PREDICTION OF GROUNDWATER QUALITY DOWNGRADIENT OF THE RECLAIMED PIT FOR THE FLAMBEAU PROJECT

Prepared for:
FLAMBEAU MINING COMPANY

Prepared by:
FOTH & VAN DYKE and Associates, Inc.
2737 S. Ridge Road
P.O. Box 19012
Green Bay, Wisconsin 54307-9012

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- **APPENDIX A** Revised Table No. 5-1 from the Mining Permit Application for the Kennecott Flambeau Project
- **APPENDIX B** In-Pit Model Calculations
1.0 INTRODUCTION

This report addresses whether or not groundwater quality impacts will result from the reclamation of the open mine pit that will be created as part of the Flambeau Project near Ladysmith, Wisconsin. This question was initially addressed in the environmental impact report (KEIR) (Foth & Van Dyke 1989a) for this project. Supplementary information on groundwater flow directions and velocities during and after mining have been provided in a modeling report by Prickett (1989). The groundwater quality impact of the Type I stockpile was demonstrated to be insignificant in another supplementary report, by Foth & Van Dyke (1989b).

The KEIR concludes that neither the mining operation, itself, nor the creation and operation of the Type II stockpile will create groundwater quality impacts. The mine pit, when in existence, will cause the formation of a cone of depression in the water table. Thus, during the time the mine is in existence, all groundwater will flow toward the open pit, making it impossible for any groundwater-borne compounds to leave the mine vicinity. As for the Type II stockpile, it will be underlain with an impermeable liner and a leachate collection system, thereby preventing compounds from moving downward from the stockpile to the water table. Underneath the stockpile, therefore, no groundwater-borne compounds will be able to move downward to the water table.

Since the mine pit as well as both the stockpiles are incapable of impacting groundwater quality, the only remaining groundwater quality issue, then, is the one relating to the reclaimed pit. The waste characterization study described in the KEIR showed the possibility that several parameters in the reclaimed pit could become elevated. This report determines that four of these—copper, manganese, iron, and sulfate—would be elevated
sufficiently to be measurable and predictable. These concentrations would occur in the bottom of the pit in the layer of Type II waste rock, the most leachable of the materials returned to the pit.

In order to evaluate what, if any, impact these compounds will have on water quality, it is necessary to consider the results of the modeling conducted by Prickett (1989). He, assisted by the staff of Engineering Technologies Associates, Inc. of Ellicott City, Maryland, created a two-dimensional, cross-sectional flow model of the reclaimed pit. This model clearly shows that the groundwater within the waste rock below the saprolite layer in the reclaimed pit flows downwards and toward the river pillar. He showed that as long as the river pillar is relatively highly permeable, the pillar itself acts as a sink, drawing all the up-gradient bedrock groundwater toward it, and then discharging it to the river at an average discharge rate of 2 gallons per minute (gpm).

The only situation which could change this flow pattern would be a change in the river pillar permeability, caused by grouting during mining operations. If such a permeability change would occur, the potential would exist for a small amount of the groundwater emanating from the Type II waste rock in the reclaimed pit to move upward past the saprolite layer and escape the pit in the shallow outwash to the northwest.

Such grouting would occur, however, only in response to a need to cut down flows to the open pit so as not to overload the wastewater treatment plant. Inasmuch as the wastewater treatment plant has been significantly over-designed with respect to capacity, there is no possibility that a grouting effort will ever be undertaken to reduce the flows through the river pillar to less
than those predicted by Prickett. The wastewater plant is designed to handle the flows he predicted, and more.

Therefore, since there is no likelihood that the pillar permeability will ever be reduced to a level below that used by Prickett in his predictions, there also is no possibility that the groundwater emanating from the Type II waste rock in the reclaimed pit will do anything but move straight toward the Flambeau River through the river pillar. Thus, the only flow regime evaluated in this report is the direct route through the river pillar. The studies described herein conclude that only one parameter, sulfate, would depart the reclaimed pit at concentrations higher than present-day background groundwater quality conditions. The report further concludes that the sulfate concentration increase would not be of concern because no sulfate increase would be detectable beyond the Flambeau River. Since the proposed compliance boundary is beyond the river, no sulfate exceedences are possible at the point of standards application. As to the river itself, the incremental increases in the river water of parameters in groundwater entering the river from the pit will be so small as to be unmeasurable. Thus, no impact on the river will occur.

Following this introduction, Section 2.0 of the report discusses how the source term concentrations for copper, manganese, iron, and sulfate were derived. Section 3.0 discusses the transport of these constituents downgradient of the pit through the river pillar and into the river. Section 4.0 of the report presents the report’s evaluation of the potential impacts. Section 5.0 is a list of the references cited.
2.0 SOURCE TERM CALCULATIONS

Type II wastes, consisting of saprolite and waste rock containing more than one percent sulfur, will be temporarily stockpiled above grade in a lined, twenty-seven acre site. Reactions between the stockpiled wastes and precipitation produce leachate which will be collected and treated, along with pit contact water, in an on-site wastewater treatment facility. The slurried lime and sulfide precipitate produced in the facility will be spread on the stockpiled wastes. The precipitate reacts with the leachate in the stockpile, forming additional leachate by dissolution and secondary minerals by precipitation.

Following the completion of mining operations, these wastes and precipitates will be backfilled into the bottom of the open pit. As these materials are being backfilled, groundwater and precipitation will restore the groundwater levels to the approximate premining steady state elevations. When the steady state groundwater levels have been attained, groundwater will flow from the east to the west through the backfilled materials within the pit. Reactions between the groundwater and the wastes will result in the release of certain substances from the wastes to the groundwater which will then be transported with the groundwater from the pit.

The models described in this report include one which formulates the generation of the leachate within the stockpiled wastes, and one which formulates the reactions between the backfilled wastes and groundwater. Also discussed are the generation of the Type II wastes and the precipitate, and the expected reactions between the stockpiled wastes and the applied slurried precipitate.
The output of the first model is a time-based generation of leachate within the stockpiled wastes. The output of the second model is a time-based release of substances from the backfilled pit to the downgradient groundwater.

2.1 Model Inputs

The inputs to the model describing the unsaturated generation of leachate within the stockpiled wastes include the quantity of waste stored in the stockpile and the time during which the wastes are added to the stockpile. In addition, the quantity and periodicity of the precipitative inputs to the stockpile are utilized in the model. The leachate percolates through the wastes until it intersects the leachate collection system which will be installed beneath the system and above the impervious liner.

The leachate thus generated and collected will be piped to the surge pond. From there it will be sent to the wastewater treatment facility where, along with the pit contact water, it will be treated with lime and sulfide. This treatment removes substances to a level which will more than meet the requirements for the discharge of these waters to the Flambeau River. A by-product of the treatment will be the generation of sulfide precipitate produced from lime. This precipitate will be applied to the stockpiled wastes in a slurried form on a daily basis. The precipitate applied to the stockpile will react with precipitation and leachate producing additional leachate of a somewhat alkaline nature and secondary minerals.

