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31

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by

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About this Report

This report is the output of one of the components of the project entitled “Management of Sulfidic Mine Wastes” which was developed by the Australian Centre for Minesite Rehabilitation Research (ACMRR), now the Australian Centre for Mining Environmental Research (ACMER), in consultation with industry. The project, which was sponsored by BHP Minerals, Environment Australia, Iluka Resources Limited, MIM Holdings Limited, Normandy Mining Limited, Pasminco Century Mine Limited, Placer Dome Asia Pacific Pty Ltd, Renison Bell Limited, Rio Tinto and Western Metals NL, commenced in March 1998 and was completed in February 2000.

The Chief Investigators were Dr. John W. Bennett and Dr. M. Josick Comarmond of the Australian Nuclear Science and Technology Organisation and Dr. John J. Jeffery of Environmental Geochemistry International Pty Limited.

ACMER commissioned the Australian Minerals Industries Research Association (AMIRA) to manage this component (P488) of the project, and this was undertaken on behalf of AMIRA by Mr. Dennis O’Neill of Resource Futures Pty. Ltd.

Further information on this report and other reports from the project can be obtained from –

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Introduction

The concept of designing new mining operations to minimise the cost and environmental impact associated with their future closure has gained widespread acceptance in the mining industry in recent years. Research and development continues to move towards the goal of being able to determine with sufficient certainty how sulfidic wastes from a particular site will behave. Predictive models are in the process of being developed at a number of research centres around the world to enable the effect of dump design parameters and waste management options on pollutant release rates in the short to long term to be determined.

A key parameter required in describing the behaviour of sulfidic mine wastes, particularly waste rock, is the rate at which the material oxidises under whatever conditions may apply to that material. The primary objective of the work reported here was to determine whether laboratory-scale measurements of oxidation rates could be shown to be sufficiently close to field measurements that laboratory data could be used in predictive models of full scale waste piles. To achieve this objective, measured data were collected and sets of values measured at different size scales were compared. The specific objectives of the work were to:

1. Compile from literature searches and unpublished data, estimates of oxidation rates of sulfidic material obtained under controlled laboratory conditions;
2. Compile from literature searches and unpublished data, estimates of oxidation rates of sulfidic material obtained from field measurements;
3. Intercompare the estimates and identify any systematic differences between field and laboratory measurements;
4. Identify any shortcomings in the techniques used and the application of these data in the management of sulfidic mine wastes; and
5. Report findings to industry.

The work described in this report has been carried out jointly by the Australian Nuclear Science and Technology Organisation (ANSTO) and Environmental Geochemistry International Pty Ltd (EGi). The work has been funded through the Australian Centre for Mining Environmental Research (ACMER) with support from BHP Minerals, Environment Australia, Iluka Resources Limited, MIM Holdings Limited, Normandy Mining Limited, Pasminco Century Mine Limited, Placer Dome Asia Pacific Pty Ltd, Renison Bell Limited, Rio Tinto and Western Metals NL.

Sources of Data

Data enabling oxidation rates of sulfidic waste materials to be determined at the laboratory and field scales were sought from a wide range of sources. Requests for data were sent to individual mining companies, to national research programs and a commercial database provider. Published literature was searched, including journals, conference proceedings, reports and theses. Data were also obtained from databases held by EGi and ANSTO. In order to meet the main aim of this study, particular attention was paid to data from measurements made at different size scales on the same or similar material.

Despite there being a considerable body of acid mine drainage/acid rock drainage literature which falls under the category generally referred to as ‘prediction’, such literature almost invariably confines itself to laboratory techniques. When references are made to field scale information, the data provided is usually incomplete (for example, if concentrations of chemical species in drainage are given without the corresponding flow data, fluxes of chemical species cannot be determined) or found on examination to be paradoxical.

Three publications were found that were considered to be of value in the study reported here.

The first publication reported a study of drainage from ore taken from copper-nickel resources of the Duluth Complex in Minnesota, USA (Lapakko 1994). The second case was taken from the Canadian Cinola Project studies of long term acid generation at different size scales (Norecol, Dames and Moore 1994). The third source of information considered here was a Masters of Applied Science thesis (Frostad 1999) on the prediction of acid rock drainage for the Red Mountain Project in British Columbia, Canada.

In order to make best use of the information available from ANSTO and EGi, the data sets from each group were compared to find individual mine sites where oxidation rates could be obtained for waste rock, measured at different scales. Only two sites were identified where valid comparisons could be made.

Another set of data was provided by measurements made for Boliden AB on waste rock from the Aitik Mine in northern Sweden.

Conclusions and Recommendations

The conclusions made here are based on the available data. Few measurements had been made using the same material types across the scales being considered. Good data were particularly lacking at the field scale. One recommendation of the work is that better experiments need to be designed and carried out to address issues of scale-up.

The primary objective of the work has been achieved, in that it can be concluded from the information presented in this report that laboratory-scale measurements of oxidation rates of sulfidic mine wastes have been shown to be sufficiently close to field measurements that the laboratory rates could be used with confidence in predictive models of full scale waste piles.

The validity of the previous conclusion has been found to be independent of particle size distribution in the materials measured, particularly where oxidation rates only need to be known to within an order of magnitude. In general, measurements of oxidation rate will produce the same results, irrespective of whether they are made according to standardised humidity cell procedures or in columns, as long as all the material is supplied with oxygen, the water infiltration rate is high enough to keep the water residence time reasonably short and there is not a significant loss of sulfate in the material through precipitation of secondary minerals. This is not to say, however, that particle size is not an important determinant of oxidation rate. The apparent insensitivity to particle size distribution is because the techniques are in effect measuring the maximum value of the intrinsic oxidation rate which is dominated by small particles. It needs to be stressed that the particle size distribution will affect the change in the intrinsic oxidation rate over time as sulfide is consumed, but none of the techniques described here set out to measured such a dependency.

Because humidity cells contain only small particles, they provide a useful means to measure the maximum oxidation rate of a particular material. However, in order to provide data on the time-dependent behaviour of oxidation rates which can be taken to be representative of the material in full-sized dumps, laboratory measurements need to be made on samples with a particle size distribution up to about 200 mm. Consequently, it is recommended that such a measurement program be run for long enough to determine the dependence of intrinsic oxidation rate on sulfide sulfur content as the particles oxidise. The resulting data should be used to test and, if necessary, modify the functional dependence of the intrinsic oxidation rate currently used in models which are to be applied to full-scale dumps.

The most significant shortcomings of the measurement procedures reported here were:

- the lack of recognition of the need to keep the residence time of water in a system short, compared with the expected rate of change of oxidation rate and associated processes (particularly seasonal changes), and
- the failure in most cases to quantify the likelihood of secondary mineralisation in a system and the effect that this may have on the interpretation of measurements.

An attempt has been made in this report to provide sufficient information on each of these matters to be of assistance in the design of any future measurement programs.

Early in the process of compiling data for use in this work, it became clear that there was a dearth of well-designed measurements which could be used to compare oxidation rates of materials at different size scales. Many previous programs have focussed on measuring the concentration of chemical species in effluent, without also recording the effluent flow rates which are also necessary to determine chemical fluxes. It is recommended that a minimum set of parameters to be measured in any laboratory or field test should include direct measurements of effluent flow and concentrations of sufficient chemical species to check for secondary mineralisation in the system.

It is recommended that measurement programs using large columns, test piles or full sized dumps include instrumentation to enable pore gas oxygen concentrations to be determined throughout the system. This information can be used either to assure that all the material is free to oxidise or to determine the region of the system which is oxidising.

If it can be demonstrated that there are circumstances where it is important to take more accurate account of the dependence of oxidation rate on temperature than is afforded by the current approach, it is recommended that a program of work be undertaken to establish the validity of the Arrhenius equation for bulk materials and to find more appropriate values of the activation energy of dominant sulfides.

In considering questions of scale-up, it has been concluded that test piles do not provide any information on oxidation rates which cannot be measured in well-designed laboratory columns under controlled conditions.

There should now be discussions between modellers, experimental scientists and the mining industry to ensure that the remaining scientific questions related to the management of sulfidic mine wastes are well-posed and that the required information is identified. Appropriate measurement programs should then be instigated to provide the information and supply data to enable predictive models to be tested.

1 INTRODUCTION

The concept of designing new mining operations to minimise the cost and environmental impact associated with their future closure has gained widespread acceptance in the mining industry in recent years. There are many issues associated with the concept which link the life-cycle stages of a new mine, from feasibility to decommissioning and closure. Of interest will be design elements which facilitate closure and have the potential to bring additional benefits during operation (Hicks 1998).

One area of operations where there remains significant room for improvement is in the management of sulfidic mine wastes. The oxidation of sulfides in waste piles may lead to the release of ecologically detrimental levels of pollutants into surface and ground waters. Research and development continues to move towards the goal of being able to determine with sufficient certainty how sulfidic wastes from a particular site will behave. Achievement of this goal will enable decisions on the management of the wastes to be made confidently at the design stage and during operation. Adequate management would ensure that pollutant levels entering the ecosystem from the wastes would be at acceptable concentrations throughout the mine life and beyond closure.

Predictive models are in the process of being developed at a number of research centres around the world to enable the effect of dump design parameters and waste management options on pollutant release rates in the short to long term to be determined. The expectation is that the models will be used, for example, to determine the optimum geometry for particular dumps and stockpiles to minimise pollutant generation, to assess the value of selective placement, to assist in the design of covers and predict how pollutant generation will change with time.

