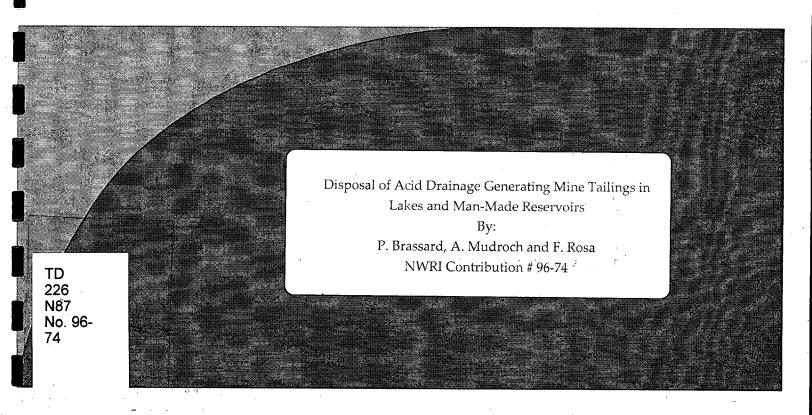
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DISPOSAL OF ACID DRAINAGE GENERATING MINE TAILINGS IN LAKES AND MAN-MADE RESERVOIRS

P. Brassard, A. Mudroch and F. Rosa

MANAGEMENT PERSPECTIVE

Recent research of economical and environmentally safe disposal of the tailings and waste rock indicated subaqueous disposal of these materials as a possible solution. However, the research also indentified negative effects of the tailings disposed on the bottom of temperature-stratified lakes on biota and water quality. Further, prevention of oxidation of sulfides in disposed tailings with the subsequent migration of metals and trace elements into lake water can not be achieved in shallow lakes and lakes with oxygenated bottom waters. Consequently, subaqueous disposal of acid generating tailings and waste rock into chemically stratified lakes with an anoxic layer of bottom water was suggested as a suitable technique.

A study was initiated at the National Water Research Institute to evaluate the economical and environmental feasibility of the disposal of acid generating mine tailings and waste rock into natural meromictic lakes and man-made reservoirs. The objectives of the study were to collect sufficient data for development of a model for the estimation of the capacity of a well characterized meromictic water body to contain acid drainage generating mine tailings, and to predict the changes that would occur in water chemistry and the tailings after their disposal.

The results of the study of an abandoned mining pit at Ignace, Ontario, clearly indicated that the pit has the characteristics of a meromictic water body. Data collected during the study were used in the modeling of changes of water quality in the pit and oxydation of the tailings after their disposal into the pit. The results of the modeling showed that the diffusion of oxygen through the water column is sufficiently low to maintain the tailings disposed on the bottom of the pit under anoxic conditions for a long period of time. In addition, the model showed that the amount of calcite in the tailings on the bottom of the pit would be sufficient to neutralize the generated acid for a period of several thousand years.

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P. Brassard*1, A. Mudroch and F. Rosa²

- ¹ Department of Chemistry, McMaster University, 1280 Main St. West, Hamilton, Ontario, L8S 4M1, Canada
- National Water Research Institute, 867 Lakeshore Rd., P.O. Box 5050, Burlington, Ontario L7R 4A6, Canada

ABSTRACT

A simple model is proposed to predict the rate of oxidation of acid drainage generating mine tailings disposed on the bottom of a meromictic pit near Mattabi mine near Ignace, Ontario, Canada. Oxygen consumption is limited by diffusion across the thermocline and can only reach a maximal value dependent on depth and morphometry of the water body. The standard acid-base accounting method is used to characterize the neutralization potential of the tailings. Theoretical calculations show that the amount of calcite needed to neutralize the generated acid is not straightforward and is related to desired ambient pH. The oxidation and subsequent acid generation does not depend on the amount of impounded tailings because the oxygen flow is limited. The tailings at the bottom of the pit would generate the acid equivalent, at most, to 383 kg of calcite per year at pH 6. Neutralization potential, however, increases with the total amount of tailings. If the pit was filled with the tailings to a depth of 16 m, the amount of calcite in the tailings would be sufficient to neutralize the generated acid for a period of several thousand years. The impoundment of tailings thus appears to be a practical and feasible technique for environmentally-safe disposal of the tailings, as long as the meromictic character of the pit can be maintained.

KEYWORDS: mine tailings, acid drainage, subaqueous disposal

INTRODUCTION

Many base and precious metal ores and surrounding rock contain sulfide minerals. Tailings and waste rock generated by mining and extraction of the metals from these ores contain different quantities of sulfides. During exposure to air and water, the water insoluble sulfides in the tailings and waste rock become converted to water soluble sulfates. These sulfates acidify surface and groundwater which subsequently become contaminated by different metals and trace elements leached from the tailings and waste rock. Uncollected and untreated acid drainage can further contaminate surface and groundwater and negatively affect the receiving ecosystem within and downstream of the mining area.

For several past years, the Canadian mining industry, in cooperation with federal and provincial government agencies, has sponsored the research of economical and environmentally safe disposal of acid generating mine tailings and waste rock. The results of the research indicate that the subaqueous disposal of acid generating mine tailings is a possible solution. However, some problems, such as the effects of tailings disposed on the bottom of the lake on benthic organisms and other biota and the food chain in the lake, resuspension and transport of tailing particles, etc., remain to be solved before the technique for the subaqueous disposal of the tailings and waste rock into lakes and man-made reservoirs can be accepted as the final solution for the prevention of acid mine drainage.

One of the major tasks in the subaqueous disposal of acid generating tailings and waste rock is to prevent oxidation of sulfides in disposed material with the subsequent migration of metals and trace elements into the overlying water. Suitable conditions for subaqueous disposal of tailings would thus be found in a lake (or a man-made reservoir) with sufficiently deep layer of anoxic bottom water, containing high concentrations of sulfides and a sulfate-reducing microbial population. Such conditions exist in natural meromictic lakes.

