacted extensively with tailings in an environment containing abundant oxygen. The majority of water stored in tailings basins was used to grind, separate, and process minerals and may have been derived previously from groundwater resources within the region. Thus, the fluid penetrating into tailings typically contains, in addition to dissolved oxygen, relatively large amounts of dissolved Ca, Mg, and HCO₃ and may contain significant amounts of other elements, including Na, SO_4 , F, and Cl.

Nevertheless, application of a siderite oxidation model describes reasonably well the changes that take place during seepage of such waters through tailings (compare Figures 4 and 1). In particular, the large increases in HCO_3 , Ca, and Mg concentrations that occurs during seepage of water from National's tailings basin can be effectively simulated by reacting tailings basin water with a combination of siderite, dolomite, and rhodochrosite. Moreover, the high Mn and Fe concentrations in Inland seeps and wells can be effectively simulated by reacting the their tailings basin fluid with siderite and rhodochrosite, but in the absence of dolomite.

It is likely that future development of the computer simulations, allowing provision of sulfur oxidation effects in tailings basin waters, will also permit us to model the compositional changes in other basins where sulfur oxidation is also an important process (LTV, USX). At present, however, the close correlation between the observed and predicted chemical trends provided by a siderite oxidation model provide us with a degree of confidence that we now have a means to assess and predict redox and pH in wide variety of chemical environments involving taconite tailings. As discussed by Berndt *et al* (1997a,b) and Berndt (1998), As, Mo and Mn and F mobilities are affected strongly by changes in major element chemistry, pH and redox potential. It is likely, therefore, that coupling the siderite oxidation reaction to reactions involving adsorption of Mo, As, and F will permit us to assess transport of these important elements in a reasonably quantitative fashion (Berndt, 1998).

Groundwater/Tailings Interaction

The composition of water that evolved during our groundwater/tailings experiments is provided in appendix V and shown in Figures 7 through 10. The results reveal that the composition of groundwater during the experiments gradually approached the composition of the original pore fluid. These trends suggest that the groundwater injected into the column was affected mostly by a gradual remixing with the original pore fluid. Even a generally non-reactive component such as Cl, for example, rebounded to values approaching the original Cl concentrations during the course of each experiment. This type of behavior for Cl and the other elements is a clear indication that the major process responsible for changes in fluid chemistry during our groundwater experiment involves mixing between the injected fluid and the original pore fluid.

This type of result was not entirely surprising because the permeability of tailings is not uniform and some "streaming" could not be avoided during the injection of the groundwater. In effect, the groundwater that was injected would seek the highest permeability routes possible and avoid the least permeable zones in the column. After flow of groundwater was stopped, water remaining in the low-permeability zones was free to exchange diffusionally with water in the high-permeability zones, and result in the observed mixing patterns. Because flow rates in these experiments were very slow (e.g., <50 mls/wk), the amount of water passing through the column during the entire experiment was less then one pore volume. Noticeably lacking during the intrusion of groundwater into our columns, however, is any significant reaction between the tailings as would be indicated by increases in HCO_3 , Ca, or Mg above values found in the original pore fluid. This is exactly what one should expect in a system where acid generation is driven by availability of oxygen (equation 1): because the groundwater that was injected had no dissolved oxygen, reaction 1 could not proceed in the forward direction, and no significant dissolution of tailings resulted.

In terms of Mn, As, Mo, and F mobility (Figure 10), dissolved concentrations during experiments were generally intermediate to those in the initial groundwater or pore fluid concentrations. As for the major elements, the longer the experiment was carried out, the closer the values approached the original pore fluid values. This indicates to us that the incursion of groundwater into tailings does not result in significant release of these elements from the tailings. Simple mixing and associated minor desorption/adsorption readjustments are the dominant process controlling the chemistry of the fluids during incursion of groundwater into tailings.

Rainwater/Tailings Interaction

In the rainwater/tailings experiments, reacted process waters were replaced by deionized water to simulate infiltration from local runoff. In contrast to the groundwater experiments, water used in these experiments was freely exposed to the atmosphere prior to infiltration into the columns. The chemical composition of water derived in these experiments is presented in appendix VI and shown graphically in Figures 11 through 14.

In these experiments, deionized water was permitted to flow through the columns at a rate of approximately 400 mls/week for a period of 11 weeks (more than twice the amount needed to replace all of the water present in the column with deionized water). Cl and Br concentrations could be used to determine the degree of "short circuiting" that occurred in the columns. Samples were then periodically collected with the column operating in a static (non-flow) mode for the next 12 weeks in order to establish longer term equilibration between taconite tailings and recently oxygenated waters. After this period, continuous flow was again initiated at a rate of 500 mls /week to further rinse F and other mobile trace elements from the column. Analyses of samples from this last portion of the experiments were not complete at the time this document was written.

Perhaps the most remarkable aspect of the results shown in Figures 11 through 13 is the tremendous ability of minerals in the tailings to generate high alkalinity and dissolved cation concentrations water. In the rainwater experiment where National's tailings were exposed to the oxygenated rainwater, for example, the alkalinity of water penetrating the column increased from 0 to 4 mmolal. Alkalinity in experiments involving tailings from Inland and LTV increased by even more, up to approximately 6 mmolal. The low Cl concentrations in the reactant fluids from these experiments rule out mixing to account for the large increase in alkalinity and dissolved cations. In addition, a siderite oxidation process can only account for no more that a 4 mmolal increase in alkalinity. Thus, introduction of oxygenated de-ionized water into tailings previously inhabited by process waters gives rise to another chemical process that increases the alkalinity of the fluid above that which siderite oxidation alone can account for.

Cation and anion adsorption processes offer one possibility to account for this excess alkalinity. In particular, dilution has three effects on the chemical equilibration between fluids and mineral surfaces (Dzombak and Morel, 1990): (1) it changes the acid-base speciation on the mineral surfaces, (2) it changes the speciation of the element in the fluid, and (3) it affects the coulombic energy of ion adsorption. The net effect of these processes is to promote desorption of ions from the mineral surfaces. In effect, cations and anions may "co-desorb" from the surfaces of tailings and increase the activity of dissolved species in the fluid.

Trace element concentrations in fluids collected from our rainwater/tailings experiments (Figure 14) provide some support for such a process. Mo, for example, is an element that was generally adsorbed to the tailings during reaction of process waters with tailings (Berndt and Lapakko, 1997a,b), but this element appears to be preferentially released during infiltration by dilute water (Figure 14). The trace element composition of dilute fluids such as rainwater reacting with tailings reflects to some degree the past history of the tailings. In effect, cations and anions deposited onto mineral surfaces when the pores were inhabited by process waters, tend to desorb later into dilute fluids infiltrating the system.

The precise order in which anions and cations can be expected to desorb from tailings is not yet well understood at this point in our study, but geochemical models are being constructed to simulate the process as illustrated in Figure 15. Iron oxide minerals in this simulation are first equilibrated with process waters and then removed from the system and placed into a solution containing deionized water. By allowing the minerals to re-equilibrate with the deionized water, we can determine the relative order in which species can be expected to desorb from tailings.

In the case we modeled (Inland process waters; Figure 16), we found that Mo desorbed much more readily than the other species included in the model. As and F concentrations in the dilute water were similar to those that had existed in the process water suggesting these species also have a tendency to desorb gradually from tailings. W, which was also considered in the model, behaved in a fashion similar to that of Mo. These results are strikingly similar to the results obtained from the rainwater/tailings experiments, despite the fact that no provision was made for reaction with other minerals in the tailings. We feel it is likely, therefore, that a process similar to this will occur when tailings placed in a pit are infiltrated by surface runoff.

Fluoride in tailings basins

From a geochemical perspective, the behavior of fluoride in process waters has been particularly difficult to quantify. Berndt and Lapakko (1997a, b) found that process waters at LTV were supersaturated with respect to CaF_2 , while those at Inland were close to saturation and those at National were consistently below saturation. In general, very high Ca seeps from USX and LTV tailings basins were found to have very low F concentrations, and were consistently close to saturation with respect to the mineral fluorite. However, Berndt (1998) found several widely variable thermodynamic solubility constants were available to "predict" fluorite saturation (Brown and Roberson, 1977; Hem, 1985; Wolery, 1992; Johnson et al, 1991), and that whether or not water from Inland's tailings basin was saturated depended on which thermodynamic constants were used in the calculation. No firm conclusion can be made, therefore, on where, when, or even if fluorite saturation provides and effective limit on fluoride mobility in taconite tailings basins.

Since tailings generally contain large amounts of F (200 ppm) and because of the ambiguity associated with F geochemistry, further experimentation on the mobility of F was considered necessary. New column experiments were performed to determine exactly how much F could be readily leached from tailings and also to provide further information on the mechanism of F leaching. Because the case for or against fluorite saturation in tailings was ambiguous for Inland, we selected Inland's tailings for the experiments. Results from these experiments are depicted in Figure 17, where F concentrations are presented as a function of the number of pore volumes passed through the column.

If pore waters were efficiently displaced by the deionized water and if no reaction occurred between tailings and the new pore fluid, one would expect the concentrations of all elements to drop to concentrations below detection after only one pore volume of fluid had passed through the column. This was very nearly the case for unreactive anions (e.g., Cl, Br, data not shown), indicating that there was little short-circuiting of flow in these experiments. Despite this, the concentrations of F, Ca, Mg, and HCO₃ (Figure 17) in the effluent were maintained at detectable or high concentrations throughout the experiments even after 8-10 pore volumes of fluid (see Figure 17) had passed through the column. This indicates that significant reaction occurs during flow of deionized water through the tailings, similar to what was shown by our rain water experiments described above.

In terms of F mobility, the concentration of F in experiments 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 F begin to decrease, and even then, it decreased quite gradually depending upon the amount of fluid passed through the column. That the concentration of F in our experiments depended solely on the amount of fluid that passed through the column indicates that an adsorption/desorption process controls F mobility in Inland's tailings rather than a mineral dissolution process.

The experimental data also permit quantification of the total amount of fluoride that can be leached from taconite tailings. In general, it appears that the amount of F adsorbed to deposited tailings is approximately twice that present in the initial pore fluid (e.g., F(adsorbed)/F(dissolved) = 2 in freshly deposited tailings). For Inland, at the time our tailings sample was collected, this amounts to approximately 2 ppm leachable F (on a mass basis), or approximately 1% of the total F typically found in taconite tailings (200 ppm) (see Berndt and Lapakko, 1997 a,b).

Fluoride source

An important question that must be asked is, "What factors control the amount of mobile F in taconite tailings?" A partial answer to this question was provided by results of Berndt and Lapakko (1997a) and Jakel et al (1998) who measured F in taconite processing streams at Inland and LTV. It was determined in both studies that the scrubber water was the predominant source of F in taconite processing streams. Engesser (1998) has made similar observations.

A possible mechanism for F mobilization in taconite processing streams is presented schematically in Figure 18. In general, F in unprocessed ore is immobile because it is bound in relatively insoluble minerals such as fluorapatite, amphibole, and clay minerals (Zhu and Sverjensky, 1991). Support for this notion can be found in the fact that Biwabik Iron Formation waters typically have low F concentrations (Table 3). During mineral processing, most of these F bearing minerals are separated from the ore and disposed along with tailings into the tailings basins. If all of the F-bearing minerals were treated in this fashion, then the concentration of F 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 F bearing minerals present in ore will always be streamed along with the concentrate into the pellitization plant. Materials are heated to extremely high temperatures during pelletization.

F in apatite and silicates can be converted quickly to HF (in the presence of H_2O vapor) (Zhu and Sverjensky, 1991) which is highly volatile. Gases 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 as dissolved F. The resulting scrubber waters are mixed back into the process streams, where some of the fluoride may combine with Ca and precipitate as fluorite and where some may also adsorb onto the surfaces of the tailings.

By this mechanism, the amount of mobile F generated during processing of taconite will depend on the efficiency in which F bearing minerals can be removed from the concentrate. Engesser (personal communication) suggests that F concentrations in tailings process waters may be intrinsically related to the grain size of the natural ore. For finer grain sized ores, separation of ore and non-ore minerals will be more difficult to separate, and there will be a greater tendency for some of the F-bearing minerals to be routed into the agglomerator indurator. This effect may account for the low F in National Steel's process water compared to Inland or LTV (Engesser, personal communication).

Origin of Snively Pit pore fluids

Chemistry of water from the Snively Pit is presented in the appendix VII. Both pore (well) and surface (sump) water are of similar types with very high SO_4 and high alkalinity. Both waters have, therefore, apparently been exposed to oxidized sulfide minerals, and are most similar, in this regard, to water from the USX tailings basin (Lapakko and Jangunich, 1991; Berndt and Lapakko, 1997a,b). The dissolved concentrations of all trace elements (As, Mo, B, and F are extremely low), while Mn concentrations are significant.

Several chemical indicators suggest that the pore fluid is composed of surface water that has infiltrated the tailings. In particular, differences that do exist in the surface and pore waters in the Snively Pit are consistent with reactions that generally take place within tailings. For example, $SO_4^{=}$, HCO_3^{-} , Ca, and Mg concentrations are all higher in the pore fluid compared to water at the surface, while K, Na, Rb, and Cs, are all less. These chemical changes are exactly what would be predicted if the surface water from the pit were to react with tailings in a closed environment (see above, and Berndt and Lapakko, 1997a). However, fluids currently reacting with tailings in the Snively Pit are atypical of any of the other waters that we collected from Biwabik Iron Formation aquifers or of any of most other waters that result from tailings/water interaction (except at USX, see Lapakko and Jagunich, 1991 and Berndt and Lapakko, 1997a). We believe that the unusual chemistry is a local by-product of the extensive mining and mineral processing activities that have occurred in the vicinity of the Snively Pit. Since the area around the Snively pit has been actively mined for many years, the precise source of the high SO_4^{-1} fluids is not known.

Conclusions

(1) Redox potential and pH in tailings basins appear to be influenced by oxidation of siderite (FeCO₃) to iron oxide. Models performed using this reaction correctly predict the compositions of water currently existing in the Biwabik Iron Formation and the compositions of process waters seeping through tailings in tailings basins. The conditions brought on by this reaction result in increased solubility of $MnCO_3$ and increased sorption of Mo, As, and F.

(2) Experiments indicated that intrusion of tailings by groundwater leads to mixing with only minor mineral/fluid reaction (owing to the lack of oxygen in groundwater) and, correspondingly, to low level mobilization of As, Mo, Mn, and F.

(3) Infiltration of tailings by local runoff derived from precipitation potentially introduces significant oxygen into taconite tailings, and leads, therefore, to renewed oxidation of siderite, dissolution of carbonate minerals in the tailings, and possible remobilization of F, Mo, and As.

