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AN OXYGEN CONSUMPTION SURVEY OF THE SULPHIDE TAILINGS AT CULLATON LAKE, N.W.T.

Final Report to:

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1.0 INTRODUCTION

The Cullaton Lake property is a former gold mine that has been decommissioned. The focus of this investigation is the non-flooded portion of the tailings impoundment that occupies an area of approximately 6 hectares adjacent to the former mill site. The tailings were covered by a coarse-grained layer of gravel-boulder sandy till mixed with blast rock. The purpose of the cover was two-fold: firstly, to decrease oxygen migration into the tailings and, secondly, to provide thermal insulation to encourage the development of permafrost conditions in the tailings. It was expected that permafrost conditions in the tailings would prevent oxidation of the sulphide minerals and subsequent impact on the quality of water adjacent to the tailings. BEAK was contracted by Homestake Canada Inc. to provide a rapid assessment of the oxidation status of the non-flooded tailings using a newly developed field technique referred to as an Oxygen Consumption Measurement.

The purpose of this investigation was to measure the rates of oxidation of the existing tailings under the coarse-grained cover. These measurements were made over a one week period in July 1996 at 17 locations across the covered tailings. Control measurements were also made on a small area of uncovered tailings and on tailings with the cover temporarily removed by excavating a small diameter hole through the cover material. The resulting oxygen consumption measurements were used to calculate the rate of sulphide mineral oxidation in the tailings. The effects of the present cover were compared to the probable condition in uncovered tailings. The implications of the existing conditions and recommendations for further action are discussed.

2.0 FIELD SITE BACKGROUND

The Cullaton Lake tailings impoundment is located at the former Cullaton Lake Gold Mines Ltd. location in the district of Nunavut, Keewaitin Sub-District of the Northwest Territories. The property is located approximately 620 km north of Thompson, Manitoba and 416 km northwest of Churchill, Manitoba. The site is underlain by continuous permafrost that develops a moderate active zone during the summer season. The property is owned by Homestake Canada Inc. and has been under care and maintenance since September 1985 when production ceased. As part of their Abandonment and Restoration Plan, the tailings impoundment was covered with a waste rock and overburden cover to act as an oxygen diffusion barrier and to promote the development of permafrost conditions in the tailings and subsequently limit sulphide mineral oxidation.

The tailings impoundment consists of two tailings derived from two distinct ore bodies, the Shear Zone and the "B" Zone ores. The "B" Zone deposit is a gold bearing iron formation located in a turbiditic sedimentary basin that forms part of the Rankin Inlet - Ennadi Archean greenstone belt . Pyrrhotite and pyrite are the dominate sulphide minerals present, with minor amounts of arsenopyrite and chalcopyrite. The Shear Zone is a discontinuous ridge of orthoquartzite with gold mineralization found in altered shears, breccias, pyritic shears, and pyritic sericitic impure quartzite. The dominate sulphide mineral in the Shear Zone is pyrite (Clulow 1996).

3.0 METHODS AND MEASUREMENTS

On site work was conducted during the period of July 25th through July 31st. During this time testing equipment was installed and oxygen consumption method measurements were conducted.

The Oxygen Consumption Method testing procedure consists of the installation of 7" O.D., thin-wall aluminum tubing vertically through the tailings cover and into the tailings below (see Appendix A for a detailed description of the method). This establishes a well defined testing area on the tailings. Aluminum tubes are usually installed by pounding with a sledge and collar system but the cobbley nature of the cover precluded tube installation using this method. To facilitate installation, the cover was manually excavated and the underlying tailings exposed. The tubes were then pounded into the tailings until remaining stick-up was approximately equal to the cover thickness at that location. The cover was replaced both around and in the tube and compacted to approximate the original cover composition. The tube was then left approximately 48 hours to allow for the re-establishment of steady-state oxygen profiles.

A small headspace (0.01 to 0.02 m) above the cover surface was maintained in the tube. This headspace was capped for a short period of time, usually 1 to 2 hours, for the actual oxygen consumption determination. Time series data for oxygen concentration in the headspace and ambient temperature were collected using a laptop computer and datalogger system. Ambient temperature data was recorded to allow for data correction of errors induced due to temperature fluctuations.

The cover thickness at the Cullaton Lake site has been reported at 1.5 m. However during this visit and the installation of 17 oxygen consumption method test points the greatest cover thickness encountered was 0.90 m. Table 1 details the cover thickness at the testing point locations.

TABLE 1: COVER THICKNESS AT TESTING LOCATIONS

	Thickness (m)
TRANSECT 1	
A	61
B	89
C	71
D	70
E	62
F	68
G	69
H	58
J	62
Average	**68**
TRANSECT 2	
A	72
B	67
C	60
Average	**76**
TRANSECT 3	
A	90
B	90
C	88
Average	**89**