A key parameter required in describing the behaviour of sulfidic mine wastes, particularly waste rock, is the rate at which the material oxidises under whatever conditions may apply to that material. Oxidation rates of sulfidic mine wastes have been measured at a range of size scales, from bench-top studies, through small and large columns, to test piles and in full-scale waste piles. The primary objective of the work reported here was to determine whether laboratory-scale measurements of oxidation rates could be shown to be sufficiently close to field measurements that laboratory data could be used in predictive models of full scale waste piles. To achieve this objective, measured data were collected and sets of values measured at different size scales were compared. A clear advantage of being able to use laboratory measurements is that they can be made at an early stage in the mine life-cycle and can be made on a large number of samples, therefore allowing decisions to be made on the management of sulfidic wastes as part of the overall design of mine operations.

The specific objectives of the work were to:

1. Compile from literature searches and unpublished data, estimates of oxidation rates of sulfidic material obtained under controlled laboratory conditions;
2. Compile from literature searches and unpublished data, estimates of oxidation rates of sulfidic material obtained from field measurements;
3. Intercompare the estimates and identify any systematic differences between field and laboratory measurements;

4. Identify any shortcomings in the techniques used and the application of these data in the management of sulfidic mine wastes; and
5. Report findings to industry.

The work described in this report has been carried out jointly by the Australian Nuclear Science and Technology Organisation (ANSTO) and Environmental Geochemistry International Pty Ltd (EGi). The work has been funded through the Australian Centre for Mining Environmental Research (ACMER) with financial support from the following sponsors: BHP Minerals, Iluka Resources Limited, MIM Holdings Limited, Normandy Mining Limited, Pasminco Century Mine Limited, Placer Dome Asia Pacific Pty Ltd, Renison Bell Limited, Rio Tinto and Western Metals NL. The project was managed by the Australian Mineral Industries Research Association (AMIRA).

2 BACKGROUND

2.1 Sulfide Oxidation

Pyrite and other sulfidic minerals commonly occur in many of the base metal, precious metal and coal deposits which are mined around the world. Sulfidic materials below cut-off grade are routinely consigned to waste rock dumps or and sulfidic wastes from ore processing are piped to tailings storage facilities. In these piles the sulfides may be exposed to air and undergo oxidation reactions, generating sulfate and iron salts and possibly mobilising trace metals present in the wastes. The initial stage of the oxidation of pyrite can be summarised by the following reaction:

$$FeS_2 + 7/2\, O_2 + H_2O \Rightarrow Fe^{2+} + 2\, H^+ + 2\, SO_4^{2-} \qquad [1]$$

A more complete presentation of the pyrite oxidation reactions is provided in Appendix A. Similar oxidation reactions can be written for other sulfides, such as pyrrhotite.

The presence of metal species in drainage waters from sulfidic waste piles may cause receiving ecosystems to be adversely affected. The need is to be able to predict whether particular mine wastes are going to present an ecological risk and if so to plan to manage the wastes to reduce the risk to acceptable levels. To meet the need numerical models are required which can be used with confidence to predict the chemical composition of drainage waters from full-sized waste piles.

2.2 Intrinsic Oxidation Rate

The intrinsic oxidation rate (IOR) is the rate of oxidation of material at a point in a system (column, stockpile, dump), under the particular conditions which pertain to that point. The IOR is a function of many parameters, such as oxygen concentration, sulfide sulfur concentration, temperature, pH, sulfide mineral morphology, microbial ecology etc. Since it is currently impossible to predict the functional dependence of the IOR by measuring individual material characteristics, the only reasonable approach is to make direct measurements of oxidation rate, either of samples in the laboratory or in-situ. Laboratory measurements can be designed to provide the functional dependence of the IOR on any of the parameters which are judged to be important.

Field measurements of the IOR are usually expressed as the mass of oxygen consumed per cubic metre of material per second [kg(O_2) m^{-3} s^{-1}]. If the mass or bulk density of the material is known then the IOR can be expressed as the mass of oxygen consumed per mass of material per second [kg(O_2) kg(material)$^{-1}$ s^{-1}].

The use of the IOR in predictive modelling of sulfidic piles has been well described by Ritchie (1994a). The IOR is the property of the material which enables oxidation and primary pollutant generation rates in a system to be described as a function of space and time.

Various forms of the functional dependence of the IOR have been proposed. For example, there are two limiting forms for the dependence on oxygen concentration. The first is a linear dependence, in which the IOR is zero when there is no oxygen present and is at a maximum at atmospheric oxygen concentration. At the other limit, the IOR is constant, irrespective of oxygen concentration, but is zero when there is no oxygen present. Ritchie (1994b) has shown that the overall oxidation rate in a waste rock dump is comparatively insensitive to detailed changes in the intrinsic oxidation rate unless the IOR is very low. It follows that in many situations knowledge of the detailed properties of the IOR are not required for the practical purposes of decision-making in the management of sulfidic wastes. Generally the IOR only needs to be known to within an order of magnitude.

2.3 Measurement Techniques

2.3.1 Static Tests

During the past 20 years chemical testing procedures have been developed to help identify different waste types and how they might be managed. Initially the approach was to characterise the acid forming and acid neutralising properties of sulfidic mine waste materials. Procedures such as the net acid production potential (NAPP), acid neutralising capacity (ANC) and the net acid generation (NAG) test have been added to the suite of tests and have been widely adopted as the basis for characterising wastes according to their acid generating potential. A classification system developed by EGi is presented in Table 1.

The procedures just mentioned are often referred to as static tests since they provide no indication of the rates of sulfide oxidation, acid generation or acid neutralisation in a material. Because they give no rate information, static test results have not been collected for use in this report.

Table 1. Geochemical waste rock classes

Waste Type	Final NAG pH	NAPP [kg H_2SO_4/t]
potentially acid forming (PAF)	< 4.5	+ ve
non acid forming (NAF)	≥ 4.5	- ve
acid consuming (AC)	≥ 4.5	< -100
uncertain[#]	≥ 4.5 < 4.5	+ ve - ve

[#] further testing required

2.3.2 Humidity Cell and Column Tests

The pyrite oxidation reaction given by Equation 1 suggests two means of determining the pyritic oxidation rate of a sample of material. The first is to measure the sulfate production rate and use the stoichiometry of the reaction to calculate the oxidation rate, according to Equation 2 below.

$$\text{oxygen consumption rate } [\text{kg}(O_2)\ \text{kg(material)}^{-1}\ \text{s}^{-1}] = 0.583 \times \text{sulfate production rate } [\text{kg}(SO_4)\ \text{kg(material)}^{-1}\ \text{s}^{-1}] \qquad [2]$$

The second means is to measure the oxygen consumption rate in a system directly. Practical applications of these methods will be discussed below.

So called ‘kinetic tests’ aim to provide some of the rate information required. The most widely used laboratory procedures are the humidity cell and column leach tests. In both systems the usual method of operation is to pass water through the oxidising material and chemically analyse the leachate. A humidity cell testing procedure has been incorporated into a United States of America ASTM standard (White and Sorini 1997). The column leach test procedure used by EGi is described in Appendix B. A description of column design and operation which includes the facility to measure oxygen consumption rates has also been described by Garvie and Taylor (1999).

The main difference between humidity cells and columns is that the former attempt to prevent precipitation of any oxidation/neutralisation products by regular flushing of the system, whereas columns may operate at high ionic strengths and precipitation may occur. Notwithstanding this difference of intent however, many of the comments made in the rest of this report concerning columns may equally apply to humidity cells

The size of columns is usually determined by the maximum particle size which is to be included in the material being tested. Humidity cells typically contain 1 kg of material and columns have been operated which contain tonnes of waste rock. Columns are usually run in the laboratory under controlled conditions but have also been set up outdoors, exposed to ambient climatic conditions.

Kinetic tests may be designed to quantify a range of parameters such as: acid generation rate, sulfate release rate, rate of neutralisation, metal release rate, time to produce acid leachate and time to consume the carbonates and sulfides. Tests are typically run for months and often years, allowing time-dependent effects on that time-scale to be seen.

Information on sulfide oxidation rates can be obtained from the tests by two methods. The first equates the sulfate release rate to the sulfate production rate which, in turn, relates to the pyritic oxidation rate using the stoichiometry of Equation 1. An important assumption in this method is that the flux of sulfate in leachate from a humidity cell or column is proportional to the sulfate production rate in the system. In a system where the infiltration rate or oxidation rate have changed it will take some time for the assumption to be valid (even assuming that sulfate is conservative in the system and that none is lost by precipitation). That time cannot be less than the residence time of water through the system. The residence time is the time taken by a conservative pollutant (or tracer) to travel from the top of the system to the bottom, under the ambient, constant infiltration rate. Equation 3 provides a means of determining the residence time. As a rule of thumb, the water-filled volume fraction of waste rock is typically between 0.15 and 0.25. The residence time can be considered to be a characteristic time-scale for any changes in the system to be fully represented in drainage.

$$\text{residence time (s)} = \text{height of the system (m)} \times \text{water-filled volume fraction / infiltration rate (m s}^{-1}\text{)} \qquad [3]$$

The second method can be used in suitably designed columns where the oxidation rate can be measured directly by sealing the system from the air and monitoring the decrease of oxygen contained in the known gas volume within the column. In designing such a column it is important to incorporate a means of maintaining the gas pressure inside the column equal to the outside pressure, primarily to reduce the risk of air entering the column through any leaks in the system. The oxygen consumption method assumes that the sulfidic oxidation rate is the only one that consumes oxygen in the system.

Both methods require oxygen to be freely available throughout the material at all times. Only under these conditions can the volume or mass of oxidising material be known. It can be readily shown that in many systems the supply of oxygen to the reaction sites may be limited by the oxygen diffusion coefficient of the material, confining oxidation to a fraction of the total quantity of material. To ensure that oxygen is freely available in columns, all columns should be designed to enable pore gas oxygen concentration measurements to be made to check that oxygen is not limiting oxidation anywhere. In materials with a high oxidation rate it may be necessary to maintain an air flow through a column.

