OXIDATION RATES AND POLLUTION LOADS IN DRAINAGE; CORRELATION OF MEASUREMENTS IN A PYRITIC WASTE ROCK DUMP

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Abstract: There are several methods by which the oxidation rate in a pyritic waste rock dump may be inferred. Pore gas oxygen concentration profiles, temperature profiles, and drainage-monitoring data have been analyzed to quantify the oxidation processes occurring in a waste rock dump at the Aitik Mine in northern Sweden. Analysis of oxygen concentration profiles showed that material in some regions of the portion of the dump investigated had an intrinsic oxidation rate (IOR) of about $10^{-8}$ kg m$^{-3}$ s$^{-1}$ which was some 60 times greater than that of material in other regions. A comparison with pollution loads from measurements in the cutoff drain indicates that if 14% of the dump has an IOR of $10^{-8}$ kg m$^{-3}$ s$^{-1}$ then 86% has an IOR that contributes little to the total pollution load from the dump. The higher IOR found for the Aitik waste rock dump material is about eight times lower than the highest value found for waste rock at Rum Jungle in northern Australia. It is stressed, however, that the comparatively low IOR of the Aitik waste rock dump material still generates significant pollution loads in drainage. The case study presented emphasizes the utility of using temperature and oxygen profile measurements together with flow and concentration measurements to characterize pollution generation and drainage from a dump.

Additional Key Words: acid mine drainage, oxygen concentration, temperature, gas diffusion, sulfate.

Introduction

The primary process that leads to pollution generation in a pyritic waste rock dump is the oxidation of the pyrite. For this reason it is important to have data on the rate at which this reaction proceeds in a dump. The overall dump oxidation rate, which is the space integral of the oxidation rate over the dump at any one time, is a direct measure of the primary pollution generation rate in the waste rock dump and a major determinant of pollution loads in drainage from the dump. The intrinsic oxidation rate (IOR), for any one particular type of waste rock, is a function that relates the oxidation rate to any parameters that might be considered relevant, such as the oxygen and pyrite concentrations, the dump temperature, local pH, and so forth. An approximation to this function is required in most modeling of dump behavior.

There are several methods by which the oxidation rate in a pyritic waste rock dump may be inferred. One is the analysis of oxygen concentration profiles within the dump. Analysis is straightforward if diffusion is the dominant oxygen transport process. The IOR, in units of kilograms of oxygen consumed per cubic meter of rock per second, is readily inferred from the pore gas oxygen concentration profiles and the diffusion coefficient for oxygen in the waste rock.

Another approach is to measure the temperature rise brought about by the exothermic oxidation process. Interpretation of temperature measurements may be made difficult by the effects of seasonal variations in solar radiation and uncertainties about the boundary conditions at the base of the dump. Despite this, reasonable estimates of oxidation rates have been derived by this means (Harries and Ritchie 1981).

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The third approach is to measure the rate of output of chemical species in drainage water and infer the oxidation rate in the dump (for example, Galbraith 1991). Sulfate makes a good tracer for the oxidation of pyrite because it is a direct product of the reaction and is abundant, reaching concentrations of a few grams per liter. Care must be taken however to ensure that it is conservative through the system. The average sulfate load, in units of tonnes per year, can be measured relatively easily if good measurements of sulfate concentration and flow rate of drainage from the dump are available.

The application of these techniques to a waste rock dump at the Aitik copper mine in northern Sweden is discussed in this paper.

**Background and Field Measurements**

### Aitik Waste Dumps

The Aitik Mine is located near the town of Gällivare in the north of Sweden, about 100 km north of the Arctic Circle. Aitik is operated by Boliden Mineral AB and is Europe’s largest copper mine. The openpit operation which was begun around 1960 now produces approximately 14 million tonnes of waste rock per year and about the same quantity of mill tailings. The waste rock from the pit has been disposed of by end-dumping from trucks in dumps which currently average about 25 m in height and cover an area of about 400 ha.