The quantity and composition of the backfilled wastes and precipitates returned to the pit, and the quantity and composition of the recharging groundwater and precipitation, are the inputs for the model that predicts the in-pit reactions between the wastes and groundwater.
2.1.1 Type II Waste Generation

Type II waste materials will be generated in two phases. The first phase, Phase I, will consist of waste rock and saprolite removed from the western half of the open pit. Phase II wastes will consist of the same materials, but will differ in relative proportions of them. The Phase II wastes will be removed from the eastern end of the pit subsequent to the removal of the Phase I wastes, as shown on Table No. 4-2 of the Revised Mining Permit Application for the Flambeau Project (KMINE) (Foth & Van Dyke 1989c).

As seen in Table No. 2-1, a total of 3,122 kilotons of Type II waste will be removed during the mining operation. All of these wastes will be stockpiled in the lined Type II stockpile. Quarterly production figures for the combined Phase I and II wastes are also listed in Table No. 2-1. The wastes will be stockpiled in two phases, the first of which, Phase I, will cover 15.53 acres. Phase II of the stockpiling will cover an additional 11.47 acres. Phase I stockpiling will initially occur through the third quarter of the second year of operations. From that time until the cessation of operations at the end of the third quarter of the sixth year, stockpiling at various rates will occur in both phases, but mainly in the Phase II area.

2.1.2 Leachate Generation

The most important factor in leachate generation is the input of precipitation to the stockpiled wastes. Average monthly precipitation data, corrected for losses due to evapotranspiration, were added to the wastes on a quarterly basis in the model (see KMINE, Appendix N, p. 28 for data). The quarters used in the model were January-March, April-June, July-September, and, October-December. In the model it was assumed that the net
**TABLE NO. 2-1**

In-Pit Model Output

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<th>MANGANESE (mg/L)</th>
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**TOTALS:**

6.92E+12  7.17E+11  2.00E+10  2.14E+12
precipitation was of uniform quantity during the entire quarter. Also, it was assumed that runoff would generate leachate, since it will be in contact with the wastes and will be collected by part of the leachate collection system.

The precipitation and runoff that will be collected by the Phase I stockpile for the above listed quarters will be $6.14 \times 10^6$, $5.27 \times 10^6$, $7.49 \times 10^6$, and, $8.68 \times 10^6$ liters per quarter, respectively. The precipitation and runoff that will be collected by the combined Phase I and II stockpiled wastes will be $1.09 \times 10^7$, $9.16 \times 10^6$, $1.30 \times 10^7$, and, $1.51 \times 10^7$ liters per quarter, respectively (see Table No. 2-1).

Wet-dry leaching experiments were performed on a typical Type II waste (sample WR-5) as part of the waste characterization studies. These experiments simulate the reactions that will occur when precipitation reacts with the wastes. Mathematical relationships have been developed between the quantity of five parameters—copper, iron, manganese, sulfate, and pH—that will be leached from these materials, and the leach cycle number (see Table Nos. 3.5-18 and 3.5-19 in the KEIR). No other relationships were developed because no other parameters that would be of concern leached from the waste rock in any elevated concentration.

Each leaching test was conducted for a period of 80 days during which time leachate samples were collected and analyzed following a geometrically increasing time scale (samples were collected at the conclusion of cycles 1, 2, 4, 8, and, 16). The results of the analyses of these samples has revealed that the quantities of materials leached decreased according to negative power functions of the leaching cycles. The calculated numerical relationships
for the leaching of the rock chips, which will make up an estimated 97-98 percent of the stockpiled waste rock, are:

\[
\begin{align*}
\text{Cu (ug/g)} & = (437.6)(\text{cycle \#})^{-1.81}, & r^2 = 0.93 \\
\text{Fe (ug/g)} & = (168.0)(\text{cycle \#})^{-2.11}, & r^2 = 0.93 \\
\text{Mn (ug/g)} & = (3.86)(\text{cycle \#})^{-1.71}, & r^2 = 0.94 \\
\text{SO}_4 (\text{mg/g}) & = (1.40)(\text{cycle \#})^{-1.78}, & r^2 = 0.92
\end{align*}
\]

The numerical relationship between leachate pH, which was measured during each of the 16 cycles, and leaching cycle number is:

\[
\text{pH (su)} = (2.86)(\text{cycle \#})^{0.14}, \quad r^2 = 0.92
\]

Similar relationships were observed for the leaching of the rock powder. However, due to irregularities in the data, only the leached amounts of copper and manganese could be quantified simply. The calculated relationships for these metals are:

\[
\begin{align*}
\text{Cu (ug/g)} & = (314.8)(\text{cycle \#})^{-1.13}, & r^2 = 0.81 \\
\text{Mn (ug/g)} & = (2.64)(\text{cycle \#})^{-1.54}, & r^2 = 0.88
\end{align*}
\]

Due to the fact that only a minor proportion of the waste rock will be powder, and the fact that the leaching relationships of the powder are similar to the rock chips, only the data from the rock chip leaching experiments have been used in modeling the leachate generation.

The results of the analyses also revealed that significant statistical mathematical relationships exist between the quantities of leached copper, iron, manganese, and, sulfate and leachate pH. These calculated relationships show that the quantities of metals leached from the rock chips decrease with increasing pH following negative power functions. These relationships are:
It is assumed that the leaching characteristics of the Type II saprolite will be similar to that of the waste rock.

2.1.3 Precipitate Generation

Bench tests performed as part of the Preliminary Engineering Report for Wastewater Treatment Facilities (Foth & Van Dyke 1989d) have shown that precipitate production from the planned wastewater treatment plant will vary with the length of exposure of Type II material to wetting and drying cycles. Precipitate production during the studies ranged from 9,000 pounds of dry precipitate per million gallons of wastewater to 60,000 pounds per million gallons. The higher value corresponds to the initial wetting of Type II material used for the bench tests, while the lower value represents the third and final wetting. The second wetting produced an estimated production rate of 30,000 dry pounds per million gallons.

Given the bench test results, it is projected that the actual rate of precipitate production at the maximum wastewater treatment plant capacity of 800 gpm will be closer to 30,000 dry pounds per million gallons. At the estimated average annual flow rate of 296 gpm, average daily precipitate production over the life of the project is expected to be equivalent to approximately 11,100 dry pounds per million gallons.
The projected quarterly generation of wastewater from the open pit and Type II stockpile are listed in Table No. 2-2. The values for the pit inflow data were derived from Prickett (1989). The other values were calculated from data presented in the KMINE document. The values take into account the changes in pit inflow, variations in quarterly precipitation and runoff (listed as "precipitation"), the successive opening of Phases I and II within the pit, and the expansion of the stockpile when Phase II of the stockpile is opened.