Meromictic lakes exist in the temperate zone of the North American continent. Studies of a meromictic lake near Syracuse, New York, revealed high concentrations of nitrogen, phosphorus, sulfate and sulfide in anoxic bottom waters (1, 2, 3). In the 45-m deep lake, the monimolimnion extended from about 20 m water depth to the bottom. Below 17 m, oxygen was absent and sulfide present in the water. The studies indicated that a large standing stock of bacterioplankton and zooplankton at the top of the monimolimnion and at the base of the epilimnion existed as relatively isolated units in the lake food chain, and that the food webs in the epilimnion closely resembled those in non meromictic lakes (4). Meromictic lakes would thus provide suitable conditions for the subaqueous disposal of acid generating mine tailings and waste rock. Surface waters, unaffected by materials disposed on the bottom of a meromictic lake, can be managed to continue to support plankton and fish populations similar to a non meromictic lake. The knowledge of the biogeochemical processes in a natural meromictic lake, before and after the disposal of mine tailings, will allow the modelling and design of man-made reservoirs managed as meromictic lakes which can be used for the disposal of mine tailings.

Many pits have been generated by surface mining. For example, Lyons et al. (5) anticipated between twenty and forty completed open pit mines in Nevada within next twenty years. After filling with water, these "pit lakes" will contain a large volume of water, and their unusual shape will have a profound effect on their physical limnology and hence their biogeochemical dynamics. Once filled with water, deep pits with a relatively small surface area may become meromictic and therefore suitable for the disposal of acid drainage generating mine tailings and waste rock.

This study was carried out to estimate the quantity of acid drainage generating mine tailings which can be safely disposed on the bottom of a meromictic pit, and to assess the rate at which the tailings become oxidized after their disposal. The objective of the study was to develop a model for the estimation of the capacity of a well characterized meromictic water body to contain acid mine tailings.

MATERIALS AND METHODS

The Crown Pillar pit (Figure 1) is an artificial lake dug out near the mining operations at Mattabi Mines Inc., Ignace, Ontario, Canada. It is approximately 300 m long by 180 m wide with a single deep spot at 24 m. The pit is surrounded by bentonite dykes to prevent infiltration of acid drainage from the nearby tailings. Several profiles of temperature, conductivity, pH, and O₂ concentration were collected in the spring and summer of 1993 and 1994 with a hydrolab multi probe and an automatic logger to establish the meromictic character of the pit. Stability of the thermocline was evaluated by anchoring the hydrolab probe at 12 m depth and logging data every hour for the whole year.

Acid mine tailings from the nearby operation at the Noranda Group mine (i.e., Mattabi Mines Inc.) were taken as representative of the type of waste that would be impounded. The fraction of pyritic sulfur in the tailings was obtained by using the McLachlin (6) method outlined in METHOD #1 of the MEND report (7). The approach is to selectively dissolve pyrrhotite by washing the sample with hot Hcl. The remaining sulfides are then digested with nitric acid, the digest is evaporated to dryness, and the residue dissolved in dilute Hcl. The concentration of iron was measured with inductively coupled plasma instead using the spectrophotometric method given by the authors of the method (7). The determination of the total concentrations of different elements in the tailings was carried out by x-ray fluorescence spectrometry using pressed pellets made from the tailings. The results of the analysis are shown in Table 1. The concentration of total inorganic carbon for calculating neutralisation potential were estimated from total Ca and assuming Ca to be all in CaCO₃ form.

Table 1. Results of analysis of Mattabi tailings.

Fe(Pyrite)	Fe(Pyrite)	S(Pyrite)	S(Pyrrotite)	total S	total Ca
μg.g ⁻¹	*	*	%	*	ક
508	12.7	7 14.6	10.6	25.2	0.46

RESULTS AND DISCUSSION

Generally, meromictic lakes differ from others in a) being permanently stratified, and b) having a high concentration of dissolved salts. Three

distinctive segments in a meromictic lake are (1) the surface water (also referred to as epilimnion), often resembling the water quality of a eutrophic lake; (2) the chemocline, a segment of water separating the epilimnion from the bottom water; and (3) the monimolimnion, a segment of anoxic water above the lake bottom containing relatively high concentrations of dissolved salts. Although temperature changes and mixing of the epilimnion can occur, the monimolimnion is stabilized by its density derived from dissolved salts, and full circulation of the water occurs rarely in the lake.

A similar stratification exists in the pit. The three major layers vary in size during the season (Figures 2a and 2b). The epilimnion, mixed by wind, is well oxygenated and the hypolimnion is always anoxic, with high conductivity and a constant temperature near 4°C. During summer and fall (Figure 2b) the epilimnion occupies a large portion of the volume. The temperature, conductivity and pH remain constant until the onset of a narrow thermocline at about 15 m. Conductivity rises and oxygen drops sharply thereafter. During winter and spring, the layer in the first 2 m has uniform properties probably arising from wind mixing following ice melt. The thermocline extends from 2 m to about 8 m and shows temperature sharply declining from about 9.5°C to 4°C. From 8 m and deeper lies a stable hypolimnion where temperature is relatively constant. A stratified lake under similar circumstances would suffer an overturn in the fall resulting in complete mixing and oxygenation of the hypolimnion.