It is important to be aware that using sulfate flux (concentration × flow) in leachate as a measure of the rate of sulfidic oxidation is only valid if there is no significant loss of sulfate in the system through precipitation of sulfate minerals. Whether species such as gypsum [$CaSO_4.2H_2O$] or jarosite [$KFe_3(SO_4)_2(OH)_6$] will form will depend on the mineral composition of the material and the concentration of dissolved chemical species in the pore water, including the pH. A brief discussion of the formation of secondary minerals is presented in Appendix C and further information can be found in Alpers et al. (1994). Loss of sulfate in a system due to secondary mineralisation will lead to an underestimate of oxidation rates. Also, if there are pre-existing sulfate minerals, their dissoultion during a test could lead to an over-estimation of the oxidation rate.

2.3.3 Test Piles

Test piles have been seen by some to be an intermediate scale between columns and full-sized dumps. As will be seen in later discussion, the principal parameter which is usually scaled up from columns is the maximum particle size, with test piles usually being constructed of run-of-mine material. They are constructed outdoors and are subject to climatic conditions.

Test piles typically range in size from some hundreds of tonnes to thousands of tonnes of material and range in height from about 1 metre to several metres. They are usually constructed on a low permeability base so that drainage flows can be monitored, collected and chemically analysed.

Interpretation of the data from test piles is subject to the same constraints as has already been described for columns, that is, that there is no significant loss (or gain) of sulfates through secondary mineralisation and that oxygen is freely available throughout the system. For this reason any measurement program in a test pile should make provision for pore gas oxygen concentrations to be measured.

The matter of response time for test piles is also important. In many circumstances the height of a pile and the rainfall rate at a site can mean that the residence time of water through the centre of a pile is a year or more. As a consequence, test piles generally need to be operated for periods of several years to obtain meaningful information. Furthermore, information cannot be obtained on variations in rates which occur on time-scales less than the residence time, which generally precludes their usefulness in observing the effects of seasonal variations in parameters, such as temperature.

The design and operation of test piles used by EGi at a number of mine sites is described in Appendix D.

2.3.4 Full Scale Dumps

There are several reasons why attempts to estimate sulfide oxidation rates within full scale waste rock dumps (greater than, say, one million tonnes), ore stockpiles, and tailings storage facilities may be unsuccessful. First may be a lack of information on oxygen distribution in particular dumps so that the fraction of material in a dump contributing to measured sulfate fluxes is unknown. Second is the issue of secondary mineralisation which may control sulfate fluxes. These two issues have already been discussed. A third issue relates to the mechanics and time-scale of water transport in dumps. Even assuming that all drainage flow from a full sized dump, stockpile or tailings storage facility could be intercepted, monitored and analysed, the residence time of water in such systems is generally of the order of a few years. As mentioned in the previous section, this residence time determines the time-scale over which data must be collected to provide meaningful information about the system being measured Since the oxidation process in a dump is also time dependent, interpretation of such field drainage data requires great care.

ANSTO has developed a method which can be used to estimate oxidation rates in dumps and stockpiles based on monitoring changes in oxygen concentration as a function of depth and time. The method takes advantage of conditions created within a dump during probe hole drilling, in which compressed air is used to clear cuttings from the hole. A consequence of drilling is that a significant volume of the dump surrounding a recently installed probe hole can be well aerated. Once drilling stops, the oxygen which has been blown into the pore space will be consumed by sulfidic oxidation until the concentration returns to a steady profile which is characteristic of the dump. Measuring the rate at which the oxygen concentration falls at a number of depths in a hole soon after installation provides a direct measure of the oxidation rate of the dump material (for example, Bennett 1994).

The method for installing probe holes and measuring pore gas oxygen concentration profiles in waste piles has been described by Garvie and Taylor (1999). The method for estimating oxidation rates from measured oxygen concentration profiles is described in Appendix E. The approach described here does not take into account the effect of diffusion of oxygen from the aerated zone into the rest of the dump or the possibility of poor aeration of the dump where a hole has been drilled through material having a very low gas permeability. Both of these effects would lead to an overestimate of the oxidation rate by this method.

Oxidation rates can also be determined from an analysis of the shape of a measured pore gas oxygen concentration profile. Since the time-scale for the oxidation of pyrite is generally much longer than the time-scales for gas transport, one-dimensional oxygen transport into the dump by diffusion from the surface (in the absence of advection) can be described as:

$$D\frac{\partial^2 C}{\partial x^2} - S^*(x) = 0 \qquad [4]$$

where D is the diffusion coefficient of the dump material
C is the pore gas oxygen concentration
x is the depth below the surface
S^* is the intrinsic oxidation rate.

If an analytical function can be found to fit a measured oxygen concentration profile, and the assumptions on which Equation 4 is based are satisfied, then the intrinsic oxidation rate can be easily found by calculating the second derivative or curvature of the function at a given depth.

3 SOURCES OF DATA

Data enabling oxidation rates of sulfidic waste materials to be determined at the laboratory and field scales were sought from a wide range of sources. Requests for data were sent to individual mining companies, to national research programs and a commercial database provider. Published literature was searched, including journals, conference proceedings, reports and theses. Data were also obtained from databases held by EGi and ANSTO. In order to meet the main aim of this study, particular attention was paid to data from measurements made at different size scales on the same or similar material.

It was necessary to undertake a critical assessment of the validity of the available data. Although experiments may not necessarily have been undertaken with the specific aim of measuring oxidation rates, data were considered for inclusion if there was enough information for the rates to be evaluated. Data to be included in the study needed to satisfy the following criteria:

1. sufficient information to evaluate an oxidation rate in the units of $kg(O_2)\ m^{-3}\ s^{-1}$ or $kg(O_2)\ kg(material)^{-1}\ s^{-1}$;
2. information on the mass or volume of material which was oxidising; and
3. sufficient information to be assured that precipitation of sulfate minerals in the system would not significantly affect oxidation rate evaluations through the application of Equation 2.

A consequence of applying these criteria was that many potential sources of oxidation rate data were rejected. Each of the sources of information included in this study will be discussed in turn.

3.1 International Kinetic Database

The International Kinetic Database (IKD, available through MDAG Publishing, Vancouver) contains summary statistics for 450 humidity cell tests of waste rock and tailings material from 61 mines and 71 column tests of waste rock and tailings material from 12 mines. The statistics have been sourced from published and publicly available summaries, files, or reports on proposed, operating and closed mines. A number of physical and chemical parameters and test results are contained in the database, including sulfate release rates.

Oxidation rate data were extracted from the IKD by applying Equation 2 to the sulfate production rate data. For each particular test, sulfate release rates were provided in the database for the entire test period as well as for the late stage period of the test (generally the last five weeks). Late stage period data were used in this study to avoid including the effect of any rapid changes in rates which sometimes appear at early times. The data were grouped according to material type (tailings and waste rock) and according to test method (humidity cell and column) for use in this work. The groupings were to enable any systematic differences in oxidation rates due to particle size distribution or to test method to be observed.

It should be noted that some of the test data included in the IKD were limited by gypsum solubility (Morin et al. 1995), leading to an underestimate of sulfide oxidation rates determined from sulfate release rates. These data were not specifically identifiable in the database and so were included in this study.

3.2 EGi and ANSTO Databases

Over a period of more than twenty years ANSTO and EGi have been involved in measurements related to the oxidation of sulfidic mine wastes. EGi has specialised in geochemical characterisation of material through static and kinetic test procedures in the laboratory. EGi has also designed and run test piles. ANSTO has focused on in-situ field measurements in full-scale waste rock dumps.

To contribute towards meeting the objectives of the study reported here, EGi and ANSTO have collated existing data and extracted oxidation rates wherever possible.

The EGi database contains the results of measurements made on 149 samples, both waste rock and tailings, from 39 sites. Sulfate release rates from the final period of testing were converted to an equivalent oxidation rate. As with the IKD, some of the oxidation rates included in the subsequent analysis may have been underestimates due to sulfate precipitation in the material. The results were grouped according to material type (waste rock or tailings) to enable the range and distribution of oxidation rate data to be compared with the results from the International Kinetic Database.

3.3 Case Studies from the Literature

An extensive literature survey was conducted with the aim of finding studies in which oxidation rate measurements had been made on at least two size scales of sulfidic material – laboratory, test piles or full scale piles.

Despite there being a considerable body of acid mine drainage/acid rock drainage literature which falls under the category generally referred to as ‘prediction’, such literature almost invariably confines itself to laboratory techniques. When references are made to field scale information, the data provided is usually incomplete (for example, if concentrations of chemical species in drainage are given without the corresponding flow data, fluxes of chemical species cannot be determined) or found on examination to be paradoxical.

Three publications were found that were considered to be of value in the study reported here.

The first publication reported a study of drainage from ore taken from copper-nickel resources of the Duluth Complex in Minnesota, USA (Lapakko 1994). The study was conducted by the Minnesota Department of Natural Resources and compared drainage from columns and five test piles over a period of years, from 1978 to 1991. The work is considered as Case 1 in this report.

Case 2 is taken from the Canadian Cinola Project studies of long term acid generation at different size scales (Norecol, Dames and Moore 1994). In 1987 City Resources (Canada) Limited initiated a program of acid generation testing as part of feasibility studies for the Cinola Gold Project located on the Queen Charlotte islands, on the north coast of British Columbia. The program was designed to quantify acid generation potential and evaluate waste rock management options for the proposed open pit gold mine. In 1990 the Mine Environment Neutral Drainage (MEND) Program and the BC Acid Mine Drainage Task Force began funding further monitoring of tests to evaluate long term material behaviour in five humidity cells, five leach columns and four on-site waste rock piles. The study was concluded in 1993.

