

OXYGEN DEPLETION OF STATIC AIR BY BACKFILL MATERIAL AT THE THOMPSON MINE

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ABSTRACT

The depletion of oxygen from airways in contact with backfill material containing pyrrhotite can create a dangerous environment in underground operations using cut and fill mining methods.

Oxygen is removed from the air via two major mass transfer processes; transfer from the air to oxygen-depleted water and transfer from the water to the solid surfaces. Both of these mechanisms are highly influenced by diffusion through the liquid phase.

Transfer from liquid to solid is directly related to the pyrrhotite content of the fill material for pyrrhotite contents greater than 7% and

inversely to the solution volume. The oxygen content of the water affects the rate of transfer according to a half-order reaction rate equation.

Removal of pyrrhotite using sizing, magnetic or flotation techniques is not likely to be a practical solution to this problem since the rate coefficient is independent of pyrrhotite content below 7%. The effects of this problem can be minimized through the use of good ditching practice for water flow control and by minimizing the height of fill poured in one lift.

All employees working in fill areas should be made aware of this problem and the importance of water flow control to minimize the risk.

INTRODUCTION

Oxygen depletion of static air has been experienced at the Thompson mine, owned

and operated by Inco Limited, with levels in mine air having been measured as low as 7% in abandoned and unventilated areas in contact with backfill material. It is clearly

dangerous to expose mining personnel to such conditions and a standard operating procedure has been adopted which requires that adequate ventilation be supplied to such areas for at least 30 minutes before allowing workers to enter.

Pyrrhotite has been labelled as the oxygen consuming component in the backfill since similar problems exist at other mines which have pyrrhotite or a high sulphide content in the fill.

This study was undertaken to identify the mineralogical factors of Thompson backfill responsible for oxygen consumption; to study the mass transfer mechanisms that control deoxygenation and to formulate several feasible solutions that might be implemented to minimize or predict the level of danger.

Testwork was conducted at Queen's University on fill material to establish the effect of such factors as size consist, pyrrhotite content, pulp density, cement content and pulp pH. Readings were then taken at the Thompson mine to correlate the laboratory findings with actual mine conditions.

OXYGEN MASS TRANSFER

Oxygen depletion can involve the following processes:

(a) the heterogeneous chemical reaction of oxygen at the pyrrhotite mineral surfaces; oxygen being transferred from air in one of the following ways:

(b) the diffusion of oxygen in air through the voids of the fill matrix, or;

(c) the dissolution of oxygen from air in oxygen-depleted water that has been in contact with pyrrhotite.

Although the diffusion of oxygen through the voids of the fill matrix can be an important consideration, there is evidence [1,2] that when significant temperature change does not occur within the fill, the rate of mass transfer via this mechanism is negligible.

Rosenblum et al. [2] have reported self heating rates below $0.07^{\circ}\text{C}/\text{h}$ for the material examined in this study, hence this mechanism is not considered to contribute to the deoxygenation problem at Thompson and has not been examined in this work.

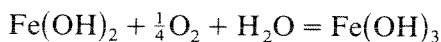
PYRRHOTITE OXIDATION REACTIONS

The oxidation of pyrrhotite requires oxygen, usually in dissolved form, and water. The reactions that take place at the surface of the mineral and in the solution in contact with the surface can be viewed to occur as a series of sequential steps as follows (for simplicity, pyrrhotite is represented here as FeS; Free Energy values are quoted in kJ/mole) [3]



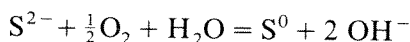
$$\Delta F_{298}^0 = -320.3 \quad (1)$$

Once ferrous hydroxide has precipitated, continued oxidation will form ferric hydroxide:



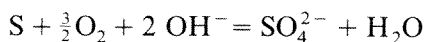
$$\Delta F_{298}^0 = -237.4 \quad (2)$$

As well, the sulphide ion that has been formed in reaction 1 can be removed from the solution according to the following oxidation reaction:



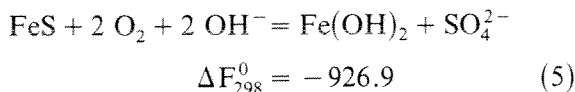
$$\Delta F_{298}^0 = -163.7 \quad (3)$$

This last step is controlled by the dissolved oxygen content and is the primary rate controlling step in removing oxygen from solution. Continued oxidation of the elemental sulphur can take place forming a series of sulph-oxy ions. Overall the reaction sequence can be represented by:

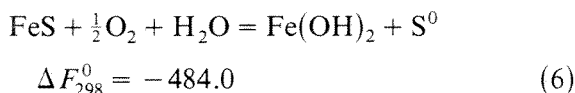


$$\Delta F_{298}^0 = -667.8 \quad (4)$$

These reactions are extremely rapid in the presence of excess dissolved oxygen and hence will dominate the control of oxygen consumption when the solution pH is high. In this case the overall reaction of stages 1, 3 and 4 would be:



However, when the solution pH is below 10, the dominant reactions will be 1 and 3 as follows:



In those situations where reaction 3 is the rate controlling step, one would expect the reaction order to be one half in terms of the dissolved oxygen content. When the reaction sequence represented by reaction 4 becomes important, then it is likely that the reaction order in terms of dissolved oxygen content will change to a value between one and two depending on solution pH.