The conductivity profile represents the sum of all dissolved chemical species in the water. It is high in the hypolimnion with a sharp decrease in the thermocline. Meromictic lakes owe their stability to the density

gradient between the hypolimnion and the upper layers. The increase in density is caused by degradation of the organic matter arising from primary productivity in the surface layers or by mineral dissolution (8). In our case it is important to maintain this density gradient to prevent the lake from turning over and exposing the hypolimnion to oxygen. The oxygen profile of the pit is separated in two main regions. The upper region comprising the mixed layer shows a nearly constant oxygen profile disturbed only by a maximum at the beginning of the thermocline. The lower region starts at the onset of hypolimnion and shows a steep decline in the concentration of dissolved oxygen, levelling off to 1 mg.1⁻¹ or similar at around 12 m.

The dissolved oxygen maximum in the epilimnion is a positive heterograde and results from oxygen saturation, and sometimes supersaturation, from the intense productivity of blue-green algae that occur deep enough to escape the turbulence of the mixed zone and still get enough light to be productive (9). Dubay and Simmons (10) observed a similar heterograde produced by macrophyte plants rooted at some depth. In the New York finger lakes, Fry (4) analyzed the food web at the top of the monimolimnion and concluded that although most of the primary productivity was due to an intense layer of bacterioplankton, the remaining food web derived its nutrition from a mixture of terrestrial detritus, phytoplankton and of the littoral vegetation. In contrast, there is little terrestrial detritus and no littoral vegetation at the Mattabi pit, and analysis of the bottom sediments in the pit revealed a relatively small concentration of organic matter. Organic residue arising from primary productivity in the surface waters is thus almost entirely mineralized before it sinks into the anoxic hypolimnion. The increase in oxygen at the heterograde is therefore compensated by degradation further down in the epilimnion, such that the compensation point for productivity lies at the beginning of the hypolimnion. It can be assumed therefore that the only major source of oxygen for the lower region of the pit is derived from the surface, and is not significantly altered by primary productivity.

The pH profile shows a profile consistent with a that of a hard water lake (11). The pH starts at approximately 8 in the epilimnion then drops to 7.5 thereafter. The slight increase in the surface water is due to primary productivity which also causes the maximum concentration of dissolved oxygen in the water column. The subsequent decrease of dissolved oxygen at the bottom of the epilimnion should coincide with an increase in total, inorganic carbon (which was not measured) resulting from mineralization. For the purpose of this analysis it is assumed the spring profile of oxygen in the pit water represents conditions occurring during the previous six months. Summer conditions are similarly represented by the oxygen profile obtained in the fall. We expect the size of the hypolimnion to be greater during the period of ice cover. Likewise, the fall oxygen profile shows an epilimnion undergoing a mixing equivalent to the overturn of a thermally stratified lake. In both cases the size of the hypolimnion underestimated.

The Oxygen Model

Simplifying assumptions were made for the transfer of oxygen to the hypolimnion. During summer, the concentration of oxygen is high (i.e., approximately 10 mg.l⁻¹) and constant down to 15 m water depth, and then abruptly drops to anoxic conditions. Stratification during summer increases the size of the anoxic layer and reduces the mixed zone. In both cases two

layers are operationally defined: a mixed layer corresponding to a zone of constant concentration of oxygen, and a diffusion layer corresponding to the combined thermocline and hypolimnion. The problem can then be simplified to one of diffusion across an initially depleted semi-infinite hypolimnion with the oxygen concentration held constant at the boundary. This simplification thus requires that i) the progression of oxygen in the hypolimnion be mainly limited by diffusion, which is a justifiable assumption since oxygen sinks/source are deemed small as explained above; ii) the overlying layers of water act like an infinite supply of oxygen to the hypolimnion below; and iii) there is no ice cover. The general solution for such a problem is already known (12) and is adapted for the present situation as:

$$C = C_0 \operatorname{erfc}\left(\frac{z - z_0}{2\sqrt{Dt}}\right) \tag{I}$$

where z is depth (m), z_0 is the onset of thermocline (m), C_0 is the concentration of oxygen at z_0 (mg.l⁻¹), t is time (sec); D, diffusion coefficient (m².sec⁻¹). The function erfc is the error function complement. Equation I with appropriate parameter value for z_0 and C_0 is adjusted to the spring and fall thermocline oxygen profiles (Figure 3). With a diffusion time, t, assumed to be six months, a best fit of the curve yields an average value of D=1.5x10⁻⁷ m².sec⁻¹ during winter and D=0.8x10⁻⁸ m².sec⁻¹ for summer (Table 2). Such value is comparable with a hypolimnetic advective coefficient of 1.7x10⁻⁷ (13). It is one to two orders of magnitude greater than the corresponding molecular diffusion of about 1x10⁻⁹ m².sec⁻¹. Now oxygen demand can be calculated at steady state for both spring and winter regimes.

Table 2. Optimization of diffusion coefficient for the four profiles in Crown Pillar pit as shown in Figure 3. Period refers to the season when the profile was taken; z_0 onset of thermocline; D_{02} diffusivity (m^2 .sec⁻¹); C_0 oxygen concentration at z_0 ; n sample size; r correlation coefficient. Numbers in parenthesis denote percent standard error.

z ₀	D ₀₂		с _о х10 ⁻⁷	, 'n	r²
7.6	1.0	(1.1)	8.3 (1.	4) 23	0.997
8.8	2.0	(0.6)	8.8 (1.	4) 58	0.997
13.0	0.1	(2.6)	9.0 (2.	6) 18	0.991
14.3	0.06	(2.6)	9.0 (7.	2) 70	0.936
	7.6 8.8 13.0	7.6 1.0 8.8 2.0 13.0 0.1	7.6 1.0 (1.1) 8.8 2.0 (0.6) 13.0 0.1 (2.6)	x10 ⁻⁷ 7.6 1.0 (1.1) 8.3 (1.8.8 2.0 (0.6) 8.8 (1.1.1) 13.0 0.1 (2.6) 9.0 (2.1.1)	x10 ⁻⁷ 7.6 1.0 (1.1) 8.3 (1.4) 23 8.8 2.0 (0.6) 8.8 (1.4) 58 13.0 0.1 (2.6) 9.0 (2.6) 18