The third source of information considered here was a Masters of Applied Science thesis (Frostad 1999) on the prediction of acid rock drainage for the Red Mountain Project. In this work Frostad carried out humidity cell and column studies using two types of waste rock, three particle size ranges and three corresponding sample sizes. Most studies were carried out in the laboratory but two large columns containing nominal 20 t samples were located outdoors at the mine site in British Columbia, Canada. Test piles were also constructed but no useful data were collected from them. The work is considered as Case 3 in this report.

3.4 New Case Studies

In order to make best use of the information available from ANSTO and EGi, the data sets from each group were compared to find individual mine sites where oxidation rates could be obtained for waste rock, measured at different scales. Only two sites were identified where valid comparisons could be made. These mines are identified as Site A and Site B in Cases 4 and 5 respectively, to maintain confidentiality of the information. At Site A, oxidation rate measurements have been made in column studies, test pile trials and in full scale dumps. At Site B they have been made in columns and in a full scale dump.

ANSTO has also been involved in studies at the Aitik Mine in Sweden as part of an overall project by the mine operator Boliden AB to develop a plan for the management of sulfidic wastes at the site. ANSTO made field measurements in a full scale waste rock dump which allowed oxidation rates to be estimated and also set up a column study. After some initial measurements the column study was taken over by two Swedish postgraduate students and some of the data were published. With the agreement of Boliden AB, one of the former students and his academic supervisor the complete column data set was made available for use in the study reported here. The Aitik work is reported as Case 6.

4 COMPILATION OF DATA

4.1 International Kinetic Database

Oxidation rates derived from sulfate production rates given in the IKD have been presented as histograms of oxidation rate versus number of results in each order of magnitude (Figures 1 and 2). Only the order of magnitude of the results has been considered to be of significance, for the reasons outlined in Section 2.2. This form of representation allows easy comparison of the range and distribution of measurements according to measurement method (humidity cells and columns) and material type (waste rock and tailings).

Figure 1 compares oxidation rates in waste rock samples obtained from (a) humidity cells and (b) columns. The humidity cell oxidation rate measurements span four orders of magnitude. The distribution was symmetric, with the peak falling between 1×10^{-11} kg(O_2) kg(material)$^{-1}$ s^{-1} and 1×10^{-10} kg(O_2) kg(material)$^{-1}$ s^{-1}. There were fewer column results but their distribution was not inconsistent with the humidity cell results.

Figure 2 compares oxidation rates in tailings samples obtained from (a) humidity cells and (b) columns. Here the humidity cell data only span three orders of magnitude, but as was found for waste rock, the peak in the distribution fell between 1×10^{-11} kg(O_2) kg(material)$^{-1}$ s^{-1} and 1×10^{-10} kg(O_2) kg(material)$^{-1}$ s^{-1}. The distribution was asymmetric, with no results below 1×10^{-12} kg(O_2) kg(material)$^{-1}$ s^{-1}. There were only a few results from column measurements but they fell in the same range as the peak of the humidity cell distribution.

A comparison of Figures 1(a) and 2(a) shows that the distribution of oxidation rates of waste rock and tailings were very similar, with the exception that there were no tailings results at the lower end of the distribution. The fact that the peak of the two distributions fell in the same range of oxidation rates suggests that there was no systematic effect of particle size on oxidation rate, although some lower rates were seen in waste rock than in tailings.

4.2 EGi Database

Figure 3(a) presents the range and distribution of oxidation rates derived from sulfate measurements made by EGi in columns of tailings from 19 sites. Figure 3(b) presents the same information for columns of waste rock, overburden and coal reject materials from 30 mine sites.

The distribution of oxidation rates in waste rock, overburden and coal reject spanned three orders of magnitude, peaked in the range 1×10^{-11} kg(O_2) kg(material)$^{-1}$ s^{-1} to 1×10^{-10} kg(O_2) kg(material)$^{-1}$ s^{-1} and did not extend below 1×10^{-12} kg(O_2) kg(material)$^{-1}$ s^{-1}. The distribution was similar to those obtained for waste rock from the IKD (Figure 1).

Figure 3(a) shows that the distribution in tailings only spans two orders of magnitude and was not symmetric, the greatest number of measurements falling in the upper range of 1×10^{-10} kg(O_2) kg(material)$^{-1}$ s^{-1} to 1×10^{-9} kg(O_2) kg(material)$^{-1}$ s^{-1}. There were fewer values in the EGi database for tailings than in the IKD tailings set (Figure 2).

4.3 Case Studies

4.3.1 Case 1 – Duluth Complex

In order to assess potential drainage problems arising from the development of copper-nickel resources of the Duluth Complex in Minnesota, USA, six test stockpiles containing low-grade ore material were constructed. The test pile studies were conducted from 1978 by the Minnesota Department of Natural Resources. The results to 1991 from five of the piles were reported by Lapakko (1994) and compared with laboratory studies. One of the aims of the study was to determine the rates of sulfate release, as part of the overall objective to relate water quality over time with sulfide sulfur content in the different materials.

Annual precipitation in the area where the test piles were constructed averages 721 mm. There is a large seasonal temperature variation, varying from an average of -14°C in January to 19°C in July, with an annual mean of 3.6°C. The ground is covered with snow for an average of 140 days per year.

The test piles contained between 815 and 1,100 tonnes of material at bulk densities between 2,040 and 2,080 kg m^{-3}. The sulfur content of three of the piles was 0.63% and the other two contained 0.79% and 1.41%. The piles were approximately 4 m high and 15 m × 25 m at the base. The material sat on a liner sloped towards a perforated plastic pipe fitted with a cumulative flow meter and a flow-weighted composite water sampler.

Lapakko reported that the test piles typically produced drainage between the middle of March and the middle of November, with an average flow season of 245 days. The average flow from the piles was quoted by Lapakko as ranging from 0.27 to 0.38 L per tonne of rock per day, although there is some uncertainty about the water infiltration rate. Using the information on the water collection area and the mass of each pile provided by Lapakko, and taking into account the number of flow days, the infiltration rate can be roughly estimated to have been from about 160 to 370 mm/year. These values seem low however compared with the annual precipitation at the site of 721 mm/year.

Three of the piles had covers placed over them and were vegetated. The covers were topsoil, coarse sand and sandy till over coarse sand. The report by Lapakko did not discuss the effect of the covers on oxidation rates in the piles, but given the nature of the cover materials, it is likely that only the topsoil could have had an effect, depending on its degree of saturation. The Lapakko data showed that the pile covered by topsoil consistently had the lowest sulfate release rate.

Column studies were carried out in the laboratory using material with similar sulfur content as the test piles. The columns each contained only 75 g of material.

Table 2 is taken from Lapakko, except that sulfate release rates in the original table have been converted to oxidation rates. The field rates were calculated by Lapakko as average rates over the entire period of record (1978 to 1991) since he found that there was little evidence of systematic changes over that 14 year period. The laboratory rates were from the last 15 to 36 weeks of the period of record. Lapakko made the comparison between field and laboratory rates based on the sulfur content of the material.

Using information provided by Lapakko it can be deduced that the residence time of water flowing through the central 4 m high section of the test piles was greater than one year. This does not affect the estimates of the oxidation rates, given the observed constancy of the sulfate release rates over years. One consequence however of the relatively long residence time of water in part of the piles was that any changes in oxidation rates in the piles due to seasonal changes, in temperature for example, could not be readily detected in sulfate fluxes in drainage.

The residence time associated with the piles also explains why Lapakko observed that sulfate flux appeared to increase with increasing water flux. Only if the change in water flux was maintained for a period of at least the residence time would the sulfate concentration re-equilibrate to indicate the actual oxidation rate in the system (assuming no sulfate precipitation).

Table 2. Comparison of field and laboratory oxidation rates of Duluth Complex ore (after Lapakko, 1994)

Test Pile	Sulfur Content (%)	Test Pile Cover	Oxidation Rate [kg(O_2) kg(material)$^{-1}$ s^{-1}]		Oxidation Rate Ratio (Test Pile/Lab)
			Test Pile	Laboratory	
1	0.63	none	2.2×10^{-12}	1.4×10^{-11}	0.16
2	0.63	topsoil	1.3×10^{-12}	1.4×10^{-11}	0.10
3	0.63	coarse sand	3.6×10^{-12}	1.4×10^{-11}	0.26
6	0.79	none	4.8×10^{-12}	1.5×10^{-11}	0.33
5	1.41	sandy till over coarse sand	6.7×10^{-12}	3.7×10^{-11}	0.18

Another factor which must be considered in the interpretation of the field data concerns the supply of oxygen to the material in the pile. The oxidation rates presented in Table 2 are sufficiently low that oxygen could be supplied by diffusion throughout a 4 m high pile, even if the material was oxidising at the highest rate measured in the laboratory. However, given that 3 of the 5 piles had vegetated covers on them, that at various times plastic sheeting had covered parts of the piles and in one case a bactericide had been applied to a pile, oxygen may not have always been available to all parts of the piles.

Table 2 shows the field oxidation rates expressed as a fraction of the laboratory rates, both sets of rates having been deduced from measured sulfate release rates. Lapakko suggested a number of possible reasons for the difference observed between the rates. These reasons include differences in temperature and particle size, and gypsum precipitation in the piles.