LIQUID PHASE MASS TRANSFER

When a liquid is brought into contact with a gas, an exchange occurs between the atmosphere and the solution. For gases of low solubility that do not react chemically with the solvent, the rate of change in concentration of dissolved gas in the liquid is [4,5]:

$$dC/dt = K_L(A/V)(C^* - C) \quad (7)$$

At a given temperature, the oxygen saturation level in water (C^*) will depend on the partial pressure of oxygen in the gas phase as follows:

$$C^* = K_H P_g \quad (8)$$

Substituting for C^* in eqn. 7, the rate becomes:

$$dC/dt = K_L(A/V)(K_H P_g - C) \quad (9)$$

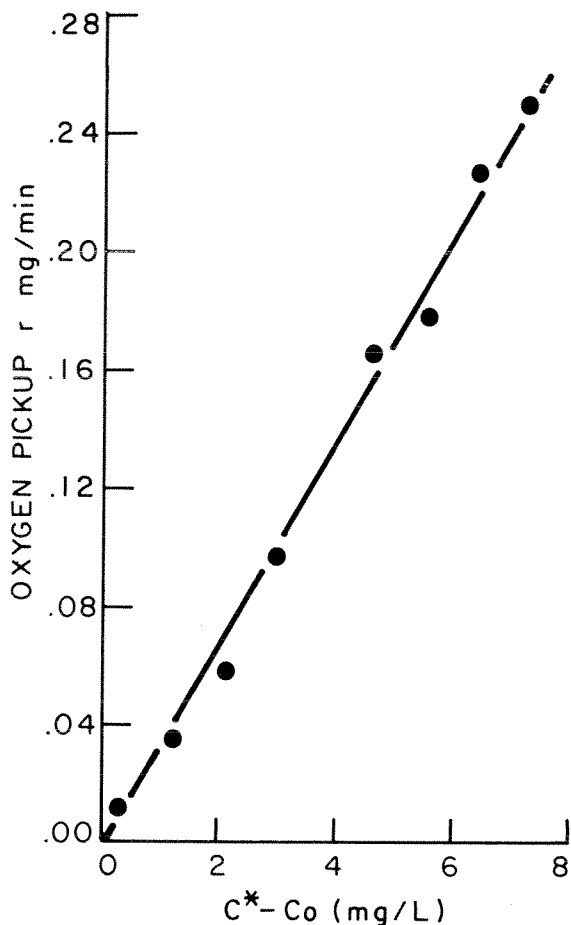


Fig. 1. The relationship between oxygen pick-up by water and oxygen deficit (temperature = 26°C).

The value of K_H is temperature dependent according to the relationship [4]:

$$K_H = 9.73 \times 10^{-4} \exp(1799/T) \quad (10)$$

The mass transfer coefficient, K_L , is also affected by temperature according to the following equation [5]:

$$K_L(T) = K_L(293) \times (1.024)^{T-293} \quad (11)$$

Thus, K_H and C^* decrease in value while K_L increases as the temperature increases. These effects cause the rate of pickup to be independent of temperature over the range between 0 and 30°C, since the effects of temperature on K_L and K_H compensate exactly for each other [4].

It has been reported [4,5] that detergents can reduce K_L for water by up to 15% depending on concentration. This effect is likely related to surface tension and viscosity changes of the solution. Hopton and Warner [6] found oxygen mass transfer coefficients of kaolinite slurries at 16% solids to be roughly half that of pure water indicating that solids content reduces the rate of oxygen absorption or desorption. For flow conditions similar to that employed in this testwork, they reported K_L to be 7.8 mm/min at 20°C for pure water.

Values of K_L in the literature range from 9.6 [7] to 4.8 [8] for turbulent flow. For laminar flow systems, K_L may be up to 1000 times lower than these levels [4,5].

Since most of these measurements have been made at normal atmospheric conditions ($P_g = 21.2$ kPa) it was considered relevant to this study to determine if K_L changes as the oxygen content of the gas phase decreases.

The rate of oxygen pickup was measured as a water jet flowed through a volume of gas of known oxygen content. The value of K_L was calculated from a knowledge of the average oxygen deficit ($C^* - C$) of the water.

The results, given in Fig. 1, show that K_L is independent of changes in the gas phase composition and that the rate of oxygen mass transfer from gas to liquid can be expressed satisfactorily by eqn. 9. A value of 15.6 mm/min was measured from the data which converts to 13.5 mm/min at 20°C. This compares almost exactly with the value reported by Hopton and Warner [6] after suitable adjustment for differences in film thickness (1.24 mm in this work; 0.70 mm in their work).

To give the measured value for K_L some practical significance, eqn. 9 has been applied to a situation that might develop in an un-ventilated area underground. The following conditions apply: consider a sealed manway 25 m long by 2 m square in which a film of water is flowing such that the interfacial area of the air and water is 12.5 m². Atmospheric conditions are 106.7 kPa (800 mm Hg) and

10°C. Thus K_L would be 10.65 mm/min and C^* would be 12.0 mg/l.

Figure 2 shows the oxygen content of the air as a function of exposure time for water flowing at 250 l/min (55 IGPM). As can be seen the rate of oxygen removal is dependent on the initial oxygen content of the water. When the oxygen level is between 1 and 3 mg/l, the passage becomes dangerous after 8–10 days of exposure. Even at high oxygen levels (5–7 mg/l) the manway will be unsafe within 2–3 weeks of sealed exposure.