For modeling it was conservatively assumed that the composition of the wastewater emanating from the open pit will be approximately equivalent to the average Type II waste rock leachate. The composition of the pit contact wastewater is considered to be equivalent to the cycle 8 waste rock leachate (see Table No. 3.5-19, KEIR), which is:

\[
\begin{align*}
\text{Cu} &= 24,000 \text{ ug/L} \\
\text{Fe} &= 4,200 \text{ ug/L} \\
\text{Mn} &= 210 \text{ ug/L} \\
\text{SO}_4 &= 60 \text{ mg/L}
\end{align*}
\]

The average steady state pit contact water flow is \(8.47 \times 10^7\) liters per quarter. Pit contact water will be collected for twenty-five quarters. It has been determined that \(5.08 \times 10^{10}, 8.90 \times 10^9, 4.45 \times 10^8,\) and, \(1.27 \times 10^{11}\) mg of copper, iron, manganese, and, sulfate, respectively, will be leached from the pit contact rocks. Stockpile leachate will be collected for twenty-eight quarters and, as shown in Table No. 2-1, \(2.14 \times 10^{12}, 7.17 \times 10^{11}, 2.00 \times 10^{10},\) and, \(6.90 \times 10^{12}\) mg of copper, iron, manganese, and, sulfate, respectively, will be leached from the stockpiled Type II wastes. Of all the metal loading, 2.3, 1.2, 2.2, and 1.8 percent, respectively, will be derived from the pit contact water.
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<th>PERIOD</th>
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<td></td>
<td>1.09E+07</td>
<td>3.02E+04</td>
</tr>
</tbody>
</table>

**TOTALS:** 1.19E+09  6.24E+08  1.81E+09  2.87E+08  6.0CE+06
In terms of flow, the waste rock leachate comprises only an average of 12.5 percent of the water that will be treated in the wastewater treatment facility. The difference in material loading between the pit and stockpile sources can be attributed to the fact that the stockpiled wastes are leached through many successive cycles and to the very considerable exposed surface area per unit mass of the stockpiled waste.

The precipitate will consist of metal hydroxides, sulfides and sulfates. Iron will be precipitated as a hydroxide, nearly all of the copper will be precipitated as a hydroxide, and approximately 75 percent of the manganese will be precipitated as a sulfide (the remaining manganese will be precipitated as a hydroxide). Sulfate will be precipitated as the mineral gypsum (a hydrous calcium sulfate) during the lime treatment of the wastewater (see Larsen, et. al., 1973, and Lanoutte, 1977).

2.1.4 Stockpiled Type II Waste Reactions

Field studies have shown that numerous secondary minerals form within and on the surface of stockpiled sulfide wastes (Nordstrom, 1982, Whiting, 1985). Some of the minerals commonly found in the central portions of stockpiles where the rates of evaporation are slow include:

- ferrihydrite, a hydrous iron oxide
- calcanthite, a hydrous copper sulfate
- ilesite, a hydrous manganese sulfate
- malachite, a hydrous copper carbonate
A mineral commonly found near the margins of sulfide stockpiles where the rates of evaporation are greater and where the pH is lowest in the stockpile is:

- jarosite, a hydrous potassic iron sulfate

Secondary minerals that form by rapid evaporation are often found on the surface and edges of sulfide stockpiles, especially near areas where seepages occur. These minerals include:

- melanterite, a hydrous iron sulfate
- copiapite, a hydrous iron sulfate
- antlerite, a hydrous copper sulfate
- cuprocoiapite, a hydrous copper iron sulfate

Minerals that form on the surfaces of sulfide stockpiles tend to be soluble and are dissolved during rain storms. Minerals that form within stockpiles tend to have lower solubilities and persist and grow during the time that the stockpile is in existence.

It is expected that, with the exception of the formation of ferrihydrite, only minor amounts of copper, manganese and sulfate will become incorporated in secondary minerals that form within or on the stockpile. Ferrihydrite is a stable mineral under all but the most acidic conditions and forms rapidly from iron hydroxide precipitates. During the lifetime of the stockpile it is expected that nearly all of the iron hydroxide precipitate that will be spread on the stockpiled wastes will be converted to ferrihydrite (Schwertmann 1985).

The major secondary minerals that will be found within and on the stockpile will be the precipitates from the applied slurried wastewater precipitate. With the exception of the iron hydroxide precipitate (ferrihydrite), many of the precipitates will
dissolve and contribute mass to the leachate. It is important to note that since the collection and treatment of the leachate will be continuous, and since the slurried precipitate will be applied to the stockpile daily, essentially all of the leached materials will be in solid form at the time that the weathered wastes are backfilled in the open pit. In addition, these solids, with the exception of ferrihydrite, will comprise the precipitate.

2.1.5 In-Pit Type II Waste Reactions

The saturated waste rock leaching studies were conducted in order to simulate the reactions that would occur if the waste materials were returned to the pit in untreated form. These materials had been previously leached during the wet-dry leaching studies. Synthetic groundwater approximating the concentration of upgradient groundwater was used to saturate the leaching columns (see Waste Characterization Studies in KEIR for details). No slurried precipitates were applied to the Type II leaching columns.

It was discovered that during the 16 saturated leaching cycles, pH decreased during the course of the leaching. In addition, the quantities of copper, manganese and sulfate leached from the waste rock chips increased. The quantity of iron leached from the chips at first increased and then decreased to the point that during cycles 8 and 16 iron was being sorbed from the synthetic groundwater (see Table No. 3.5-24 and 3.5-25 in the KEIR). The calculated relationships between leached copper, manganese and sulfate and the leach cycle number are positive power or exponential functions. These relationships are:

\[
\begin{align*}
\text{Cu (ug/g)} &= (18.4)(\text{cycle #})^{0.38}, \\
\text{Mn (ug/g)} &= (0.26)(\text{cycle #})^{0.41}, \\
\text{SO}_4 \text{ (mg/g)} &= (0.062)^{0.047}(\text{cycle #}), \\
\text{pH (su)} &= (3.77)(\text{cycle #})^{-0.051},
\end{align*}
\]

\[ r^2 = 0.92 \]
\[ r^2 = 0.85 \]
\[ r^2 = 0.92 \]
\[ r^2 = 0.95 \]
The calculated relationships between pH and the quantity of copper, manganese and sulfate leached from the rock chips are negative power functions. These mathematical relationships are not as statistically significant as were those of the wet-dry leachings. These relationships are:

\[
\begin{align*}
\text{Cu (ug/g)} &= (2.28 \times 10^5)(\text{pH})^{-7.07}, & r^2 &= 0.84 \\
\text{Mn (ug/g)} &= (4.35 \times 10^3)(\text{pH})^{-7.28}, & r^2 &= 0.74 \\
\text{SO}_4 \text{ (mg/g)} &= (13.7)(\text{pH})^{-4.07}, & r^2 &= 0.60
\end{align*}
\]

These results suggest that the Type II wastes should be treated as they are returned to the pit. Therefore the effect of liming the wastes as they were being backfilled was investigated. In order to evaluate a worst case situation, freshly ground Type II waste rock (sample WR-5) was equilibrated with distilled, deionized water and with lime bearing water that raised the solution pH to 6.5, the approximate pH of the upgradient groundwater.

The results of the "acid neutralization" tests, given in Table No. 3.5-12 (see KEIR), show that liming reduced the original copper, iron and manganese concentrations by approximately 92, 95 and 24 percent, respectively, while the concentration of sulfate doubled. As a result of this study the mining plan calls for the addition of sufficient lime slurry to the Type II wastes as they are being backfilled in order to maintain a waste contact water pH of approximately 6.5.