(4) A small fraction of the F in primary taconite ores is mobilized during mineral processing (during pelletization). Our results suggest that a large fraction of this F remains in solution and enters the tailings basin as soluble F. A significant fraction of the mobilized F is adsorbed onto the surfaces of minerals and will be deposited along with the tailings. This adsorbed F represents only a small fraction of the total F in tailings (e.g., 1% for Inland).

(5) Pore water chemistry in tailings deposited in the Snively Pit are of a high $SO_4^{=}$ and high alkalinity variety unlike any other waters sampled in our study. They appear to have been derived from surface waters which are being pumped into the Snively from a nearby active pit.

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Tables:

Table 1. Approximate detection limits for analysis by ICP-MS and ion chromatography at the University of Minnesota, Department of Geology and Geophysics.

Detection limit	ICP-MS	IC
(ppb)		
<.1	Ag, As, Ba, Cd, Co, Cr, Cs, Ga,	
	Ge, Mg, Mn, Mo, Ni, Pb, Rb,	
	REE's, Sn, Sr, Th, Tl, U, V, W	
0.1-1.0	Al, Ca, Cu, Si, Zn	
1.0-10.0	Li, K, Fe, Na, Se	Br, Cl, F, NO_2 -N,
		NO ₃ -N
10-50	В	PO_4 -P, SO_4

*REE's = rare earth elements

Table 2. Analytical procedures used in this study.

Element	Method	Preservation/Handling
Cations	ICP-MS	Filtered, 60 ml, 200 µl HNO ₃
(see Table 1)		
Anions	Ion chromatography	Filtered, Stored at approximately 4°C
(see Table 1)		
Alkalinity	Titration	Filtered, Stored at approximately 4°C
(see Table T) Alkalinity	Titration	Filtered, Stored at approximately 4°

	National (6/96 -4/98)			Inland (6/96-4/98)			LTV (6/96-4/98)			
	Discharge	Basin	Reacted	Discharge	Basin	Reacted	Discharge	Basin	Reacted	Biwabik
					· · · · ·				i	Fe-Fm
рН	8.26	8.51	7.18	8.37	8.56	7.25	8.64	8.75	7.38	7.33
Alkalinity	220	196	306	191	175	216	283	274	445	186
Eh	319	334	345	260	302	242	283	325	223	
majors(ppm)										
Al	0.00	0.00	0.00	0.43	0.40	0.01	0.01	0.51	0.00	.002
Si	16.0	7.9	10.6	10.5	3.5	6.8	8.5	6.1	10.3	5.7
Fe	0.01	0.01	0.00	0.04	0.00	4.35	0.00	0.03	1.54	0.34
Mn	0.06	0.04	0.03	0.06	0.01	4.05	0.02	0.03	0.99	0.18
Ca	32.7	24.1	75.9	30.3	27.2	40.2	15.5	20.1	67.8	44.9
Mg	36.9	34.4	28.8	45.2	38.4	36.6	30.2	35.0	72.4	22.5
Na	40.2	33.8	27.7	39.7	22.9	20.1	135.3	116.9	110.3	8.2
K	10.0	6.5	2.4	10.5	8.9	7.2	17.1	13.3	16.9	1.8
F	1.30	0.95	0.56	4.37	2.53	2.37	10.11	8.58	4.14	0.28
Cl	28.2	21.3	20.8	69.4	45.9	45.3	36.2	32.8	33.7	5.6
NO2-N	0.44	0.04	0.00	0.10	0.00	0.00	0.08	0.04	0.00	0.00
Br	0.06	0.05	0.07	0.50	0.32	0.34	0.18	0.16	0.16	0.017
NO3-N	4.59	2.16	0.30	2.02	0.64	0.42	1.76	1.02	0.39	0.41
SO4	61	51	40	60	44	29	115	117	225	34.4
trace (ppb)										
Li	15	10	8	21	9	8	94	86	36	8.9
В	75	53	37	113	62	41	342	317	444	46.3
Sc	3.5	1.7	2.9	2.5	0.7	1.6	1.8	1.1	2.2	
Cr	4.4	3.7	6.1	3.1	2.3	3.6	3.8	4.0	1.4	2.9
Co	0.2	0.2	0.4	0.2	0.3	2.6	0.2	0.3	2.8	0.4
Ni	0.7	0.4	1.2	1.0	0.7	3.3	0.8	0.9	1.5	3.9
Cu	0.7	0.5	2.3	1.1	0.7	1.1	0.9	2.1	0.7	2.8
Zn	17.1	17.2	19.6	22.5	19.3	19.6	15.0	14.8	18.0	25
As	2.2	1.4	0.4	2.9	4.6	· 3.2	4.1	9.8	4.5	0.5
Se	3.7	1.5	0.2	1.3	1.1	0.4	0.5	0.6	0.5	0.9
Rb	8.6	5.0	1.4	9.4	9.9	6.6	18.1	13.2	13.1	1.6
Sr	93	76	125.10	157	111	193	120	135	341	169
Y	0.02	0.01	0.05	0.01	0.01	0.19	0.02	0.02	0.05	
Мо	63.8	41.3	8.9	89.6	34.1	6.8	341	271	92	0.24
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.73	0.00	
Cd	0.06	0.03	0.09	0.10	0.04	0.02	0.30	0.23	0.07	0.0
Sn .	0.06	0.06	0.06	0.17	0.03	0.09	0.22	0.13	0.11	
Sb	0.06	0.03	0.00	0.11	0.02	0.01	0.27	0.19	0.01	
Те	0.00	0.00	0.00	0.06	0.00	0.01	0.01	0.01	0.00	
Cs	1.00	0.30	0.00	1.53	0.85	0.47	3.09	1.90	1.15	0.24
Ba	5.00	4.58	60.92	5.58	9.05	92.43	5.64	5.07	42.34	52.2
W	0.22	0.13	0.11	1.13	0.20	0.09	5.00	3.66	0.24	0.18
Pb	0.14	0.18	0.04	0.06	0.08	0.14	0.03	0.15	0.11	0.52
U	0.75	0.62	1.00	0.36	0.31	0.48	0.50	0.48	0.28	0.33

Table 3: Averaged chemistry of water in tailings basins and in the Biwabik Iron Formation.



Figures:





Figure 2. Schematic representation of geochemical reaction model used to describe chemical changes taking place in water reacting with tailings and of water present in the Biwabik Iron Formation. Air in this case is assumed to consist of mostly 79 % N_2 , 21 % O_2 and 0.032 % CO_2 .



Figure 3. Major element composition of Biwabik Iron Formation groundwaters. Column on the far right represents chemistry predicted when dilute water in equilibrium with the atmosphere (e.g., infiltrating rain) equilibrates at 8°C with siderite and dolomite in an environment closed from the atmosphere. The similarity between predicted and measured compositions suggests that siderite oxidation is an important process in Biwabik Iron Formation aquifers.



Fig.4. Chemical changes predicted during reaction of process waters with tailings using model described in figure 2. Process waters reacting with siderite/ankerite/rhodochrosite undergo changes similar to those observed at National's tailings basins, while process waters reacting with siderite and rhodochrosite alone undergo changes similar to those observed in Inland's tailings basin. Compare with figure 1.



Figure 5. Averaged concentrations of fluoride and manganese in and near tailings basins for National, Inland, and LTV steel mining companies. "Discharge" refers to water discharged with tailings into the tailings basin, "Basin" refers to water store in the tailings basins, and "Reacted" refers to water collected from seeps or wells at the toe of the tailings basin dikes.



Figure 6. Two-year average arsenic and molybdenum concentrations for water in and near tailings basins for National, Inland, and LTV steel mining companies. "Discharge" refers to water discharged with tailings into the tailings basin, "Basin" refers to water store in the tailings basins, and "Reacted" refers to water collected from seeps or wells at the toe of the tailings basin dikes.



National - Groundwater/Tailings Interaction





Inland - Groundwater/Tailings Interaction

Figure 8. Cation and anion concentrations during reaction of tailings from Inland Steel with our reduced, CO_2 bearing groundwater. Although the groundwater injected into the columns changes with time, it appears most of the change is due to mixing and diffusion with pore fluid still remaining in the column after the injection. Little chemical reaction with the tailings was observed.



LTV - Groundwater/Tailings Interaction





Figure 10. Mn, F, As, and Mo concentrations during reaction of tailings from National, Inland, and LTV Steel companies with our reduced, CO_2 bearing groundwater.



Figure 11. Cation and anion concentrations during reaction of tailings from National Steel with oxygenated "rainwater". "Pore fluid" represents the composition of the pore fluid prior to displacement by deionized water. The first 8 weeks of the experiment was characterized by flow of water through the column (pore volume = 2.0 liters) at a rate of 500 mls/week. This was followed by a period of 15 weeks where there was no flow except for the small amounts of fluid extracted during sampling. After 23 weeks of reaction, the flow was again continued at a rate of 500 mls/week. This experiment is still in progress.



Figure 12. Cation and anion concentrations during reaction of tailings from Inland Steel with oxygenated "rainwater". "Pore fluid" represents the composition of the pore fluid prior to displacement by deionized water. The first 8 weeks of the experiment was characterized by flow of water through the column (pore volume = 2.0 liters) at a rate of 500 mls/week. This was followed by a period of 15 weeks where there was no flow except for the small amounts of fluid extracted during sampling. After 23 weeks of reaction, the flow was again continued at a rate of 500 mls/week. This experiment is still in progress.



Figure 13. Cation and anion concentrations during reaction of tailings from LTV Steel with our oxygenated "rainwater". "Pore fluid" represents the composition of the pore fluid prior to displacement by deionized water. The first 8 weeks of the experiment was characterized by flow of water through the column (pore volume = 2.0 liters) at a rate of 500 mls/week. This was followed by a period of 15 weeks where there was no flow except for the small amounts of fluid extracted during sampling. After 23 weeks of reaction, the flow was again continued at a rate of 500 mls/week. This experiment is still in progress.


Figure 14. Mn, F, As, and Mo concentrations during reaction of tailings from National, Inland, and LTV Steel companies with oxygenated "rainwater". Flow through the columns was approximately 400 mls/week for the first 11 weeks of reaction, stopped for the period between 11 and 23 weeks, and then increased again to 500 mls/week during the for the rest of the experiments. This experiment is still in progress at the time this document was prepared.

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Figure 15: Schematic representation of reaction path calculations used to simulate desorption of oxyanions during incursion of rainwater in strata containing taconite process waters and iron oxides. Step one equilibrates process water with taconite tailings, step two transfers the iron-oxides and adsorbed species to a new tank containing deionized water, and step 3 equilibrates the deionized water with the surfaces of the iron-oxides. Results of the calculation are shown in figure 16.



Figure 16. Computed concentrations of adsorbed specie's calculated for pure water that has replaced pre-existing pore fluid (C2) divided by the concentration initially present in the pore fluid (C1). Actual modeling of desorption of ions into dilute fluids in tailings is a complicated process involving coupling of adsorption and desorption processes with mineral dissolution and precipitation calculations. This simple calculation approximates, however, the behavior observed in tailings/rain water experiments whereby Mo, F, and As were desorbed from the tailings, at values similar to, and sometimes higher than were present in the initial pore fluid.



Figure 17. Fluoride concentrations and dissolved Ca, Mg and HCO3- during leach test performed on tailings from Inland Steel.



Figure 18. Schematic diagram showing how F mobilization occurs in taconite processing plants. F is initially bound in insoluble non-ore minerals (fluorapatite, amphiboles, clays) found in the primary ore. Because ore separation is not 100% efficient, a small fraction of non-ore minerals are incorporated into the concentrate and subjected to high heat when the concentrate is pelletized. Intense heating during induration releases the F from these non-ore minerals into the air (as HF). This HF is recaptured by the plant scrubber system and introduced back into the tailings process stream as dissolved F. F introduced to the tailings stream in the scrubber waters, however, can either remain in solution, precipitate as fluorite (CaF₂), or adsorb onto the surfaces of minerals in the tailings. Because the majority of non-ore minerals are never subjected to pelletization, most of the F present in tailings remains locked in minerals and will not be released into waters that flow through the tailings.

Appendices:

Appendix I. Location map of operations involved in this study.

Mining operations included in present study Location maps for National Tailings Basin Sample sites Location maps for Inland Steel Sampling sites Location map for LTV sampling sites

Appendix II. Chemical compositions of water in and near tailings basins for the period extending from June, 1996, to April, 1998.

National Tailings Discharge Pipe National Tailings Basin at reclaim barge National Tailings Basin well #12 National Tailings Basin well #14 Inland Tailings Discharge Pipe Inland Tailings Basin Inland Tailings Basin Seeps Inland "Shallow" Well (MW6) Inland "Deep" Well (MW5) LTV Tailing Discharge Pipe LTV Tailings Basin LTV Tailings Basin Seep

Appendix III. Chemical composition of water in Biwabik Iron Formation

Appendix IV. Chemical composition of water during groundwater/tailings Experiments National Inland

LTV

Appendix V. Chemical composition of water in rainwater/tailings experiments. National Inland LTV

Appendix VI. Chemical composition of water in the Snively pit tailings disposal site, USX.

Snively Pit Pore Water Composition Snively Pit Sump Discharge to surface of tailings in Snively Pit Appendix I. Location map and sample collection sites.
Mining operations included in present study
Location maps for National Tailings Basin Sample sites
Location maps for Inland Steel Sampling sites
Location map for LTV sampling sites









Appendix II. Chemical compositions of water in and near tailings basins for the period extending from June, 1996, to April, 1998.