Temperatures were lower in the field than in the laboratory measurements. Using the Arrhenius equation[1], an activation energy for pyrrhotite (which accounts for 51% of the sulfides in the material studied) of 5.2×10^4 J/mol at pH 4 (Nicholson and Scharer 1994) and average laboratory and field temperatures of 20°C and 4°C respectively, the sulfide oxidation rate in the field could be expected to be a factor of 3 lower than those measured in the laboratory. Applying this factor to the ratios in Table 2 changes them from being in the range 0.10 to 0.33 to being in the range from 0.28 to 0.96. Whilst activation energies which are based on laboratory measurements using pure samples of pyrite cannot necessarily be applied to bulk materials in columns or in the field, it is likely that the temperature dependence of oxidation rates may contribute to some of the differences observed at the laboratory and field scale.

Lapakko suggested gypsum precipitation as a mechanism by which the sulfate release rates from the test piles might have been lower than observed from the laboratory columns, although he did not present the data explicitly to support the suggestion.

The particle size in the columns ranged from 0.053 mm to 0.149 mm in diameter and in the test piles ranged up to greater than 305 mm. This difference in particle size may also have contributed to the difference between field and laboratory rates.

4.3.2 Case 2 – Cinola Project

The stated aim of Study E of the Cinola Project was to compare acid generation rates measured in humidity cells and test piles in the field (Norecol, Dames and Moore 1994).

Four test piles were set up in the field, each containing either 20 tonnes (Pad 1) or 30 tonnes of run-of-mine waste rock. The piles were constructed in 1987 using rock from two different sources. Pad 1 was built with waste rock which had been mined in 1982 and left exposed for five years and the other piles used rock which had been freshly mined.

Each test pile consisted of an impermeable liner covered by a layer of inert quartz sand onto which the pile of waste rock was placed. The waste rock piles were around 0.9 m high on Pad 1 and 1.2 m high on the others. Each pile was drained by a pipe under the pile which fed into a plastic barrel. Samples of leachate were collected from the barrels for chemical analysis. Flows were not measured and had to be estimated, based on precipitation over the collection area of each liner which was 8 m × 8 m. Note also that complete precipitation records were not available for the test site so measurements made at a site in the same region were used, after adjustment by a relationship which was found to match the overlapping data.

Humidity cell tests were carried out using material collected from near the top of each waste rock pile approximately one month after the piles had been constructed. The samples were screened with a 4 mm hand sieve. Two sets of humidity cells were run using different methods. All cells contained 200 g of rock crushed to pass

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[1] Arrhenius Equation: the effect of temperature on reaction rate constants is given by

$\ln(k_2/k_1) = (E_a/R)*((1/T_1)-(1/T_2))$

where T_2 and T_1 are two temperatures (K), k_2 and k_1 are the rate constants at these temperatures, E_a is the activation energy (J mol^{-1}) and R is the gas constant, 8.31 J $mol^{-1}K^{-1}$.

a 2 mm screen and either humidified or dry air was passed through the cell. Leaching with deionised water was carried out once per week. The first set of columns were operated on a 3 day wet, 3 day dry, 1 day leach cycle as described by Sobek et al. (1978). The second set was operated with continuous moist air flow.

Details of the methods just described can be found in the Cinola Project report (Norecol, Dames and Moore 1994).

The Cinola Project report is supplied with a computer disk which contains the experimental data. These data have been analysed in the present work to produce the figures presented below.

Humidity Cells

The data disk provided information on the sulfate production rate from humidity cells 2-3 and 2-4, containing material from Pads 3 and 4, respectively. Using the relationship provided in Equation 2, these data were converted to oxidation rates and are presented in Figure 4.

Although the oxidation rate of the sample in cell 2-4 was consistently greater than that of the sample in cell 2-3, there was generally good agreement between the oxidation rates of the two samples, particularly at the beginning of the measurements and over the final year. Over the measurement period of nearly three years the oxidation rate of both samples fell by about two orders of magnitude, from around 10^{-9} to 10^{-11} kg(O_2) kg(material)$^{-1}$ s^{-1}.

Test Piles

Sulfate production rates from the test piles were calculated using the data provided on the disk and converted to oxidation rates using Equation 2, assuming that there was no significant precipitation of sulfate in the piles. The authors of the Cinola Project report discussed the formation of gypsum in the piles. They found that gypsum saturation was most likely to occur in the summer months and very unlikely during the winter. They concluded, however, that sulfate 'was probably not being stored extensively as gypsum'.

The results of the calculations of oxidation rates in the test piles carried out using the raw data supplied with the Cinola Project report are shown in Figure 5. A comparison of this figure with the corresponding Figure 7-13 of the Cinola Project report shows very good agreement between the relative oxidation rates as plotted over time and between the different test piles.

At a monthly rainfall of 126 mm, a typical water content of waste rock of 15 vol% and a test pile height of 1.2 m, an estimate of the residence time of water in the system is around 1.4 months. This relatively short residence time means that sulfate fluxes from the test piles will respond on that time-scale to any changes in oxidation rate within the piles. As a consequence, data from the piles can be expected to reflect any seasonal changes in oxidation rates due to changes in infiltration rates or temperature.

Comparison of Oxidation Rates at Different Size Scales

Note that Figures 4 and 5 have been plotted on the same axes to facilitate comparison of the results measured at two size scales.

Attention will be given to the results from Pads 3 and 4 which correspond with the two humidity cells 2-3 and 2-4 respectively. Both sets of data reached a peak after some time during which the systems were clearly equilibrating. At their peak, both the humidity cells and test piles gave oxidation rates close to 1×10^{-9} kg(O_2) kg(material)$^{-1}$ s^{-1}.

Over the three year measurement period the oxidation rates in the humidity cells decreased steadily to finish around 1×10^{-11} kg(O_2) kg(material)$^{-1}$ s^{-1}. The oxidation rates in the test piles exhibited greater variability, due in part perhaps to variations in water infiltration rates and temperature, the likelihood of sulfate precipitation in the piles at some times of the year, and exacerbated by the need to use estimated water flux data to calculate sulfate fluxes. Towards the end of the five year measurement period however, the minimum oxidation rates measured in Pads 3 and 4 were comparible to the rates in the humidity cells, being about 2×10^{-11} kg(O_2) kg(material)$^{-1}$ s^{-1} and 1×10^{-11} kg(O_2) kg(material)$^{-1}$ s^{-1} respectively.

The results of this study indicate excellent agreement between the oxidation rate of similar materials measured in humidity cells and test piles at the beginning of the tests. The overall rate of decrease in oxidation rates was observed however to be faster in the humidity cells than in the test piles. The slower rate of decrease in oxidation rate in the test piles over a period of five years may have been due to the continuing oxidation of the larger particles which were included in the test piles.

4.3.3 Case 3 – Red Mountain Project

One of the objectives of the work undertaken by Frostad (1999) was 'to carry out kinetic weathering tests on mine waste rock under various conditions and at different scales within the laboratory and the field to provide more confidence in scaling up laboratory data to predict the weathering characteristics of a waste dump.' Tests were conducted on samples of two types of waste rock, using masses of 1 kg, 50 kg and 20 t. Rock type HC-1 was a feldspar porphyry, estimated to contain 5-7% sulfides and rock type HC-2 was a sediment, also estimated to contain 5-7% sulfides.

Humidity Cells

Humidity cells containing 1 kg samples of waste rock which had a maximum particle diameter of 6.4 mm were operated according to a standard procedure. In the weekly cycle dry air was passed through each cell for three days, then humidified air for three days, followed on the seventh day by a distilled de-ionised water leach in which 500 mL was dripped into each cell over about one hour.

The volume of water used to irrigate the 1 kg samples was more than five times that required to completely flush the system, ensuring that the sulfate mass collected in the leachate could be taken to be indicative of the total sulfide sulfur oxidation in the rock sample over the previous week.

Data provided in Frostad have been used here to calculate sulfate release rates from the humidity cells and these rates have been converted to oxidation rates according to Equation 2 above. The results are presented in Figure 6.

The figure shows that there was no significant difference between the oxidation rate of the two different materials. Once the sulfate release rate from the cells had stabilised, after about 2 months, there was a gradual increase in the rate by around 25% over the following 8 months. The average of the oxidation rates from both rock types over the complete measurement period was 5.9×10^{-11} kg(O_2) kg(material)$^{-1}$ s^{-1}.

Laboratory Columns – 50 kg

Columns were set up in the laboratory containing 50 kg of waste rock which had a maximum particle diameter of 38.1 mm. The columns were 300 mm in diameter and 750 mm in height. The columns were operated for 31 weeks in the same way as the humidity cells, including the weekly one-hour irrigation with 500 mL of water. Aeration of the columns was discontinued after 31 weeks. Since the oxygen distribution throughout the column was unknown, data after the cessation of aeration were not included in the analysis presented below.

Oxidation rates deduced from the sulfate release rates provided in Frostad are shown for the two rock types over the first 31 weeks in Figure 6.

As found from the 1 kg humidity cells, there was no significant difference between the deduced oxidation rate of the two rock types. There was however a systematic increase in the apparent oxidation rate over the period from day 29 to day 214, rising roughly linearly by a factor of 3 in that time, from about 7×10^{-12} kg(O_2) kg(material)$^{-1}$ s^{-1} to 2×10^{-11} kg(O_2) kg(material)$^{-1}$ s^{-1}. The sharp decrease in the final value from the two columns shown on the figure cannot be explained and has not been used in the analysis just given.

In considering the implications of the apparent increase in oxidation rate, it is important to take into account the response time of the columns. Frostad found that the gravimetric water content of the column containing HC-1 material was 5.6% which equates to a volume of 2.8 L. Given that the infiltration rate was 0.5 L per week, Equation 3 gives the response time of the columns as 5.6 weeks (39 days). This means that it would have taken at least 6 weeks for any changes in oxidation rate in the system to be able to be quantified by measuring the rate of sulfate release in leachate. Since the sulfate release rate from each column was increasing throughout most of the measurement period before aeration ceased, the sulfate mass collected in each leachate sample could not be taken to be indicative of the total oxidation in the column over the previous week.