The concentrations of copper, iron, manganese, and sulfate in the pit water will mainly be functions of the pH of the water and the quantity and relative solubilities of the materials that contain these parameters. The solubility of copper hydroxide is \(2.2 \times 10^{-2}\) mg/L and that of copper sulfide is \(5.8 \times 10^{-18}\) mg/L in pure water. The solubility of ferrous hydroxide is \(8.9 \times 10^{-1}\) mg/L and that of ferrous sulfide is \(3.4 \times 10^{-5}\) mg/L in pure water.
water. At a pH of 6.5 ferric hydroxide will maintain concentrations of ferric iron at or below $3.2 \times 10^{-1}$ mg/L. The solubility of manganese hydroxide is $1.2 \times 10^{0}$ mg/L and that of manganese sulfide is $2.1 \times 10^{-3}$ mg/L in pure water. The solubility of gypsum in pure water is $2.4 \times 10^{3}$ mg/L. The solubilities of these substances will be suppressed in the pit contact water due to common ion effects.

From the above data, it is apparent that the concentration of these parameters will be dependent upon the solubilities of the soluble metal hydroxides and gypsum. The primary copper, iron and manganese sulfides, either as original rock constituents or as sulfide precipitates, are at least three orders of magnitude less soluble than their hydroxides. The solubilities of these hydroxides and sulfate, which constitute the bulk of the slurried precipitate, will control the concentrations of these parameters in the pit water and in the water that is flushed out of the pit by reestablished groundwater flow.

2.1.6 Model Input Summary

The leachate generation model provides a worst case appraisal of the leaching of the stockpiled Type II wastes. The wastes are stored by depositing successive layers of material upon one another in the lined site. The model summed the projected quantities that could be leached during cycle 1 with quantities that could be leached during cycle 2 in the next oldest quarterly deposit, and so on through all of the quarterly deposits.

The quantities of materials that could be leached from these wastes were determined in laboratory column experiments in which the wastes were successively leached with synthetic rain water, which is nearly pure water. These laboratory conditions simulated the maximum leaching that could occur, and might occur
in the field, if the quarterly accumulations of waste were deposited side by side. However, the quarterly accumulations of stockpiled wastes will be essentially deposited one on top of the other.

Leachate generated by the reactions between precipitation and the uppermost layer will percolate into the next older layer beneath it. The leaching of the second, and successive layers beneath it, will be considerably less intense than if the leaching were conducted with rain water. The reduction in leaching will be due to the common ion effect, in which the leaching of a given substance will be suppressed by the presence of significant quantities of the substance to be leached in the leaching solution.

The solubility and quantity of the most soluble substance that contains the parameter of interest will control the concentration of the parameter in solution. This control will exist until all of the soluble material has dissolved. The remaining most soluble substance will then control the parameter concentration in solution.

The major control of the in-pit concentrations of copper, iron, manganese, and, sulfate will be the precipitates of copper hydroxide, iron hydroxide (and ferrihydrite), manganese hydroxide, and, hydrous calcium sulfate (gypsum). The other materials in the wastes and precipitate containing these substances are several orders of magnitude less soluble than those listed above. Dissolution of the less soluble substances will result in parameter concentrations of essentially background levels.
2.2 Model Outputs

The outputs of the leachate generation model and the in-pit model are discussed separately below. The outputs are time based releases of materials, by leaching or dissolution, to the leachate or groundwater, respectively.

2.2.1 Leachate Generation Model

The quantities of copper, iron, manganese, and sulfate that will be included in the leachate will be a function of the quantity of waste rock leached during a given quarter, and the length of time that quantities of waste material have been in the stockpile. It was conservatively assumed that one significant leaching occurred during each quarter and that all of the material stockpiled during a given quarter was uniformly leached for the entire quarter.

The quantities of material leached was calculated by multiplying the quantity of waste deposited in the stockpile during a given period by the quantity of material that would be leached from the waste, considering the number of quarters that the materials were stockpiled. The total quantities that would be leached in a given quarter is the summation of the products of the mass of the waste times the appropriate leach cycle leaching. The results of these calculations are presented in Table No. 2-1.

The bulk concentration of copper, iron, manganese, and sulfate in the Type II waste (see Table No. 3.5-10 in the KEIR), multiplied by the total waste mass is the total quantity of each substance that potentially could be leached. These quantities are \(1.81 \times 10^{10}, 1.08 \times 10^{11}, 5.38 \times 10^7\), and \(4.25 \times 10^8\) grams respectively. The total projected quantities that would be leached from these materials are \(2.14 \times 10^9, 7.17 \times 10^{11}, 2.00 \times 10^7\), and \(6.97 \times 10^9\) grams, respectively. The above figures show that the
calculated leaching relationship overestimates the quantity of iron that could be leached from the wastes. Nearly two percent of the sulfate-sulfur could be leached from the waste in addition to more than 10 percent of the copper and more than 30 percent of the manganese. Despite the loss of metals and sulfate from the Type II waste rock and saprolite, there is no net loss from these materials since the metals and sulfate are returned to the stock-piled wastes in the form of precipitate.

2.2.2 In-Pit Model

Backfilling of the open pit will commence upon completion of the mining operations at the end of the third quarter of the sixth year of operation (period 6-3). The waste materials will be returned to the pit in this sequence: Type II waste materials at the bottom, followed in turn by Type I waste rock, saprolite, sandstone, till, and, topsoil. This sequence will be layered, and beginning with the saprolite layer, will approximate the original stratigraphic sequence of the site. The saprolite layer will be placed such that it ties in with the saprolite surrounding the pit and will be compressed to form a low permeability layer between the Type I and II materials and the overburden materials.

The Type II materials will be placed such that the lifts gently slope towards the narrow ends of the pit. This will facilitate the collection of pit inflow and precipitation, should these waters accumulate faster than the material is backfilled. Waters collected by the sump pumps installed at the narrow ends of the pit will be considered contact water and will be pumped to the wastewater treatment facility.

In addition, lime slurry will be added to the daily accumulation of Type II materials in sufficient quantity to raise the pH of
the discharge water to at least 6.5 (see KMINE and KEIR for the calculations of the quantity of lime that will be required). The liming will limit the release of substances from the backfilled Type II wastes when these materials are saturated with the incoming waters.

During the backfilling of the Type II wastes, the slurried precipitate from the wastewater treatment facility will be added to these materials in the pit rather than added to the remaining stockpiled wastes. Since the pH of the pit water will be 6.5 or greater, pH sensitive components in the precipitate will be more stable in the pit than on the stockpile where the pHs will range from 3 to 4. This is important for the stability of the copper, iron and manganese compounds. It will have little or no effect upon the solubility of gypsum, the main source of soluble sulfate. The Type II liner system will be dismantled upon the completion of the backfilling of the Type II wastes. The sand blanket and stockpile basal support materials will then be added to the top of the backfilled Type II wastes.

A copy of Table No. 5-1 (KMINE) is included in Appendix A. This table lists the sequence of, and quantity of, the backfilled wastes as a function of mine bench level.