The depletion rate is relatively independent of water flowrate. Quantitatively, the time required to reduce the oxygen level to 15% as a function of water flow would be as follows ($C_0 = 1$ mg/l):

Water flowrate (l/min)	Days to reach 15% O ₂
125	10
250	8
2000	6

A key factor, however, is the interfacial area of the flowing stream. The above calcula-

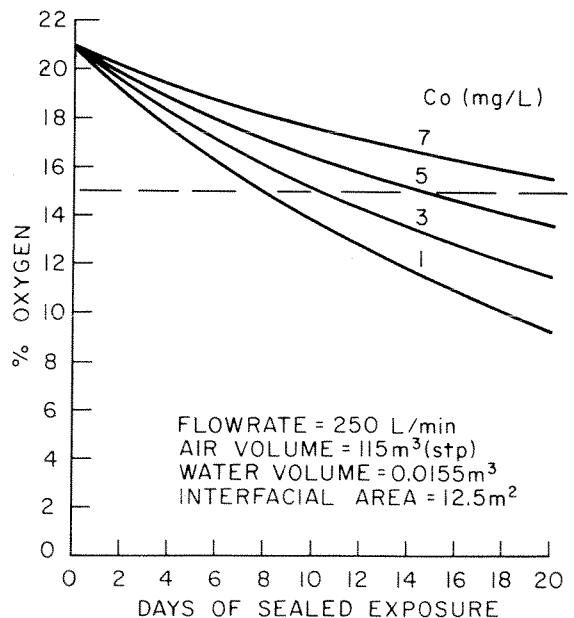


Fig. 2. The removal of oxygen from a sealed manway by flowing water deficient in dissolved oxygen.

tions assume that the water occupies only one quarter of one wall of the manway. If the stream was spread so as to yield a higher interfacial area, the time required for the passage to become dangerous would drop as follows ($C_0 = 1 \text{ mg/l}$):

A (m^2)	Days to reach 15% O_2
12.5	8
25.0	5
50.0	3

SAMPLE DESCRIPTION

Table 1 lists the chemical analysis of the fill sample used in this work indicating a pyrrhotite content of 16%.

TABLE 1

Chemical analysis of Thompson 'B' circuit backfill sample

% Fe _{Total}	13.0
% Ni	0.195
% Cu	0.012
% S	6.46
% Pyrrhotite	16.0

Table 2 compares the distribution between the magnetic and non-magnetic fractions of total sample and pyrrhotite in both 'B' and 'C' circuit samples as obtained from a Davis tube separation. While both samples recover about 96% of the pyrrhotite to the magnetic fraction, there is a distinct difference in the

TABLE 2

'B' and 'C' sandfill comparison

Fill sample	Weight %		% Sulphur		% Pyrrhotite		Pyrrhotite distribution	
	<i>B</i>	<i>C</i>	<i>B</i>	<i>C</i>	<i>B</i>	<i>C</i>	<i>B</i>	<i>C</i>
Head	100	100	6.46	8.19	15.8	19.6	100	100
Magnetics	23	63	26.71	12.49	66.3	30.0	96.5	96.0
Non-magnetics	77	37	0.33	0.88	0.7	2.0	3.5	4.0

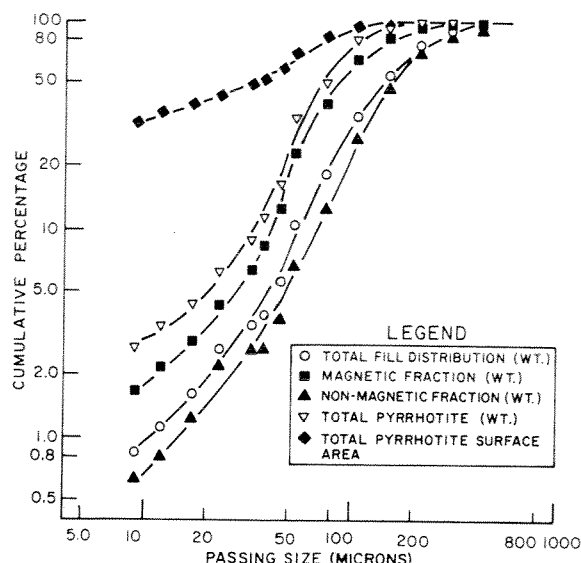


Fig. 3. Distribution of weight, pyrrhotite and pyrrhotite surface area.

weight distribution of the two samples. The magnetic fraction of the 'B' circuit constitutes only 23% of the total while the magnetic fraction of the 'C' circuit sample is 63% of the total.

Although x-ray diffraction patterns of the magnetic fraction of both samples showed the presence of hexagonal pyrrhotite, more than 90% of the pyrrhotite is of the monoclinic type.

Distributions of weight, pyrrhotite and pyrrhotite surface area for the total fill, magnetic fraction and non-magnetic fraction are presented in Fig. 3. Although the -38 micron fraction makes up only four percent of the total weight of fill, it contains over 12% of the

pyrrhotite and accounts for 54% of the total pyrrhotite surface area.

Since the size distribution and pyrrhotite consist of both 'B' and 'C' circuit were so similar, testwork concentrated on only one sample. The sample from 'B' circuit was selected since the pyrrhotite in this sample could be concentrated magnetically to a much higher content than that contained in the 'C' circuit material.

The samples were received in pulp form in sealed polyethylene containers. No gas phase was in contact with the fill material. All samples were kept in this medium until required for use. To ensure representative samples were used for duplicate tests, the sample was dried prior to riffle splitting into 1 kilogram size lots.