The Model at Steady State

The changes in the oxygen profile are examined when tailings exert a steady oxygen demand at the bottom of the pit. The long-term solution when the oxygen profile becomes constant is of main interest. At that time the total flow of oxygen at any depth is a constant and equals oxygen demand at the bottom. At any depth the flux follows Fick's law:

$$F = -D \frac{dC}{dz} \tag{(1)}$$

However, at steady state, the flow is constant throughout and equals flux multiplied by surface area:

$$F(z) A(z) = R_0 = D A(z) \frac{dC}{dz}$$
 (III)

Where F(z) is flux at depth z (g.m².sec⁻¹); A(z), the area of the pit at depth z (m²) and R_0 (g.sec⁻¹) is the oxygen consumption resulting from the oxidation of some tailings at the bottom. Following the previous discussion the model assumes a uniform mixed layer with the oxygen concentration of C_0 above the hypolimnion. The solution is:

$$-\frac{R_0}{D} \int_{z_0}^{z} \frac{1}{A(z)} dz = C - C_0$$
 (IV)

where z_0 is depth at the top of the hypolimnion (m). The function A(z) is evaluated using a cubic interpolation of bathymetry readings (Figure 4). The surface area decreases in a quasi-linear way to the bottom, probably a consequence of the excavating process in the pit and because the earthmoving equipment cannot operate past a certain slope. It is assumed that the amount of earth removed at each successive level is smaller than the previous one by a fixed amount, i.e., the amount of earth necessary to hold the equipment on the rim. If this is true the linearity between surface area and depth can be expected for most man-made pits arising from the use of excavation equipment.

A numerical solution of equation IV, when oxygen flow (R_0) is arbitrarily fixed at 2×10^{-4} g.sec⁻¹, is shown if Figure 5. The profile predicts a small variation in oxygen concentration down to approximately 20 m followed by a rapid decrease thereafter. The increase in oxygen gradient arises from the need to maintain a constant oxygen flow in spite of a decreasing surface area. A pit dug with straight and vertical walls would have a constant surface area at all depths and thus a linear decrease in oxygen concentration.

Discharging the tailings on the bottom of the pit reduces the effective depth of the hypolimnion and increases the maximal flow of oxygen to that depth. We can calculate the maximum flow of oxygen in the pit by setting the oxygen concentration to zero for that depth and solving for R₀ in equation IV. This is always true because any further consumption would result in a negative oxygen concentration at the bottom, which is impossible. If, for example, the pit was to be filled to a depth of 20 m with tailings, the maximal oxygen flow would be approximately 0.001 g.sec⁻¹. A maximum demand curve was calculated by numerical approximation using Mathcad (14) and yields a roughly log-linear curve with inflection at the top and bottom of the hypolimnion (Figure 6).

Acid-Base Accounting of Mattabi Tailings

The feasibility of storing tailings in a meromictic lake depends on the rate at which oxidation takes place. The main environmental consequence arising from the generated sulfuric acid is the lowering of pH in the environment. For a given consumption of oxygen the release of acid is best described with the oxidation of pyrite:

$$FeS_2 + \frac{15}{4}O_2 + \frac{7}{2}H_2O \implies Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$
 (V)

The tailings also contain a quantity of calcite that acts as a buffer against the generated acid:

$$CaCO_2 + 2H^+ \Rightarrow Ca^{2+} + CO_2\uparrow + H_2O \tag{VI}$$

However, the amount of carbonate is usually insufficient to neutralize all the acid. The goal is to estimate the amount of additional calcite required. The method of acid-base accounting (15) examines two principal processes: i) acid generation; and ii) acid buffering. The term Maximum Potential Acidity (MPA) is used to describe acid generation arising from equation V above. The term Neutralization Potential (NP) expresses the buffering action of calcite already present, according to equation VI. The difference between the two, i.e., the required addition of calcite, is Net Neutralization Potential (NNP).

$$NNP = NP - \frac{MPA}{\epsilon}$$
 (VII)

The equation is written such that a negative value for NNP indicates the potential to generate acid. The term ϵ is also introduced to account for the neutralization efficiency of calcite as discussed below. Although MEND (7) recognize the problem, they do not include ϵ in their treatment.

Acid-base accounting calculations are based on simplifying assumptions about the main processes involved. The model considers that:

i) sulfide minerals are the only important source of acidity;

- ii) all reactions proceed to completion;
- iii) oxygen is the only oxidant; and
- iv) calcite is the only buffer.

Biases are introduced when the composition of the tailings significantly departs from the above and also by the methods used during assays. For example, if Neutralization Potential is determined by dissolved inorganic carbon (DIC), a significant amount of siderite (i.e., FeCO₃) will cause an overestimate of NP. Similarly, an overestimate of MPA occurs when total sulfur is used as an estimate of pyrite because many neutral species, such as barite and gypsum, do not generate acids. A similar problem arises from the presence of non pyritic sulfides, such as pyrrhotite, or non-iron bearing sulfides, such as galena. A detailed analysis of the various biases imparted for the determination of acid generation potential can be found in MEND (7). For the purpose of this study, it was assumed that the acid generation in the Mattabi tailings is mainly due to pyrite.