The ore deposit at Aitik consists principally of biotite gneiss, and the waste rock also contains muscovite schist and skarn-banded gneiss. Chalcopyrite and pyrite are the dominant sulfides, with the pyrite content in the waste rock varying from 0 to 5 wt%, and averaging about 1%. The oxidation of pyrite can be taken then as the sole oxygen-consuming reaction in the Aitik dumps.

The average annual temperature at the site is just above 0°C, ranging from an average of 13.2°C in July to -13.5°C in January. The average precipitation is 680 mm/yr and the net infiltration rate into the waste rock dumps is about 500 mm/yr (Axelsson et al. 1992). From the middle of October to the middle of April the precipitation falls as snow, which then melts over a period of about 6 weeks to the end of May.

### Site Selection

The waste rock dump at the southwestern corner of the openpit pit was known to be a source of pollution and was chosen for detailed study. This dump was started around 1975 and had been left undisturbed since about 1989. The area met the criteria that the site be accessible to machinery, contain relatively old waste rock material, have had no rehabilitation works, and would be left undisturbed for the 2-yr timescale of the project. A further advantage of the site was that there was a cutoff drain that collected the drainage from the dump and provided an effective means of monitoring pollutant loads and waterflows. The site tailings dam was upstream of this dump.

### Temperature and Oxygen Measurements

Probe holes were drilled in the dump in April and August 1991 using rotary percussion airblast, with steel casing and a 140-mm eccentric bit. Once the casing was removed, the holes were lined with PVC plumbing pipe, 50 mm in external diameter, and capped at the bottom to exclude moisture and so prevent any possible perturbation of the temperature profile in the liner by vapor transport.

Nylon pressure tubing, 3/16-in internal diameter, was attached with adhesive glass filament tape to the outside of the PVC pipe. A tube ran the full length of the liner, from the bottom cap to the top of the pipe, and then one tube ran from each successive meter up to the top. These nylon tubes were to enable pore gas samples to be removed from the dump for determination of the oxygen concentration. The top of the tubes were attached to schrader valves and mounted on a brass plate.
The gap between the drilled hole and the inserted liner was backfilled using builders' sand, with the aim of limiting gas transmission between the ports since the gas diffusion coefficient of sand is not less than that of the dump material. A plug of concrete was put in the top 30 cm of the hole to prevent preferential flow of rainwater along the liner. The suitability of this liner design for temperature profile measurements has been established by Harries and Ritchie (1981).

Figure 1 shows the section of the 130 hectare dump under study and indicates the locations of the 11 probe holes. It can be seen that six holes penetrate the base of the dump.

Pore gas oxygen concentrations were determined by passing gas samples across a commercially available oxygen fuel cell. This enabled oxygen concentrations to be measured from 0% to 20.95%, with an accuracy of better than 0.05%. Temperatures were measured at meter intervals with a precision of ±0.02°C using a calibrated thermistor which was lowered down the PVC pipe. Temperature and oxygen profiles were measured at roughly monthly intervals throughout the project.

Figure 1. The relative location of the probe holes on the dump used for temperature and oxygen measurements.

**Drain and Weir Measurements**

To deduce the overall oxidation rate in any given waste rock dump from drainage measurements, it is necessary to know the total load of a relevant pollutant from the dump. This can be obtained by measuring the total water flow through the dump and the concentration of pollutant in the drainage water. Care must be taken that losses of infiltrating water, e.g., to deep ground water, are small. One must also know that the drainage does not contain pollutants from another source. In practice, if either of these complications arise, it may be accounted for if the extent of the loss or gain of pollutant can be estimated. As the flows, concentrations, and loads may vary greatly owing to seasonal factors, regular measurements must be taken at least over a 12-month period.

The glacial till below the Aitik dumps has such a low hydraulic conductivity (Axelsson et al. 1992) that essentially all the water infiltrating them appears at the toe of the dumps and may be collected in cutoff drains. All the flow from the 130 ha dump under study was collected in one drain which had been insulated with several flow weirs. Flow rates were measured at various times, the frequency of measurement depending on the season; when flow rates changed quickly during the spring snowmelt measurements were made every few days. Water samples were taken at the time of flow determination and sent to a laboratory for chemical analysis.