LABORATORY TEST PROCEDURES

Measurement of dissolved oxygen content

The measurement of dissolved oxygen content was conducted using a dissolved oxygen electrode (DOE) model 97-08 from Orion Research. Dissolved oxygen concentration could be read directly in milligrams per litre of solution on a pH meter. The meter employed was a model 520 digital pH/ion meter from Fisher Scientific.

Agitation testwork

A known weight of fill material prepared by scrubbing and filtering was contacted with distilled water for a desired time. The flasks used for these tests contained a total volume of 248 cm³ after sealing. All air present was evacuated by introducing additional water using a syringe.

Agitation was provided by rotation of the flasks on a 1 m diameter wheel at 20 rpm. A sample weight of 100 g was used for all tests

except in the pulp density series where the weights were varied to obtain different percent solids by weight.

Percolation testwork

The dissolved oxygen content of water at the inlet and outlet of a 150 mm high bed of backfill material was measured under different waterflow conditions. The waterflow through the bed was regulated using a rotary pump operated over the water percolation range of 100–750 mm/h.

RESULTS

Size consist of fill

The removal of each successively coarser mesh size from 400 to 150 mesh reduces the 12 hour oxygen demand of the backfill pulp by about 0.50 mg/l on average (Table 3).

The results also show that removing all minus 150 mesh material would reduce the fill weight by 36% and the remaining fill would contain only 4% pyrrhotite. The pyrrhotite surface area per gram of fill would be about 7 cm²/g compared with 129 cm²/g for the total fill material. However, the oxygen demand would only be decreased by about 50% from 4.73 mg/l to 2.31 mg/l. This suggests that the oxygen demand is not related simply to the available pyrrholite surface area and that some other oxygen consuming component is present in the fill material.

Pyrrhotite content

The effect of pyrrhotite content on the oxygen demand of backfill pulps was studied by varying the weight ratio of the magnetic and nonmagnetic material in each test.

A series of kinetic tests were conducted to establish a rate equation that could be used to characterize the oxidation process. The results

TABLE 3

The effect of size consist on the oxygen pickup by backfill material—12 hour contact time

Mesh size	Weight retained (%)	Pyrrhotite content (%)	Total pyrrhotite surface area		Oxygen demand (mg/l)
			(cm ² /g)	(cm ² /g) fill	
+150	64.3	3.9	188	7.4	2.31
+200	81.5	8.9	281	25.0	2.50
+270	89.5	11.7	349	40.9	3.07
+325	94.4	13.4	412	55.2	3.58
+400	96.1	14.0	440	61.6	4.17
Total	100.0	15.2	849	128.8	4.73

were found to be best described by a half-order reaction as was predicted previously:

$$dC/dt = -K_S(C - C_e)^{1/2} \quad (12)$$

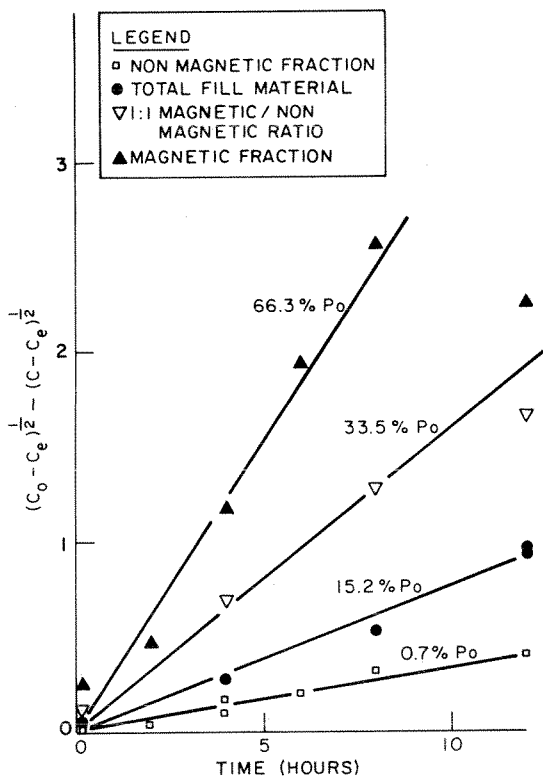


Fig. 4. The influence of pyrrhotite content on the rate of oxygen uptake by fill material (Half-order Kinetic Plots).

Upon integration the above equation becomes:

$$(C_0 - C_e)^{1/2} - (C - C_e)^{1/2} = K_S t / 2 \quad (13)$$

Figure 4 is a plot of the results in the form required by eqn. 13. Clearly the data for each fill type are consistent with the requirements of a half order reaction rate.

Figure 5 shows the half order rate constants for each material as a function of pyrrhotite content together with the rate con-

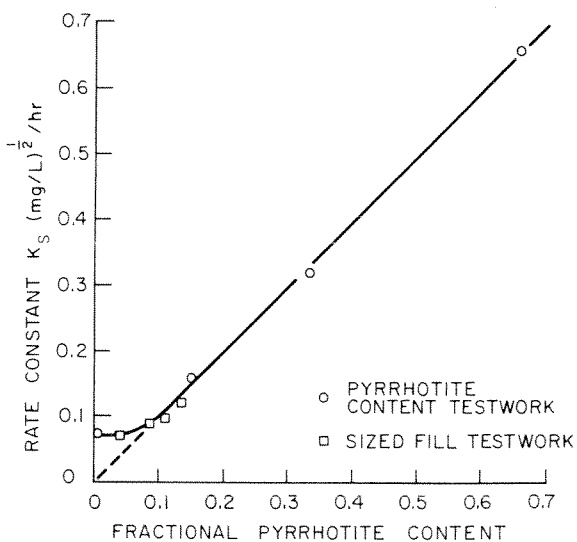


Fig. 5. The effect of pyrrhotite content on the reaction rate constant.

stants determined from a kinetic analysis of the different size fractions of the backfill. As can be seen, despite the higher specific surface area of the pyrrhotite in the total fill samples, the rate constant is a linear function of pyrrhotite content regardless of size for contents greater than about 7% by weight. The relationship can be quantified as follows:

$$K_S = 0.985f_p \quad \text{for } f_p > 0.07 \quad (14)$$

$$K_S = 0.070 \quad \text{for } f_p < 0.07 \quad (15)$$

Below 7% the overall rate constant becomes independent of pyrrhotite content suggesting that some other component in the fill also removes oxygen.