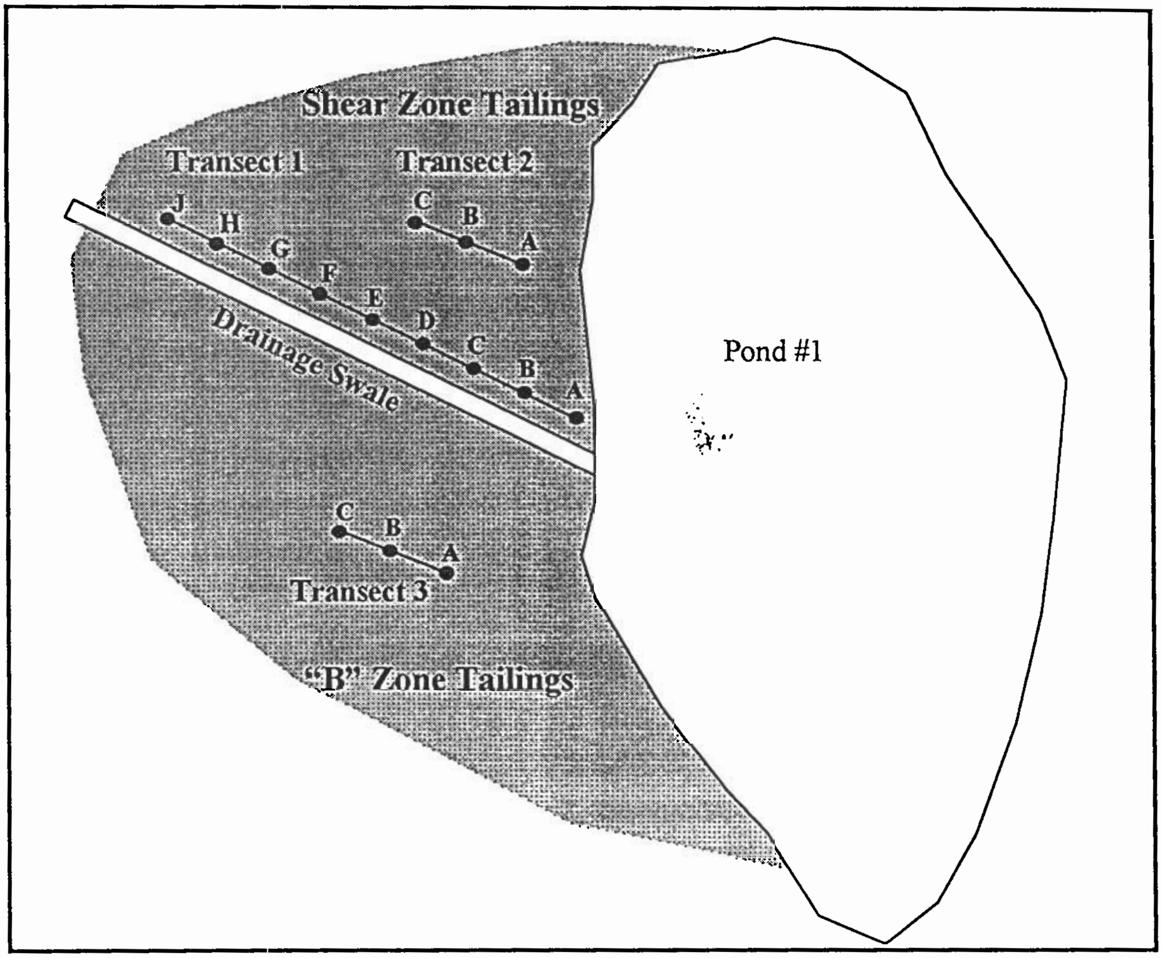
The overall average cover thickness based on observed data is considerably less than the designed thickness of 1.5 m. Two small areas located on the tailings impoundment exhibited bare tailings with no cover. One area was comprised of exposed tailings with partially established vegetation. This area was located on the "B" Zone tailings. The second area was located on the Shear Zone tailings and was comprised of exposed tailings with minor water ponding.

Three transects were installed on the Cullaton Lake tailings impoundment and are shown in Figure 1. Transect #1 is parallel to the drainage swale that bisects the impoundment. Transect #1 is located on Shear Zone tailings covered by cobbley till cover and consists of nine testing points at a 15 m spacing. These are labeled 1A-1J (to prevent possible confusion the letter "i" was not used). Tube 1A is located 3 m from the shore of Pond #1. Transect #2 is also located on the covered Shear Zone tailings. This transect consists of three testing points with a spacing of 15 m. These are identified as 2A, 2B, and 2C. Tube 2A is 25 m from the shore of pond #1. Transect #2 is parallel to Transect #1 at a distance of approximately 100 m. Transect #3 is located on the covered "B" Zone tailings. This transect also consists of three testing points with a spacing of 15 m. These are identified as 3A, 3B, and 3C. Tube 3A is approximately 50 m from the shore of pond #1. Transect #3 is also parallel to the drainage swale and is located approximately 200 m from Transect #1. In addition to the three transects two tests were performed on Shear Zone tailings without cover. One of there tests was conducted on the area of exposed tailings with minor water ponding. Despite the high moisture content evident by local ponding, this test yielded a high oxidation rate. This testing point is referred to as the control for Transect 1 and was located near testing point F. The second test on uncovered Shear Zone tailings was conducted by the manual removal of the cover and the installation of a testing point. This testing point is referred to as the control of Transect 2 and was located at Transect 2 testing point C.

3.1 Oxygen Consumption Data Collection

The sampling tubes were temporally closed with an air tight cap to measure the flux of oxygen into the tailings. Sensors located in the cap measure gaseous oxygen content in the sealed headspace of the tube as well as temperature. The measurement is conducted over 1 to 2 hours with readings recorded every minute. The resultant time series of oxygen content values are corrected for sensor drift induced by temperature fluctuations

FIGURE 1: LOCATION OF OXYGEN CONSUMPTION METHOD TRANSECTS AND TEST POINTS



and reduced to provide a value corresponding to flux of oxygen across the air-tailings boundary.

Due to the brevity of the field visit duplicate testing was not possible. Valid test data were collected on 13 of the 15 tubes installed in the cover and on both control testing points located on the Shear Zone tailings. An example of a plot of oxygen log normalized concentration over time in the headspace of the tube is shown in Figure 2.

3.2 Correction of Temperature Induced Sensor Drift

The oxygen sensors exhibit an inverse relationship between temperature and oxygen concentration reading due to the exothermic nature of the electrolytic reaction employed by the sensor in the measurement of oxygen. A decrease in ambient temperature during the test could cause a false low to be calculated for the oxygen consumption rate and conversely, warming during a test could cause a false high calculation of flux. A temperature correction factor for the sensor was developed in the laboratory. The average temperature fluctuation measured during flux measurements was always less than 3°C for any individual test. The temperature correction factor was employed on all data collected.

3.3 Calculation of Oxidation Rates and Loadings

Data derived from the oxygen consumption method provide flux values with the units of moles O_2 consumed per unit area of tailings surface per unit time. This can be converted to a mass flux of products per area of tailings surface per time based on the oxidation equations for the sulphide minerals present, and further converted into an equivalent mass of $CaCO_3$ required for neutralization.

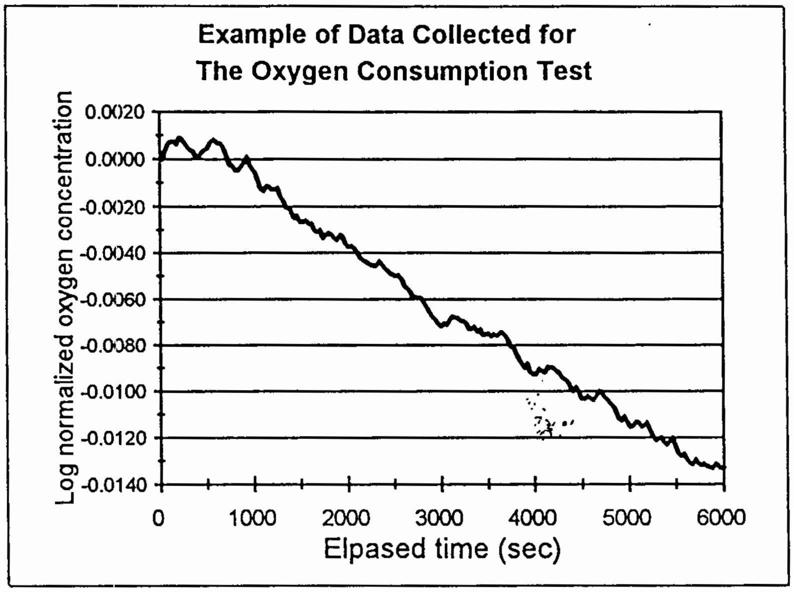
The oxidation of pyrite can be described by the following two equations

$$FeS_2 + {}^{7}/_{2}O_{2(g)} + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

$$Fe^{2+} + {}^{1}/_{4}O_{2(g)} + {}^{5}/_{2}H_2O \longrightarrow Fe(OH)_3 + 2H^+ \qquad (2)$$