The porosities of the backfilled waste materials were estimated by increasing the original material volume by the swell factor, and then reducing by the compaction factor. This porosity multiplied by the volume of wastes estimates the pore volume that will be filled by the inflowing waters. The results of these calculations are presented in Table No. 2-3 along with the estimated time required to fill the physically created pore volumes.
### TABLE NO. 2-3

Calculated Volumes and Times of Saturation of Backfilled Wastes During Remediation

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Note: WR II = Type II Waste Rock and Sandstone  
WR I = Type I Waste Rock  
SAP = Type I Saprolite  
SS = Sandstone  
TILL = Volume of Till Beneath the Water Table
The rate at which water will saturate the backfilled wastes has been calculated by summing the yearly precipitative inputs (precipitation, runoff and infiltration) with the estimated pit inflow water derived from groundwater. It is assumed that backfilling the pit will be completed in 18 months. During the backfilling the pit will receive direct precipitation and runoff. Following the completion of the backfilling, the pit will continue to receive water from precipitation but it will be by infiltrative processes (see Appendix N, KMINE for precipitative data).

Based upon data presented by Prickett (1989), it was estimated that the groundwater level above the pit would be restored in approximately 10 years following the termination of mining. It was assumed that 75 percent of the groundwater pit inflow would occur in the first 20 percent of the pit inflow time and that the quantity of inflowing water would geometrically decrease with time during the inflow. In addition, it was assumed that the first pit inflow water would enter the pit at the rate equivalent to that which occurred during the end of the mining operation, i.e., an average value of 114 gpm. The quantities of precipitative and inflow waters entering the backfilled pit during the post mining recovery of groundwater are presented in Table No. 2-4. As seen in the table, the main source of water is from precipitative sources and that during the first year of recovery the pit inflow and precipitative inputs are nearly equal.

The in-pit chemical transport model traces the movement of the water which has been in contact with the Type II wastes and the dissolution of the soluble compounds within that waste. As previously stated, the concentration of copper, iron, manganese, and, sulfate within this contact water will be a function of the most soluble substances containing these parameters. In the Type II wastes, the solubilities of copper hydroxide, iron hydroxide
TABLE NO. 2-4

Post Mining Recovery of Groundwater

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<th>Precipitative Inputs (L)</th>
<th>Pit Inflow (L)</th>
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<td>Cumulative</td>
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<td>4.10E+08</td>
<td>1.16E+05</td>
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(and ferrihydrite), manganese hydroxide, and, gypsum will determine the concentrations of these parameters.

In order to calculate the concentration of a given parameter that will exist in water that is in equilibrium with the substance containing that parameter, it is necessary to multiply the solubility of the substance by the quotient of the molecular weight of the parameter of concern (e.g., sulfate) divided by the molecular weight of the substance containing that parameter (e.g., gypsum). The calculated concentrations of copper, iron, manganese, and, sulfate that will be maintained in the contact water are 22 ug/L, 320 ug/L, 736 ug/L, and 1,360 mg/L, respectively. These concentrations are derived from the most soluble substances containing the parameters of interest, the concentrations will remain at these levels until all of the substances containing them dissolves.

The layer of Type II waste is saturated from below with inflowing groundwater and from above by precipitative water. Once this layer is saturated the soluble substances will begin to dissolve thus developing the parameter concentrations discussed above. In the model equilibrium was assumed between the wastes and the water saturating or moving through the wastes. If equilibrium were not established, then the modeled parameter concentrations would be lower. The assumption that equilibrium will be established is, therefore, a conservative one.

As the Type II wastes become saturated, water flows into them, displacing contact water with elevated concentrations of metals and sulfate into the overlying formations. By the time that the preexisting groundwater levels are reestablished (calculated to be 9.81 years) a total of 1.18 x 10^8 liters of this contact water will have been transported into the Type I waste rock and into the lower 56 percent of the Type I saprolite. It was assumed
that, since a piston flow model was used to determine chemical transport, that the contact water will displace the water that had been in the pores of these wastes without becoming diluted by, or mixing with, it.

Prickett (1989) determined that when groundwater levels have been reestablished, water will flow through the combined Type II wastes and Type I waste rock at an average rate of 1.4 gpm (2.79 x 10⁶ liters/yr). Added to this 1.4 gpm flow will be 0.6 gpm (1.19 x 10⁶ liters/yr) of water that will flow through the saprolite into these lower waste layers. A combined flow of 2.0 gpm (3.98 x 10⁶ liters/yr) will leave the pit in the Precambrian rock at the western end through the river pillar. This flow will transport elevated groundwater concentrations from the Type II wastes, and from the Type I waste rock and lower saprolite, to the Flambeau River, west of the mine site.

The waste materials have capabilities to sorb some of the parameters released from the precipitate in the Type II wastes. The capacity for the sorption of specific parameters by a given material (in micrograms) can be calculated by multiplying the weight of the material (in grams) by the sorption capability (in ug/g). The sorption capabilities were derived from the results of the saturated leaching studies (see KEIR Table No. 3.5-23 and 3.5-26 for values).

The capability of the Type I waste rock and saprolite for the sorption of iron is 1.67 ug/g and 1.51 ug/g, respectively. The calculated sorption capacities of these materials for iron are 1.64 x 10⁶ g and 1.04 x 10⁶ g, respectively (it is interesting that the Type II wastes are also capable of sorbing iron). The capability of the Type I waste rock and saprolite for the sorption of manganese is the same, 0.17 ug/g. The calculated sorption capacities of these materials for manganese are 1.67 x 10⁵ g
and $1.17 \times 10^5$ g, respectively. Only the saprolite has a capability for the sorption of copper, which is 0.11 ug/g. The calculated sorption capacity of the saprolite for copper in $7.58 \times 10^4$ g. None of the waste materials that will come in contact with the water flowing out of the Type II zone in the bottom of the pit exhibits a capacity for the sorption of sulfate.

In calculating the concentration of copper, iron or manganese in water within one of the sorbing materials, the incoming concentration was reduced to the background level by the sorption of one of the metals by the waste material. The sorption process is considered to continue in operation until the sorption capacity of the waste is reached. There is no further attenuation of metal concentration until all of the soluble source substances are dissolved. The background concentrations of copper, iron, manganese, and sulfate are 13 ug/L, 220 ug/L, 350 ug/L, and 9.9 mg/L, respectively (these are the mean concentrations for the shallow Precambrian wells presented in Table No. 3.6-12 in KEIR).

The output of the in-pit model is a time based series of parameter concentrations through the first few thousand years following the initiation of groundwater flow through the backfilled wastes. The in-pit pH will be controlled at 6.5 in perpetuity due to the liming. The output for sulfate, manganese, iron, and copper is shown on Table No. 2-5. The calculations used to compute these concentrations are included in Appendix B.

2.2.3 Model Output Summary

The output of the in-pit model suggests that the concentrations of copper, iron, and manganese that are expected to occur in the water leaving the pit are nearly the same as the background concentrations of these metals. The predicted concentration of sulfate in the water leaving the pit will be approximately 140 times
### TABLE NO. 2-5

**Predicted Parameter Concentrations of Contact Groundwater Leaving the Backfilled Pit**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration, mg/L</th>
<th>Years</th>
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<td>Sulfate</td>
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<td></td>
<td>9.9</td>
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<tr>
<td>Manganese</td>
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</tr>
<tr>
<td>Copper</td>
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<td>&gt;4,000</td>
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the background concentration. Even considering the overestimate of the materials leached from the stockpiled wastes, elevated concentrations of sulfate will exist in the water leaving the backfilled pit.