National Tailings Discharge Pipe

National Tailings Basin at reclaim barge

National Tailings Basin well #12

National Tailings Basin well #14

Inland Tailings Discharge Pipe

Inland Tailings Basin

Inland Tailings Basin Seeps

Inland "Shallow" Well (MW6)

Inland "Deep" Well (MW5)

LTV Tailing Discharge Pipe

LTV Tailings Basin

LTV Tailings Basin Seep

National: Tailings Discharged From Plant

Date	6/14/96	9/12/96	1/23/97	4/10/97	7/17/97	10/9/97	2/6/98	4/10/98					
T (C)	26	19	15	12	30	25	13	16	Nationa	al			
Cond					500		550	650	Tailing	s Dischar	ge		
									Ave	Std Dev	Max	Min	Ν
pН	8.18	8.00	8.54	8.45	8.31	8.06	8.31	8.19	8.26	0.18	8.54	8.00	8
Alk	193		249	244	194	217	209	232	220	23	249	193	7
Eh	279	386	37	466	384	na	348	337	319	137	466	37	7
majors	(ppm)												
Si	18.3	17.1	14.2	14.3	21.4	16.7	12.6	13.8	16.0	2.9	21.4	12.6	8
Fe	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.02	0.01	0.01	0.02	0.00	8
Mn	0.02	0.05	0.06	0.09	0.01	0.03	0.06	0.14	0.06	0.04	0.14	0.01	8
Ca	30.0	29.0	27.8	32.7	27.7	38.0	39.1	37.1	32.7	4.7	39.1	27.7	8
Mg	34.0	37.2	42.8	38.8	30.4	34.6	35.7	41.5	36.9	4.1	42.8	30.4	8
Na	39.2	37.5	44.1	46.9	42.4	37.4	39.1	35.1	40.2	3.9	46.9	35.1	8
K	10.5	8.4	8.7	9.9	8.7	8.2	8.9	16.5	10.0	2.7	16.5	8.2	8
F	1.24	1.18	1.14	1.29	1.40	1.10	1.55	1.48	1.30	0.16	1.55	1.10	8
Cl	30.8	27.2	26.9	29.9	24.4	25.3	29.2	32.3	28.2	2.8	32.3	24.4	8
Br	0.05	0.05	0.06	0.07	0.07	0.06	0.08	0.07	0.06	0.01	0.08	0.05	8
NO3-N	3.76	5.66	4.04	5.36	4.22	3.89	4.13	5.66	4.59	0.82	5.66	3.76	8
SO4	54	55	61	59	52	61	72	72	61	8	72	52	8
trace (p	ppb)												
Li	14	15	18	16	20	11	14	15	15	3	20	11 ^t	8
В	85	101	104	59	74	59	55	60	75	20	104	55	8
Со	0.1	0.3	0.4	0.2	0.3	0.4	0.2	0.2	0.2	0.1	0.4	0.1	8
Ni	0.4	0.6	0.9	0.6	0.0	1.3	0.8	0.8	0.7	0.4	1.3	0.0	8
Cu	0.6	0.7	0.0	0.0	0.7	1.6	1.0	1.3	0.7	0.6	1.6	0.0	8
Zn	2.6	30.0	27.4	25.8	0.9	17.3	17.7	14.8	17.1	10.9	30.0	0.9	8
Ge	0.1	0.1	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.2	0.1	8
As	1.8	3.2	2.7	2.1	2.6	0.6	1.3	3.1	2.2	0.9	3.2	0.6	8
Se	2.1	3.6	i 3.6	6.1	5.8	0.0	3.6	5.1	3.7	2.0	6.1	0.0	8
Rb	8.6	7.1	8.0	7.9	8.7	7.0	7.0)	8.6	2.3	14.1	7.0	8
Sr	98	91	109	96	75	88	83	103	93	11	109	75	8
Y	0.01	0.02	0.03	0.02	0.02	0.02	0.02	2. 0.02	2 0.02	0.01	0.03	0.01	8
Мо	68.8	70.0) 76.2	65.7	64.5	44.3	46.3	s 74.2	2 63.8	12.0	76.2	44.3	8
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.00) 0.00	0.00	0.00	0.00	0.00	8
Cd	0.08	0.06	0.02	0.05	0.05	0.09	0.05	5 0.07	0.06	0.02	0.09	0.02	8
Sn	0.19	0.00	0.00	0.00	0.00	0.00) 0.16	5 0.14	4 0.06	0.09	0.19	0.00	8
Sb	0.20	0.08	0.01	0.00	0.09	0.03	0.01	l 0.0 2	2 0.06	0.07	0.20	0.00	8
Te	0.00	0.00	0.00	0.00	0.00) 0.00) 0.00) 0.0	0.00	0.00	0.00	0.00	8
Cs	1.28	0.76	0.76	0.91	1.22	2 1.01	l 0.76	5 1.3	0 1.00	0.24	1.30	0.76	8
Ba	1.12	2.64	5.78	5.07	0.73	0.50	5 0.54	4 23.5	2 5.00	7.76	23.52	0.54	8
W	0.17	0.21	0.25	0.14	0.25	5 0.07	7 0.18	8 0.4	8 0.22	0.12	0.48	0.07	8
РЬ	0.09	0.17	0.23	0.00	0.04	0.50) 0.0	3 0.0	4 0.14	0.17	0.50	0.00	8
U	0.51	0.43	1.21	0.43	1.73	3 0.33	3 0.5	1 0.8	3 0.75	0.49	1.73	0.33	8

Date	6/14/96	9/12/96	1/23/97	4/10/97	7/17/97	10/9/97	2/6/98	4/10/98	5				
T (C)	23	20	1	1	23	16	5	9	Nationa	al			
Cond					500	500	500	400	Basin I	Reclaim			
									Ave	Std Dev	Max	Min	Ν
pН	8.74	8.67	8.20	8.66	8.78	8.48	8.15	8.38	8.51	0.24	8.78	8.15	8
Alk	178	179	230	204	186	193	215	188	196	18	230	178	8
Eh	259	389	62	479	413	409	348	314	334	129	479	62	8
majors	(ppm)												
Si	7.6	5.6	7.1	9.3	8.8	6.7	8.7	9.0) 7.9	1.3	9.3	5.6	8
Fe	0.03	0.03	0.02	0.01	0.00	0.00	0.00	0.02	2 0.01	0.01	0.03	0.00	8
Mn	0.00	0.01	0.06	0.08	0.00	0.00	0.12	0.04	4 0.04	0.04	0.12	0.00	8
Ca	23.1	20.1	22.6	21.4	20.7	25.7	33.1	25.7	7 24.1	4.2	33.1	20.1	8
Mg	35.6	32.5	35.8	35.4	32.5	33.5	38.0	31.6	5 34.4	2.2	38.0	31.6	8
Na	29.3	28.8	35.6	36.4	35.5	33.1	37.8	34.(33.8	3.3	37.8	28.8	8
K	6.2	5.8	5.9	5.9	6.5	6.2	7.3	8.2	2 6.5	0.9	8.2	5.8	8
F	0.85	0.86	0.99	0.91	1.00	0.87	1.03	1.13	3 0.95	0.10	1.13	0.85	8
Cl	18.9	18.6	22.7	21.3	20.5	21.2	24.9	22.0	6 21.3	2.1	24.9	18.6	8
Br	0.04	0.04	0.04	0.05	0.05	0.05	0.06	0.0	6 0.05	0.01	0.06	0.04	8
NO3-N	2.65	0.71	1.97	2.69	2.68	1.14	2.23	3.1	8 2.16	0.85	3.18	0.71	8
SO4	48	42	50	48	46	52	65	5:	5 51	7	65	42	8
trace (j	ppb)												
Li	8	8	12	13	13	8	9	10	0 10	2	13	8 .	8
В	49	66	74	42	41	40	60	5	2 53	13	74	40	8
Co	0.1	0.2	0.2	0.2	0.1	0.1	0.3	0.	1 0.2	0.1	0.3	0.1	8
Ni	0.3	0.6	0.3	0.4	0.0	0.3	0.6	0 .	5 0.4	0.2	0.6	0.0	8
Cu	0.9	0.5	0.0	0.0	0.5	0.3	1.5	0.	4 0.5	0.5	1.5	0.0	8
Zn	1.1	32.4	27.2	21.7	0.5	22.3	16.4	15.	9 17.2	11.4	32.4	0.5	8
Ge	0.0	0.0	0.1	0.1	0.1	0.1	0.1	. 0.	1 0.1	0.0	0.1	0.0	8
As	0.7	2.2	1.7	1.6	1.5	1.2	1.6	5 1.	0 1.4	0.5	2.2	0.7	8
Se	0.0) 1.5	1.3	3.7	0.8	0.0	1.7	2.	7 1.5	1.3	3.7	0.0	8
Rb	4.3	4.7	4.8	4.3	5.5	4.7	5.5	5 6.	4 5.0	0.7	6.4	4.3	8
Sr	63	68 68	88	76	68	82	94	1 7	0 76	11	94	63	8
Y	0.01	0.01	0.02	0.02	0.02	0.01	0.01	0.0	1 0.01	0.01	0.02	0.01	8
Мо	32.8	39.8	43.3	45.0	47.3	39.0	42.9	4 0.	.3 41.3	4.4	47.3	32.8	8
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0 0.00	0.00	0.00	0.00	8
Cd	0.05	0.03	0.00	0.03	0.00	0.08	0.05	5 0.0	0 0.03	0.03	0.08	0.00	8
Sn	0.15	0.00	0.00	0.16	0.00	0.10	0.03	3 0.0	0 0.06	0.07	0.16	0.00	8
Sb	0.07	0.04	0.01	0.00	0.05	5 0.02	0.01	0.0	0.03	0.03	0.07	0.00	8
Te	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0	0.00	0.00	0.00	0.00	8
Cs	0.22	0.23	0.18	0.26	0.53	0.28	s 0.39	9 0.3	0.30	0.11	0.53	0.18	8
Ba	3.70	4.02	5.30	3.04	2.10) 7.54	8.80	5 2.0	5/ 4.58	s 2.49	8.86	2.07	8
W	0.09	0.00	0.29	0.20	0.14	0.14	0.09	9 0.0	0.13 אין	s 0.09	0.29	0.00	8
Pb	0.08	0.18	1.04	0.02	0.0	0.00	0.0	/ 0.0	0.18	s 0.35	1.04	0.00	8
U	0.43	0.37	0.93	0.34	1.43	5 0.33	s 0.5	3 0.5	0.6 2	2 0.38	1.43	0.33	8

Date	10/9/97	2/6/98	4/10/98					
T (C)	12	8	6	Nationa	ıl			
Cond	700	550	550	Well #1	2			
				Ave	Std Dev	Max	Min	Ν
pН	7.16	7.12	7.26	7.18	0.07	7.26	7.12	3
Alk	310	281	326	306	23	326	281	3
Eh	279	407	349	345	64	407	279	3
majors	(ppm)							
Si	11.3	10.1	10.4	10.6	0.6	11.3	10.1	3
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3
Mn	0.07	0.01	· 0.01	0.03	0.04	0.07	0.01	3
Ca	82.3	69.1	76.5	75.9	6.6	82.3	69.1	3
Mg	29.9	26.9	29.6	28.8	1.7	29.9	26.9	3
Na	25.0	30.0	28.2	27.7	2.6	30.0	25.0	3
Κ	2.6	2.2	2.2	2.4	0.2	2.6	2.2	3
F	0.51	0.62	0.54	0.56	0.06	0.62	0.51	3
Cl	21.3	21.1	20.0	20.8	0.7	21.3	20.0	3
Br	0.07	0.07	0.07	0.07	0.00	0.07	0.07	3
NO3-N	0.49	0.21	0.21	0.30	0.17	0.49	0.21	3
SO4	39	43	38	40	3	43	38	3
trace (j	ppb)							
Li	8	7	8	8	1	8	7	3
B	28	43	40	37	8	43	28	3
Co	0.3	0.2	0.7	0.4	0.3	0.7	0.2	3
Ni	1.2	0.8	1.8	1.2	0.5	1.8	0.8	3
Cu	0.7	5.0	1.2	2.3	2.3	5.0	0.7	3
Zn	23.6	20.8	14.4	19.6	4.7	23.6	14.4	3
Ge	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3
As	0.5	0.5	0.1	0.4	0.2	0.5	0.1	3
Se	0.0	0.7	0.0) 0.2	0.4	0.7	0.0	3
Rb	1.3	1.4	1.4	5 1.4	0.1	1.5	1.3	3
Sr	138	111	127	125.10	0 13.73	137.90	110.60	3
Y	0.05	0.04	0.05	5 0.05	0.01	0.05	0.04	3
Мо	8.1	10.0	8.1	7 8.9	1.0	10.0	8.1	3
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3
Cd	0.09	0.04	0.13	3 0.09	0.05	0.13	0.04	3
Sn	0.00	0.11	0.0	5 0.06	0.06	0.11	0.00	3
Sb	0.01	0.00	0.00	0.00	0.01	0.01	0.00	3
Te	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3
Cs	0.00	0.00	0.0	1 0.00	0.01	0.01	0.00	3
Ba	63.49	57.57	61.7	1 60.92	2 3.04	63.49	57.57	3
W	0.05	0.12	0.1	5 0.11	0.05	0.15	0.05	3
РЬ	0.05	0.04	0.0	4 0.04	0.01	0.05	0.04	3
U	0.68	0.98	1.3	3 1.00	0.33	1.33	0.68	

Date	10/9/97	2/6/98	4/10/98							
T (C)	12	8	10	Nationa	al					
Cond	450	500	500	Well #1	4					
				Ave	Std Dev	Max	Min	Ν		
pН	7.24	7.08	7.45	7.26	0.19	7.45	7.08	3		
Alk	337	337	303	326	20	337	303	3	÷	
Eh	453	па	351	402	72	453	351	2		
majors	(ppm)									
Si	12.8	13.2	11.3	12.4	1.0	13.2	11.3	3		
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3		
Mn	0.01	0.01	0.11	0.04	0.05	0.11	0.01	3		
Ca	89.3	89.6	72.2	83.7	9.9	89 .6	72.2	3		
Mg	30.4	30.3	24.2	28.3	3.6	30.4	24.2	3		
Na	5.8	6.0	4.7	5.5	0.7	6.0	4.7	3		
K	1.2	1.0	1.0	1.0	0.1	1.2	1.0	3		
F	0.13	0.12	0.11	0.12	0.01	0.13	0.11	3		
Cl	6.7	7.2	5.3	6.4	1.0	7.2	5.3	3		
Br	0.06	0.06	0.04	0.05	0.01	0.06	0.04	3		
NO3-N	0.82	0.66	0.13	0.53	0.36	0.82	0.13	3		
SO4	16	18	15	16	1	18	15	3		
trace (p	pb)									
Li	8	8	6	7	1	8	6	3		
B	7	13	0	7	6	13	0	3		
Co	0.3	0.2	0.3	0.3	0.1	0.3	0.2	3		
Ni	1.3	0.9	1.4	1.2	0.3	1.4	0.9	3		
Cu	0.7	10.1	3.2	4.7	4.9	10.1	0.7	3		
Zn	35.8	48.4	15.6	33.3	16.5	48.4	15.6	3		
Ge	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3		
As	0.2	0.2	0.3	0.2	0.0	0.3	0.2	3		
Se	0.0	0.3	0.0	0.1	0.2	0.3	0.0	3		
Rb	1.0	0.6	0.6	0.7	0.3	1.0	0.6	3		
Sr	101	96	76	90.87	13.33	100.50	75.65	3		
Y	0.06	0.04	0.03	0.04	0.02	0.06	0.03	3		
Mo	0.4	0.4	0.3	0.4	0.1	0.4	0.3	3		
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3		
Ca	0.10	0.07	0.03	0.07	0.04	0.10	0.03	3		
Sn	0.00	0.05	0.06	0.04	0.03	0.06	0.00	3		
50	0.01	0.01	0.01	0.01	0.00	0.01	0.01	3		
Te	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3		
Cs D	0.00	0.01	0.00	0.00	0.01	0.01	0.00	3		
ы	51.16	52.58	39.14	47.63	7.38	52.58	39.14	3		
W	0.00	0.04	0.00	0.01	0.02	0.04	0.00	3		
PD	0.08	0.03	0.07	0.06	0.03	0.08	0.03	3		
U	0.12	0.24	0.26	0.21	0.08	0.26	0.12	3		