Maximum potential acidity: First, the equivalent amount of sulfur from measured pyritic iron was calculated (see Material and Methods for the determination of the concentrations of the iron):

$$M_{S} = M_{Fe} \left[2 \frac{AW_{S}}{AW_{Fe}} \right]$$

$$M_{S} = 1.143 M_{Fe}$$
(VIII)

The equivalent consumption of oxygen to oxidize this pyrite is obtained from equation V:

$$M_{O_2} = M_{Fe} \left[\frac{\frac{15}{4} FW_{O_2}}{AW_{Fe}} \right]$$

$$M_{O_2} = 2.14 M_{Fe}$$
(IX)

In the above equations, M_x is the mass of compound x expressed in percent total mass; FW_{02} , formula weight of molecular oxygen (32 g.mol⁻¹); AW_{Fe} is atomic weight of Fe (56 g.mol⁻¹); AW_s , atomic weight of S (32 g.mol⁻¹). Table 1 shows that pyrite sulfur accounts for only 14.6% of the total mass of the tailings. The complete oxidation of this pyrite requires an amount of oxygen equivalent to 27.1% of total tailing mass. It is the accepted norm to express MPA as equivalent tonnes of $CaCO_3$ per kilotonne tailings. The maximum potential acidity is:

$$MPA = 31.25 M_{\rm s} \tag{X}$$

Neutralization potential: The neutralization potential is a measure of the buffer present in the tailings before oxidation takes place and expressed as calcite equivalent. The NP is expressed in tonnes CaCO₃ per kilotonne tailings with the following:

$$NP = \frac{8.33 \ M_C}{W} \tag{XI}$$

where M_c is measured inorganic carbon (mg), and W is the sample weight (g). The concentration of total Ca in Table 1 is given at 0.46%. If all of calcium came from calcite the concentration would be 1.15% or 11.5 mg.g⁻¹. Neutralization potential is thus, at most, 95.8 tonns of calcite per kilotonne of tailings (equation XI). It is important to note here that the neutralization of acidity by the presence of calcite does not affect the

oxygen demand of the tailings. The addition is only required to stabilize the pH at an acceptable value. Such value for pH has a direct impact on the real neutralization power of the added calcite because even if equation 6 states that one mole $CaCO_3$ should neutralize one mole of SO_4 (ϵ =1), the actual neutralization efficiency is probably less (7, 16). Since dissolution of calcite forms three pH-dependent species, i.e., H_2CO3 , HCO_3 , and CO_3^{2-} , each one neutralizing a different amount of acid, the overall neutralization efficiency of calcite is specific to the final pH of the solution can be calculated as a titration of carbonates with a strong acid (SO_4^{2-}) in the presence of a solid ($CaCO_3$), a well known system (17).

It is necessary to solve the charge balance:

$$2 C_a = C_t (2 - \alpha_1 - 2\alpha_2) + H^+ - \frac{K_w}{H}$$
 (XII)

where C_a is concentration of acid $(M.1^{-1})$; C_t is total calcite $(M.1^{-1})$; H^+ , hydrogen ion $(M.1^{-1})$; K_w , dissociation constant for water (10^{-14}) ; α_1 speciation ratio for HCO_3^{s-} ; α_2 , for CO_3^{2-} . Total carbon can be expressed as the solubility product $(K_s=10^{-8.22})$ of $CaCO_3$:

$$C_{l} = \left[\frac{K_{s}}{\alpha_{2}}\right]^{5} \tag{XIII}$$

The speciation ratios are related to the dissociation constants for carbonates and pH:

$$\alpha_2 = \frac{K_1 K_2}{H^2 + H K_1 + K_1 K_2} \tag{XIV}$$

$$\alpha_1 = \frac{H K_1}{H^2 + H K_1 + K_1 K_2} \tag{XV}$$

where K_1 is first dissociation constant for carbonates (10^{-6.4}) and K_2 the second constant (10^{-10.4}). Finally, the neutralization efficiency is:

$$\epsilon = \frac{c_a}{c_b} \tag{XVI}$$

For constant pressure and temperature, equations XII to XVI yield ϵ as a unique function of pH. When $\epsilon=1$, one mole of calcite can neutralize one mole of sulfuric acid, but only at pH 4.5 or lower. Release of leachates at such a low pH is unacceptable. A more realistic pH of 6, near natural water value, would require a ratio ϵ of 0.6 to 0.8, or about 66% more calcite than at pH 4. The ratio ϵ of 0.625 suggested (16) yields a pH near 6.8, which is quite acceptable.

Acid-Base Accounting Applied to a Meromictic Pit

The general equation for acid base accounting must be altered to reflect the conditions under which tailings oxidize at the bottom of a meromictic pit. Contrary to the usual calculations where the total amount of sulfide S is expected to react completely, oxidation in the pit is limited, not by the amount of S present, but by the limitation of oxygen consumed. It follows that the actual amount of tailings deposited is not immediately important. The amount of calcite required to neutralize the acid should therefore be solely a function of the oxygen flow and should also be expressed as a rate.

There are two steps involved in neutralization. First, the tailings are deposited on the bottom of the pit and the calcite already present neutralizes the acid until it is exhausted. Then, in the second step, calcite is added continuously in proportion to the acidity generated. We calculate the rate of calcite addition, R_{ca} (t.yr⁻¹), directly from maximum oxygen flow R_0 (g.sec⁻¹):

$$R_{MPA} = \frac{R_{o_2} 8 FW_{CaCo_3} 31.56}{\epsilon 15 FW_{o_2}}$$

$$R_{MPA} = 52.6 \frac{R_{o_2}}{\epsilon}$$
(XVII)

Then, from the calcite already present (NP) and the total tailings impounded (in kt), the time required to consume the buffer and, therefore, the period before any supplement is required is calculated. This period is defined as the transition period, TP (yr)

$$TP = \frac{NP M_t}{R_{MPA}} \tag{XVIII}$$

Information on the actual speed of processes at the bottom of the pit can be obtained. For example, if it is decided to fill the bottom of the pit up to a depth of 16 m, and assuming specific gravity of the tailings to be 2 and the known volume of the pit at that depth to be 5.452x10⁴ m³, the calculated load of tailings is 109 kt. Using the maximal oxygen consumption for the tailings at that depth, the rate of calcite addition and transition period can be calculated (Table 3). The transition period is very large and shows that oxidation of tailings is essentially delayed as long as the meromictic character of the pit is maintained.