Pulp pH and cement content

Figures 6 and 7 show that pulp pH and cement content play important roles in determining the rate of deoxygenation. As outlined previously, the rate controlling step at pH values above 10 is considered to be reaction 4 so the reaction order should change from 1/2 to 2. This behaviour is confirmed by the data shown in Fig. 6 in which all dissolved oxygen is completely removed from

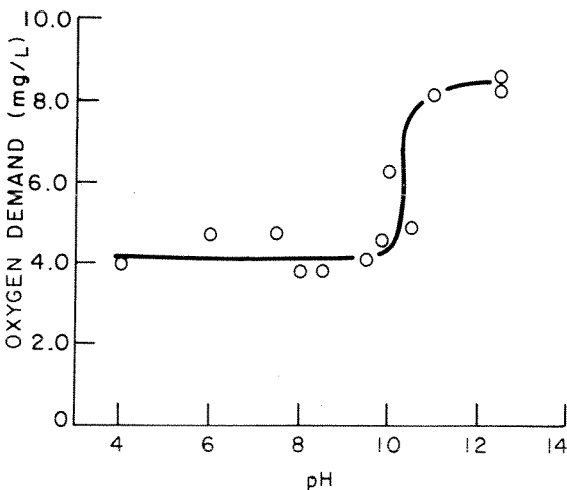


Fig. 6. The effect of pulp pH on oxygen demand of total fill material for 12 hour contact time.

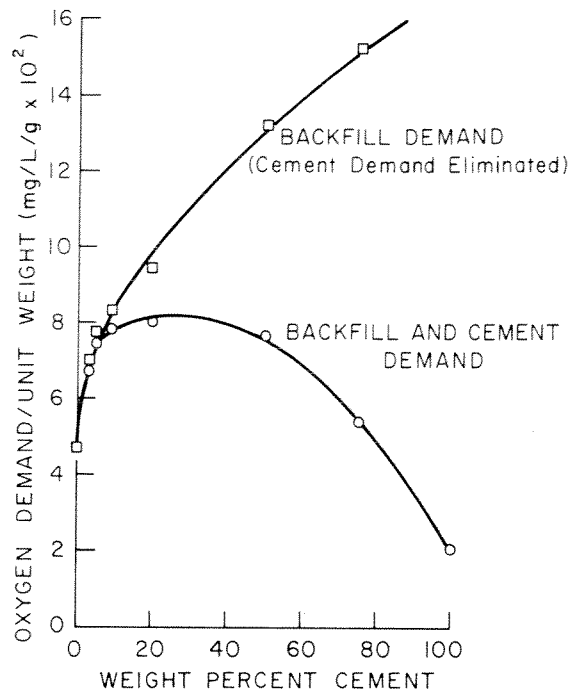


Fig. 7. The effect of cement addition on oxygen demand of fill material for 12 hours contact time.

solution within 12 hours at pH levels above 10.

The effect of cement on the oxygen demand was examined since it is added to the fill to obtain desired strength characteristics. As can be seen in Fig. 7, cement, on its own, consumes oxygen. Thus the oxygen demand due to fill material has been calculated by accounting for the contribution to the total demand from the presence of cement.

The addition of cement affected pulp pH in these tests, greatly increasing the reactivity of the fill material. In all cases when cement was added, the final solution pH increased to 12.0–12.2 and the average oxygen demand increased from 4.73 mg/l (0% cement) to about 8 mg/l in accord with the pH test series.

The influence of cement content thus confirms the important role of pH in increasing the oxygen demand. Moreover, these tests indicate that calcium ions may affect the

TABLE 4

The effect of pulp density on the half-order rate constant for oxygen depletion by backfill material

% Solids by weight	Contact time (hours)	C_0 (mg/l)	C (mg/l)	$(C_0 - C_e)^{1/2} - (C - C_e)^{1/2}$ (mg/l) ^{1/2}	K_S (mg/l) ^{1/2} /h	Weight of pyrrhotite per unit volume of water (g/cm ³)
18	12	9.40	6.40	0.552	0.092	0.04
32	12	9.28	4.55	0.947	0.158	0.07
43	8	8.66	4.69	0.806	0.202	0.12
52	6	9.02	4.85	0.830	0.277	0.17

oxygen consumption above that due to pH changes. The 12 hour oxygen demand of the fill at 75% cement content is almost double that at 20% cement content despite a similar final pH value.

Pulp density and percolation rate

All the previous tests were conducted at a solids content of 32% to ensure adequate and convenient solids-liquid contact.

This test series was conducted to apply the findings to a range of practical pulp density levels. However, a maximum of 52% solids could only be studied by this method due to solids settling problems at higher densities.