Because of the different water residence times between the humidity cells and columns, it is not valid to compare the results from each. Comparisons could only have been made if the sulfate release rates had equilibrated to the extent that the time-scale of changes was less than the water residence time in the columns. This condition may have been met within a further six months since the apparent oxidation rate of the columns would have then equalled the rate measured in the humidity cells if the observed rate of increase in the sulfate release rate from the columns had continued.

The reason for the long response time of the 50 kg columns was the low infiltration rate applied. In scaling up from the 1 kg humidity cell to the 50 kg column it would seem reasonable that the leaching rate should have also been scaled up to achieve a shorter response time and to reduce the possibility of secondary mineral precipitation in the column. If the scaling had been on the basis of surface area then the volume applied each week would have needed to have been 9 times greater to achieve a response time of less than a week.

Sulfate and calcium concentrations provided by Frostad demonstrate that gypsum precipitation was controlling sulfate release rates in drainage from the column containing HC-1 material from early in the measurement period. For this reason, oxidation rates could not be validly determined from drainage chemistry. In the column containing HC-2 material the system was close to saturation with respect to gypsum.

In conclusion, useful data to enable a comparison of oxidation rates measured at different particle size distributions could only have been obtained from the 50 kg columns if they had been run longer, under aerated conditions and if the weekly irrigation rate had been increased to prevent gypsum saturation.

Field Columns – 20 t

Field ‘cells’ or columns were set up outdoors at the Red Mountain project site in north-western British Columbia. The annual precipitation at the mine site is around 1880 mm and the mean annual air temperature is about 0°C.

The columns were square in cross-section, 2.5 m × 2.5 m, and were 1.5 m high. They contained about 20 tonnes of each rock type. The maximum particle diameter in column HC-1 was 400 mm and in column HC-2 it was 320 mm.

The columns were set up in 1994 but no useful data were collected in 1995 due to operational difficulties. As a consequence data were obtained only in 1996 and even then it was a very limited set because the water in the columns was frozen for nine months of the year, up until the middle of June.

Frostad determined the water content of the HC-1 column to be 1,620 L and of the HC-2 column to be 2,650 L. The measured flows through the HC-1 and HC-2 field cells in the period 13 June 1996 to 19 September 1996 were 1208 L and 258 L, respectively. These two flow rates can be taken to represent the annual infiltration rate in each column. Using this information, the residence time of the HC-1 column was 1.3 years and of the HC-2 column was 10.3 years. Given that conditions in the columns change markedly with the seasonal changes at the site (no water flow for almost 9 months and large temperature variations), these long response times mean that it would not be valid to use sulfate release rates in leachate collected over three months as a measure of oxidation rates in the columns.

Comparison of Oxidation Rates at Different Size Scales

The data presented in Figure 6 allows a comparison to be made of oxidation rates determined from measurements made by Frostad in two types of material (HC-1 and HC-2), with particle size distributions up to a maximum diameter of 6.4 mm and 38.1 mm.

It can be seen that for each of the particle size distributions the two types of material produced rates which were not significantly different from each other.

Although the deduced oxidation rates in the columns containing the larger sized materials was always less than those in the columns containing the smaller sized materials, the rate of increase of the larger sized materials was greater at early times in the measurement period than that of the smaller sized materials. However, because sulfate release rates in the 50 kg column of HC-1 material can be shown to have been controlled by gypsum precipitation and the 50 kg HC-2 column was close to saturation, sulfate production rates could be expected to reach a plateau, invalidating their use in deducing oxidation rates. Once gypsum saturated is reached in a system, sulfate release rates will be proportional to water flow rates (since the concentration of sulfate will be constant).

The apparent increase in oxidation rates of the materials in the humidity cells and columns has not been explained.

The apparent agreement, to well within an order of magnitude, between inferred oxidation rates of materials with two particle size distributions must be viewed with caution. The issue of gypsum precipitation in the 50 kg columns means that oxidation rates in the material in those columns is likely to have been higher than the oxidation rates inferred from sulfate production rates. It is likely however that better agreement would have been found if the 50 kg columns had been operated for longer and if the irrigation rate applied to the 50 kg columns had been high enough to prevent gypsum precipitation.

No useful data were obtained from measurements made using material with a larger particle size distribution.

4.3.4 Case 4 – Site A

At Site A measurements have been made at three different size scales: column measurements, test piles and in waste rock dumps.

Columns and test piles each contained one of three run-of-mine potentially acid forming (PAF) material types which had been assessed as having either a low capacity for acid generation (PAF-LC), a moderate capacity (PAF-MC), or a high capacity (PAF-HC).

Column Measurements

Summary data from the column measurements are shown in Table 3. The main piece of information is the oxidation rate which was determined from the sulfate release rate in the last measurement period of each test, using Equation 2. Also shown is the pH of leachate. Information has been provided on the geochemical waste type, as described in Table 1, and the maximum particle diameter in the column. The columns have been operating for 100 weeks and are continuing.

It is important to note that there is not a strong correlation between maximum particle size in a column and the relative oxidation rate. In each of the cases in Table 3 the difference between the fastest and slowest oxidation rates was less than a factor of 3. The difference in rates between material <39 mm and <19 mm was not more than a factor of 1.5.

The oxidation rates of columns AC16, AC17 and AC18 have been plotted against time in Figure 7. This graph indicates that the rates corresponding with the three different particle size distributions remained similar to each other over the measurement period. Over the same period the pH of leachate from the three columns also remained similar and fell from about 3.5 at the beginning to about 2.0 at the end.

Figure 8 shows the deduced oxidation rate versus time in three columns which contained material with the same maximum particle size (<39 mm) and each of the three geochemical types (columns AC10, AC13, AC16). It can be seen that there was a significant difference between the oxidation rate of the different materials, which spanned a range of around 1½ orders of magnitude.

It is clear from the results presented in Figures 7 and 8 that oxidation rate was strongly dependent on the material type and largely independent of particle size distribution.

Table 3. Column results using waste rock from Site A

Column Number	Geochemical Waste Type	Particle Diameter (mm)	Leachate pH after 100 weeks	Oxidation Rate after 100 weeks [$kg(O_2)\ kg(material)^{-1}\ s^{-1}$]
AC10	PAF-LC	<39	6.0	1.3×10^{-11}
AC11	PAF-LC	<19	5.5	1.9×10^{-11}
AC12	PAF-LC	<3.2	7.6	6.7×10^{-12}
AC13	PAF-MC	<39	2.5	1.1×10^{-10}
AC14	PAF-MC	<19	2.3	1.6×10^{-10}
AC15	PAF-MC	<3.2	2.8	7.3×10^{-11}
AC16	PAF-HC	<39	2.1	3.2×10^{-10}
AC17	PAF-HC	<19	2.0	4.3×10^{-10}
AC18	PAF-HC	<3.2	2.0	4.0×10^{-10}

Test Piles

Sulfate release rates from test piles have been measured over a period of nearly 100 weeks at Site A. The piles were constructed according to the description in Appendix D. Each pile measured 10 m × 10 m at the base, was 3 m high and contained about 500 tonnes of run-of-mine material. The three piles reported here each contained one of the three different geochemical waste types used in the column study. The only water infiltration through the piles came from rainfall. Rainfall at the site is high and falls throughout the year, leading to a response time in the piles of about 7 weeks, if it is assumed that 90% of rain infiltrated the piles and that the water content of the piles was 15% by volume. There was a two month period of exceptionally low rainfall at the site about half way through the two year measurement program.

Maximum sulfate concentrations in effluent from the test piles were found to range up to around 40 g/L. These high levels, in conjunction with the low pH of the leachate, are consistent with acid bas accounting results which showed that the materials had very low acid neutralising capacity and implied that there were little or no carbonate minerals in the piles. Clearly sulfate concentrations were not limited by secondary mineralisation and could therefore be used to infer oxidation rates.

A summary of results from the three test piles is presented in Table 4. The table shows the material type and the pH in leachate after 14 weeks and after 98 weeks. The table also gives the oxidation rate and standard deviation averaged over the period from week 14 to 98, where oxidation rates were deduced from sulfate release rates using the relationship given by Equation 2.

Table 4. Test pile oxidation rates at Site A

Test Pile	Material Type	Leachate pH at week 14	Leachate pH at week 98	Oxidation Rate averaged from week 14 to 98 [$kg(O_2)\ kg(material)^{-1}\ s^{-1}$]
AP1	PAF-LC	3.9	3.3	$(1.5 \pm 0.8) \times 10^{-11}$
AP2	PAF-MC	3.8	2.3	$(7.2 \pm 4.5) \times 10^{-11}$
AP3	PAF-HC	3.2	1.9	$(2.0 \pm 1.1) \times 10^{-10}$

Sulfate release rates in the first 8 weeks were less than the average over the remainder of the measurement period and the pH was significantly higher in the first 8 weeks. After this early period the pH in leachate from each pile fell gradually over time. The sulfate release rates continued to show significant variation with time but this is likely to have been due to variations in the rainfall rate. Figure 9 shows oxidation rates in the test piles versus time.

In relating sulfate release rate from the test piles to oxidation rate, the assumption has been made that all of the material in the pile was oxidising. This in turn requires that oxygen was available to all parts of the piles throughout the measurement period. If the assumption is not met and only a fraction of the mass of material was oxidising then oxidation rates deduced from sulfate production rates would be underestimated.