Assuming that complete oxidation occurs as described in equations 1 and 2 the overall reaction can be written as:

FIGURE 2: PLOT OF LOG NORMALIZED OXYGEN CONCENTRATION VERSUS TIME FOR A TYPICAL OXYGEN CONSUMPTION TEST



$$FeS_2 + {}^{15}/_{4}O_{2(g)} + {}^{7}/_{2}H_2O \longrightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \tag{3}$$

Similarly the oxidation of pyrrhotite can be described as:

$$Fe(1\text{-}x)S + (2\text{-}({}^{x}/_{2}))O_{2(g)} + xH_2O \longrightarrow 2SO_4^{2-} + (1\text{-}x)Fe^{2+} + 2xH^+ \tag{4}$$

Where x varies between 0 and 0.125 depending on the crystallographic structure. For the purposes of calculating acid production estimates for this study the oxidation of pyrrhotite can be described by the sulphide reaction:

$$FeS + 2O_{2(g)} \longrightarrow SO_4^{2-} + Fe^{2+} \tag{5}$$

Similar to the Fe^{2+} generated by the oxidation of pyrite, the Fe^{2+} generated in equation (5) can be further oxidized as described in equation (2). Thus the overall oxidation of pyrrhotite can be written as:

$$FeS + {}^{9}/_{2}O_2 + {}^{5}/_{2}H_2O \longrightarrow SO_4^{2-} + Fe(OH)_3 + 2H^+ \tag{6}$$

From Equation (3) it can be seen that the consumption of 1 mole of O_2 through pyrite oxidation can ultimately generate 1.07 moles of acid. Similarly one mole of O_2 consumed through pyrrhotite oxidation can generate 0.44 moles of acid. It is this generated acid that can lead to the degradation of receiving waterbodies due to acidification and mobilization of trace metals such as zinc and nickel that are often associated with mine tailings.

The buffering of the acid generated from the above equations is usually reported as the mass of equivalent calcite ($CaCO_3$) required for neutralization. The equation that governs this buffering can be expressed as:

$$CaCO_3 + H^+ \longrightarrow Ca^{2+} + HCO_3^- \tag{7}$$

From equation (7) we see that one mole of calcite is required for the neutralization of one mole of acid generated under near neutral conditions.

4.0 RESULTS

Data derived from the oxygen consumption method provide a measurement of the flux of oxygen with the units of moles O_2 consumed per unit area of tailings surface per unit time. This can be converted to a mass flux of products per area per time based on the oxidation equations for the sulphide minerals present (equations 3, and 6), and further converted into an equivalent mass of $CaCO_3$ required for neutralization. Based on these manipulations the results for the Cullaton Lake tailings impoundment are listed in Tables 2a-c. Results for the "B" Zone tailings were calculated assuming the sulphide minerals oxidizing are 1) pyrite only and 2) a mixture of pyrite and pyrrhotite in equal proportions.

TABLE 2a: OXYGEN CONSUMPTION VALUES AND EQUIVALENT RATES OF ACID GENERATION GIVEN AS $CaCO_3$ IN TONNES PER HECTARE PER YEAR FOR TRANSECT 1, SHEAR ZONE TAILINGS

Test Location	Moles $O_2/m^2/a$	Equiv. $CaCO_3$ (tonnes/ha/a)
Control	128	73-137
Tube A	33	19-35
Tube B	22	13-24
Tube C	14	8-15
Tube D	12	7-14
Tube E	3	2-3
Tube G	7	4-8
Tube H	3	2-3

TABLE 2b: OXYGEN CONSUMPTION VALUES AND EQUIVALENT RATES OF ACID GENERATION GIVEN AS $CaCO_3$ IN TONNES PER HECTARE PER YEAR FOR TRANSECT 2, SHEAR ZONE TAILINGS

Test Location	Moles $O_2/m^2/a$	Equiv. $CaCO_3$ (tonnes/ha/a)
Control	82	47-88
Tube A	2	1-2
Tube B	<0.1	<0.09
Tube C	7	4-7

Note: The calculated range for equivalent $CaCO_3$ is based on the oxidation of pyrite as described in equations 1 and 2.

TABLE 2c: OXYGEN CONSUMPTION VALUES AND EQUIVALENT RATES OF ACID GENERATION GIVEN AS $CaCO_3$ IN TONNES PER HECTARE PER YEAR FOR TRANSECT 3, "B" ZONE TAILINGS

Test Location	Moles $O_2/m^2/a$	[1]Equiv. $CaCO_3$ (tonnes/ha/a)	[2]Equiv. $CaCO_3$ (tonnes/ha/a)
Tube A	9	5-10	5-7
Tube B	9	5-10	5-7
Tube C	12	7-13	7-10

Note: [1] Assumes only pyrite present.
[2] Assumes equal parts of pyrrhotite and pyrite present.

5.0 DISCUSSION

5.1 Effect of Cover

The application of the waste rock and overburden cover can potentially lower oxidation rates and subsequent acid generation by acting as a thermal blanket promoting permafrost development in the tailings, by acting as a diffusion barrier for oxygen transport, and by limiting evapotransporation and providing a higher moisture content in the underlying tailings. The effectiveness of the applied cover to limit oxidation of the "B" Zone and Shear Zone tailings can be examined by comparing the test results on covered tailings to that for the control tests. The cover reduced the oxygen consumption rates by approximately one order of magnitude for the Shear Zone tailings area. While no control test was available for comparison in the "B" Zone tailings area it can be assumed that a similar reduction in rates is occurring there. The cover thickness on the "B" Zone tailings was, on average, slightly thicker than that of the Shear Zone area. This might imply a greater effectiveness due to the increased diffusion resistance caused by a thicker cover. Local variation in the measured oxygen consumption rate are dominantly due to variation in cover thickness, tailings mineralogy, and moisture profiles within the tailings and the cover.