Sulfate concentrations were measured to determine the dump oxidation rate for the reasons given above. This
approach requires the sulphate to be conserved in the system. The most common reason for the removal of sulphate from solution flow in dumps is the precipitation of gypsum when the calcium concentration is above the gypsum solubility limit. Ion analysis of the Aitik drainage waters showed the calcium concentrations to be well below this limit.

Analysis of Oxygen Profiles

The rate of pollutant production from the oxidation of pyrite in a waste rock dump can be deduced from estimates of the rate of oxygen consumption in the dump, which in turn is derived from an analysis of measured pore gas oxygen concentration profiles.

Where oxygen diffusion is the sole supply mechanism, oxygen is transported from regions of higher pore gas oxygen concentration to regions of lower concentration. A section of measured profile with constant gradient indicates that oxygen is being transmitted without consumption, whereas a curved profile denotes a region where oxygen is being consumed.

Oxygen profiles can be interpreted qualitatively to infer the dominant gas transport mechanism in a dump and the relative magnitude of pyritic oxidation rates in different regions. Vertical profiles in which the oxygen concentration decreases monotonically with depth are consistent with oxygen being supplied from the top surface by diffusion, higher gradients implying higher oxygen consumption rates in the dump. This is discussed more completely below. Zones of relatively higher oxygen concentrations at depth suggest that either advective transport processes are dominant or there is significant diffusion from the sides. Advection will be accompanied by elevated temperatures resulting from the heat generated by higher oxidation rates.

If it can be assumed that the gas diffusion coefficient does not vary greatly with location, as is most usually the case in waste rock dumps, then it follows that different gradients in the oxygen concentration profiles are due to different oxidation rates.

In the absence of advection (including convection), one-dimensional oxygen transport into the dump by diffusion from the surface can be described as

$$\varepsilon_g \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - S(x, t),$$  \hspace{1cm} (1)

where \( C \) is the pore gas oxygen concentration, \( t \) is time, \( x \) is distance, \( D \) is the oxygen diffusion coefficient, \( \varepsilon_g \) is the gas-filled pore space, and \( S \) is the volume oxygen absorption rate.

The analytical approach requires a knowledge of the diffusion coefficient of the dump material but this does not present such a big problem as it might seem. The primary requirement in characterizing an oxidising dump is to establish oxidation rates to within an order of magnitude so a variation in \( D \) by some factors is of little consequence. In practice, the values of \( D \) fall within a narrow range because the diffusion coefficient is largely governed by a fixed parameter, the coefficient for diffusion of oxygen in air (under the narrow range of temperature and pressure encountered), and one that has a narrow range of variation, the gas-filled porosity of the dump. The gas diffusion coefficient is not expected to show much spatial variation in any given dump either because of the relative uniformity of porosity and moisture content found in typical waste rock dumps.

In most waste rock dumps the timescale for oxidation of pyrite is much longer than the timescales for gas transport. The oxygen profiles are then pseudo steady state and equation 1 can be simplified to

$$D \frac{\partial^2 C}{\partial x^2} - S(x) = 0.$$

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So, if an analytic function can be found to represent a particular oxygen concentration profile well, and the assumptions on which equation 2 is based are satisfied, then the volume oxygen absorption rates or oxidation rates (S) can be easily found by calculating the second derivative or curvature of the function at a given depth.

Results

Oxygen Results

Typical results from the pore gas oxygen concentration measurement program are presented in figures 2 and 3. In general, the oxygen concentration fell monotonically from the surface of the dump, indicating that the oxygen supply mechanism to the sites of pyritic oxidation was dominated by diffusion.