Table 3. Calculated parameters for oxidation of 109 kt tailings impounded at 16 m water depth in Crown Pillar pit: R_{02} oxygen flow; R_{ca} rate of calcite addition; TP transition period

Month	R_{02} g.sec ⁻¹	R _{ca} kg.yr ⁻¹	TP yr x10³	Season
MAY 1993	2.27x10 ⁻³	199	53	Winter
MAY 1994	4.37x10 ⁻³	383	27	
OCT 1993	4.48×10 ⁻⁴	39	268	Summer
NOV 1995	4.39x10 ⁻⁴	38	237	

In their study on diffusion of gases into uncemented uranium tailings, Reardon and Moddle (18) found a relation between CO₂-gas diffusion and degree of air porosity. The relation can be converted to oxygen diffusion assuming that the diffusivity ratio in two different media is the same for any nonreactive gas. The authors write oxygen diffusivity as:

$$D_{O_2} = 3.98 \times 10^{-5} (\epsilon - 0.5/0.95)^{1.7} T^{3/2}$$
 (XIX)

where ϵ is the air porosity ratio and T (°K) is temperature. For the study pit the hypolimnion is constantly at 4°C and air porosity ϵ =0. Their equation is, however, limited to ϵ =0.06 (i.e., 94% water saturation), giving a minimal value for D₀₂ 8.0 x 10⁻⁵ (m².sec⁻¹). Assuming an homogeneous and uncemented mass, diffusion in the impounded tailings is therefore at least 2 order of magnitudes greater than the equivalent tranquil water

column. However, in reduced tailings, the diffusion of O₂ and CO₂ brings about cementation by gypsum and melanterite, forming a hardpan 20 to 30 cm below the surface. Blowes et al. (19) calculated a diffusion coefficient of 1.3x10⁻⁸ m².sec⁻¹, a value close to our summer diffusion coefficient (Table 3), which is probably an underestimate since their tailings were not submerged. Thus, it is considered that impounded tailings at the bottom of a meromictic pit behave like two well mixed compartments above and below the hardpan.

CONCLUSIONS

The model presented here is based on the assumption that acid generation is limited by oxygen demand and that oxygen sources other than from the surface of the pit are not significant. The diffusion of oxygen from the surface follows simple diffusion in a tranquil column. Diffusion is so low in the water column that oxygen reaching the mass of the tailings can be assumed to be entering two well mixed compartments separated by a restriction due to the formation of a hardpan. Under these conditions meromictic pits can store and neutralize acid generating tailings for long periods of time without further treatments.

REFERENCES

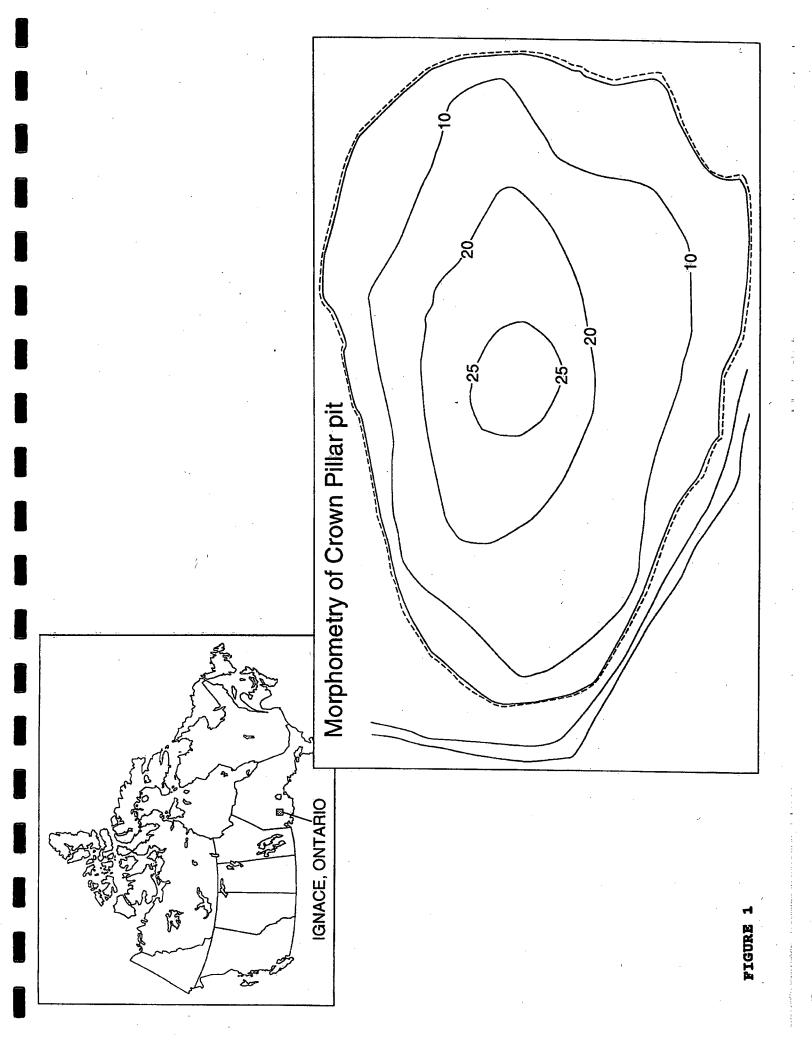
- 1. Deevey E.S., Nakai N. and Stuiver M., Fractionation of sulfur and carbon isotopes in a meromictic lake. Science, 130, 407-408 (1963).
- Turano V.S. and Rand M.C., Some chemical observations on Fayetteville Green Lake, New York. In: Some Aspects of Meromixis, Jackson D.F. (ed.), Dept. Civ. Eng., Syracuse Univ., N.Y., 151-187 (1967).
- 3. Torgersen T., Hammond D.E., Clarke W.B. and Peng T.H., Fayetteville Green Lake, New York: ³H-³He water mass ages and secondary chemical structure. *Limnol. Oceanogr.*, **26**, 110-122 (1981).
- 4. Fry B., Sources of carbon and sulfur nutrition for consumers in three meromictic lakes of New York State. Limnol. Oceanogr., 31, 79-88 (1986).
- 5. Lyons W.B., Doyle G.A., Petersen R.C. and Swanson E.E., The limnology of future pit lakes in Nevada: The importance of shape. In: Tailings and Mine Waste, 1994 Balkema, Rotterdam, ISBN 90 5410 3647 (1994).
- 6. McLachlin C.G., Increasing gold recovery from Noranda milling ore. Appendix 2 - Quantitative determination of pyrite and pyrrhotite in Noranda ore and mill products. Am. Inst. Min. Met. Eng. Trans., 112, 593-596 (1934).
- 7. MEND, New methods for determination of key mineral species in acid generation prediction by acid-base accounting. MEND project 1.16.1c, April 1991, Publisher CANMET, Ottawa, Ontario, Canada (1991a).
- 8. Cole G.A., Textbook of Limnology, 3d edition. The Mosby Co., St. Louis (1983).
- 9. Eberly W.R., Further studies on the metalimnetic oxygen maximum with special reference to its occurrence throughout the world. *Invest.*Indiana Lakes Streams, 6, 103-139 (1964).