Pore gas oxygen concentrations were measured in the centre of the piles, towards the base, using gas sampling tubes which were laid into the piles during construction, as shown in Figure D.2 (Appendix D). Measurements showed that in piles AP1 and AP3 oxygen concentrations were around 20 vol%, near to the concentration in air of 21 vol%, and in pile AP2 the concentrations were around 15 vol%. These results indicate that all the material in piles AP1 and AP3 was supplied with sufficient oxygen to oxidise at the same rate throughout. In the case of pile AP2 however, the measurements showed that oxygen concentrations in the interior of the pile were significantly lower than in air so that, although all the material was able to oxidise, material inside the pile may have been oxidising at a lower rate, depending on the functional relationship between intrinsic oxidation rate and oxygen concentration.

Waste Rock Dumps

Oxidation rates were determined as a function of depth in a total of 6 probe holes distributed over 2 waste rock dumps at Site A, using the technique described in Appendix E. As a means of presenting the results of a large number of individual values in a meaningful manner, Table 5 shows for each probe hole: the range of depths over which measurements were made, the number of values obtained, the range of oxidation rates and the median value. The median oxidation rates in the final column have been converted from units of $kg(O_2)\ m^{-3}\ s^{-1}$ to $kg(O_2)\ kg(material)^{-1}\ s^{-1}$ (using a typical dump dry bulk density of 1,700 $kg\ m^{-3}$) to enable comparison with other values given in this report.

Probe Hole AD1 was installed in waste rock which had been in place for a few months and holes AD2 to AD6 were in material which had been in place for up to 4 years.

Table 5 shows that variations in oxidation rates measured at different depths in a hole can be at least as great as from hole to hole. This result is simply a consequence of the history of dump construction. The instrumented parts of the dumps had been constructed over a period of time by end-dumping of material removed from the mine pit, with no attempt to selectively place materials with different geochemical properties.

Table 5. Oxidation rates measured in waste rock dumps at Site A

Probe Hole No.	Depth Range (m)	Number of Values	Range of Oxidation Rate [kg(O_2) m^{-3} s^{-1}]	Median Oxidation Rate [kg(O_2) m^{-3} s^{-1}]	Median Oxidation Rate [kg(O_2) kg(material)$^{-1}$ s^{-1}]
AD1	0.2 – 6.5	18	1.1×10^{-6} to 6.2×10^{-6}	2.1×10^{-6}	1.2×10^{-9}
AD2	10.7 – 19.7	9	3.0×10^{-7} to 3.8×10^{-6}	2.4×10^{-6}	1.4×10^{-9}
AD3	0.9 – 15.9	12	4.0×10^{-7} to 2.4×10^{-6}	1.6×10^{-6}	9.2×10^{-10}
AD4	1.6 – 49.6	13	3.8×10^{-8} to 2.4×10^{-6}	2.9×10^{-7}	1.7×10^{-10}
AD5	1.0 – 45.0	20	8.9×10^{-8} to 2.2×10^{-6}	2.9×10^{-7}	1.7×10^{-10}
AD6	0.8 – 19.3	19	6.6×10^{-8} to 5.0×10^{-7}	1.8×10^{-7}	1.0×10^{-10}

The complete set of oxidation rates determined from field measurements are represented in Figure 10.

Comparison of Oxidation Rates at Different Size Scales and Material Types

Figure 7 shows the oxidation rate in test pile AP3 versus time as well as the rates measured in the three columns of the same material. It can be seen that there was little difference between the rates measured in the test pile containing run-of-mine material and the column rates except over a few short periods. At the beginning of the measurement period the deduced rates were low in the pile, representing the period when sulfate release rates from the test pile were reaching equilibrium with the generation rate. Equilibrium would be expected to be reached on a time-scale of the water residence time for the system, which was shown earlier to be around 7 weeks. At certain other times, for example around week 60 and at the end of the measurement period, it can be seen in the figure that the oxidation rate in the pile appeared to be lower than measured in the columns. In general, variations in test piles can be expected to be greater than seen in laboratory measurements due to the greater variation in parameters such as irrigation rate and temperature.

Comparing Figures 8 and 9 provides further evidence of the good agreement between oxidation rates measured using laboratory columns (in this case columns with a maximum particle size of 39 mm) and test piles, for each of three material types.

Comparing the histogram in Figure 10 with the results presented in Figures 8 and 9 shows that over three quarters of the rates measured in the field were within the range measured in the laboratory and test piles. The other 23 % of the field measurements produced oxidation rates which were greater than 1×10^{-9} kg(O_2) kg(material)$^{-1}$ s^{-1}, apparently representing material in the dumps which had a higher oxidation rate than the materials which had been used in the columns and test piles.

Good agreement has been found between oxidation rate measurements made in the laboratory and in test piles of material from Site A. Measured oxidation rates were found to depend on the geochemical classification of the material. For a particular material, rates measured at a range of particle size distributions up to run-of-mine were found to be largely independent of particle size distribution.

It has been demonstrated that any of the laboratory or test pile oxidation rate measurements could be applied with confidence to full-scale dumps at Site A if the location of different material types in a dump were known.

4.3.5 Case 5 – Site B

At Site B measurements have been made on waste rock at two different size scales: column measurements and in waste rock dumps.

Column Measurements

Data from the column measurements are shown in Table 7. The table presents oxidation rates determined from sulfate release rates, at the maximum and in the final period of each test. The pH of column leachate at the end of each test period is also shown. The column of maximum oxidation rates in the table have been presented as a histogram in Figure 11(a).

Waste Rock Dumps

Oxidation rates were determined at a total of 25 locations in four probe holes in waste rock at Site B. Measurements yielded rates in units of kg(O_2) m^{-3} s^{-1} which were converted to units of kg(O_2) kg(material)$^{-1}$ s^{-1} using a typical dump dry bulk density of 1,700 kg m^{-3}. Figure 11(b) presents the results as a histogram.

Comparison of Oxidation Rates at Different Size Scales

The field technique produces a value for the oxidation rate which can be considered to be a maximum rate for the materials encountered. These field rates can reasonably be compared then with the maximum values seen in the laboratory.

Both sets of oxidation rates presented in Figure 11 span two orders of magnitude and in each case the greatest number of results falls between 1×10^{-10} and 1×10^{-9} kg(O_2) kg(material)$^{-1}$ s^{-1}. The number of measurements in both sets is small, however, particularly in the case of the laboratory measurements, making meaningful comparisons between to the two distributions difficult.

The results seem to indicate that the field and laboratory measurements were generally made on similar materials, but that some materials were intercepted in the field which had lower oxidation rates than any samples used in the columns.

4.3.6 Case 6 – Aitik Mine

The Aitik Mine in northern Sweden is owned by Boliden AB and is Europe's largest copper mine. By the time of mine closure there is expected to be in excess of 200 Mt of sulfidic waste rock. As part of the process of developing a management plan for the waste rock dumps, ANSTO undertook a program of studies which included field measurements (for example Bennett et al. 1992), numerical modelling and column measurements. The column studies were continued past ANSTO's involvement by Boliden AB (Strömberg et al. 1994, Strömberg 1997).

Table 7. Column results using waste rock from Site B

Column Number	Test Period (weeks)	Oxidation Rate – maximum [kg(O_2) kg(material)$^{-1}$ s^{-1}]	Oxidation Rate – at end [kg(O_2) kg(material)$^{-1}$ s^{-1}]	Final Leachate pH
BC1	35	1.5×10^{-9}	2.1×10^{-11}	2.5
BC2	85	2.7×10^{-10}	1.2×10^{-11}	2.3
BC3	68	6.5×10^{-10}	3.9×10^{-12}	2.1
BC4	85	6.1×10^{-11}	1.9×10^{-12}	6.8
BC5	68	2.5×10^{-10}	7.7×10^{-12}	2.8
BC6	35	2.7×10^{-10}	2.4×10^{-11}	2.7
BC7	68	2.4×10^{-10}	2.4×10^{-11}	2.5
BC8	68	7.7×10^{-10}	2.9×10^{-11}	2.2
BC9	85	1.2×10^{-11}	9.6×10^{-13}	4.5

Column Measurements

Strömberg and Banwart (1999) have provided a comprehensive description and analysis of studies undertaken on six large columns of Aitik waste rock. One of the objectives of the work was to quantify oxidation rates of the sulfidic material.

The six columns, labelled C1 to C6 contained three types of waste rock (two columns of each type) which had been collected from the open cut mine soon after blasting. The samples were characterised as biotite gneiss with some skarn minerals (Sample 1 in columns C5 and C6), gneiss with some mica schist (Sample 2 in C1 and C4) and mica schist with some gneiss (Sample 3 in C2 and C3).

Between 1450 kg and 1830 kg of sample were loaded into each column. Particles larger than 0.2 m were removed. The temperature of the columns was maintained between 4°C in winter and 10°C in summer by a water jacket. The columns, which had a diameter of 0.8 m, were irrigated with de-ionised water at a rate of 0.7 m year^{-1}. Oxygen was made freely available throughout the material by gently blowing air through the base of the columns. Pore gas sampling ports were installed at several depths in the columns to allow oxygen concentrations to be measured.

The moisture content in one of the columns was measured after 17 months of operation and was found to be 11 vol%, giving a residence time for water in the columns of around 14 weeks.

Oxidation rates were quantified by measuring the sulfate flux from the columns and also by periodically sealing the columns and determining the oxygen consumption rate. The columns were run for nearly 3½ years.

Figure 12 has been produced after Strömberg and Banwart (ibid.), using data supplied by them to the authors of this report.