The measured profiles fell into two groups. There was a region near the edge of the dump (probe holes A1, A2, A5, A10, and A11; see figure 2 for example) where there were high gradients in the oxygen concentration profiles and in the central part of the dump the gradients were low (A3, A4, A6, A7, A8, and A12; see figure 3 for example). In the absence of any significant heating in the dump (see below) and making the assumption that the diffusion coefficient of the waste rock does not vary greatly with location, then it is reasonable to conclude that pyritic oxidation rates are relatively high in the region where the gradients are high, and are relatively low where the gradients are low.

The oxygen profiles in the material oxidizing at the higher rate indicate that oxygen was supplied by diffusion and that the rate was not limited by the oxygen supply rate. This means then that the rate is not dependent on the geometry of the dump or the location of the material in the dump, but is a property of the material itself. Clearly, such material may occur anywhere in the dump.

The oxygen profiles in the region with low oxidation rate settled down in a few weeks after installation of the holes. In the regions of high oxidation rate, however, the profiles were variable with time, as shown in figure 2. Whilst the changes were significant with respect to the accuracy with which the oxygen concentrations were measured, they were still relatively small. As a consequence, it was possible to use the region with the greatest gradient to establish a reasonable upper bound on the oxidation rate within the dump.

Figure 2. Pore gas oxygen concentrations measured in probe hole A1.

Figure 3. Oxygen concentrations measured in probe hole A7 between April 1991 and January 1992.
Following the method described above, functions of a suitable form were constructed and fitted using a least-squares method to the data points of the oxygen profiles measured in hole A1 over a 2-yr period, from April 1991 to April 1993. Since the oxygen concentration (mole fraction) at the surface of the dump is fixed at 20.95% (atmospheric), the fitted curves were constrained to pass through this point.

Figure 4 presents an example of the graphical results of the best fit of the predetermined function to data measured in the top 6.2 m of hole A1 in May 1992. (The measured profile indicates no oxygen consumption in the waste rock below this depth.) In the figure the axes have been normalized so that the atmospheric oxygen concentration (20.95%) = 1 and the depth of 11.22 m = 1. The normalized data and error estimates are also shown. The function clearly describes the measured pore gas oxygen concentration profiles very well. The second derivative or curvature of the fitted curve at a chosen depth was determined and converted to the volume absorption rate or oxidation rate. The oxygen diffusion coefficient in the dump, D, was taken as $4.1 \times 10^{-6}$ m$^2$ s$^{-1}$, taking the gas-filled porosity as 0.28 and using the curve of Papendick and Runkles (1965). This procedure produced a set of oxidation rates at a series of depths and time.

The oxidation rates thus determined from the hole A1 profiles ranged from $(3.1 \pm 0.2) \times 10^{-9} \text{ kg m}^{-3} \text{ s}^{-1}$ to $(4.3 \pm 0.3) \times 10^{-8} \text{ kg m}^{-3} \text{ s}^{-1}$, with an average volume absorption rate for the high oxidation region of the dump of close to $1 \times 10^{-8} \text{ kg m}^{-3} \text{ s}^{-1}$.

Another method for quantifying oxidation rates in the dump from the measured pore gas oxygen concentration profiles involved obtaining the oxygen fluxes into the top surface of the dump. The gradient of the pore gas oxygen concentration at the surface for each measured profile was determined graphically, and the surface oxygen fluxes were estimated using the oxygen diffusion coefficient given above. The surface oxygen fluxes varied with location, with two distinct classes of surface oxygen fluxes being seen in the test area. In keeping with the earlier analysis, higher fluxes were found at the edge of the dump, with lower fluxes in the central region. The average values of surface oxygen flux into the dump were found to be $(15 \pm 9) \times 10^{-8} \text{ kg m}^{-2} \text{ s}^{-1}$ at A1, A2, A5, A10, and A11 and $(0.25 \pm 0.25) \times 10^{-8} \text{ kg m}^{-2} \text{ s}^{-1}$ at A3, A4, A6, A7, A8, and A12. The standard deviation on the averages represents flux variations with location and time, although a clear seasonal pattern was not seen.