The data presented in Table 4 have been analysed using the half-order kinetic equation discussed above to determine the K_S value. As

can be seen, the half-order rate constant, K_S , is directly related to percent solids.

In a similar fashion, this equation can also be used to evaluate the data from the percolation testwork. Table 5 contains the results of these calculations. By plotting $(C_0 - C_e)^{1/2} - (C - C_e)^{1/2}$ versus the mean resident time of water in contact with the fill, the rate constant K_S can be determined from the slope (see Fig. 8). A value of 3.25 (mg/l)^{1/2}/h was obtained.

CORRELATION OF THE DATA

In order to correlate the different testwork data, the K_S values obtained in each series are plotted in Fig. 9 as a function of pyrrhotite weight per unit volume of solution. All of the

TABLE 5

The effect of percolation rate on the rate of oxidation of backfill material

Percolation rate (cm/h)	Residence time (h)	Inlet C_0 (mg/l)	Outlet C (mg/l)	Rate of oxidation (mg/h)	$(C_0 - C_e)^{1/2} - (C - C_e)^{1/2}$ (mg/l) ^{1/2}
9.9	0.773	8.34	2.73	2.52	1.299
17.8	0.430	8.53	5.03	2.83	0.702
28.3	0.200	8.79	7.20	2.77	0.290
72.7	0.105	8.14	7.33	2.68	0.150

% Solids = 74

Volume of water in the bed = 348 cm³

Weight of fill in the bed = 1000 g

Weight of pyrrhotite = 0.45 g/cm³

per unit volume of water

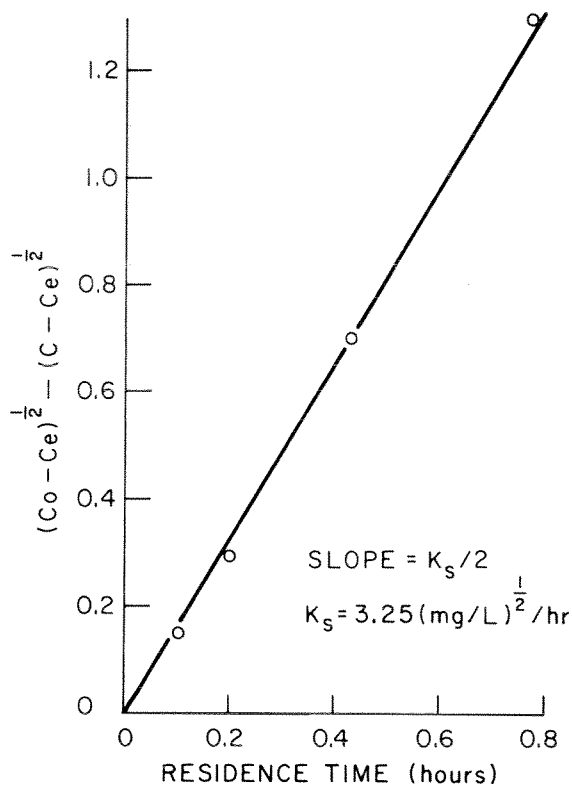


Fig. 8. Kinetic analysis of the percolation rate testwork.

agitation test results give a relationship between K_S and this ratio as follows:

$$K_S = 2.01 f_p \left(\frac{\% \text{ solids}}{100 - \% \text{ solids}} \right) \quad \text{for } f_p > 0.07 \quad (16)$$

Figure 9 shows, however, a serious discrepancy between the K_S value predicted from the agitation tests for 74% solids and that obtained in the percolation tests. The value obtained in the latter testwork is about 3.5 times higher than that predicted from the agitation testwork.

Although it is possible that reaction products impeded the rate of reaction in the agitation testwork, we believe that the important explanation for this occurrence relates to the transfer of oxygen from the solution to the solid surface by liquid phase diffusion in the agitation testwork.

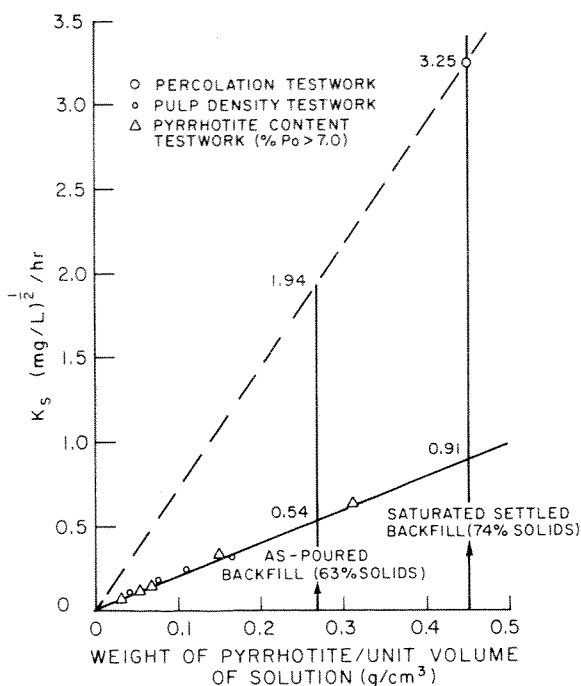


Fig. 9. The effect of pyrrhotite: solution volume ratio on the rate constant for pyrrhotite oxidation by dissolved oxygen.

Reaction product effects are unlikely since the level of total oxidation in these tests is small and the concentration of reaction products in solution would not be high enough to slow the reaction to the extent observed. Secondly, the formation and dissolution or removal of solid precipitants at the solid surface would lead to solid phase diffusion. Since no significant correlation was observed with pyrrhotite specific surface area, solid phase diffusion cannot be rate controlling.