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u U

Results: Inland Tailings Discharged From Plant

Date	6/15/96	9/13/96	1/23/97	7/18/97	10/10/97	2/5/98	4/9/98						
Tempera	t 33	21	11	31	27	17	20						
Conduct	ivity			650	750	650	750						
	,							Average Std.	Dev	Max	Min N	ſ	
лH	8 46	8 61	8 40	8 32	8 23	8 52	8 08	8 37	0.18	8 61	8.08	7	
	162	182	213	170	217	196	200	101	21	217	162	7	
AIK	102	206	215	222	217	190	200	260	106	217	74	5	
	Course En	500	74	222	512	lia	270	200	100	222	/4	2	
majors	(ppm)	0.0	0.4	10.5	10.0	10.5	10.1	10.5		10.5	.	-	
51	11.3	9.8	9.4	12.5	10.2	10.5	10.1	10.5	1.1	12.5	9.4	7	
Fe	0.01	0.10	0.00	0.00	0.17	0.00	0.00	0.04	0.07	0.17	0.00	7	
Mn	0.05	0.07	0.05	0.06	0.11	0.05	0.06	0.06	0.02	0.11	0.05	7	
Ca	25.1	27.8	27.0	34.6	32.0	32.9	32.7	30.3	3.6	34.6	25.1	7	
Mg	37.9	42.6	47.4	45.6	42.0	50.4	50.8	45.2	4.7	50.8	37.9	7	
Na	34.5	33.5	37.8	33.9	47.7	44.1	46.3	39.7	6.2	47.7	33.5	7	
K	9.1	10.2	8.3	14.4	12.8	8.7	10.2	10.5	2.3	14.4	8.3	7	
F	2.88	2.30	2.76	5.60	7.62	5.24	4.17	4.37	1.91	7.62	2.30	7	
Cl	51.9	60.5	58.9	84.5	76.3	71.8	81.9	69.4	12.5	84.5	51.9	7	
Br	0.33	0.40	0.39	0.63	0.58	0.53	0.62	0.50	0.12	0.63	0 33	7	
NO3-N	1.06	1 84	1 22	1 09	4 63	2.06	2 23	2 02	1 25	4 63	1.06	7	
504	51	52	50	57	4.05 60	2.00	2.23	2.02	1.20	7.05	51	7	
304	_ L)	52	78	57	00	/4	/1	00	9	74	51	1	
trace (p	po)	24		10								-	
Li	16	24	20	19	20	22	28	21	4	28	16	7	
В	92	141	66	212	97	87	96	113	49	212	66	7	
Co	0.2	0.1	0.2	0.3	0.2	0.2	0.3	0.2	0.1	0.3	0.1	7	
Ni	0.8	0.6	1.0	0.7	1.6	1.1	1.2	1.0	0.3	1.6	0.6	7	
Cu	2.0	0.2	0.0	1.4	1.3	1.2	1.3	1.1	0.7	2.0	0.0	7	
Zn	45.9	28.8	27.9	2.9	20.9	12.7	18.4	22.5	13.6	45.9	2.9	7	
As	3.8	2.5	2.8	3.8	1.9	2.7	2.7	2.9	0.7	3.8	1.9	7	
Se	0.4	0.7	2.6	1.0	0.0	2.1	2.7	1.3	1.1	2.7	0.0	7	
Rb	8.3	9.1	7.2	13.8	11.5	7.6	8.4	9.4	2.4	13.8	7.2	7	
Sr	167	152	118	206	180	145	133	157	30	206	118	7	
v	0.02	0.01	0.02	0.01	0.01	0.02	0.01	0.01	-0.01	0.02	0.01	7	
Mo	0.02 86 2	85.0	76.9	67.9	72 6	0.02	142.8	80.6	25 2	142 9	679	4	
NIO A -	0.0	0.00	/0.0	07.0	72.0	33.0	142.0	0.00	20.0	142.0		7	
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00			1	
Ca	0.13	0.08	0.14	0.00	0.10	0.07	0.19	0.10	0.00	0.19	0.00	/	
Sn	0.54	0.09	0.00	0.17	0.08	0.13	0.17	0.17	0.17	0.54	0.00	7	
Sb	0.32	0.13	0.03	0.16	0.05	0.04	0.06	0.11	0.10	0.32	2 0.03	7	
Te	0.32	0.08	0.00	0.00	0.00	0.00	0.00	0.06	0.12	0.32	2 0.00	7	
Cs	1.46	1.60	1.06	2.54	1.65	0.90	1.50	1.53	0.53	2.54	0.90	7	
Ba	7.29	6.10	4.32	7.03	6.30	3.32	4.71	5.58	1.49	7.29	3.32	7	
W	0.84	0.87	1.95	1.57	0.53	1.10	1.08	1.13 .	0.48	1.95	5 0.53	7	
Pb	0.01	0.09	0.00	0.14	0.00	0.01	0.20	0.06	0.08	0.20	0.00	7	
U	0.30	0.15	0.60	0.47	0.12	0.41	0.49	0.36	0.18	0.60	0.12	7	
(F	6.95	113	0.92	0.4	4 0.38	0.62	0.63	6.58					
Peel	0.01	10.5%	47.4		1 11	2 . 74	2 . 50	0 66					
REAL	0.80	0.78	0.89	0.5	6 0.6	0 0.10	1 0.50						
Pisen Li		0.70	0 85	0.5	4 6.6	6 0.7	1 0.50	0.64					
Br	0.8	8 0.18	0.47			7	0	-8 -15					
		70	2 6 4	(4,05	5 0.	0.1	8 0.5	0 0.63					
((1+3)	12 0.8	37 0.12	5 0.1		. 1	· 12	4 4.1	7 2 4,51					
(1.1.20	/	- 2.	2.1	rc si	60 1.	62 3.2		10 2,53					
1 r	-7 - 28	8 2.2	5 5 9	55 2.	,4 9 2.	89 3.2	6 2.	10					
1		2 2.5	9 51	-87		C							
U	2.4			-70									
			56	10									
9-					6.	57 0.8	D F.12	0.89					
TYP	6.9	8 1.45	1.0	1 0.0		Λ Α	Δ	Λ					
KCIBr			A	N									
	Λ.												

Date	6/15/96	9/13/96	1/23/97	4/11/97	7/18/97	10/10/97	2/5/98	4/9/98					
Temperat	21	17	1	1	24	11	4	6					
Conductiv	ity				500	500	550	550	Basin Recla	im			
									Average St	d. Dev. N	Max N	1in. N	
pН	8.76	8.70	8.73	8.20	8.79	8.58	8.14	8.61	8.56	0.25	8.79	8.14	8
Alk	162	172	188	104	181	193	197	203	175	32	203	104	8
Corrected	Eh 297	398	81	384	290	348	na	319	302	106	398	81	7
majors (pp	om)												
Si	2.7	4.2	5.0	3.3	1.7	3.5	3.9	3.4	3.5	1.0	5.0	1.7	8
Fe	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.00	8
Mn	0.01	0.01	0.00	0.07	0.00	0.00	0.00	0.01	0.01	0.02	0.07	0.00	8
Ca	27.8	26.0	27.9	17.3	28.7	29.2	32.2	28.9	27.2	4.4	32.2	17.3	8
Mg	38.5	38.2	39.8	22.0	40.0	41.4	45.5	41.7	38.4	7.0	45.5	22.0	8
Na	20.3	21.7	22.7	11.5	25.1	26.3	30.1	25.9	22.9	5.5	30.1	11.5	8
К	9.5	9.5	9.9	5.3	8.8	9.3	10.2	9.0	8.9	1.5	10.2	5.3	8
F	2.44	2.59	2.55	1.31	2.49	2.89	3.26	2.70) 2.53 *	0.56	3.26	1.31	8
Cl	44.4	47.2	49.7	23.1	47.3	51.8	56.1	47.9	45.9	9.9	56.1	23.1	8
Br	0.29	0.31	0.33	0.17	0.34	0.38	0.41	0.36	o 0.32	0.07	0.41	0.17	8
NO3-N	0.41	0.07	1.07	0.70	0.45	1.24	0.27	0.91	0.64	0.41	1.24	0.07	8
SO4	43	40	43	29	47	45	50	54	44	8	54	29	8
trace (ppb)												
Li	10	11	11	0	8	11	13	11	9	4	13	0	8
В	60	76	62	27	61	60	81	72	2 62	16	,81	27	8
Co	0.2	0.3	0.4	0.5	0.3	0.2	0.4	0.2	2 0.3	0.1	0.5	0.2	8
Ni	0.7	0.6	0.6	0.5	1.1	0.5	0.8	0.0	5 0 .7	0.2	1.1	0.5	8
Cu	1.2	0.9	0.0	0.0	1.4	0.5	0.6	0.1	7 _ 0.7	0.5	1.4	0.0	8
Zn	4.2	33.0	28.7	31.2	0.8	22.3	19.0	14.9	9 19.3	12.1	33.0	0.8	8
As	3.1	7.4	5.4	3.8	4.5	6 4.6	4.6	3.4	4.6	1.4	7.4	3.1	8
Se	0.6	0.4	2.7	1.5	0.7	0.8	0.9	1.:	5 1.1	0.7	2.7	0.4	8
Rb	9.8	10.5	11.1	6.4	10.0) 10.5	11.4	9.:	2 9.9	1.6	11.4	6.4	8
Sr	104	112	121	67	120) 112	132	11	7 111	20	132	67	8
Y	0.01	0.01	0.01	0.02	0.00) 0.00	0.01	0.0	1 0.01	0.01	0.02	0.00	8
Мо	48.9	48.1	42.0	16.1	28.9	27.7	33.0	28.	5 34.1	11.4	48.9	16.1	8
Ag	0.00		0.00	0.00	0.00) 0.00	0.00	0.0	0.00	0.00	0.00	0.00	7
Cd	0.07	0.04	0.00	0.03	0.01	0.01	0.13	0.0	3 0.04	0.04	0.13	0.00	8
Sn	0.20	0.03	0.00	0.00	0.00	0.00) 0.00	0.0	0 0.03	0.07	0.20	0.00	8
Sb	0.06	0.03	0.00	0.00	0.03	3 0.01	0.01	0.0	1 0.02	0.02	0.06	0.00	8
Te	0.00	0.01	0.00	0.00	0.00	0.00) 0.00	0.0	0.00	0.00	0.01	0.00	8
Cs	0.93	1.08	0.97	0.39	0.93	3 0.87	0.83	0.7	7 0.85	0.21	1.08	0.39	8
Ba	9.30	8.90	11.00	4.63	9.6	5 9.36	5 10.53	9.0	3 9.05	1.93	11.00	4.63	8
W	0.14	0.21	0.67	0.03	0.1	3 0.16	0.14	0.1	1 0.20	0.20	0.67	0.03	8
Pb	0.01	0.17	0.27	0.00) 0.0	4 0.07	0.06	0.0	1 0.08	0.09	0.27	0.00	8
U	0.25	0.18	0.46	0.15	5 0 .7 3	3 0.10) 0.24	0.3	6 0.31	0.21	0.73	0.10	8

Seeps	Inland	Inland	Inland	Inland	Inland					
Date	6/15/96	4/.11/97	7/18/97	10/10/97	4/9/98					
Temperat	18	1	19	10	11					
Conductiv	ity		600	750	600	Seep				
						Average	Std. Dey.	Max	Min.	N
pН	7.46	7.72	7.83	7.43	7.17	7.52	0.26	7.83	7.17	5
Alk	179	199	291	303	nd	243	63	303	179	4
-Corrected	Eh 328	355	419	315	289					
majors (pp	om)									
Si	3.3	3.9	5.3	4.4	4.9	4.4	0.8	5.3	3.3	5
Fe	0.02	0.02	0.00	0.00	0.00	0.01	0.01	0.02	0.00	5
Mn	0.00	3.58	1.71	3.83	3.06	2.44	1.59	3.83	0.00	5
Ca	30.0	27.1	41.3	41.1	39.8	35.9	6.8	41.3	27.1	5
Mg	33.3	32.9	54.9	58.2	45.3	44.9	11.8	58.2	32.9	5
Na	9.1	15.8	, 19.6	19.0	22.8	17.3	5.2	22.8	9.1	5
K	6.7	6.8	9.9	8.2	10.1	8.4	1.6	10.1	6.7	5
F	1.18	1.78	3.02	2.27	2.69	2.19	0.73	3.02	1.18	5
Cl	17.0	20.4	44.0	45.5	48.2	35.0	15.0	48.2	17.0	5
Br	0.12	0.16	0.33	0.34	0.37	0.26	0.12	0.37	0.12	5
NO3-N	0.22	0.30	0.22	0.37	0.70	0.36	0.20	0.70	0.22	5
SO4	22	20	42	33	41	32	10	42	20	5
trace (ppb)									
Li	4	0	26	2	2	7	11	26	0	5
В	40	34	52	37	41	41	7	52	34	5
Со	0.1	4.4	1.0	4.0	2.7	2.4	1.9	4.4	. 0.1	5
Ni	0.7	2.2	1.0	2.2	1.7	1.6	0.7	2.2	0.7	5
Cu	0.9	4.3	1.7	3.8	1.9	2.5	1.5	4.3	0.9	5
Zn	3.1	23.0	2.8	21.4	16.2	13.3	9.8	3 23.0	2.8	5
As	0.5	0.7	0.8	0.5	0.5	0.6	0.1	0.8	0.5	5
Se	0.0	0.0	1.0	0.0	0.2	0.2	0.4	1.0	0.0	5
Rb	8.6	8.0	12.0	10.5	10.1	9.8	1.6	5 12.0	8.0	5
Sr	97	127	167	156	148	139	27	167	97	5
Y	0.02	0.03	0.03	0.02	0.04	0.03	0.01	0.04	0.02	5
Мо	5.1	1.5	13.7	3.8	11.1	7.0	5.1	13.7	1.5	5
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5
Cď	0.00	0.00	0.00	0.00	0.03	0.01	0.01	0.03	0.00	5
Sn	0.14	0.01	0.31	0.00	0.09	0.11	0.13	0.31	0.00	5
Sb	0.01	0.00	0.00	0.00	0.00) 0.00) 0.00	0.01	0.00	5
Te	0.00	0.00	0.00	0.00	0.00) 0.00) 0.00	0.00	0.00	5
Cs	0.23	0.40	1.00	0.63	0.86	6 0.62	2 0.32	2 1.00	0.23	5
Ba	0.51	17.40	45.29	30.09	65.33	3 31.72	2 24.98	65.33	0.51	5
W	0.00	0.04	0.12	0.00	0.10	5 0.00	5 0.0 [°]	7 0.16	0.00	5
Dh										
rυ	0.03	0.00	0.07	0.00) 0.0	5 0.03	3 0.03	3 0.07	0.00	5