Figure 4. Function fitted to the pore gas oxygen concentration data measured in probe hole A1 in May 1992.
The shape of the oxygen profiles at the bottom of A1 implies a flux through the base of the dump. The average value of this flux was estimated to be $2 \times 10^{-8}$ kg m$^{-2}$ s$^{-1}$. The net oxygen flux (oxygen consumed in the dump) is then simply the difference between the surface and bottom oxygen fluxes, which was found to be $13 \times 10^{-8}$ kg m$^{-2}$ s$^{-1}$. The flux through the base of the dump in the central region of the dump was taken to be negligibly small, because the gradients at the bottom of the profiles show no indication of such a flux, and because neglecting any flux through the base leads to an overestimate rather than an underestimate of pollution generation in the dump.

The total amount of oxygen consumed in the whole dump can be estimated by using either the surface flux values or the volume oxygen absorption rates. Assuming that all the oxygen diffusing into the dump surface was consumed by pyritic oxidation, then oxygen consumption can be converted into sulfate production using the overall stoichiometry of the reaction of oxygen with pyrite (1 kg oxygen $\rightarrow$ 1.714 kg sulfate).

Three estimates of the pollution generation rate from the 130 ha dump which drains into the cutoff drain have been made, which effectively put upper and lower bounds on the rate:

1. The average volume absorption rate of $1 \times 10^{-8}$ kg m$^{-3}$ s$^{-1}$ obtained from hole A1 was applied to the whole dump. At this rate of absorption, diffusion will limit oxidation to the top 15 m of the dump, so the effective thickness of the 130-ha dump is taken to be 15 m. This gives an annual sulfate production rate of 10,500 t/yr.

2. An estimate of 10,000 t/yr of sulfate was obtained by applying the average surface flux at A1, A2, A5, A10, and A11 ($15 \times 10^{-8}$ kg m$^{-2}$ s$^{-1}$) to the whole dump.

3. A lower bound was estimated by using the average of the six lowest oxygen fluxes (A3, A4, A6, A7, A8, and A12). The average of these fluxes, $0.25 \times 10^{-8}$ kg m$^{-2}$ s$^{-1}$, was applied to the whole dump and yielded a rate of 180 t/yr of sulfate.

The results are summarized in table 1, expressed in units of tonnes per hectare per year.

<table>
<thead>
<tr>
<th>Description of Method Used for the Estimate</th>
<th>Sulfate production</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen volume absorption rate at A1 applied to whole dump. Rate = $1 \times 10^{-8}$ kg m$^{-3}$ s$^{-1}$</td>
<td>80.9</td>
</tr>
<tr>
<td>Average surface flux at A1, A2, A5, A10, and A11 applied to whole dump. Flux = $15 \times 10^{-8}$ kg m$^{-2}$ s$^{-1}$</td>
<td>76.9</td>
</tr>
<tr>
<td>Average flux at A3, A4, A6, A7, A8, and A12 applied to whole dump. Flux = $0.25 \times 10^{-8}$ kg m$^{-2}$ s$^{-1}$</td>
<td>1.4</td>
</tr>
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</table>

**Oxidation Rates From Temperature**

Whilst oxidation rates can in principle be obtained from measured temperature profiles, where heat is generated by the pyritic oxidation reaction, this has been found to be too difficult with the Aitik data owing to a number of factors as outlined below.
The ambient average monthly temperatures at the Aitik site range from -13.5°C in January to 13.2°C in July. The near-surface temperatures in the dump follow the ambient ones closely when they are positive, but once the surface freezes the dump temperatures do not drop below -5°C. During the months when the dump surface is warming up, the temperature in the dump is highest at the surface, but as the surface cools down, the temperature peak travels deeper into the dump. The attenuation and phase shift of the Fourier components of the temperature signal at the surface depend on the thermal properties of the dump.

Figure 5 shows the temperature profiles measured in hole A1 over a 10-month period and illustrates how the large seasonal swing in surface temperatures affects the temperature of the dump to a depth of at least 10 m. Because the average ambient temperature at the site is close to 0°C, the temperature of about 2.5°C which is seen in the lower part of the dump can be attributed to heating due to pyritic oxidation. This is a relatively small signal, especially when compared with the temperature fluctuations due to insolation in the top half of hole A1, where the oxidation has been found to be occurring.