Thus, liquid phase diffusion of oxygen is the important effect. To confirm this suggestion, it is interesting to compare the reaction rate measured by Rosenblum et al. [2] on a sample of 'B' circuit sandfill in contact with air (point A in their Fig. 6). At 8% moisture and 40°C they obtained an oxygen consumption rate of 0.076 mg/min for a 1 kg sample in a static test condition. They further showed

that the oxygen consumption rate of tailing material is relatively constant between 5 and 15% moisture but decreases at higher water levels.

Projecting our agitation data (Eqn. 16) to 85% solids gives a K_S value of 1.80 (mg/l)^{1/2}/h. At 40°C, the saturation oxygen content of water in contact with air is 6.5 mg/l. From the equation: $r = K_S (C^* - C_e)^{1/2}$; a value of 0.074 mg/min is calculated for r . The similarity between the two values is indeed remarkable and confirms the likelihood of significant liquid phase diffusion in the agitation testwork.

The practical application of eqn. 16 is thus limited to situations in which there is no water flow through the settled backfill. When water is flowing in contact with the fill, however, the actual rate of oxygen removal from the water will be higher and is predicted from the dotted line plotted in Fig. 9 to have a rate constant as follows:

$$K_S = 7.15 f_p \left(\frac{\% \text{ solids}}{100 - \% \text{ solids}} \right) \quad \text{for } f_p > 0.07 \quad (17)$$

CONFIRMATION AT INCO-THOMPSON

The equations developed from the data have been confirmed from measurements taken at the Thompson T1 Mine in stope 234 on the 3200 level on March 23 and 24, 1982. Access to this stope was via a manway of 1.5 m in diameter with constant fresh air supply. About 10,000 dry tons of sandfill were poured on March 23rd at 63% solids to a height of 3.7 m (\approx 12 ft.). The cross sectional area of the stope is estimated to be about 1700 m². Approximately 50% of the sandfill came from 'B' circuit and the total pyrrhotite content of the fill was 17%. No cement was added to this sandfill.

Oxygen transfer from air to water

After the pour a large quantity of "clear" water ran off the top of the sandfill. A portion of this water flowed down the access manway. This flow was estimated at the time of measurement to be about 20 l/min with an average interfacial area between the points of measurement of 2.6 m². At the top of the manway a sample of water flowing from the fill contained 6.9 mg/l (10°C and 106 kPa). At these conditions the saturated oxygen content is 12.5 mg/l. The value of K_L at 10°C predicted from eqn. 11 is 1.065 cm/min. Thus, the oxygen content of the water 20 meters down the manway after suitable integration of eqn. 7, is calculated to be 11 mg/l.

A concentration of 10.6 mg/l was obtained from a sample taken at this point which is in good agreement with the predicted value and confirms the practical application of eqn. 7 to predict oxygen transfer from air to a flowing stream of water.

Oxygen transfer from water to solids

Measurements were also taken at various points within the sandplant to confirm the equations developed for backfill oxidation. The plant water used in the sandplant contained 10.0 mg/l of oxygen at 15°C and 97.9 kPa (734 mm Hg). For these conditions the saturated oxygen concentration is 10.3 mg/l.

At the time of measurement, the backfill had been prepared for use approximately 5 hours earlier and had settled in the storage tanks in which a minor desliming operation was also carried out. The fill material settled to a saturated pulp density of 74% solids and was removed from the tank using a MARCONAFLOW[®] jet which added sufficient fresh water to pump the fill to an agitated mixing tank for cement addition. The density of the fill pumped underground was typically 63% solids.

Thus, while in the settling tank, the backfill would consume dissolved oxygen according to eqn. 16 since agitation and flow are negligible prior to repulping. At 74% solids and 17% pyrrhotite, the rate coefficient at 22°C would be $0.973 \text{ (mg/l)}^{1/2}/\text{h}$. Assuming this coefficient responds to temperature in a similar fashion to a diffusion coefficient [9] then K_S at 15°C is predicted to have a value of $0.80 \text{ (mg/l)}^{1/2}/\text{h}$.

Substituting this value into eqn. 13 and assuming C_0 is 10 mg/l an oxygen concentration value of 1.64 mg/l is determined for the pulp water removed from the storage tank after 5 hours of contact. The pulp, however, is diluted with fresh water upon removal from the storage tank with the pulp density changing from 74% solids to 63% solids. Thus a sample taken of the slurry in the agitated mixing tank should contain 5.0 mg/l.

A measured value of 5.40 mg/l was obtained from a sample taken during the transfer of slurry from the storage tank to the mixing tank. Thus the application of eqn. 13 together with eqn. 16 for static pulp conditions is a valid approach to use in evaluating the depletion of dissolved oxygen by backfill material.

ALTERNATE SOLUTIONS

Removal of fine size material

Removal of the fine size fractions would reduce considerably the pyrrhotite content of the fill and lower the oxygen consumption. However, because there is no correlation between the pyrrhotite surface area and the rate of oxidation, fines removal does not produce the expected degree of reduction. For example, when the minus 38 micron material is removed (4% weight loss), lowering the pyrrhotite surface area by 54%, there is only a 12% reduction in oxygen demand.

Thus elimination of fine sizes is not an

efficient method to use since significant oxidation still occurs.

Removal of pyrrhotite

A more effective way to reduce the oxidation rate would be to lower the pyrrhotite content of the backfill directly.