Date	9/13/96	4/11/97	7/18/97	10/10/97	2/5/98	4/9/98					
Temperat	17	4	16	10	4	10					
Conductiv	600	500	550	600	500	500	Shallow V	Well			
							Average	Std. Dev.	Max	Min.	N
pН	6.91	7.31	7.18	7.11	7.50	7.02	7.17	0.21	7.50	6.91	6
Alk	217	230	245	220	196	186	216	22	245	186	6
Corrected	189	207	154	160	na	256	193	41	256	154	5
majors (pp	m)										
Si	6.4	6.5	7.2	5.9	6.0	8.9	6.8	1.1	8.9	5.9	6
Fe	10.80	8.62	11.30	11.85	11.49	2.34	9.40	3.64	11.85	2.34	6
Mn	4.12	4.26	4.00	4.20	3.76	6.08	4.40	0.84	6.08	3.76	6
Ca	34.8	34.5	38.4	33.9	32.1	48.0	36.9	5.8	48.0	32.1	6
Mg	36.2	36.2	40.4	37.1	35.3	26.8	35.3	4.5	40.4	26.8	6
Na	17.8	19.1	20.6	22.0	24.6	19.7	20.6	2.4	24.6	17.8	6
К	9.8	9.1	11.0	8.8	9.3	3.0	8.5	2.8	11.0	3.0	6
F	3.11	3.38	3.27	3.39	3.58	1.64	3.06	0.71	3.58	1.64	6
Cl	46.9	46.8	52.4	47.1	51.6	49.1	49.0	2.5	5 52.4	46.8	6
Br	0.32	0.35	0.40	0.37	0.40	0.38	0.37	0.03	0.40	0.32	6
NO3-N	0.08	0.05	0.12	0.50	0.22	0.40	0.23	0.18	0.50	0.05	6
SO4	13	20	23	12	18	28	3 19) 6	5 28	12	6
trace (ppb)										
Li	0	0	0	2	0	3	3 1	. 1	3	0	6
В	42	34	47	45	66	30) 44	13	3 66	30	. 6
Co	2.6	3.5	2.2	1.9	2.7	2.4	5 2.6	6 0.5	5 3.5	1.9	6
Ni	2.0	1.9	2.7	0.9	15.6	2.3	3 4.2	2 5.0	5 15.6	0.9	6
Cu	0.0	0.0	0.6	0.1	1.3	0.0	5 0.4	l 0.5	5 · 1.3	0.0	6
Zn	32.9	24.8	2.9	25.6	20.8	16.0) 20.5	5 10.3	3 32.9	2.9	6
As	7.3	4.5	8.1	5.6	4.8	1.	5 5.3	3 2.3	3 8.1	1.5	6
Se	1.1	0.2	1.8	8 0.0	0.0	0.0	0.5	5 0.8	3 1.8	0.0	6
Rb	11.4	7.3	10.6	6.3	6.7	1.0) 7.2	2 3.1	7 11.4	1.0	6
Sr	215	185	227	161	155	230	5 196	5 34	4 236	155	6
Y	0.35	0.22	0.26	5 0.2 3	0.23	0.2	3 0.25	5 0.0	5 0.35	0.22	6
Мо	6.9	8.4	5.8	8 8.0	6.8	6.	5 7.1	1 1.0	0 8.4	5.8	6
Ag	0.00	0.02	0.00	0.00	0.00	0.0	0.00	0.0	1 0.02	2. 0.00	6
Cd	0.01	0.00	0.00) 0.01	0.04	0.1	5 0.04	4 0.0	6 0.15	0.0 0	6
Sn	0.01	0.00	0.39	0.07	0.22	0.0	3 0.12	2 0.1	5 0.39	0.00	6
Sb	0.01	0.00	0.00	0.00) 0.00	0.0	1 0.0	0.0	1 0.01	0.00	6
Te	0.14	0.00) 0.00	0.00) 0.00	0.0	1 0.0	3 0.0	6 0.14	4 0.00	6
Cs	0.52	0.76	i 1.20	0.62	2 0.57	0.0	2 0.6	2 0.3	8 1.20) 0.02	6
Ba	124.40	114.00) 135.4(0 110.50) 127.30) 91.4	4 117.1	7 15.5	2 135.40) 91.44	6
W	0.04	0.00) 0.0	7 0.03	3 0.10) 0.0	6 0.0	5 0.0	3 0.10	0.00	6
Pb	0.11	0.00) 0.0	5 0.02	2 0.1	0.0	3 0.0	5 0.0	5 0.1	1 0.00	6
U	0.03	0.03	3 0.0	8 0.00	0.0	l 0.7	2 0.1	5 0.2	8 0.72	2 0.00) 6

Date	9/13/96	4/11/97	7/18/97	10/10/97	4/9/97					
Temperat	12	5	13	9	10					
Conductiv	ity		500	550	500	Deep Wel	I (MW 5)			
						Average	Std. Dev.	Max	Min.	N
pН	6.72	7.23	6.99	7.07	7.30	7.06	0.23	7.30	6.72	5
Alk	181	197	181	199	213	194	14	213	181	5
Corrected	283	382	337	279	174	291	78	382	174	5
majors (pp	m)									
Si	9.9	9.4	9.7	10.3	6.1	9.1	1.7	10.3	6.1	5
Fe	1.19	0.01	0.17	0.70	11.18	2.65	4.79	11.18	0.01	5
Mn	4.36	5.43	5.98	6.58	3.90	5.25	1.11	6.58	3.90	5
Ca	53.4	51.0	50.9	52.0	35.5	48.6	7.4	53.4	35.5	5
Mg	25.9	28.9	27.8	28.6	38.0	29.8	4.7	38.0	25.9	5
Na	31.1	18.8	18.8	18.8	23.7	22.2	5.4	31.1	18.8	5
Κ	3.1	3.5	3.5	3.3	9.5	4.6	2.8	9.5	3.1	5
F	0.56	1.36	1.54	1.59	3.53	1.72	1.09	3.53	0.56	5
Cl	50.1	49.1	52.3	50.6	53.5	51.1	1.8	53.5	49.1	5
Br	0.36	0.38	0.41	0.39	0.41	0.39	0.02	0.41	0.36	5
NO3-N	1.81	0.22	0.19	1.12	0.15	0.70	0.74	1.81	0.15	5
SO4	73	35	31	31	26	39	19	73	26	5
trace (ppb))									
Li	4	4	74	4	1	17	31	74	1	5 `
В	44	27	41	34	48	38	8	48	27	5
Co	4.1	2.3	3.4	2.4	1.9	2.8	0.9	4.1	1.9	5
Ni	3.9	2.1	2.8	2.4	9.0	4.0	2.8	9.0	2.1	5
Cu	0.8	0.0	0.8	0.6	0.5	0.5	0.3	0.8	0.0	5
Zn	53.7	21.6	4.3	30.0	14.3	24.8	18.7	53.7	4.3	5
As	2.6	3.3	3.3	2.2	4.3	3.2	0.8	4.3	2.2	5
Se	1.0	0.0	0.9	0.0	0.9	0.6	0.5	1.0	0.0	5
Rb	1.6	1.7	1.4	1.1	7.1	2.6	2.5	7.1	1.1	5
Sr	225	266	293	251	177	242	44	293	177	5
Y	0.29	0.25	0.31	0.27	0.26	0.28	0.02	0.31	0.25	5
Мо	3.4	8.1	6.5	6.8	6.7	6.3	1.7	8.1	3.4	5
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5
Cd	0.03	0.00	0.00	0.01	0.10	0.03	0.04	0.10	0.00	5
Sn	0.10	0.00	0.00	0.00	0.13	0.05	0.06	6 0.13	0.00	5
Sb	0.04	0.00	0.02	0.01	0.01	0.02	0.02	2. 0.04	0.00	5
Te	0.05	0.00	0.00	0.01	0.00	0.01	0.02	2 0.05	0.00	5
Cs	0.04	0.05	0.02	0.01	0.54	0.13	0.23	0.54	0.01	5
Ba	128.30	126.00	133.20	109.40	120.30	123.44	9.12	133.20	109.40	5
W	0.14	0.25	0.21	0.12	0.16	0.18	0.05	5 0.25	0.12	5
Pb	0.21	0.00	0.11	1.35	0.03	0.34	0.57	7 1.35	0.0 0	5
U	0.58	2.09	2.32	0.39	0.05	1.09	1.04	2.32	2. 0.05	5

LTV: Process Waters Discharged From Plant

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	LTV	LTV	LTV	LTV	LTV	LTV	LTV	LTV					
Date	6/14/96	9/12/96	1/23/97	4/10/97	7/17/97	10/10/97	2/5/98	4/9/98					
Temper	29	21	11	14	31	23	14	18					
Conduc	tivity				900	800	95 0	900	Tailing	Discharge	•		
								•	Ave.	St. Dev N	Aax N	Min N	
pН	8.66	8.51	8.37	8.68	8.56	8.64	8.99	8.67	8.64	0.18	8.99	8.37	8
Alk	260	233	289	301	277	264	370	273	283	40	370	233	8
Eh	259	347	30	391	323	270	319	322	283	110	391	30	8
majors	(ppm)												
Si	10.5	7.7	7.7	7.7	10.8	9.0	7.2	7.8	8.5	1.4	10.8	7.2	8
Fe	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	8
Mn	0.02	0.03	0.03	0.03	0.02	0.02	0.02	0.03	0.02	0.01	0.03	0.02	8
Ca	10.7	18.0	21.2	14.5	15.3	14.6	11.7	17.6	15.5	3.4	21.2	10.7	8
Mg	22.4	29.3	34.9	33.1	30.8	30.5	28.9	31.5	30.2	3.7	34.9	22.4	8
Na	155.6	108.2	137.6	134.8	129.5	119.8	182.9	114.0	135.3	24.3	182.9	108.2	8
K	18.5	16.5	16.4	17.1	22.0	12.9	15.5	18.0	17.1	2.6	22.0	12.9	8
F	10.01	9.25	10.34	8.97	10.15	10.54	10.88	10.78	10.11	0.69	10.88	. <mark>8.97</mark>	8
Cl	39.9	36.0	39.7	36.3	39.3	34.5	34.0	30.2	36.2	3.4	39.9	30.2	8
Br	0.16	0.16	0.18	0.19	0.22	0.19	0.19	0.17	0.18	0.02	0.22	0.16	8
NO3-N	1.36	1.15	2.74	2.11	1.30	1.24	1.71	2.47	1.76	0.61	2.74	1.15	8
SO4	112	108	124	112	112	113	127	111	115	7	127	108	8
trace (ppb)											٢	
Li	83	85	-91	64	265	44	71	48	94	71	265	44	8
В	392	. 447	334	270	434	294	362	204	342	84	447	204	8
Co	0.1	0.3	0.2	. 0.3	0.2	0.2	0.5	0.2	0.2	• 0.1	0.5	0.1	8
Ni	0.7	0.9	1.1	0.7	0.5	0.8	1.0	0.6	0.8	0.2	1.1	0.5	8
Cu	2.5	1.1	0.0) 0.6	0.8	0.5	1.2	0.8	0.9	0.7	2.5	0.0	8
Zn	1.4	27.7	24.5	5 22.1	0.1	15.3	14.9	14.1	15.0	10.1	27.7	0.1	8
As	5.4	5.4	2.8	3 2.1	6.4	4.7	4.6	1.5	4.1	1.8	6.4	1.5	8
Se	0.0) 1.1	0.8	s 0.9	0.0	0.0	1.1	0.0	0.5	0.5	1.1	0.0	8
Rb	22.5	20.6	5 18.4	15.9	22.7	13.2	15.7	16.3	18.1	3.5	22.7	13.2	8
Sr	86	5 129	167	105	137	107	85	144	120	29	167	85	8
Y	0.01	0.02	2 0.03	3 0.02	0.01	0.02	0.03	0.01	0.02	0.01	0.03	0.01	8
Mo	368	342	2 434	315	355	307	326	282	. 341	46	434	282	8
Ag	0.00) 0.00) 0.00) 0.00	0.11	0.00	0.00	0.00	0.01	0.04	0.11	0.00	8
Cd	0.33	3 0.27	0.39	0.22	0.23	0.41	0.30	0.26	0.30	0.07	0.41	0.22	8
Sn	0.54	0.50	0.00) 0.23	0.26	0.1 3	0.06	0.03	0.22	0.21	0.54	0.00	8
Sb	1.00	0.26	0.0	5 0.03	0.42	2 0.16	0.12	0.11	0.27	0.32	1.00	0.03	8
Te	0.05	5 0.02	2 0.0	0.00	0.00) 0.00	0.00	0.00	0.01	0.02	0.05	0.00	8
Cs	4.4() 3.68	3 2.99	2.44	4.48	3 2.49	1.80) 2.43	3.09	0.99	4.48	1.80	8
Ba	7.50) 7.70) 8.9	1 4.94	2.81	2.30	4.65	6.27	5.64	2.37	8.91	2.30	8
W	4.70	J 2.7	/ 3.9	s 3.91	7.64	5.11		o 3.81	5.00	1.89	8.06	2.77	8
Pb	0.1	1 0.03	5 0.00	0.04	0.0	0.00	0.01		2 0.03	0.04	0.11	0.00	8
U	0.4	1 0.3	B 0.70	ь 0.26	o 0.78	s 0.33	3 0.47	/ 0.58	s 0.50	0.19	0.78	0.26	8