The concentrations of copper, iron, manganese, and, sulfate presented in this report are greater than those presented in the KEIR. These differences are the result of the pit inflow quantities being several times lower in Prickett (1989) than those reported in the KEIR. The reduction in flow results in less precipitate being produced and, therefore, the precipitate has less effect on the pH of the leachate in the stockpile. The pH of the leachate is the main factor governing the concentration of sulfate in the water leaving the backfilled pit since nearly all of the leached sulfate will become incorporated in the very soluble mineral gypsum.

The quantities of the metals leached from the wastes are also pH dependent but the metals form compounds that are not as soluble as gypsum. Of greater importance to the concentration of the metals--especially copper and manganese--in the water leaving the pit, is the fact that a lower pit inflow results in higher concentrations of metals in the waters treated in the wastewater treatment facility. This results in a change in the relative proportions of hydroxide and sulfides in the precipitates. Lower metal concentrations in the leachate favors the formation of greater quantities of sulfides, which are several orders of magnitude less soluble than the hydroxides for a given metal.
3.0 TRANSPORT CALCULATION

The cross-sectional flow model produced by Prickett (1989) for flow through reclaimed pit clearly demonstrates the downward nature of all the vertical hydraulic gradients through the saprolite layer overlying the waste rock. Under these conditions, all of the groundwater flowing through the Type II waste rock in the reclaimed pit will exit the pit through the Precambrian rock in the river pillar and flow directly into the bed of the Flambeau River.

Since this flow path is very short and occurs entirely within fractured crystalline rock, there will be little if any dispersion or retardation of the dissolved constituents in the groundwater. As described above, the dissolved constituents that will be added to the background crystalline groundwater by the Type II material in the pit will be copper, manganese, iron, and sulfate. Since there will be no dispersion, dilution, or retardation, in the river pillar, the concentrations of these constituents in the groundwater leaving the pit will be the same as the concentrations entering the river bed. As shown above in Section 2.2.2, these concentrations are:

- Copper - 0.014 mg/L
- Manganese - 0.522 mg/L
- Iron - 0.32 mg/L
- Sulfate - 1,360 mg/L

The metal concentrations are not statistically different from the background groundwater quality in the shallow bedrock as presented in the KEIR. In that document, the mean background concentration of copper is 0.013 mg/L, manganese is 0.35 mg/L, and iron is 0.22 mg/L. If, as is a common statistical practice, the standard deviation of the data is added to the mean to create a
reasonable upper bound for the range in which the data may be said to routinely occur, the numbers for background copper, manganese, and iron are 0.031 mg/L, 0.54 mg/L, and 0.43 mg/L, respectively. Thus it can be seen that the predicted concentrations for these compounds in the groundwater emanating from the Type II waste rock in the reclaimed pit are well within the range for background norms at the site.

The background concentration of sulfate is 9.9 mg/L. With the standard deviation added to define the upper bound, it is 18.4 mg/L. This is statistically different from the predicted 1,360 mg/L of sulfate in the groundwater emanating from the Type II waste rock in the reclaimed pit.

Two of the same four parameters routinely occur in measurable concentrations in the Flambeau River water itself. According to the KEIR, the average river concentrations are:

- Copper – <0.005 mg/L
- Manganese – <0.05 mg/L
- Iron – 0.40 mg/L
- Sulfate – 10 mg/L

Thus the river has higher background concentrations of iron than does the groundwater. It has a sulfate concentration similar to the groundwater, and manganese and copper concentrations less than the groundwater.
4.0 POTENTIAL IMPACTS TO WATER QUALITY

At the Flambeau site there are, theoretically, two types of impacts which could result from altered groundwater quality. The first impact would be to the groundwater itself, while the second would be the potential effect of altered groundwater quality on the surface water quality in the Flambeau River.

As shown below, neither of these possibilities is viable.

4.1 Groundwater

The default groundwater standards in NR 182.075(1)(A)2a are the federally-defined MCLs (maximum contaminant levels), which are based on the national primary and secondary drinking water standards. Primary standards are defined for those compounds that can cause health-related problems in drinking water. Secondary standards are defined for those compounds that can cause only aesthetic problems (i.e., taste and odor) in drinking water.

None of the compounds for which primary standards have been defined will be found in measurable concentrations in the groundwater emanating from the Type II waste rock in the reclaimed pit.

Three of the compounds for which secondary standards have been defined—copper, manganese, and iron—will be found in measurable concentrations above the standards, but at concentrations which are also comparable to naturally occurring concentrations. In such cases, NR 182.075(1)(a)2.b. states:
Where the baseline concentration of a substance subject to a state or national drinking water standard exceeds the MCL, set by state or national drinking water standards, the groundwater quality standard shall be the baseline concentration of that substance......

While sulfate at 1,360 mg/L, is above the background concentration of 9.9 mg/L, and above the standard of 250 mg/L, this is not a problem. Sulfate will not exceed the MCL beyond the Flambeau River, which is only 140 feet from the edge of the mine pit. In addition, since the river will serve as a very effective hydraulic boundary and the river pillar acts as a sink for groundwater, it is assured that the elevated sulfate concentrations will never be able to travel more than 140 feet from the reclaimed pit. Furthermore, since sulfate cannot travel more than 140 feet, and since the compliance boundary has been proposed at a distance of 1,200 feet, it will not be possible for sulfate exceedences to occur at the compliance boundary.

4.2 Surface Water

Not only do the four parameters pose no threat to the groundwater itself, they also do not threaten the Flambeau River in any way. To illustrate the lack of river impact, a calculation was made of the effect the groundwater will have upon the concentration of these substance in the Flambeau River.

According to the KEIR, the mean flow in the river is 1,855 cubic feet per second (cfs). According to Prickett (1989), the groundwater flow into the river from the waste rock zone in the reclaimed pit will be 2.0 gpm, or 0.0045 cfs. When these factors are applied, the incremental increase in river concentrations would be:
Copper - 0.000000034 mg/L
Manganese - 0.0000013 mg/L
Iron - 0.00000078 mg/L
Sulfate - 0.0033 mg/L

Clearly there is no potential adverse impact. The predicted increase in river concentrations would be so low that they would not even be detectable in the water by today's sophisticated analytical laboratory techniques. Since all the known potential adverse health and environmental impacts from these compounds occur well above the detection levels for the compounds, it must be concluded that the groundwater emanating from the Type II waste rock in the reclaimed pit will pose no threat to the Flambeau River.
5.0 REFERENCES


APPENDIX A

Table No. 5-1 from the Mining Permit
Application for the Flambeau Project, Revised
December 1989
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**TOTALS:** 3,122 1,079 759 829 1,979 7,768
APPENDIX B

In-Pit Model Calculations
1. INTRODUCTION

a. The model calculated the transport of sulfate, manganese, iron, and copper from the saprolite (SAP), Type I waste rock (WRI), and Type II waste materials (WRRII). The latter include both waste rock and saprolite.

b. The concentration of sulfate, manganese, iron, and copper was considered to be a function of the most soluble solid phase that contained each parameter. These were gypsum (hydrous calcium sulfate), manganese, iron hydroxide (ferrihydrite), and copper hydroxide, respectively.

c. A piston flow of water, and consequent transport of these materials, was modeled. This assumes that water containing background concentrations of the parameters replaces a certain volume of water within the backfilled wastes and that an equal volume of water containing dissolution products of the soluble substance leaves the wastes.