5.2 Implications for Water Quality

The oxidation of Shear and "B" Zone tailings have been investigated by column leach studies at 25°C (Davé 1992), and later at cooler temperatures of 2°C and 10°C (Clulow 1996). The data from Clulow (1996) provides correlation between sulphate and selected metals released during the laboratory leaching test. Nickel and zinc were selected for comparison because of the good correlation with sulphate shown in the data reported by Clulow (1996) and because these metals are relatively mobile and less affected by neutralization of low pH waters. Other dissolved species such as ferrous iron, copper and arsenic may also be of concern but were not considered here. A summary of sulphate to metal ratios for nickel and zinc for both "B" Zone and Shear Zone tailings are given in Table 3.

TABLE 3: CORRELATION BETWEEN SULPHATE AND SELECTED METALS FOR COLUMN LEACH EXPERIMENTS REPORTED BY CLULOW (1996)

	Shear Zone	“B” Zone
*SO_4/Ni	1,600	15,000
No. of Points	22	8
R^2	0.83	0.3
SO_4/Zn	3,200	N/A
No. of Points	22	
R^2	0.73	

* Concentrations reported in mg/L

N/A - Zinc concentrations below detection limit of 0.002 mg/L

To project these ratios to actual field conditions the sulphate loadings resulting from sulphide mineral oxidation are estimated from the measured oxygen consumption rates and the stoichiometry of the sulphide mineral oxidation reactions. The estimated loading rates can be converted to approximate annual pore water concentrations by dividing the loading rate by an estimated annual infiltration rate appropriate for the site. This calculation provides an indirect indication of maximum potential pore water concentrations. It is important to remember that these values represent a theoretical possible loading and that they only consider chemical interactions as present in the column leach studies of Clulow (1996). These concentrations are not predictions of actual pore water concentrations but are to be viewed as comparative scenarios to gain insight into the effectiveness of the applied cover and possible future impacts only. Estimated maximum potential pore water concentrations are listed in Tables 4 and 5. These values are based on the measured oxygen consumption rates and correlation between sulphate and selected metal concentration reported by Clulow (1996) for column leach tests conducted in the laboratory at 10°C.

The range of concentrations are based on the two tests performed on two sites of uncovered tailings located on the Shear Zone section of the tailings impoundment. These estimated values suggest that the cover may be reducing pore water metal concentrations by more than an order of magnitude in the Shear Zone tailings.

Similar calculations were conducted on data collected from the "B" Zone tailings. The ranges reported in Table 5 represent two scenarios 1) the sulphide mineral component of the "B" Zone tailings is a mixture of pyrite and pyrrhotite in equal proportions and 2) the sulphide mineral component is pyrite only. A control test was not conducted on the "B" Zone tailings. Estimated potential pore water concentration values reported for exposed "B" Zone tailings were calculated using the ratio of exposed to covered oxygen consumption rates measured for the Shear Zone tailings. From values reported in Table 5 it can be seen that the cover may be responsible for decreasing the estimated maximum potential pore water concentrations by approximately an order of magnitude.

5.3 Contrasts Between the Shear and "B" Zone Tailings

The depositional history of the Shear Zone and "B" Zone ore deposits and the resulting tailings mineralogy have been reported by Davé (1992) and by Clulow (1996). From the

TABLE 4: ESTIMATED MAXIMUM POTENTIAL PORE WATER CONCENTRATIONS FOR SHEAR ZONE TAILINGS

Species	SHEAR ZONE TAILINGS	
	Exposed (mg/L)	Covered (mg/L)
Ni	263-411	14-38
Zn	129-202	7-19

TABLE 5: ESTIMATED MAXIMUM POTENTIAL PORE WATER CONCENTRATIONS FOR "B" ZONE TAILINGS

Species	"B" ZONE TAILINGS	
	Exposed (mg/L)	Covered (mg/L)
Ni	26-37	2.4-3.4
Zn	0.10-0.15	<0.015

material characterization for column leaching tests by Clulow (1996) the "B" Zone tailings contain, on average 2.31% S and the Shear Zone tailings contain, on average 0.4% S. The higher sulphur content, an indication of higher sulphide mineral content in the "B" Zone would suggest that it is this portion of the impoundment that would be experiencing greater oxidation rates and therefore contributing greater loadings to the pore water. However, the column leaching experiments of Clulow (1996), and data from this study indicate that the Shear Zone tailings represent a more important concern for metal loadings. The average measured oxygen consumption rate for all tests on the covered Shear Zone tailings was approximately 12 moles O_2 / m^2 / year. This is very similar to the average value measured for the "B" Zone tailings of 10 moles O_2 / m^2 / year. This finding indicates that despite the notably higher sulphide mineral content of the "B" Zone tailings the oxygen consumption rates are approximately equal. This may be explained by the presence of a slightly thicker cover on average, over the "B" Zone tailings. The average cover thickness for test points on the "B" Zone tailings was 0.89 m. The average cover thickness for the test points located on the Shear Zone tailings was 0.69 m. This increased cover thickness on the "B" Zone tailings may have contributed to a greater cover effectiveness by increased diffusion resistance.

Despite the variable cover thickness on the Shear and "B" Zone tailings, an overall decrease in oxygen consumption rates of approximately one order of magnitude was observed for all tests conducted compared to the uncovered Shear Zone tailings.

6.0 CONCLUSIONS

The existing cover on the tailings at Cullaton Lake is on the order of 0.70m thick. The cover material is a cobbely till with the finest fraction being a sandy loam. In theory, this type of material would not be expected to act as an efficient oxygen barrier to reduce sulphide mineral oxidation in the underlying tailings. The measured oxygen consumption rates, however, suggest that the oxidation rates below the cover are about a factor of ten lower than those measured for exposed tailings. This reduction in oxidation rates may be the result of decreased oxygen diffusion through the cover but may also be from the lower temperatures in the tailings due to the thermal insulating properties of the cover or due to increased moisture in the tailings resulting from decreased evaporation rates through the cover. It is probable that the lower oxidation rates result from a combination of all these processes. The data do suggest, however, that a thicker layer of cover material would result in lower rates of oxidation and hence lower rates of metal loadings to the local subsurface water.

7.0 RECOMMENDATIONS

It is suggested that the cover thickness be increased to meet the original specification of approximately 1.5m if better thermal insulation and increased resistance to diffusive transport of oxygen are to be achieved. Additional oxygen consumption measurements could be conducted after construction of the final cover to confirm the increased effectiveness of the thicker cover.

8.0 REFERENCES

Clulow, V. (1996). Column leaching characteristics of Cullaton Lake B and Shear Zone Tailings. Phase 2: Cold temperature leaching Final Report. Final Report to Homestake Canada Ltd.