Date	6/14/96	9/12/96	1/23/97	4/10/97	7/17/97	10/10/97	2/5/98	4/9/98					
T (C)	22	19	1	1	24	13	3	6					
Cond.					800	750	1000	750	Basin R	eclaim			
							,		Ave.	St. Dev I	Max	Min N	I
pН	9.06	8.66	8.68	8.56	8.91	8.81	8.75	8.55	8.75	0.17	9.06	8.55	8
Alk	256	262	280	259	276	283	309	266	274	17	309	256	8
Eh	266	388	72	436	296	348	379	415	325	117	436	72	8
majors	(ppm)												
Si	3.5	5.3	7.3	7.4	4.3	6.5	8.2	6.5	6.1	1.6	8.2	3.5	8
Fe	0.00	0.02	0.02	0.18	0.00	0.02	0.00	0.00	0.03	0.06	0.18	0.00	8
Mn	0.00	0.00	0.07	0.08	0.00	0.00	0.04	0.01	0.03	0.03	0.08	0.00	8
Ca	18.2	19.2	26.1	20.9	18.5	18.0	21.4	18.5	20.1	2.7	26.1	18.0	8
Mg	34.2	33.5	39.6	35.1	33.2	33.5	38.2	32.4	35.0	2.6	39.6	32.4	8
Na	119.0	119.5	125.0	105.4	113.0	120.8	127.6	105.1	116.9	8.4	127.6	105.1	8
K	12.4	15.7	13.9	12.0	14.2	14.6	12.1	11.1	13.3	1.6	15.7	11.1	8
F	7.93	9.33	9.23	7.53	7.87	9.15	9.65	7.98	8.58	0.83	9.65	7.53	8
Cl	35.5	37.1	36.3	32.5	32.2	31.0	31.9	26.0	32.8	3.6	37.1	26.0	. 8
Br	0.14	0.16	0.16	0.16	0.17	0.18	0.17	0.14	0.16	0.01	0.18	0.14	8
NO3-N	0.79	0.46	1.36	1.40	0.79	1.78	1.40	0.17	1.02	0.55	1.78	0.17	8
SO4	109	118	132	114	109	116	128	108	117	9	132	108	8
trace (ppb)												
Li	46	64	78	55	307	43	58	37	86	90	307	3,7	8
В	319	453	326	280	330	226	336	263	317	67	453	226	8
Co	0.1	0.1	0.3	0.6	0.4	0.2	0.2	0.2	0.3	0.2	0.6	0.1	8
Ni	0.4	0.6	1.1	1.2	0.5	1.0	1.1	0.9	0.9	. 0.3	1.2	0.4	8
Cu	1.4	0.9	0.0	0.5	11.0	0.7	1.3	0.9	2.1	3.6	11.0	0.0	8
Zn	2.3	26.3	28.4	12.2	1.5	21.3	14.0	12.3	14.8	10.1	28.4	1.5	8
As	9.3	21.9	6.2	5.9	11.3	10.3	7.4	5.9	9.8	5.3	21.9	5.9	8
Se	0.0	0.9	0.9	0.0	0.9	0.0	1.0	1.3	0.6	0.5	1.3	0.0	8
Rb	12.3	17.4	13.6	11.6	15.3	15.0	11.2	9.6	5 13.2	2.6	17.4	9.6	8
Sr	100	133	189	136	142	122	150	113	135	27	189	100	8
Y	0.02	0.02	0.02	0.04	0.02	0.01	0.03	0.02	0.02	0.01	0.04	0.01	8
Мо	263	316	323	259	257	264	273	215	5 271	34	323	215	8
Ag	0.01	0.00	0.00	5.80	0.00	0.00	0.00	0.00	0.73	2.05	5.80	0.00	8
Cd	0.29	0.28	0.27	0.16	0.08	0.37	0.19	0.23	0.23	0.09	0.37	0.08	8
Sn	0.11	0.00	0.00	0.06	0.61	0.00	0.16	0.08	B 0.13	0.20	0.61	0.00	8
Sb	0.63	0.24	0.04	0.02	0.25	0.18	0.09	0.08	3 0.19	0.20	0.63	0.02	8
Te	0.09	0.00	0.00	0.00	0.00) 0.00	0.00) 0.00	0.01	0.03	0.09	0.00	8
Cs	1.90) 2.60	1.87	1.54	2.26	5 2.10) 1.45	5 1.45	5 1.90	0.41	2.60) 1.45	8
Ba	4.00) 7.03	7.35	6.04	4.56	5 3.33	4.24	4.00	5.07	1.52	7.35	3.33	8
W	2.70) 3.20	3.46	1.98	3 4.71	4.61	5.13	3.50	3.66	1.08	5.13	1.98	8
Pb	0.06	5 0. 03	0.00	0.09	0.79	0.00	0.18	3 0.0 3	3 0.15	0.27	0.79	0.00	8
U	0.33	3 0.32	0.68	0.21	1.02	2 0.24	0.50) 0.53	3 0.48	0.27	1.02	2 0.21	

Date	6/14/96	9/12/96	1/23/97	4/10/97	7/17/97	10/10/97	2/5/98	4/9/98					
T (°C)	13	14	11	10	11	14	10	10					
Conduc	tivity				1100	1200	1150	1250	Seep				
									Ave.	St. Dev l	Max	Min l	N
pН	7.23	7.70	7.30	7.41	7.31	7.45	7.38	7.28	7.38	0.15	7.70	7.23	8
Alk	530	415	427	342	439	462	450	500	445	57	530	342	8
Eh	161	380	33	237	213	186	244	329	223	105	380	33	8
majors	(ppm)												
Si	11.2	9.3	10.0	10.5	9.3	10.2	10.6	11.1	10.3	0.7	11.2	9.3	8
Fe	2.18	0.09	0.73	1.73	1.20	1.50	2.42	2.49	1.54	0.85	2.49	0.09	8
Mn	1.43	1.23	0.82	0.69	1.00	0.94	0.88	0.91	0.99	0.24	1.43	0.69	8
Ca	96.3	57.0	65.9	50.9	67.3	68.7	65.6	70.6	67.8	13.3	96.3	50.9	8
Mg	109.0	65.4	68.7	49.0	70.9	72.3	69.8	74.1	72.4	16.7	109.0	49.0	8
Na	90.9	106.8	140.0	110.4	113.5	106.7	106.7	107.4	110.3	13.7	140.0	90.9	8
K	15.4	16.2	20.9	16.4	17.3	16.3	16.3	16.2	16.9	1.7	20.9	15.4	8
F	1.77	4.40	4.60	4.75	4.79	4.29	4.33	4.17	4.14	0.98	4.79	1.77	8
Cl	31.7	31.9	36.2	35.5	35.7	34.6	32.4	31.4	33.7	2.0	36.2	31.4	8
Br	0.12	0.16	0.16	0.18	0.17	0.16	0.18	0.17	0.16	0.02	0.18	0.12	8
NO3-N	0.18	0.19	0.43	0.47	0.09	1.47	0.11	0.16	0.39	0.46	1.47	0.09	8
SO4	284	207	263	169	237	217	206	220	225	36	284	169	8
trace (j	opb)												
Li	29	27	30	19	109	22	29	23	36	5 30	109	,19	8
В	383	468	515	457	455	338	453	483	444	57	515	338	8
Co	5.1	1.9	3.7	1.6	4.0	2.4	2.0	1.6	2.8	3 1.3	5.1	1.6	8
Ni	1.9	1.5	0.9	1.7	1.3	1.2	1.7	1.5	1.5	5 0.3	1.9	0.9	8
Cu	1.2	1.1	0.0	0.0	0.8	0.8	0.9	0.6	0.7	0.5	1.2	0.0	8
Zn	7.8	28.9	30.2	23.7	5.0	17.7	18.1	12.5	18.0) 9.3	30.2	5.0	8
As	3.7	2.2	4.8	5.8	4.9	3.7	5.9	4.7	4.5	5 1.2	5.9	2.2	8
Se	0.0	0.2	2.2	0.7	0.0	0.0	0.3	0.4	0.5	5 0.7	2.2	0.0	8
Rb	11.3	15.7	17.1	12.5	13.6) 11.4	11.8	11.7	13.1	2.2	17.1	11.3	8
Sr	450	257	369	303	354	322	338	336	34	56	450	257	8
Y	0.07	0.03	0.04	0.05	0.03	0.04	0.05	0.05	0.03	0.01	0.07	0.03	8
Mo	15	129	123	106		2 80	90) 84) 0.00	92	2 35	129	15	8
Ag	0.00	0.00	0.00							0.00	0.00	0.00	8
Ca	0.04	0.12	0.07	0.09		0.09			0.0	/ 0.03	0.12	0.03	ð
Sn	0.17	0.13	0.40			0.09				0.13	0.40		, ð
30 T-	0.04	0.01	0.00								0.04		ð
1e	0.00	0.00	0.00							J 0.01	0.01		ð
	1.00	1.72	1.43								1.72	2 0.91	8 0
Da W	40.00	20.81	39.00	45.2	43.15	7 45.42 2 0.10	2 48./C	5 - 51.73	0 42.34 0 0 0	4 9.31 4 0.31	51.75	20.81	8 0
W Dh	0.11	0.18) 0.14) 0.04		2 U.Z. 7 A A) 0.2/) 0.1	+ U.21 1 0.12	0.72	0.11 2 0.00	δ o
r0 11	0.03		0.48		0 0.10	J U.U.		7 0.00) 0.1) 0.1	1 U.10 9 A 19	0.40	5 0.00 5 0.11	ð 0
U	0.10	0.21	0.44	F 0.15	• U.O	0.1	U.2	/ 0.1	, 0.2	o U.18	0.00	J U.II	ð

Appendix III. Chemical composition of water in Biwabik Iron Formation

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Biwabik Iron Formation Groundwater Chemistry

Loc.		CALUMET #2	CALUMET #3	NASHV	AUK #3	NASHWAUK #4	KEEWATIN #1	KEEWATIN #2	SCRANTON	BUHL #1	BUHL #2	KINNEY #2	MT. IRON #2	Average	Std. Dev.	Min.	Max.
Date	•	3/0/58	3/0/38		1/96 7	3///30 7	3/0/98	9	5/0/96	74	70	איוו ונ ר	375		1		
	1	796	8 14	6	, 80	7 22	7 57	1 27	7 29	673	6.95	7.25	7.3	7 11	043	6.73	814
	maka CaCO3	161	154	2	07	167	206	199	198	195	211	158	191	186	22	154	211
F	ma/kg CaCOJ	0.23	0.20		78	049	0.24	017	0.23	0.14	0.20	0.17	0.26	0.28	0.19	0.14	0.78
à	mg/xg	23	64		1	17	15	83	15.0	37	7.6	1.8	114	5.6	4.5	1.5	15.0
	mg/kg	< 015	0.025	0		< 015	< 015	0.024	0.026	0.018	0.034	< 015	0.049	0.017	0.011	< 015	0.049
NOI	ing/kg	0.27	0.11	0.	74	0.21	0.51	0.42	0.83	0.010	0.054	0.19	0.46	0.017	0.011	0.11	0.017
1103-1 604	ma/kg	78	16.8	1	1 1	95	10.51	106.0	80.1	41 0	35.0	22.3	35.6	34.4	317	7.8	106.0
304	iiig/kg	7.0	10.0			7.5	10.5	100.0	00.1	41.5	55.0	11.0	55.0				1000
Si	mg/kg	3.7	3.9		.9	5.7	4.2	5.0	5.0	7.3	7.1	10.7	5.3	5.7	2.0	3.7	10.7
Fe	mg/kg	0.08	0.14	0	07	0.00	0.19	0.10	0.01	0.04	0.16	2.91	0.02	0.34	0.85	0.00	2.91
Mn	mg/kg	0.05	0.09	. 0	06	0.06	0.69	0.28	0.00	0.00	0.31	0.33	0.11	0.18	0.21	0.00	0.69
Ca	mg/kg	32.7	34.3	4	7.6	34.7	47.7	69.6	47.7	45.8	47.3	41.3	45.3	44.9	10.1	32.7	69.6
Mg	mg/kg	15.0	16.0	2).2	19.1	17.3	28.5	36.1	25.2	25.5	20.6	24.5	22.5	6.2	15.0	36.1
Na	mg/kg	7.1	7.2	7	.2	4.7	7.7	8.5	11.2	8.8	9.6	6.7	12.0	8.2	2.1	4.7	12.0
K	mg/kg	2.4	2.7	2	.1	2.1	1.1	1.6	1.9	2.1	2.0	0.5	1.1	1.8	0.7	0.5	2.7
Li	µg/kg	17.6	21.2	8	.4	5.8	7.5	8.7	5.8	7.0	5.3	6.1	4.2	8.9	5.4	4.2	21.2
В	µg/kg	105.7	106.3	2	1.0	15.4	46.9	68.9	18.7	28.1	16.6	31.1	44.9	46.3	33.4	15.4	106.3
Al	µg/kg	5.2	1.1	0	.6	1.5	2.0	3.0	1.7	0.6	0.6	2.1	1.0	1.8	1.3	0.6	5.2
Cr	µg/kg	1.0	2.7		.5	3.3	3.0	3.5	3.3	3.1	4.0	1.2	2.1	2.9	1.1	1.0	4.5
Co	µg/kg	0.6	0.2	0	.1	0.1	0.7	0.6	0.1	0.1	0.7	0.6	0.4	0.4	0.3	0.1	0.7
Ni	µg/kg	1.4	20.8	1	.7	1.3	1.6	2.9	4.4	1.5	3.8	1.6	1.6	3.9	5.7	1.3	20.8
Cu	µg/kg	1.1	2.8	2	.4	10.1	2.1	1.5	5.3	4.0	0.6	0.3	0.3	2.8	2.9	0.3	10.1
Zn	µg/kg	21	20	1	9	23	48	19	35	25	28	16	17	25	9	16	48
As	µg/kg	0.7	0.7	0	.4	0.3	0.3	0.2	0.2	0.1	0.2	1.9	0.5	0.5	0.5	0.1	1.9
Se	µg/kg	0.0	1.5	0	.7	1.0	0.0	2.6	1.5	1.3	0.8	0.0	0.4	0.9	0.8	0.0	2.6
Rb	µg/kg	1.1	1.3	0	.9	0.7	0.5	1.0	1.3	3.5	3.7	0.6	2.3	1.6	1.1	0.5	3.7
Sr	µg/kg	356	425	1:	28	85	126	217	104	121	103	82	108	169	116	82	425
Мо	µg/kg	0.72	0.66	0.	13	0.05	0.16	0.26	0.13	0.01	0.04	0.28	0.18	0.24	0.24	0.01	0.72
Cd	µg/kg	0.0	0.0	0	.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Cs	µg/kg	0.04	0.05	0.	07	0.05	0.07	0.04	0.13	0.88	0.74	0.07	0.53	0.24	0.32	0.04	0.88
Ba	µg/kg	139.4	135.4	20	0.0	8.8	160.7	36.1	0.1	1.0	28.5	7.9	36.0	52.2	61.3	0.1	160.7
w	µg/kg	0.10	0.00	0.	33	0.08	0.30	0.06	0.32	0.35	0.07	0.30	0.06	0.18	0.14	0.00	0.35
TI	µg/kg	0.01	0.00	0.	02	0.00	0.03	0.01	0.02	0.02	0.01	0.03	0.02	0.02	0.01	0.00	0.03
РЪ	µg/kg	0.18	0.41	0.	53	0.44	2.80	0.31	0.57	0.33	0.07	0.06	0.06	0.52	0.78	0.06	2.80
U	µr/kr	0.31	0.35	0.	40	0.72	0.11	0.22	0.51	0.24	0.37	0.13	0.23	0.33	0.18	0.11	0.72