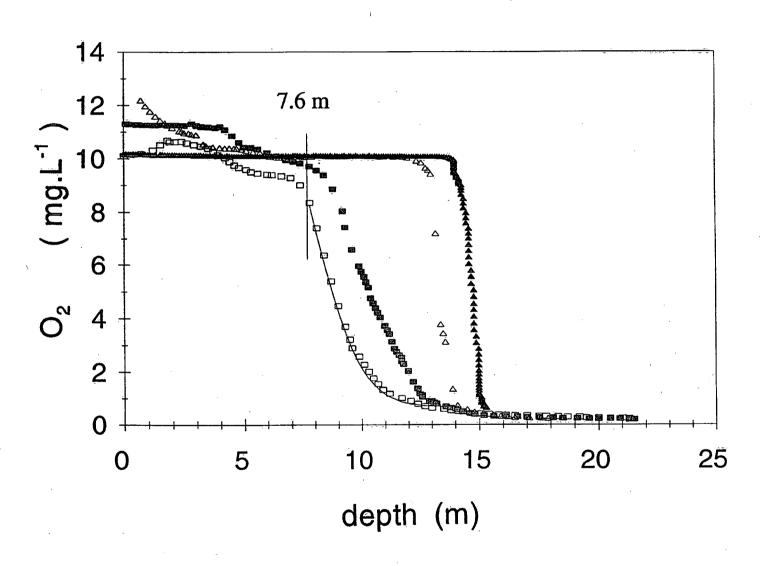
- 10. Dubay C.I. and Simmons G.M., The contribution of macrophytes to the metalimnetic oxygen maximum in a Montane, oligotrophic lake. Amer.

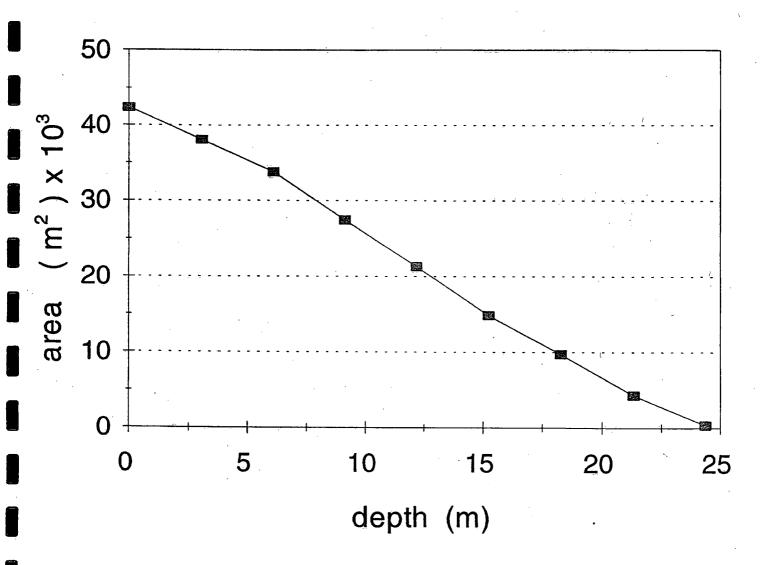
 Midland Naturalist, 101, 108-117 (1979).
- 11. Wetzel R.G., Limnology, 2nd Edition, Saunders College Publishing, New York (1983).
- 12. Crank J., The mathematics of diffusion, Second edition, Oxford Science Publications, Oxford University Press (1975).
- 13. Quay P.D., Broeker W.S., Hesslein R.H. and Schindler D.W., Vertical diffusion rates determined by tritium tracer experiments in the thermocline and hypolimnion of two lakes. Limnoligy and Oceanography, 25, 201-218 (1980).
- 14. Mathsoft Inc., MATHCAD Version 2.5 User's Guide. Mathsoft, Inc, Cambridge, MA, U.S.A. (1989).
- 15. MEND, Acid rock drainage prediction manual. MEND project 1.16.1b,
 March 1991, Publisher CANMET, Ottawa, Ontario, Canada (1991b).
- 16. Brady K.B.C. and Hornberger R.J., A manual for premining prediction of coal mine drainage quality Draft. Unpubl. report for the Pennsylvania Dept. of Environmental Resources, Bureau of Mining and Reclamation, Pennsylvania, U.S.A. (1990).
- 17. Stumm W. and Morgan J., Aquatic Chemistry, John Wiley & Sons, Inc., New York (1981).
- 18. Reardon E.J. and Moddle P.M., Gas diffusion measurement on uranium mill tailings: implication to cover layer design. *Uranium*, 2, 111-131 (1985).
- 19. Blowes D.W., Reardon E.J., Jambor J.L. and Cherry J.A., The formation and potential importance of cemented layers in inactive sulfidemine tailings. Gechimica et Cosmochimica Acta, 55, 965-978 (1991).