Davé, N. K. (1992). Column Leaching Characteristics of Cullaton Lake B and Shear Zone Tailings. Phase I: Room Temperature Leaching. Division Report MSL 92-4. Prepared for International Corona Corporation.

APPENDIX A

Ronald V. Nicholson, Bo Elberling, Gary Williams, (1995). A New Oxygen Consumption Technique to Provide Rapid Assessment of Tailings Reactivity in the Field and Laboratory. Proc. Sudbury '95 Mining and the Environment. May 28 - June 1st, 1995. Sudbury ON. Vol. 3, pp 999-1006.

A New Oxygen Consumption Technique to Provide Rapid Assessment of Tailings Reactivity in the Field and the Laboratory[1]

Ronald V. Nicholson[2], Bo Elberling[3] and Gary Williams[4]

Abstract: The rate of sulphide mineral oxidation in tailings is affected by chemical kinetics at the particle surface and the transfer of oxygen from the atmosphere into the tailings. When sulphide mineral waste is the only oxygen consuming material present, the rate of oxidation within the tailings can be estimated by measuring the flux of oxygen through the tailings surface. A technique has been developed to measure oxygen consumption at the surface. The method involves insertion of a 20 cm diameter thin-walled aluminum tube into the tailings, placement of a cap to temporarily seal the head space from the atmosphere and measurement of the oxygen concentration in the air volume above the tailings over a one to two hour period. The observed rate of oxygen depletion is used to calculate the oxygen flux through the tailings surface. Laboratory and field measurements of oxygen consumption agree well with oxidation rates estimated from sulphate release rates. This method provides a simple and rapid measurement technique that can be used to monitor tailings oxidation and identify relative "hot-spots" that may require immediate intervention to reduce loadings from acidic drainage. The method can also be applied to the evaluation of non-oxygen-consuming covers by comparing pre- and post-construction oxidation rates across the tailings.

Key Words: Tailings, Sulphide, Oxidation, Measurements, Field rates

Introduction

The most common method of evaluating the effects of sulphide oxidation in tailings has been to collect and analyze water samples from wells below the water table and squeezed solid samples above the water table (1, 2, 3, among others). The water chemistry, sometimes in combination with solids analysis, is used to infer the acid generation history of the tailings. Many years of data collection may be required to estimate the rates of oxidation or acid generation because of the interaction of complex chemical reactions and non-steady hydrologic transport of dissolved species. It is also difficult to evaluate short-term variations in the rate of oxidation because of expected natural variations. This is especially critical for rehabilitation activities such as construction of a cover that may require a number of years of monitoring to determine the degree of improvement provided by the cover. There is a need for measurements that provide more immediate indication of acid generation rates in order to assess the effects of rehabilitation activities in the short-term in addition to current long-term monitoring practices.

Previous attempts to measure instantaneous oxidation rates in the field were described by David (4), Elberling et al. (5) and David and Nicholson (6). David (4) and David and Nicholson (6) estimated

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[1] Paper presented at Sudbury '95, Conference on Mining and the Environment, Sudbury, Ontario, May 28th - June 1, 1995

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the rates of tailings oxidation with two independent methods. One estimate was based on the total dissolved masses of iron and sulphate that occurred in the zone above the water table for which the residence time was estimated from known infiltration rates (mass balance method). The oxidation rate was then calculated as the mass of oxidation product per unit area divided by the time for oxidation in the six-year-old tailings. The other estimate of oxidation rate was made from a calculation of oxygen diffusion using Fick's first law (oxygen gradient method). Oxygen-gas concentration-gradients were measured in the shallow subsurface of the tailings. The degree of water saturation of the tailings across the same zone were also measured to estimate the effective diffusion coefficient for oxygen gas in the tailings. The calculated flux was given in the mass of oxygen entering a unit area of the tailings surface per unit time was compared to the mass flux calculated from the mass of oxidation products produced since deposition of the tailings.

It was recognised that both of these methods have inherent uncertainties that can affect the calculated rates. The mass balance method is subject to errors when precipitation and dissolution reactions occur for iron and sulphate. It was also recognised that use of water saturation to estimate the diffusion coefficients will tend to over-estimate oxygen flux values vertically through the tailings. However, in spite of the uncertainties, the two methods provided results that compared well on a relative basis from place to place. The rates revealed anticipated trends with higher values in areas that were well drained and lower values in areas with high degrees of water saturation. Almost three-orders-of-magnitude difference in rates were observed between drained areas and those with a wet low-sulphur slimes layers near the ground surface. Elberling et al. (5) demonstrated that the oxygen gradient method also provided spatially consistent trends for rates in an area in the vicinity of ponded tailings with an increase in rates by more than a factor of 100 from the edge of the pond to a distance of a few hundred metres from the pond. These methods appear to provide useful results in comparing oxidation rates across a site. Unfortunately, these measurement methods also require detailed sampling and laboratory analysis. The oxygen gradient method is by far simpler than the mass balance method but sampling at any site may require significant effort to obtain the necessary data.

An innovative and efficient method has been developed to estimate oxidation rates in tailings by measuring the rate of oxygen consumption that occurs at the tailings surface. This method was first demonstrated in the laboratory where the oxygen consumption rates correlated well with rates estimated from mass balance for sulphate produced and the oxygen gradient method (7). The results of the laboratory studies suggested that steady-state oxidation rates were attained within two days after flushing the tailings column with water and that the consumption measurements required only one hour of monitoring that could be conducted daily without altering the ambient rates of oxidation. The oxygen consumption method was then adapted for field measurements and tested for a variety of conditions.

The field measurements are presented here with a description of the measurement techniques, the theory relating the measurements to rates of oxidation and the results of some application of the oxygen consumption method at field test sites. The implications of the results are discussed in the context of the conceptual models of rate controls on oxidation rates in a field setting and the use of fine-grained covers to inhibit oxidation and acid generation.

Theory of Oxygen Consumption Measurements

The oxidation of sulphide minerals involves the consumption of oxygen with production of various species of iron and sulphur that may differ as a result of environmental conditions. Most of the field and laboratory evidence suggests that the most common products of oxidation in tailings are ferrous iron (Fe^{2+}) and sulphate (SO_4^{2-}). If we consider pyrrhotite as the primary sulphide waste, the oxidation reaction can be written as;

$$Fe_{1-x}S_{(s)} + (2-\frac{x}{2})O_{2(g)} + xH_2O \rightarrow SO_4^{2-} + (1-x)Fe^{2+} + 2xH^{+} \qquad (1)$$

Oxygen Consumption Rates and Sulphide Oxidation Rates

The flux of oxygen through the surface of tailings is equal to the amount of oxygen consumed in a vertical column of tailings under steady-state conditions. Oxidation rates have previously been estimated by evaluating the oxygen profile and the effective diffusion coefficients with depth based on the degree of saturation (5). An alternative method to determine the rate of sulphide oxidation uses the decrease in the oxygen concentration with time in the headspace of a chamber covering the tailings surface.