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Appendix IV. Chemical composition of water during groundwater/tailings Experiments

National Inland

LTV

Results: National Tailings + Groundwater

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Weeks	P. Fluid	G. Wat	1	3	7	12	16	20	25	30
pН	7.98	7	7.42	7.33	7.25	7.95	7.8	8.01	8 -	
Alk	350) 196	232	227	241	251	276	273	282 -	
								*		
majors (ppn	n)									
Si	19.9	5.1	12.8	12.7	14.8	14.5	14.5	15.7	15.3	15.6
Fe	0.02	0.23	0.03	0.00	0.01	2.60	2.05	3.24	0.04	0.00
Mn	0.28	0.46	0.63	0.61	0.90	0.63	0.72	0.57	0.52	0.46
Ca	31.4	71.2	68.0	67.9	67.6	63.9	62.9	68.1	65.6	62.8
Mg	62.6	5 28.6	29.5	31.0	32.8	35.4	38.0	42.4	45.1	47.6
Na	39.9	8.7	15.3	15.4	17.0	18.1	19.8	22.0	23.7	26.1
К	1.7	1.6	2.2	1.5	1.4	1.3	1.5	1.6	1.7	1.8
F	1.08	0.86	1.04	1.02	0.99	0.98	0.94	0.93	0.96	0.99
Cl	28.7	7.7	6.6	7.3	15.7	15.0	10.0	29.4	37.0	44.3
Br	0.070	0.027	0.024	0.024	0.027	0.029	0.034	0.049	0.630	0.074
SO4	51.8	3 104.3	85.6	85.6	85.3	84.7	83.8	76.3	67.8	58.9
trace (ppb)		· 0	14	0	o	0	0	10	10	10
	177	0 0 1 71	14	9 47	0 64	02	0	10	12	10
B	1/1		40	07	04	93	00	75	97	128
Cr Ma	1.0		0.0	0.2	0.0	0.4	0.2	0.0	0.7	1.4
Mu	20	5 410 5 707	25	340	197	2220	0/4	405	445	522
Fe Co	20) 282	33	14	12	2440	2108	2200	20	. 0
CO NG	1.		0.4	1.2	0.9	0.5	0.5	0.5	4.0	0.0
	0	$\begin{array}{c} 0.0 \\ 0.6 \end{array}$	24	1.7	0.0	2.5	2.5	1.1	2.5	2.5
Cu Zn	0.: 7.	· · · · ·	2.4	51	57	21.0 60	2. 9 61	71	2.0	40
	03	+ 73 4 0.06	0.14	013	0.16	0.15	013	031	0 17	40
A c	0.5	- 0.00 0 0 5	1.6	0.15	1 1	1.2	1 1	1.6	0.17	12
Se	0.	7 0.0	0.0	0.0	0.0	0.0	03	0.1	0.0	0.0
Rb	0. 1 (6 12	15	13	13	0.9	1.0	1.1	1.1	1.4
Sr	44	7 236	200	197	219	221	227	253	280	312
Y Y	0.0	1 0	0.01	0.01	0.02	0.02	0.02	0.06	0	012
- Mo	19.	8 0.0	3.8	4.3	4.9	5.4	6.2	6.4	6.2	7.2
Ag		0 0	0	0	0	0	0	0	0	
Cd	0.	0.0	0.0	0.0	0.0	0.6	0.2	0.0	0.1	0.0
Sn	1.	8 1.7	0.2	0.1	0.1	0.4	0.2	2.3	0.2	
Sb		0 0	0.01	0.01	0	0	0	0	0	
Cs	0.1	7 0.06	0.20	0.11	0.20	0.10	0.11	0.12	0.12	0.12
Ba	16.	5 73.6	13.8	17.5	30.8	5.0	6.5	4.9	4.6	5.5
W	0.0	5 0.00	0.03	0.08	0.08	0.15	0.14	0.09	0.13	0.13
Pb	0.0	1 0.86	0.17	0.00	0.01	0.66	0.63	0.42	0.04	0.04
U	0.0	3 0.15	0.09	0.08	0.04	0.04	0.04	0.05	0.10	0.11

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Weeks	P. Fluid C	G. Wat.	1	3	7	12	16	20	25	30
pН	7.67	7	7.35	7.32	7.26	8.05	8	8.31	7.96	
Alk	399	196	255	303	321.2	332	400	406	444	
majors (ppr	n)						•			
Si	22.1	5.1	14.1	14.3	17.3	16.9	18.0	18.2	19.1	19.0
Fe	0.02	0.23	0.36	0.01	0.00	1.41	1.15	0.96	0.047	0.00
Mn	0.31	0.46	0.63	0.52	0.30	0.21	0.23	0.18	0.17	0.18
Ca	53.7	71.2	75.4	78.6	77.4	72.7	70.3	70.0	68.1	63.5
Mg	86.4	28.6	35.2	41.4	49.5	55.3	61.1	78.7	83.8	84.3
Na	18.2	8.7	11.9	12.7	14.2	14.6	15.3	18.0	19.08	20.0
К	1.6	1.6	1.8	1.6	1.6	1.5	1.4	1.5	1.61	1.6
F	2.70	0.86	1.16	1.26	1.52	1.62	1.78	2.07	2.25	2.23
Cl	71.5	7.7	13.8	17.1	24.2	25.7	31.6	44.6	49.6	54.5
Br	0.433	0.027	0.023	0.060	0.108	0.126	0.188	0.280	0.310	0.335
SO4	54.1	104.3	100.0	96.0	⁻ 87.7	82.3	77.6	69.4	65.4	50.8
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trace (ppb)	7	8	Q	7	٥	7	7	0	11	10
Li B	281	71	י רד	75	128	117	144	163	106	256
D Cr	1.6	03	0.2	15	0.0	0.5	0.5	105	150	250
Mn	281	0.J 418	758	0.0 /30	282	102	214	167	1.5	180
Fe	201	787	531	16	202	1244	1170	1003	45	109
	03	0.5	21	20	12	1244	A 1	1095	· 15	20
Ni	0.5	0.5	0.8	1.0	0.8	3.0	4.1	1.1	2.1	2.0
	0.7	6.4	0.0	0.2	0.0	20.8	4.0	23	0.0	11
Zu Zn	98 0	75	0.2 A	63	57	29.0	104	<i>2.3</i> 55	78	57
Ge	0.27	0.06	0 12	0 14	0 14	0.24	0.19	017	0 19	57
As	2.6	0.5	3.4	1.2	1.7	3.1	2.7	3.0	2.5	2.1
Se	1.5	0.0	0.0	0.0	0.0	0.0	0.6	0.0	1.1	0.0
Rb	1.4	1.2	1.8	1.4	1.7	1.2	1.3	1.4	1.4	1.4
Sr	328	236	243	253	301	291	298	367	395	414
Y	0.01	0	0.01	0.01	0.02	0.03	0.02	0.02	0.01	
Мо	13.5	0.0	3.6	3.7	5.6	6.5	8.1	8.7	9.6	9.9
Ag	0	0	0	0	0	0	0	0	0	
Cd	0.0	0.0	0.0	0.0	. 0.0	18.9	0.2	0.0	0.1	0.1
Sn	3.0	1.7	0.0	0.1	0.3	0.5	0.2	0.2	0.2	
Sb	0	0	0	0.02	0	0.01	0.02	0	0	
Cs	0.22	0.06	0.35	0.25	0.29	0.16	0.16	0.18	0.20	0.17
Ba	33.7	73.6	9.3	15.2	29.5	4.2	12.0	2.4	2.6	2.4
W	0.22	0.00	0.06	0.01	0.14	0.27	0.15	0.18	0.23	0.49
Pb	0.01	0.86	0.00	0.07	0.01	3.79	1.48	0.45	0.10	0.24
U	0.04	0.15	0.04	0.02	0.04	0.05	0.05	0.08	0.11	0.17

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	LTV	LTV	LTV	LTV	LTV	LTV	LTV	LTV	LTV	LTV
Weeks	P. Fluid	G. Wat.	1	3	7	12	16	20	25	30
pН	7.9	7	7.5	7.44	7.42	7.89	7.89	8.03	8.12	
Alk	452	196	284	292.3	333.7	339.5	395	386	415	
majors (ppn	n)									
Si	20.4	5.1	14.6	14.3	16.6	16.3	15.9	17.0	16.8	17.0
Fe	0.01	0.23	0.22	0.00	0.00	1.48	1.02	1.31	0.03	0.01
Mn	0.14	0.46	0.28	0.28	0.22	0.15	0.24	0.27	0.22	0.17
Ca	49.5	71.2	65.6	67.3	65.9	64.4	68.9	71.8	73.4	65.2
Mg	73.2	28.6	37.5	43.8	45.7	50.0	53.2	58.3	62.4	64.4
Na	79.0	8.7	26.3	28.5	31.7	33.8	37.7	42.0	46.0	47.7
К	5.0	1.6	2.8	2.5	2.8	2.8	3.0	3.5	3.9	4.1
F	5.49	0.86	1.90	2.20	2.31	2.43	2.67	2.70	2.98	3.03
Cl	50.7	7.7	13.6	12.0	14.2	15.4	20.6	27.7	35.0	42.2
Br	0.190	0.027	0.026	0.034	0.036	0.038	0.070	0.085	0.100	0.140
SO4	76.6	104.3	86.6	87.0	82.5	85.2	90.2	78.1	73.3	58.4
trace (ppb)										
Li	37	8	26	28	28	35	40	53	54	53
B	679	71	138	144	185	211	252	215	339	470
Cr	0.2	0.3	0.2	0.8	0.5	0.4	0.3	0.8	1.0	0.6
Mn	132	418	235	255	211	133	228	268	196	195
Fe	26	282	276	20	7	1513	856	1161	· 13	2
Co	0.6	0.5	0.3	0.7	0.9	0.9	0.6	0.4	0.2	1.3
Ni	0.2	0.8	0.2	0.7	0.9	2.4	1.1	2.0	0.5	2.3
Cu	0.4	6.4	1.5	0.1	0.4	14.2	2.6	7.1	0.6	1.3
Zn	38	75	3	59	39	78	63	78	43	43
Ge	0.02	0.06	0.3	0.31	0.42	0.38	0.41	0.38	0.4	
As	1.0	0.5	1.1	0.6	1.7	1.1	1.1	0.9	0.5	1.0
Se	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3
Rb	5.3	1.2	3.0	2.8	3,8	2.7	3.1	3.5	3.6	4.2
Sr	704	236	260	280	334	330	394	469	464	518
Y	0.01	0	0.01	0.01	0.02	0.02	0.02	0.04	0.11	
Мо	6.9	0.0	3.7	4.0	4.7	3.9	4.0	3.5	3.4	4.0
Ag	C) 0	0	0	0	0.01	0	0	0.01	
Cd	0.0	0.0	0.0	0.0	0.0	0.5	0.2	2.4	0.0	0.0
Sn	1.2	2. 1.7	0.2	0.3	0.2	0.5	0.1	0.3	0.1	
Sb	C) (0	0.02	0	0	0	0	0	
Cs	0.74	0.06	0.59	0.47	0.74	0.39	0.42	2. 0.53	0.49	0.47
Ba	19.2	2 73.6	9.8	20.0	32.4	5.1	6.9	6.8	6.0	6.6
W	0.54	0.00	0.35	0.18	0.39	0.40	0.38	0.37	0.42	0.31
Pb	0.00	0.86	0.35	0.06	0.00) 1.08	0.37	0.55	0.04	0.03
U	0.04	4 0.15	0.0 0	0.03	0.03	0.00	0.00	0.04	0.03	0.04

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Appendix V. Chemical composition of water in rainwater/tailings experiments.