Two methods of recovery could be investigated—flotation or magnetic separation. Magnetic separation would clearly be preferred from a capital and operating cost viewpoint. However, the presence of magnetite in significant quantity in the 'C' circuit backfill limits the purity of the pyrrhotite concentrate and the weight recovery of the sandplant product. Because of this limitation, it is estimated that a 15% reduction in backfill production would occur. This is not acceptable.

Using flotation, a concentrate grade of 80% pyrrhotite at 95% recovery is likely achievable. With minor adjustments to the sandplant operation, the total production of backfill could be maintained at present production levels. It is doubtful, however, if this process could be justified since the decrease in oxidation rate would be only about 50% after pyrrhotite is removed.

Preoxidation of the pyrrhotite

A few tests were run to attempt to oxidize the pyrrhotite surface to the extent where further reaction would be impeded by reaction products. While it is possible to reduce the oxygen demand of a pyrrhotite slurry to near zero by high speed agitation for 15–20 minutes, upon repulping of the solids with fresh water the oxidation process is renewed.

In a percolating environment, reduced oxygen consumption from this proposal is unlikely.

Modification to filling practices

The large difference between the oxidation rates of liquid phase diffusion controlled reac-

tions and those in which significant water flow occurs, points out the validity of the observation made by Patton [10] concerning heat generation and depth of fill placement. By placing fill in 4 m lifts, the amount of water that must percolate through the fill is reduced; the majority of pulp water leaves by surface runoff. Reducing the residence time of water in contact with the fill will reduce the overall oxygen consumption rate.

Once the fill is in place and settled to its final moisture content, it is important to minimize the flow of mine water through or in contact with the backfill material. The elimination of water flow is, of course, not possible in practice. However, the control of water flow through open manways and drifts using ditches and/or water flow channels is a method which could be employed to divert water away from dangerous regions and to minimize the surface area of the water/air interface.

Sealing techniques could also be used to prevent direct contact between an air passage and the backfill material. Polyethylene liners or a layer of cement or shot-crete could be used to inhibit air diffusion through the fill matrix. This might be a useful practice for backfill material containing pyrrhotite at levels above 20%. Unfortunately, if water seeps through the fill (water flow from backfill should always be encouraged to prevent hydraulic pressure build-up) then the transfer of oxygen from the air to the oxygen deficient water can still occur.

CONCLUSIONS

Oxygen depletion of air passages by oxygen deficient water is a primary mode of oxygen transfer in cut and fill underground mining operation using backfill containing pyrrhotite. The rate of deoxygenation is related to the oxygen deficit of the water by the following

equation:

$$\frac{dC}{dt} = K_L \frac{A}{V} (C^* - C)$$

where K_L equals 13.5 mm/min at 20°C. This rate is independent of temperature over the range of 5–40°C.

Oxygen removal can be very rapid from a sealed manway with water flowing at moderate flow rates. A hazardous situation can exist within 3 days depending upon water/air surface area, water flow and initial oxygen concentration.

Oxygen is removed from water by reaction with pyrrhotite contained in the backfill material. The rate of removal is controlled by liquid phase diffusion unless water is percolating through the fill. The rate of oxygen removal from the water by the fill material is related to the oxygen content by a half order reaction equation.

The rate constant K_S is a function of the pyrrhotite content and the pulp density as follows:

$$K_S = 2.01 f_p \left[\frac{\% \text{ solids}}{100 - \% \text{ solids}} \right] \quad f_p > 0.07$$

$$K_S = 0.141 \left[\frac{\% \text{ solids}}{100 - \% \text{ solids}} \right] \quad f_p < 0.07$$

When water is percolating through the fill at typical flow rates, the rate constant K_S is 3.5 times higher than the values predicted above.

Although the oxidation rate is directly related to the pyrrhotite content for values above 7%, there is no correlation with available surface area suggesting that solid state diffusion does not play a significant role in the reaction mechanism.

The oxygen demand of backfill is sensitive to pulp pH and cement content. The reaction order may become equal to two at pH levels above 10.0. Calcium ion concentration appears to increase the oxygen demand independent of pH effects.

Simply removing the pyrrhotite using sizing techniques, magnetic separation or flotation

will not eliminate the oxygen depletion problem. Another mineral is present in the fill that consumes oxygen at considerable rates.

In view of the health hazards revealed by this work, underground workers at Inco-Thompson have been made aware of the need for exercising extreme care in entering sealed areas of the mine in contact with cut and fill stopes. All such areas should be well-ventilated with an air line for at least 30 minutes duration before entering. Self-breathing apparatus should be available for use and carried by each individual upon entering such an area. The use of life lines and a buddy system should be implemented when areas are considered particularly hazardous.

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NOTATION

A	interfacial area (cm^2)
C	dissolved oxygen concentration (mg/l)
C_e	equilibrium dissolved oxygen concentration (mg/l)
C_0	initial dissolved oxygen concentration (mg/l)
C^*	saturated dissolved oxygen concentration (mg/l)
f_p	fractional pyrrhotite content
K_H	Henry's Law Constant (mg/l-kPa)

K_L	gas/liquid oxygen mass transfer coefficient (mm/min)
K_S	liquid/solid oxygen mass transfer coefficient ($\text{mg/l}^{1/2}/\text{h}$)
P_g	partial pressure of oxygen (kPa)
r	reaction rate (mg/min)
T	temperature (K)
t	time (minutes)
V	volume of solution (cm^3)

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