Assuming steady-state consumption rates, Elberling et al. (7) showed that the concentration of oxygen (*C*) in the headspace can be described as a function of time with the following equation:

$$\ln\left(\frac{C}{C_0}\right) = -t(kD_{eff})^{0.5}\frac{A}{V} \qquad (2)$$

Where C_0 is the original atmospheric concentration at the surface, t is time, k is the first-order rate constant for sulphide mineral oxidation, D_{eff} is the effective diffusion coefficient for oxygen in the tailings, A is the area, and V is the volume of the gas reservoir. The slope of the plot of $\ln(C/C_0)$ versus time gives the value of $(kD_{eff})^{0.5}$ when A/V is known. This term can then be substituted into:

$$F_s = C_0(kD_{eff})^{0.5} \qquad (3)$$

to calculate the flux of oxygen at the surface. The flux will depend on both the kinetic rate constant and the diffusivity. The k value represents an average oxidation rate constat in the oxidation zone and D_{eff} represents a harmonic mean of the D_{eff} from the surface to the depth where oxidation takes place. Both parameters may change with depth and are difficult to evaluate in the field. Although computer models of tailings oxidation require estimates of both k and D_{eff} with depth, the oxygen consumption method does not require an evaluation of these values or of the relative importance of these parameters.

Oxygen Measurements

Gas reservoirs used to measure oxygen rates in the field consisted of thin-walled aluminum cylinders (0.18 m I.D.) of various lengths (0.5-0.7 m) which were manually driven into the tailings leaving the top 0.01 to 0.02 m of the columns above the tailings surface. An oxygen sensor, ports for temperature and pressure measurements, and a pressure release port were sealed into an aluminum cap and placed on top of the column to form a closed gas reservoir above the tailings surface during the measurement (Figure 1).

The cap was installed only for the short measurement periods, ensuring exposure to atmospheric oxygen and ambient gas diffusion between measurements. The oxygen concentrations in the headspace was monitored every 300 sec in periods of 6000 sec which is a short period compared to the ambient oxidation duration. Measurements were made with a voltmeter which was connected to the

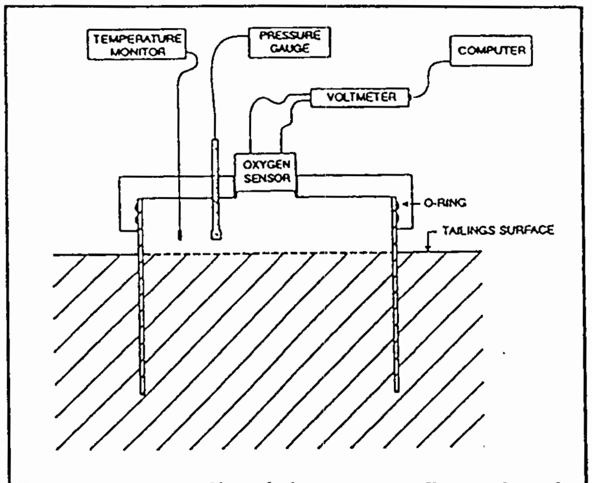

Figure 1 - Details of the cap-configuration for the measurements of oxygen consumption rates.

electrochemical gas sensor. The gas sensor provides a voltage output which is linearly related to the absolute concentration of O_2. The accuracy of the sensor is 0.1% O_2. During measurements over time, the output from the voltmeter was recorded on a portable computer.

Williams (8) tested the accuracy of the sensor over a range of conditions observed in the present field study, including variation in temperature and drop in headspace pressure due to oxygen consumption. The laboratory results indicate a linear drop in sensor response with decreasing pressure and increasing temperature. For the range of pressure and temperature variations observed during field measurements, the variation in the sensor response was insignificant.

The sensitivity of the oxygen consumption rate measurements in the field was tested by measuring the atmospheric oxygen concentration before and after the consumption measurements. The maximum change in the measured atmospheric oxygen concentrations equals ±0.1 moles O_2 $m^{-2}year^{-1}$ representing a drift in measurements and is assumed to be the lower detection limit for the current method of monitoring oxygen consumption rates.

Experimental Setup

The oxygen consumption rates were monitored at 26 test sites in one existing tailings over an area of 10 ha on a tailings that was inactive since 1986. At nine sites along a line that progressed from the tailings discharge zone to a ponded area (D1-D9), the consumption rates were monitored several times over a two-month period. The 26 test sites illustrated different oxygen availability and included variation in the presence of fine-grained layers and the depth to the water table. Two additional column configurations were established along the transect at sites D2 through D7. One column at each site included a 20 cm thick fine-grained sand layers over the tailings. In the other column, 20 cm of the uppermost oxidized zone was removed and replaced by unoxidized tailings (Figure 2). The fine sand was obtained by sieving < 80 mesh material from the sand and gravel quarry adjacent to the tailings. No attempt was made to obtain "ideal" cover material. At sites D2, D4, and D7, additional columns similar to the others

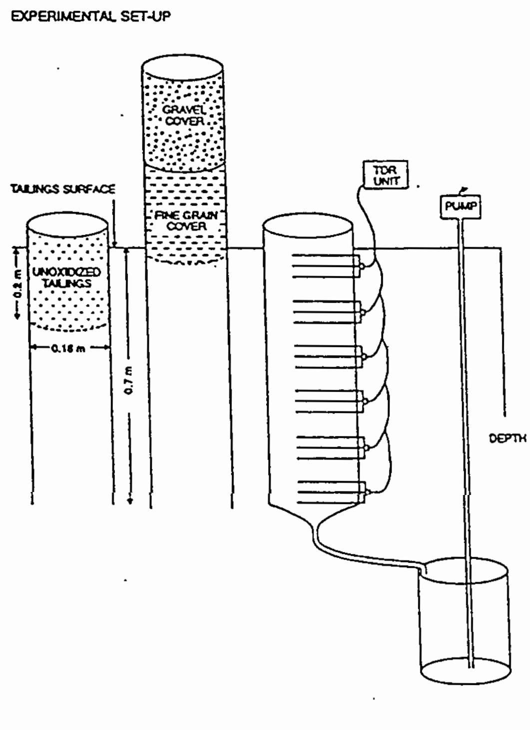

Figure 2 - Experimental setup showing the column configurations including sites with fine grained cover, sites with unoxidized tailings at the surface, and the lysimeter for the collection of effluent.

were installed as lysimeters in order to flush and collect the effluent for total sulphate analyses. Every week, the lysimeters were flushed with a minimum of eight volumes of de-ionized water to remove resident pore water. Flushing and collection of the effluent was made within eight hours. The effluent was filtered and the electrical conductance measured in the field. Samples were analyzed for SO_4^{2-}. Prior to measurements, the lysimeters were flushed with 60 times pore volumes in order to limit the influence of the secondary solid phases, such as gypsum ($CaSO_4 \cdot 2H_2O$) on the sulphate concentrations monitored during oxidation measurements. During the initial flushing, the sulphate concentration and the conductivity in the flush water dropped to a level approaching that of de-ionized water (less than 0.01 ppm SO_4^{2-}). The lysimeters were loosely covered to prevent sulphate contamination from local rainfall that is affected by locally elevated SO_2 levels.