- 0.6 gpm, or $1.19 \times 10^6$ L/yr, enters the wastes stored below the saprolite layer and combines with the 1.4 gpm, or $2.79 \times 10^6$ L/yr of water flowing into these wastes from the eastern end of the pit. A total of 2.0 gpm, or $3.98 \times 10^6$ L/yr, flows out of these wastes through the western end of the pit, known as the river pillar.

d. During the recharge of the backfilled wastes, groundwater flows into the wastes from below and precipitation and runoff water into the wastes from above.
- The $1.18 \times 10^8$ L of groundwater that will enter the base of the WRII will result in an upward displacement of $1.18 \times 10^8$ L of water into the WRI and into the lower 56 percent of the SAP.

- This displacement will decrease the total quantity of soluble materials with the lower portion of the WRI.

- It was assumed that groundwater flow through the stockpiled wastes would not commence until the former groundwater levels were reestablished. Lateral groundwater flow through the wastes would begin at that time. The three waste layers--SAP, WRI, and WRII--would respond chemically as five separate layers. These layers are: 1) the upper 44 percent of the SAP layer containing $3.55 \times 10^7$ L pore volume which would be filled with water containing only background concentration of chemicals; 2) the lower 56 percent of the SAP layer containing $4.59 \times 10^7$ L of pore volume which would be filled with the water displaced from the WRII layer; 3) the WRI layer containing $7.21 \times 10^7$ L pore volume which would also be filled with water displaced from the WRII layer; 4) the upper 47 percent of the WRII layer containing $1.07 \times 10^8$ L of pore volume which would be filled with water in equilibrium with the soluble compounds; and 5) the lower 53 percent of the WRII layer containing $1.18 \times 10^8$ L of pore volume which would be filled with water in equilibrium with the soluble compounds but differing from the upper portion of the WRII in that the quantity of soluble compounds would have been depleted by the quantity of dissolved minerals that were displaced into the WRI and SAP layers.
These five layers are referred to as SAPA, SAPB, WRI, WRIIA, and WRIIB, respectively.

The 0.6 gpm flowing through the two SAP layers would displace $3.55 \times 10^7$ L/yr and $4.59 \times 10^7$ L/yr from the SAPA and SAPB, respectively.

The 1.4 gpm flowing through the WRI and WRII layers would displace $6.76 \times 10^5$, $1.00 \times 10^6$, and $1.11 \times 10^6$ L/yr from the WRI, WRIIA, and WRIIB, respectively.

e. It was assumed that equilibrium would be established instantly between the inflowing groundwater and the soluble compounds. Also, it was assumed that there would be no suppression of the solubilities of these compounds due to common ion effects.

f. Some of the layers sorb some of the dissolved chemicals. Copper is sorbed by the SAP layer, manganese by the SAP and WRI layers, and iron by the SAP, WRI, and WRII layers. Sulfate is not sorbed by any of the layers.

- It was assumed that the sorption reactions occur instantly.

- No desorption reactions were used in the model.

- It was assumed that the measured concentrations of these chemicals in the shallow Precambrian wells represents concentrations that are in equilibrium with these crystalline rocks. The reduction in concentrations of a given chemical due to sorption processes is the initial concentration minus the background concentration.
2. SULFATE

a. A total of $8.60 \times 10^{12}$ mg of sulfate in the form of gypsum will be contained within the WRII layer.

b. The solubility of gypsum in pure water is 2,400 mg/L. Sulfate derived from the dissolution of gypsum will have a concentration of $100/176 \times 2,400 = 1,360$ mg/L.

c. The background concentration of sulfate in the shallow Precambrian wells is 9.9 mg/L.

d. The quantity of sulfate contained within the pore water of each sublayer at the time lateral groundwater flow commences will be:

- **SAPA**: $3.5 \times 10^7$ L x 9.9 mg/L = 3.52 x $10^8$ mg
- **SAPB**: $4.59 \times 10^7$ L x 1,360 mg/L = 6.24 x $10^{10}$ mg
- **WRI**: $7.21 \times 10^7$ L x 1,360 mg/L = 9.81 x $10^{10}$ mg
- **WRII**: $2.25 \times 10^8$ L x 1,360 mg/L = 3.06 x $10^{11}$ mg

e. The amount of sulfate displaced from WRIIB to fill the pores in WRI and SAPB is:

$$6.24 \times 10^{10} \text{ mg} + 9.81 \times 10^{10} \text{ mg} = 1.61 \times 10^{11} \text{ mg}$$

Therefore, the quantity of sulfate contained in WRIIA and WRIIB is:

- **WRIIA**: $6.97 \times 10^{12}$ mg x 0.47 = 3.32 x $10^{12}$ mg
- **WRIIB**: $(6.97 \times 10^{12} \text{ mg} \times 0.53) - 1.61 \times 10^{11} = 3.49 \times 10^{12}$ mg
f. The rate of removal of sulfate from each layer is:

\[
\begin{align*}
\text{SAPA} & : 5.21 \times 10^5 \text{ L/yr} \times 9.9 \text{ mg/L} = 5.16 \times 10^6 \text{ mg/yr} \\
\text{SAPB} & : 6.72 \times 10^5 \text{ L/yr} \times 1,360 \text{ mg/L} = 5.16 \times 10^6 \text{ mg/yr} \\
\text{WRI} & : 6.76 \times 10^5 \text{ L/yr} \times 1,360 \text{ mg/L} = 5.16 \times 10^6 \text{ mg/yr} \\
\text{WRIIA} & : 1.00 \times 10^6 \text{ L/yr} \times 1,360 \text{ mg/L} = 5.16 \times 10^6 \text{ mg/yr} \\
\text{WRIIB} & : 1.11 \times 10^6 \text{ L/yr} \times 1,360 \text{ mg/L} = 5.16 \times 10^6 \text{ mg/yr}
\end{align*}
\]

The length of time required to dissolve and remove all of the sulfate contained in a given sublayer is equal to the quantity of sulfate contained within that sublayer divided by the rate of removal (values listed in 2.d and 2.e divided by those in 2.f). The calculated times are:

\[
\begin{align*}
\text{SAPB} & : 8.42 \text{ years} \\
\text{WRI} & : 132 \text{ years} \\
\text{WRIIA} & : 3,010 \text{ years} \\
\text{WRIIB} & : 2,850 \text{ years}
\end{align*}
\]

h. The concentrations of sulfate in the groundwater leaving the pit through the river pillar is a function of the time required to move the sulfate from each layer (2.g, above), the concentration of sulfate in equilibrium with gypsum, and the background concentration of sulfate. The time based concentrations are:

\[
\begin{align*}
0-8.42 \text{ years} & : 1,360 \text{ mg/L} \\
8.42-132 \text{ years} & : 1,100 \text{ mg/L} \\
132-2,850 \text{ years} & : 832 \text{ mg/L} \\
2,850-3,010 \text{ years} & : 317 \text{ mg/L} \\
3,010+ \text{ years} & : 9.9 \text{ mg/L}
\end{align*}
\]
3. **MANGANESE**

a. A total of $2.47 \times 10^{10}$ mg of manganese in the form of manganese hydroxide and manganese sulfide will be contained within the WRII layer.