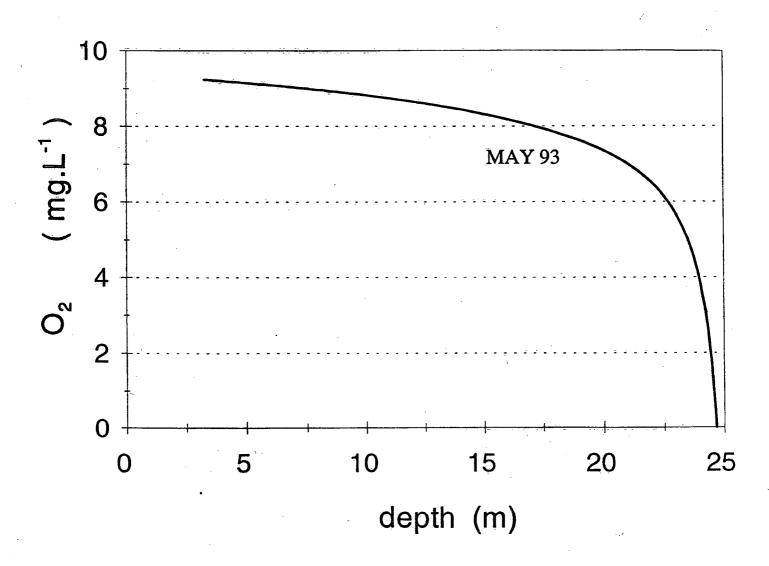
FIGURE CAPTIONS

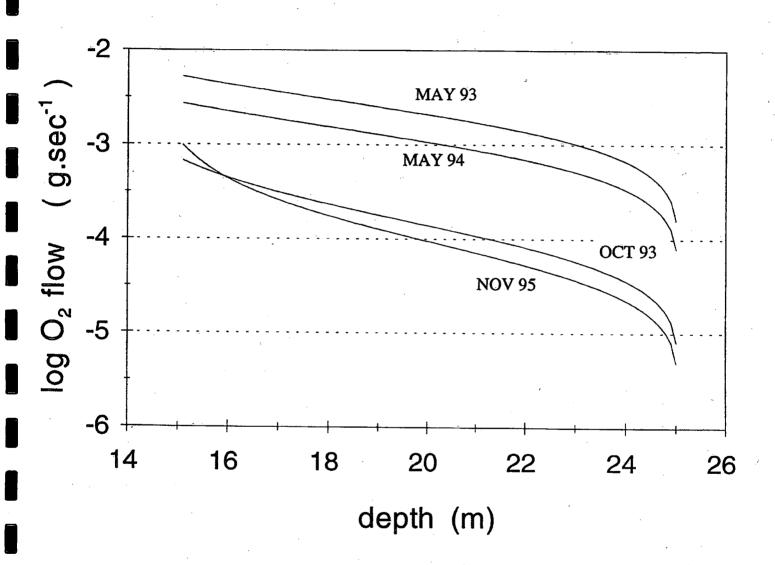
- Figure 1. Bathymetric map of the Crown Pillar pit, Ignace, Ontario, Canada.
- Figure 2. Profiles at the deep point in Crown Pillar pit taken in a) May 1993 to represent winter conditions, and b) October 1993, to represent summer conditions.
- Figure 3. Adjustment of the model to the four profiles taken in the spring and fall in Crown Pillar pit: □ May 1993; May 1994; △ October 1993; ▲ November 1995. Adjustment of the diffusion model is shown only for the May 1993 profile. Vertical line shows onset of thermocline. See Table 2 for optimized parameter.
- Figure 4. Area profile of the pit with spline fit.
- Figure 5. Solution of equation IV showing oxygen profile in the pit under assumed constant oxygen demand of $2x10^{-4}$ g.sec⁻¹. Conditions are for the May 1993 profile.
- Figure 6. Maximum oxygen flow at depth for the four profiles. Calculation assume pit to be filled with tailings to the indicated depth.













Canada Centre for Inland Waters P.O. Box 5050 867 Lakeshore Road Burlington, Ontario L7R 4A6 Canada

National Hydrology Research Centre 11 Innovation Boulevard Saskatoon, Saskatchewan S7N 3H5 Canada

St. Lawrence Centre 105 McGill Street Montreal, Quebec H2Y 2E7 Canada

Place Vincent Massey 351 St. Joseph Boulevard Gatineau, Quebec K1A 0H3 Canada

Centre canadien des eaux intérieures

Case postale 5050 867, chemin Lakeshore Burlington (Ontario) L7R 4A6 Canada

Centre national de recherche en hydrologie

11, boul. Innovation Saskatoon (Saskatchewan) S7N 3H5 Canada

Centre Saint-Laurent

105, rue McGill Montréal (Québec) H2Y 2E7 Canada

Place Vincent-Massey

351 boul St-Joseph Gatineau (Québec) K1A 0H3 Canada