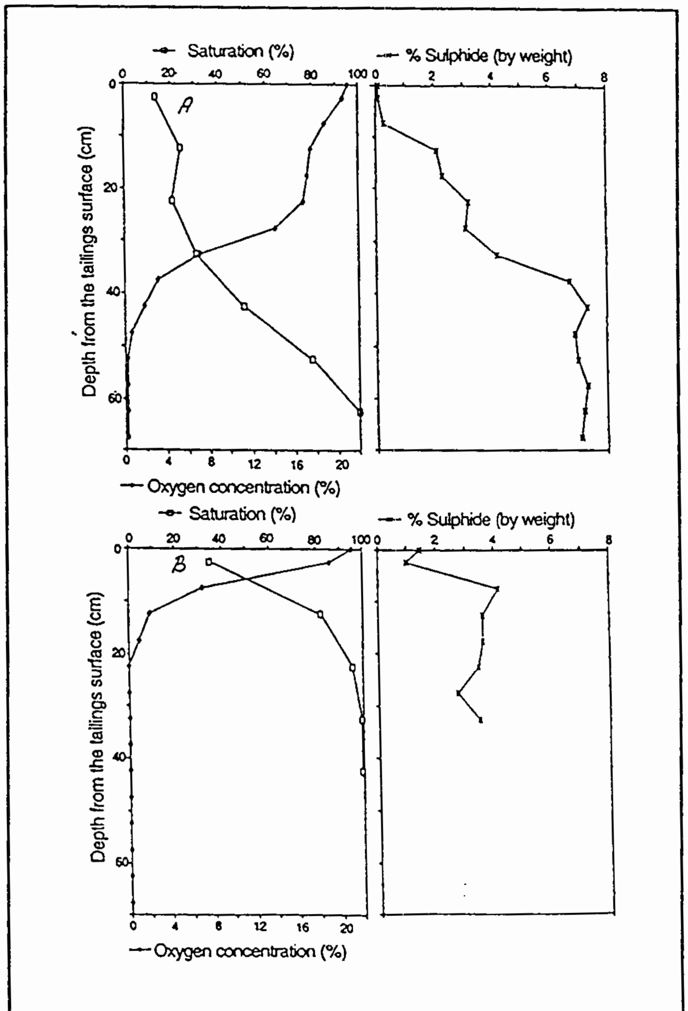

Figure 3 - Water saturation, oxygen concentration, and solid sulphide content in profiles at site D2 near the tailings discharge area (A) and site D7 near the tailings pond (B).

Time domain reflectometry (TDR, Tektronix 1502B,C) was used to estimate the volumetric water content at 0.1 m intervals. Drive-type piezometers were installed at sites in order to evaluate temporal water table fluctuations.

Results

Laboratory studies of pyrrhotite oxidation in columns have previously shown that the oxygen consumption rates correspond well with rates measured from the release of sulphate in leach water. Differences in the values of oxidation between the two estimates were within 40% of mean values (8). The results of the field studies provide strong supporting evidence to suggest that the oxygen consumption method yields values that are consistent with expected spatial trends and with anticipated effects of moist cover layers. The results presented here show that water table depth can have a very influential effect on oxidation rates. The results also indicate that oxidation rates decrease with increasing exposure time to the atmosphere. Finally, inclusion of a fine-grained layer as little as 20 cm thick can reduce oxidation rates by more than two orders of magnitude.

The pore-gas oxygen concentration decreased from atmospheric concentration (20.9%) to less than 2% within the upper 60 cm of all profiles. The decreasing oxygen concentration with depth was due to the supply of oxygen controlled by the diffusivity of the tailings and the uptake of oxygen by sulphide oxidation. At site D2, the depth to the water table was approximately 0.65 m and low degrees of saturation were observed near the surface (Figure 3). Although the current distribution of sulphide

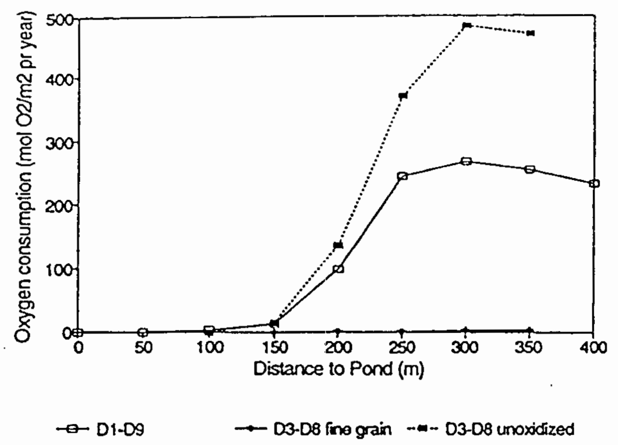

Figure 4 - Oxygen consumption rates versus the distance to the pond for the sites D1-D9, including sites with fine grained cover and unoxidized tailings on the surface.

minerals partly is a result of the history of the tailings deposition site, D2 in the tailings discharge area represents a typical profile with an upper oxidized zone and a lower unoxidized zone. Near the pond, where there is a shallow water table, the oxidized zone is limited to the upper 20 cm of the tailings.

The results from the oxygen consumption measurements at sites D1-D9, including experiments with fine-grained layers and unoxidized tailings are summarized in Figure 4. The oxygen consumption varies from 250 moles O_2 $m^{-2}year^{-1}$ at sites where the water table is below the oxidation zone to less than 0.1 moles O_2 $m^{-2}year^{-1}$ closer to the pond where the water table approaches the ground surface. When unoxidized tailings were placed on the tailings surface, the distance oxygen has to diffuse in order to reach the oxidation zone is decreased approximately by a factor of two and oxygen consumption values were as high as two times the ambient rates in oxidized tailings. These results are consistent with modelling results presented by Elberling et al. (9). Closer to the pond, the oxidation zone is situated closer to the ground surface and this effect decreases. No differences were observed between sites with and without unoxidized tailings at sites with depths to water table less than 0.2 m.