b. Twenty five percent of the total manganese will be the soluble compound manganese hydroxide. The solubility of the hydroxide is $1.2 \text{ mg/L}$, of which $0.725 \text{ mg/L}$ is manganese ($1.2 \times \left[\text{55/91}\right]$).

c. The background **concentration of manganese** is $350 \text{ mg/L}$.

d. The quantity of manganese contained within the pore water in each sublayer at the time lateral groundwater flow commences will be (no sorption considered):

\[
\begin{align*}
\text{SAPA} & : 3.55 \times 10^7 \text{ L} \times 0.350 \text{ mg/L} = 1.24 \times 10^7 \text{ mg} \\
\text{SAPB} & : 4.59 \times 10^7 \text{ L} \times 0.725 \text{ mg/L} = 3.33 \times 10^7 \text{ mg} \\
\text{WRI} & : 7.21 \times 10^7 \text{ L} \times 0.725 \text{ mg/L} = 5.23 \times 10^7 \text{ mg} \\
\text{WRII} & : 2.25 \times 10^6 \text{ L} \times 0.725 \text{ mg/L} = 1.63 \times 10^8 \text{ mg}
\end{align*}
\]

The SAPB layer has a sorption capacity of $6.55 \times 10^7$ mg for manganese ($1.17 \times 10^8$ mg X 0.56). Layer WRI has a sorption capacity of $1.67 \times 10^8$ mg for manganese. There is more than enough sorption capacity in each layer to sorb all the manganese displaced into these layers from the WRIIB displacement. Therefore, the manganese concentrations in layers SAPB and WRI will be $0.350 \text{ mg/L}$, the background concentration.
e. The amount of soluble manganese displaced from WRIIB to fill the pores in WRI and SAP is:

\[ 5.23 \times 10^7 \text{ mg} + 3.33 \times 10^7 \text{ mg} = 8.59 \times 10^7 \text{ mg} \]

Therefore, the quantity of soluble manganese contained in WRIIA and WRIIB is:

\[
\begin{align*}
\text{WRIIA} & \quad (2.00 \times 10^{10} \text{ mg} \times 0.25) \times 0.47 = 2.35 \times 10^9 \text{ mg} \\
\text{WRIIB} & \quad ([2.00 \times 10^{10} \text{ mg} \times 0.25] \times 0.53) - 8.56 \times 10^7 \text{ mg} \\
& \quad = 2.56 \times 10^9 \text{ mg}
\end{align*}
\]

f. The rate of removal of soluble manganese from each layer is:

\[
\begin{align*}
\text{SAPA} & \quad 5.21 \times 10^5 \text{ L/yr} \times 0.350 \text{ mg/L} = 1.82 \times 10^5 \text{ mg/yr} \\
\text{SAPB} & \quad 6.72 \times 10^5 \text{ L/yr} \times 0.350 \text{ mg/L} = 1.35 \times 10^5 \text{ mg/yr} \\
\text{WRI} & \quad 6.76 \times 10^5 \text{ L/yr} \times 0.350 \text{ mg/L} = 2.37 \times 10^5 \text{ mg/yr} \\
\text{WRIIA} & \quad 1.00 \times 10^6 \text{ L/yr} \times 0.725 \text{ mg/L} = 7.25 \times 10^5 \text{ mg/yr} \\
\text{WRIIB} & \quad 1.11 \times 10^6 \text{ L/yr} \times 0.725 \text{ mg/L} = 8.05 \times 10^5 \text{ mg/yr}
\end{align*}
\]

g. Only the soluble manganese in layers WRIIA and WRIIB will contribute to the concentration of manganese above background in the groundwater leaving the pit. The time required to dissolve and remove all the manganese in these two sublayers can be calculated by dividing the quantity of soluble manganese in each layer by the removal rate (values in 3.e divided by those in 3.f). The calculated times are:

\[
\begin{align*}
\text{WRIIA:} & \quad 4,000 \text{ years} \\
\text{WRIIB:} & \quad 3,920 \text{ years}
\end{align*}
\]
h. The concentration of soluble manganese in the groundwater leaving the pit through the river pillar is a function of the time required to remove the manganese from each layer (3.9g above), the concentration of manganese in equilibrium with manganese hydroxide, and the background concentration of manganese. The time based concentrations are:

- 0-3,920 years: 550 ug/L
- 3,920-4,000 years: 445 ug/L
- 4,000+ years: 350 ug/L

4. **IRON**

a. A total of $8.84 \times 10^{11}$ mg of iron in the form of iron hydroxide and the mineral ferrihydrite (a hydrous iron oxide) will be contained within the WRIT layer.

b. The solubility of these compounds is limited since they are stable and sparingly soluble materials. A concentration of 320 ug/L of iron is supported in solution by these compounds. This is approximately the solubility of ferric iron under these conditions.

c. The background concentration of iron in the shallow Precambrian wells is 220 ug/L.

d. All of the modeled waste materials sorb iron. It is assumed that the equilibrium concentration that the water will maintain is 220 ug/L.

e. The rate of removal of iron from these waters is:

$$3.98 \times 10^6 \text{ L/yr} \times 0.320 \text{ mg/L} = 1.27 \times 10^6 \text{ mg/yr}$$
f. The time required to reduce the 320 ug/L to the background concentration of 220 ug/L is:

\[ 8.84 \times 10^{11} \text{ mg} / 1.27 \times 10^6 \text{ mg/yr} = 696,000 \text{ years} \]

The calculated time suggests that approximately 700,000 years will be required to reduce the initial concentration supported by these sparingly soluble materials.

5. COPPER

a. A total of \(2.64 \times 10^{12}\) mg of copper, mainly in the form of copper hydroxide, will be contained within the WRII wastes.

b. The solubility of copper hydroxide is 22 ug/L. The concentration of copper in equilibrium with copper hydroxide in pure water is 14 ug/L (\((64/100) \times 22\)). Copper hydroxide is less soluble than iron hydroxide at near-neutral pH conditions.

c. The background concentration of copper in the shallow Precambrian wells is 13 ug/L.

d. Since there is no statistical difference between the background concentration of copper and the copper supported in solution by copper hydroxide, there is little sense in modeling the changes in copper.

e. For the sake of completeness, the rate of removal of copper from the wastes, ignoring sorption, is:

\[ 3.98 \times 10^6 \text{ L/yr} \times 0.014 \text{ mg/L} = 5.57 \times 10^7 \text{ yrs} \]
f. The time required to reduce the 14 ug/L to the background concentration of 13 ug/L is:

\[ 2.64 \times 10^{12} \text{ mg} / 5.57 \times 10^4 \text{ mg/yr} = 4.74 \times 10^7 \text{ yrs} \]

The calculated time suggests that approximately 47 million years will be required for the complete removal of the rather insoluble copper hydroxide.