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National

Inland

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Results: National Tailings + "Rainwater"

	Nat	Nat	Nat	Nat	Nat	Nat						
Weeks	0	9	13	18	23	27						
рН	7.89	7.7	7.8	8.19	8.17							
Alk	323	212	207	218	217							
majors (ppm)												
Si	19.9	15.7	17.1	18.4	18.8	16.4						
Fe	0.02	0.04	0.02	0.16	0.08	0.00						
Mn	0.28	0.17	0.29	0.29	0.28	0.18						
Ca	31.4	19.0	19.5	21.2	21.3	16.4						
Mg	62.6	28.4	30.3	33.4	34.4	31.9						
Na	39.9	21.7	19.4	19.4	19.4	11.7						
К	1.7	3.8	3.2	3.8	3.6	2.4						
F	1.08	0.79	0.88	0.85	0.85	0.75						
Cl	28.7	2.3	3.7	5.7	3.7	9.2						
Br	0.070	0.000			1.830	0.000						
SO4	51.8	2.4	0.8	0.6	1.0	0.1						
trace (ppb)												
Li	6	5	4	6	8	4						
В	171	155	107	126	117	59						
Cr	1.6	0.2	0.3	0.0	1.2	0.3						
Mn	258	162	264	256	263	194						
Fe	20	46	22	171	89	0						
Со	1.1	0.0	0.3	2.0	0.9	1.6						
Ni	0.3	0.3	0.2	2.0	0.4	0.9						
Cu	0.9	0.1	0.3	6.0	53.6	23.3						
Zn	74	48	50	114	116	40						
Ge	0.34	0.13	0.12	0.14	0.16							
As	0.9	2.6	3.5	2.8	2.2	2.9						
Se	0.7	0.0	0.0	0.0	0.0	0.0						
Rb	1.6	2.3	1.8	2.2	2.2	1.5						
Sr	447	180	178	203	199	144						
Y	0.01	0	0	0.02	0							
Мо	19.8	33.8	35.6	31.3	31.0	25.9						
Ag	0	0	0	0.05	0							
Cd	0.0	0.0	0.0	1.4	0.2	0.1						
Sn	1.8	0.2	0.1	0.3	0.9							
Sb	0	0	0	0	0							
Cs	0.17	0.22	0.16	0.20	0.16	0.12						
Ba	16.5	105.0	52.5	41.3	16.0	5.6						
W	0.05	0.16	0.16	0.10	0.17	0.39						
Pb	0.01	0.00	0.03	2.47	0.00	0.06						
U	0.03	0.17	0.08	0.19	0.14	0.30						

Results: Inland Tailings + "Rainwater"

	Inl	Inl	Inl	Inl	Inl	Inl						
Weeks	0	9	13	18	23	27						
pН	7.69	7.46	7.59	8.57	8.04							
Alk	375	435	330	344	335							
majors (ppm)												
Si	22.1	17.0	15.9	16.9	17.1	15.0						
Fe	0.02	0.55	0.16	0.74	0.02	0.01						
Mn	0.31	0.36	0.32	0.39	0.35	0.24						
Ca	53.7	38.9	33.9	35.9	37.1	33.4						
Mg	86.4	80.8	59.3	61.6	63.3	37.2						
Na	18.2	11.3	8.5	8.7	9.0	78						
К	1.6	1.0	0.8	0.9	0.9	0.8						
F	2.70	3.20	4.05	3 85	3 50	1 70						
Cl	71.5	5.5	4.3	4 8	51	7.0						
Br	0.433	0.057	0.028	0.030	0 270	0.019						
SO4	54.1	0.8	17	17	1 9	0.015						
		0.0		1.7	1.7	0.5						
trace (ppb)												
Li	7	5	4	5	5	A						
В	281	174	97	107	152	57						
Cr	1.6	2.0	00	06	0.6	02						
Mn	281	316	282	342	313	258						
Fe	36	477	167	1260	12	2.0						
Co	0.3	0.3	0.2	1.0	0.8	12						
Ni	0.7	0.7	0.6	1.0	1 1	1.2						
Cu	0.4	0.2	0.2	1.8	0.5	0.5						
Zn	98	54	52	68	66	37						
Ge	0.27	0.25	0.22	0.19	0 17	51						
As	2.6	7.2	3.7	6.1	51	49						
Se	1.5	0.0	0.0	0.0	0.0	0.5						
Rb	1.4	0.8	0.7	0.8	0.7	0.7						
Sr	328	203	154	167	172	144						
Y	0.01	0	0.01	0.01	0.01	•••						
Мо	13.5	7.1	8.0	9.3	9.3	19.3						
Ag	0	0	0	0	0							
Cd	0.0	0.0	0.0	0.1	0.1	0.0						
Sn	3.0	0.1	0.1	0.1	0.1	0.0						
Sb	0	0	0	0	0							
Cs	0.22	0.12	0.13	0.13	0.13	0.10						
Ba	33.7	27.8	19.8	1.5	0.9	0.5						
W	0.22	0.05	0.20	0.17	0.12	0.16						
Pb	0.01	0.01	0.02	0.40	0.12	0.04						
U	0.04	0.04	0.05	0.07	0.08	0.13						

	LTV	LTV	LTV	LTV	LTV	LTV	
Weeks	0	10	11	18	23	27	
pН	7.5	7.55	7.62	8.09	8		
Alk	432	359	331	348	350		
majors (ppn	n)						
Si	20.4	13.4	13.1	14.3	14.5	13.1	
Fe	0.01	0.37	0.30	1.65	0.02	0.00	
Mn	0.14	0.25	0.24	0.33	0.17	0.22	
Ca	49.5	36.3	37.9	40.5	40.6	37.9	
Mg	73.2	47.4	42.5	47.1	46.7	30.3	
Na	79.0	42.0	38.4	39.3	39.8	30.5	
К	5.0	3.7	3.5	3.6	3.5	3.0	
F	5.49	8.60	7.40	7.32	6.70	3.31	
Cl	50.7	2.0	4.3	7.9	5.1	3.2	
Br	0.190	0.018	0.015	0.015	0.00	0.000	
SO4	76.6	2.5	1.6	0.2	0.7	0.8	
trace (ppb)							
Li	37	56	49	52	49	40	
В	679	198	148	143	205	112	
Cr	0.2	0.0	0.0	0.1	0.0	0.2	
Mn	132	221	211	296	170	225	
Fe	26	356	285	1450	21	0	
Co	0.6	0.1	0.3	1.0	0.4	5.5	
Ni	0.2	0.5	0.6	1.9	1.5	2.0	
Cu	0.4	0.1	0.2	7.3	0.5	2.0	
Zn	38	48	53	121	55	41	
Ge	0.02	0.3	0.24	0.5	0.52		
As	1.0	0.6	0.6	0.3	0.1	0.3	
Se	0.0	0.0	0.0	0.0	0.0	0.0	
Rb	5.3	3.2	3.1	3.1	3.0	2.7	
Sr	704	343	306	334	328	249	
Y	0.01	0	0.01	0.01	0		
Мо	6.9	60.4	59.7	28.2	21.2	34.6	
Ag	0	0	0	0.01	0		
Cd	0.0	0.0	0.1	0.8	0.0	0.1	
Sn	1.2	0.2	0.1	0.3	0.1		
Sb	0	0	0	0	0		
Cs	0.74	0.42	0.45	0.42	0.43	0.32	
Ba	19.2	44.7	21.2	11.0	2.8	2.1	
W	0.54	0.52	0.63	0.67	0.72	0.72	
РЬ	0.00	0.00	0.04	1.20	1.40	0.20	
U	0.04	0.01	0.01	0.02	0.01	0.02	

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Appendix Chemical composition of water in the Snively pit tailings disposal site. USX.

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Snively Pit Pore Water Composition

Snively Pit Sump Discharge to surface of tailings in Snively Pit

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-	USX	USX	USX	USX	USX					
Date	11/22/96	9/10/97	10/11/97	2/6/98	4/10/98					
Location	well	well	well	well	well					
T °C	6	9.5		7	9					
						Ave	Std Dev	Max	Min	Ν
рн	8.16	7.40	7.32	7,52	7.32	7.54	0.35	8.16	7.32	5
	342	335	338	335	329	336	5	342	329	5
En majors (no	296 m)	258	295	288	322	292	23	322	258	5
	(11)	0.00	0.01	0.00	0.00	0.04	0.00			_
Si	0.20	0.00	0.01	0.00	10.2	0.04	0.09	0.20	0.00	5
P	0.08	9.2	9.5	10.4	10.3	9.7	0.0	10.4	9.2	5
Fe	12 50	0.00	0.00	0.00	0.01	2.02	0.03	12.00	0.00	5
Mn	1.87	1.02	1.07	1 22	1.61	2.90	0.34	12.50	0.17	5
Ca	125.0	111 7	109 1	108.3	102.2	111 3	0.57	125.0	1.02	ວ 5
Mg	94.6	91.4	90.0	91.9	86.0	90.8	3.2	94.6	86.0	5
Na	22.2	20.9	19.7	20.5	19.0	20.4	12	22.2	19.0	5
к	9.0	8.7	8.7	9.2	9.6	9.0	04	9.6	87	5
F	0.16		0.24	0.24	0.25	0.22	0.05	0.25	0.16	4
CI	15.7		15.1	13.0	11.7	13.9	1.9	15.7	11 7	4
NO2-N	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	4
Br	0.06		0.07	0.06	0.05	0.06	0.01	0.07	0.05	4
NO3-N	0.48		0.18	0.22	2.99	0.97	1.35	2.99	0.18	4
SO4	383		360	371	338	363	19	383	338	4
trace (ppb))									
Li	12	9	9	9	9	10	1	12	9	5
Ве	0	0	0	0	0	0	0	0	0	5
B	43	45	22	40	14	33	14	45	14	5
SC т:	0.1	4.3	2.5	2.9	2.8	2.5	1.5	4.3	0.1	5
	0.4	6.8	8.7	0.3	10.4	5.3	4.7	10.4	0.3	5
v Cr	0.0	0.0	0.1	10.0	0.1	0.2	0.3	8.0	0.0	5
Co	0	0.0 1 A	1.0	12.7	1.0	4.3	5.0	12.7	0.8	5
Ni	13.8	2.6	24	27	3.0 2.8	2.1	0.9	3.0 12.9	1.3	5
Cu	3.4	1.1	0.4	1.0	0.9	13	12	34	2.4	5
Zn	39.2	1.3	2.7	18.5	17.6	15.8	15.3	39.2	13	5
Ge	0.2	0.0	0.0	0.1	0.1	0.1	0.1	0.2	0.0	5
As	4.8	0.5	0.1	0.3	0.3	1.2	2.0	4.8	0.1	5
Se	0.1	0.3	0.0	0.8	0.0	0.2	0.3	0.8	0.0	5
Br		67	61	49	50	57	8	67	49	4
Rb	6.9	7.0	3.5	7.2	7.4	6.4	1.6	7.4	3.5	5
Sr	290	301	250	251	224	263	32	301	224	5
Y	1.31	0.04	0.03	0.03	0.01	0.28	0.57	1.31	0.01	5
MO	1.5	0.5	0.3	0.1	0.2	0:5	0.6	1.5	0.1	5
Ag	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5
	0.16	0.00	0.00	0.22	0.17	0.11	0.10	0.22	0.00	5
Sh	0.24	0.01	0.01	0.05	0.12	0.09	0.10	0.24	0.01	5
Te	0.01		0.00	0.00	0.00	0.00	0.00	0.01	0.00	5
Cs	0.01	0.00	0.00	0.00	0.00 0.00	0.00	0.00	0.01	0.00	5
Ba	43.34	31 69	27.28	25 57	0.00 22 12	30.20	0.09 7 QQ	00.0	0.33	5
Ŵ	10.04	01.00	21.20	20.07	20.10	JU.20	1.30	40.04	23.13	э
	0.30	0.08	0.01	0 00	0 10	0 12	0 12	0 20	0 00	5
Pb ·	0.30 1.37	0.08 0.08	0.01 0.03	0.00 0.01	0.19	0.12	0.13	0.30	0.00	5 5

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Date Location T (C)	USX 11/22/96 sump 7	USX 9/10/97 sump 9.5	USX 10/11/97 sump	USX 2/6/98 sump 6	USX 4/10/98 sump 9				·	
ъH	9 07	7 07	7 4 4	0.07		Ave	Std Dev	Maximum	Minimum	Ν
Alk	219	240	7.11	6.87	7.19	7.26	0.47	8.07	6.87	5
Eh	308	240	204	204	270	249	20	270	219	5
maiors (ppm)	000	530	552	299	299	326	39	390	299	5
Al	0.03	0.00	0.00	0.00	0.00	0.01	0.04	0.00		
Si	7.2	7.6	7.8	7.8	0.00 7 A	0.01	0.01	0.03	0.00	5
Р	0.00	0.00	0.01	0.00	0 00	0.0	0.2	1.8	7.2	5
Fe	0.00	0.02	0.00	0.07	0.00	0.00	0.00	0.01	0.00	5
Mn	3.32	1.38	1.58	8.59	2.07	3.39	3 00	8.59	0.00	5 5
Ca	85.8	81.4	82.6	97.7	81.8	85.9	6.8	97.7	81.4	5
Mg	75.1	70.5	70.6	75.3	64.0	71.1	4.6	75.3	64.0	5
Na	24.9	19.5	19.1	23.2	22.5	21.9	2.5	24.9	19.1	5
K F	24.9	16.8	16.1	24.5	21.0	20.7	4.2	24.9	16.1	5
	0.17		0.22	0.19	0.25	0.21	0.04	0.25	0.17	4
	5.7 0.12		6.6	8.2	8.3	7.2	1.3	8.3	5.7	4
Br	0.12		0.00	0.56	0.10	0.19	0.25	0.56	0.00	4
NO3-N	11.30		3 00	10.00	0.05	0.05	0.01	0.05	0.04	4
SO4	333		295	340	· 0.00	8.39	4.27	12.73	3.99	4
trace (ppb)			200	0-0	210	209	33	340	270	4
Li	10	9	8	13	10	10	· 2	13	0	c
Be	0	0	0	0	0	0	0	13	0	5 5
В	28	35	42	30	6	28	14	42	6	5
Sc	0.1	3.2	2.2	2.5	2.0	2.0	1.2	3.2	0.1	5
	0.1	1.2	3.9	13.9	12.2	6.3	6.4	13.9	0.1	5
V Cr	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1	0.0	5
Co	4.3	0.2	0.0	8.3	0.3	2.6	3.6	8.3	0.0	5
Ni	22.1	1.9	2.2	15.2	3.2	9.0	9.4	22.7	1.9	5
Cu	22	0.6	1.5	5.9 10 0	1.1	2.9	1.9	5.9	1.1	5
Zn	36.7	0.8	19.8	15.5	136	3.3 17 2	4.3	10.9	0.6	5
Ge	0.1	0.0	0.1	0.0	0.1	0.1	13.0	30.7	0.8	5
As	6.6	1.8	1.5	0.4	0.7	2.2	2.5	6.6	0.0	5 5
Se	2.5	0.7	0.0	5.5	0.0	1.7	2.3	5.5	0.4	5
Br		44	33	48	44	42	7	48	33	4
Rb	27.7	23.5	18.8	35.7	27.6	26.6	6.2	35.7	18.8	5
Sr	206	278	241	219	223	233	28	278	206	5
Mo	0.03	0.03	0.03	0.03	0.03	0.03	0.00	0.03	0.03	5
Aa	5.3	2.5	2.2	0.6	2.1	2.6	1.7	5.3	0.6	5
Cd	0.00	0.00	0.00	0.10	0.00	0.02	0.04	0.10	0.00	5
Sn	0.49	0.00	0.00	0.04	0.00	0.02	0.02	0.05	0.00	5
Sb	0.00	0.00	0.00	0.00	0.04	0.12	0.21	0.49	0.00	5
Те	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5 5
Cs	5.98	4.18	3.49	5.44	4.64	4.75	0.99	5.98	3 40	5
Ba	31.30	33.10	30.45	17.64	32.57	29.01	6.44	33.10	17.64	5
W	0.06	0.02	0.00	0.12	0.05	0.05	0.05	0.12	0.00	5
Pb .	0.59	0.00	0.13	0.09	0.12	0.19	0.23	0.59	0.00	5
U	0.52	0.93	0.76	0.42	1.62	0.85	0.47	1.62	0.42	5