The near-surface effective diffusion coefficient was decreased by a factor of 100 or more below the fine-grained sand layer that maintained an 80% saturation value. This is consistent with the expected change in the D_{eff} from the theoretical relationship between the effective diffusion coefficient and degree of saturation. The importance of the water content might even be greater if near-saturated conditions within the fine-grained cover could be obtained and maintained over extended periods of time. This factor of 100 reduction could conceivably be improved if more appropriate engineering selection of cover material were made.

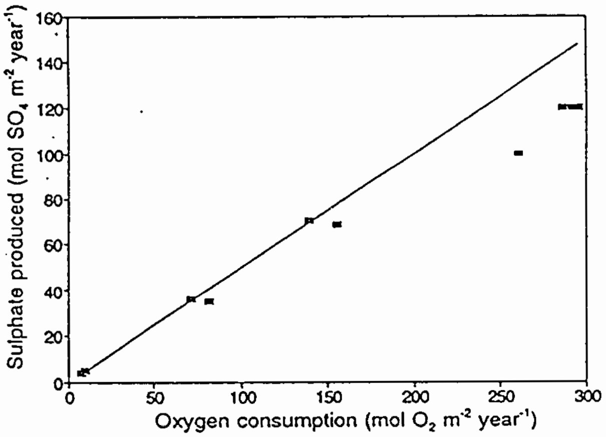

Figure 5 - Sulphate produced versus oxygen consumed. The 1:2 relationship is shown as a solid line.

Two moles of consumed O_2 produces approximately 1 mole of SO_4^{2-} assuming that the oxygen is only consumed by the sulphur component of FeS and that oxygen is the only oxidation agent for the sulphide oxidation. A 2:1 linear relationship between sulphate produced and oxygen consumed was observed at low oxidation rates (Figure 5). At higher rates, the oxygen consumption rate deviates from the sulphate production rates. The lower than expected sulphate production suggests that complex reactions such as incomplete transformation of sulphur species to sulphate may play a role. This is certainly consistent with laboratory studies that have identified elemental sulphur when oxidation rates are high (10). In any case, the oxygen consumption rates generally reflect closely the release rates for sulphate.

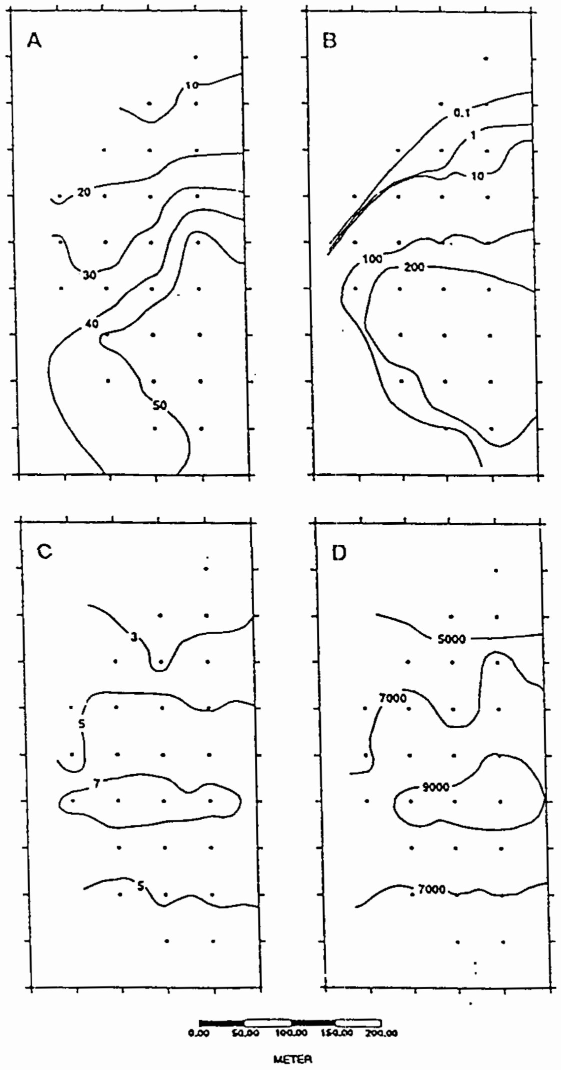

Figure 6 - Spatial trends in: (A) depth to the water table (cm); (B) oxygen consumption rate (moles O_2 m^{-2}year^{-1}); (C) sulphate concentration (g/L); and (D) the electrical conductivity of the water at the water table (μS).

Oxygen consumption rates are compared to the depth to the water table, the sulphate concentration, and the conductivity measurements at all 26 sites (Figure 6). The water chemistry measurements were based on water samples collected at the water table. A general level in oxidation rate of around 200 moles O_2 m^{-2}year^{-1} was observed in the southeastern part of the test area and a gradual decrease to the lower limit of the measurable oxidation rate towards north and northwest. The spatial trend in oxidation rates are consistent with the changes in the depth to water table with decreasing rates towards the pond. The trends in the water chemistry data also correlate with the oxidation rates but are somewhat shifted towards the pond, corresponding to the general near-surface flow direction.

Conclusions

The results of this field study indicated that oxygen consumption measurements provide a reasonable estimate of oxidation rates in sulphide tailings. There was a good agreement between oxygen uptake and the production of sulphate resulting from sulphide mineral oxidation. The oxygen consumption method can be used to measure rates over a range of three orders of magnitude.

This study showed that oxygen consumption rates exhibit consistent trends in time and space. Rates of oxidation are affected by depth to the water table, the presence of moisture-retaining non-sulphide layers at the surface and the age of exposed tailings at the surface. Rates of oxidation decreased by a factor of 1000 from a well-drained areas and deeper water table to the edge of the tailings pond. Placement of a 20 cm thick fine-sand layer produced rate reductions of more than 200 times. Rates of oxidation of fresh unoxidized tailings were as high as two times the rate observed in the existing tailings that had been exposed to the oxygen at surface for about eight years.

The demonstrated link between oxygen consumption measurements and sulphate release rates indicates that simple diffusion theory applies to oxygen transfer in tailings. These results support the use of simple diffusion models in more complex models of sulphide tailings oxidation and subsequent acid generation. In any case, models require measurements to compare to calculated rates of oxidation. The oxygen consumption method provides a rapid method for assessing field rates of oxidation in tailings in addition to the assessment of covers used to inhibit acid generation in both tailings and waste rock.

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