A further difficulty with any analysis of the temperature data is that the boundary condition at the base of the dump is unknown. Water is flowing close to the interface between the dump and the original ground surface and will have affect measured temperature distributions, but not enough is known about the system to be able to quantify this reliably.

**Flows, Concentrations and Loads**

Figure 6 shows a typical result for the monitoring in the cutoff drain of drainage flow rates and sulfate concentrations. The instantaneous load is the product of the flow and concentration. The average annual load was obtained by integrating the load over the period. A careful analysis of the water balance and drainage data showed that a constant sulfate load was coming from the tailings dam, underflowing the waste rock dump and entering the cutoff drain. This load was subtracted from the total load in the drain to give a value of 12.1 t ha⁻¹ yr⁻¹ for the annual sulfate.
production of the waste rock dump. As presented in table 1, the annual sulphate production rate from the high and low IOR material in the dump has been estimated to be 80.9 t ha\(^{-1}\) yr\(^{-1}\) and 1.4 t ha\(^{-1}\) yr\(^{-1}\), respectively. The drain data implies, then, that 14% of the dump is composed of the high IOR material and the rest has the low IOR.

Figure 6. Typical data from drainage monitoring.

**Discussion and Conclusions**

In a large dump where gas transport is dominated by diffusion, any appreciable pyrite oxidation rate leads to a reduction in the oxygen concentration in the pore gas. The present case study has provided a quantitative estimate of oxidation rates of the bulk waste rock material from an analysis of the measured oxygen profiles. These oxidation rates were used to estimate the overall sulfate production rate in the dump. If sulfate is conserved in the system then the sulfate load in the drain will be a direct measure of the overall oxidation rate in the dump, shifted in time by some function which depends on the transit time of the solution through the dump. This transit time is short, of the order of a few years in typical dumps, compared with the time to oxidize the whole dump.

Analysis of oxygen concentration profiles showed that material in some regions of the dump investigated had an IOR of about \(10^{-8} \text{ kg m}^{-3} \text{ s}^{-1}\) which was some 60 times greater than that of material in other regions. A comparison with pollution loads from measurements in the cutoff drain indicates that if 14% of the dump has an IOR of \(10^{-8} \text{ kg m}^{-3} \text{ s}^{-1}\) then 86% has an IOR that contributes little to the total pollution load from the dump.

The temperature rise in the dump from heat produced in the pyritic oxidation reaction was too small to extract the oxidation rate from the temperature profiles, particularly in the top 6 m of the dump, where the changes caused by seasonal temperature changes were large. Hence, although in principle the oxidation rate can be extracted from both the temperature and oxygen concentration profiles in the dump, in practice it was possible to use only one of these methods.
It is important to note that the "high" IOR found for the Aitik waste rock dump material is about eight times lower than the highest value found for waste rock at Rum Jungle in northern Australia (Harries and Ritchie 1981). It should be stressed, however, that a comparatively low IOR such as that found for the Aitik waste rock dump material still generates significant pollution loads in drainage. The main reason is that in the early history of the dump, which may last for many years, a low IOR means that a large region of dump is involved in oxidation.

The case study presented here has emphasized the utility of using pore gas oxygen profile measurements together with flow and concentration measurements to characterize pollution generation and drainage from a dump. In general, oxygen and temperature measurements provide information on rate processes within the dump, while the flow and concentration measurements provide data on pollution generation rates integrated over the whole dump. The set of measurements is complementary. Concentration measurements without flow rates and an overall water balance for the dump lead, at best, to a qualitative assessment of the environmental impact of the waste rock dump or of the effectiveness of rehabilitation measures. Oxygen measurements without temperature measurements can lead to wrong conclusions on gas transport mechanisms. Even with data on both oxygen concentrations and temperature distributions it may be in practice that quantitative estimates of the oxidation rate can be extracted from only one set of data.

**Literature Cited**


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