A summary of the oxidation rate determinations are shown in Table 9. The table shows the pH of leachate at the start of measurements and at the end. Oxidation rates found by oxygen consumption measurements were averaged over all measurements made in each column. Oxidation rates from sulfate production rates were averaged over measurements made in the last five weeks of operation. It should be noted that during the course of the measurement period column C5 was artificially acidified after one year, bringing the final pH down to 3.4. The leachate from column C6 which contained the same type of material fell to a final pH of only 5.6.

Table 9. Oxidation rate of Aitik waste rock determined in columns by two different methods

Column No. (Sample No.)	pH start – pH finish	Oxidation Rate [kg(O_2) kg(material)$^{-1}$ s^{-1}]	
		by oxygen consumption	by sulfate production
C5 (1)	7.3 – 3.4	9.6×10^{-12}	1.0×10^{-11}
C6 (1)	7.5 – 5.6	6.1×10^{-12}	5.4×10^{-12}
C1 (2)	7.2 – 3.3	1.5×10^{-11}	2.4×10^{-11}
C4 (2)	7.5 – 7.1	2.4×10^{-12}	2.3×10^{-12}
C2 (3)	7.3 – 7.0	3.5×10^{-12}	1.6×10^{-12}
C3 (3)	7.6 – 6.9	4.9×10^{-12}	1.6×10^{-12}

It can be seen from Table 9 that there was good agreement between the two methods of determining oxidation rates. Strömberg and Banwart found that although columns C1, C5 and C6 were consistently at saturation with respect to gypsum, gypsum precipitation was small. The small amount of gypsum precipitation accords with the mineralogy of the material which showed that calcite was the only carbonate mineral and that it was present in only very low concentrations, about 0.1 % of the total.

Field Measurements

A total of 11 probe holes were installed in a full-sized waste rock dump at Aitik, distributed over an area of 150 m by 250 m. Pore gas oxygen concentration and temperature profiles were monitored in the probe holes over a period of more than two years. A description of some of the measurements and their interpretation can be found in Bennett et al (1992). One of the conclusions from the work was that around 85 % of the Aitik waste rock was either not oxidising or oxidising at a very low rate. Pore gas oxygen concentration measurements showed that levels were close to atmospheric throughout most of the 18 m thick dump, with only some regions showing significant oxygen consumption.

At only one location could the shape of the oxygen concentration profiles be analysed using the method based on Equation 4. Bennett et al. (1994) found that the oxidation rates at that location ranged from $(3.1 \pm 0.2) \times 10^{-9}$ kg(O_2) m^{-3} s^{-1} to $(4.3 \pm 0.3) \times 10^{-8}$ kg(O_2) m^{-3} s^{-1}, with an average of close to 1×10^{-8} kg(O_2) m^{-3} s^{-1}. The average rate is equivalent to 6×10^{-12} kg(O_2) kg(material)$^{-1}$ s^{-1}, taking a typical value for the bulk density of waste rock as 1,700 t m^{-3}.

Comparison of Oxidation Rates at Different Size Scales

It can be seen that the rates determined from measurements in a full-sized dump fall within the range of oxidation rates measured in the laboratory columns (Table 9).

In making the comparison between the column and field measurements it should be noted that the waste rock types used in the column were selected because they were expected to be generators of pollutants and were therefore not representative of the range of material types found in the waste rock dumps. It is for this reason that none of the columns contained material which oxidised at a very low rate, even though such material was observed from field measurements to make up over 80% of the dump

5 SUMMARY OF DATA COMPARISONS

One of the approaches taken in this work was to extract oxidation rates from databases of laboratory measurements, where the measurements had been made on tailings and waste rock and using humidity cells and columns.

From the International Kinetic Database it was found that the oxidation rates of the two types of materials were very similar and that it could be concluded that there was no systematic effect of particle size on oxidation rate.

The set of tailings data in the EGi database was similar to the IKD tailings set. The rates for waste rock, overburden and coal reject in the EGi database showed a greater proportion of results at the upper end of the distribution but there were significantly fewer results in the data set.

It is clear from the databases of measurements that the oxidation rate of sulfidic material can span four orders of magnitude.

Measurements on Duluth Complex material appeared to show that oxidation rates in test piles were only between 10% and 33% of the rates measured in columns. However, no account was taken in this study either of temperature effects on oxidation rates in the field compared with rates in the laboratory or of the likelihood of gypsum precipitation in the test piles. The lower average temperatures in the field could have resulted in lower oxidation rates in the piles and gypsum precipitation could have led to an underestimate of oxidation rates in the piles as measured by sulfate release rates.

In the Cinola work comparisons were made between measurements made in humidity cells and test piles in the field. There was very good agreement between oxidation rates of similar materials measured at the two size scales early in the respective measurement periods. Although the rates in the test piles varied over time, due to seasonal variations in water infiltration rates (which had to be estimated due to the lack of on site monitoring of rainfall or drainage flows) and possibly also to temperature variations, it appeared that the rate of decrease of oxidation rate in the humidity cells was faster than in the piles. The differences in the rate of change of oxidation rates became apparent about two years after the measurements had begun. We have proposed that the results could be due to differences in particle size distribution between the two systems.

The work at Red Mountain highlighted a number of difficulties in undertaking measurements at different size scales and in the field. Two size scales in the laboratory seemed to show agreement between oxidation rates to within an order of magnitude but secondary mineralisation was a problem in the larger scale columns, leading to an underestimate of rates in the larger ones. Consideration of the residence time of water in the larger columns however suggested that the agreement could have been much closer if the measurements had been continued for longer and if the water infiltration rate had been high enough to prevent gypsum precipitation. An attempt to measure the oxidation rate of 20 t samples in the field was not successful due to the very short period over which data was collected, the long residence time of water in the columns and the effect of seasonal temperature variations on the system. The objective of the work to address the issue of scale-up from the laboratory to the field could not be achieved due to this lack of data.

Site A provided the best data on the variation of oxidation rate with particle size distribution for three well-characterised materials. The oxidation rate of three particle size distributions were measured in laboratory columns and that of run-of-mine material was measured in test piles in the field. It was found that the greatest dependence of oxidation rate was on material type as characterised by static tests (net acid generation, net acid production potential and acid neutralising capacity) and that there was little or no dependence on particle size distribution. There were more variations over time in the data from the test piles than from the columns, due to variations in the rainfall rate at the field site. Unlike other test pile measurements described in this report, the ones made at Site A benefited from a high annual rainfall rate and a fairly constant temperature throughout the year. These were also the only test piles which were instrumented to enable pore gas oxygen concentrations to be monitored.

Measurements of oxidation rates in full-sized dumps at Site A showed a substantial overlap with rates seen in the column and test pile measurements. About one quarter of the measurements in the dumps were up to an order of magnitude greater than the other measurements. Because the material types were not known at the measurement locations in the dumps, it cannot be ascertained whether the higher values were associated with a different material type oxidising at higher rates than seen in the other measurements or whether there is a systematic error in the measurement technique which led to the over-estimation of oxidation rates in certain conditions.

Interpretation of the results from Site B column and full-sized dump measurements was difficult because of the statistical uncertainties associated with the small number of values in each case. No meaningful conclusions could be made.

The Aitik column measurements provided good data on the oxidation rates of three types of waste rock from the mine. There was good agreement between the two independent methods of measuring sulfate release rates and oxygen consumption rate. A measurement of oxidation rate at a location in a full-sized dump fell within the range spanned by the column measurements. There was however no information on the type of material in the dump at the measurement location.

6 DISCUSSION

This study has identified a number of issues which may affect the validity of the different measurement techniques used to obtain oxidation rates at different size scales. This section will address each of the issues with the aim of recommending how the measurements could be improved.

6.1 Oxygen Supply

An assumption which must be made in deducing oxidation rates from sulfate release rates from humidity cells, columns or test piles is that all of the material is free to oxidise. The assumption is likely to be valid in humidity cells and columns which are aerated by blowing air through the material. In test piles the validity of the assumption is questionable and should always be tested, since it is possible that the intrinsic oxidation rate of material is high enough that in a 3 or 4 metre high pile diffusion cannot supply oxygen to all parts of the pile. The same may be true of columns which are not aerated, depending on the oxidation rate of the material, the porosity, the degree of saturation and the distance over which oxygen must diffuse to reach all parts of the sample.

Of the cases studied here, only the test piles at Site A and the Aitik columns were instrumented to allow pore gas oxygen concentrations to be measured in the system. It is recommended that such instrumentation should be installed in all test piles and in some columns, depending on the conditions which were outlined in the previous paragraph.

6.2 Sulfate Release

As has already been stated several times, the determination of oxidation rates from sulfate release rates is based on the assumption that there is no significant loss of sulfate from the system. Whilst this assumption has been acknowledged in the case studies presented here, none of the workers, except at Site A, have attempted to quantify any loss of sulfate in their systems through precipitation. It is recommended that the question of sulfate loss should be addressed in any further work in which conditions make secondary mineralisation likely. Where sulfate precipitation is found to be significant, the method of measuring oxygen consumption rates in columns to determine oxidation rates should be employed.

An additional assumption used in this report that pyrite is the only sulfidic mineral contributing to the production of sulfate. Where there are other sulfides which are oxidising at a significant rate or there is dissolution of sulfate minerals, they need to be accounted for in relating sulfate release rate to oxidation rate.

6.3 Water Residence Time

Long water residence times in columns and test piles have the potential to make the interpretation of some measurements impossible. The water residence time needs to be short compared with the rate of change of conditions within the system being measured so that information on rates and trends can be obtained from sulfate fluxes in leachate.

The water residence time is also a factor in determining the length of time over which a measurement program needs to be conducted. Any change in the system, such as a change in irrigation rate, will take at least the residence time to propagate through the system and for sulfate fluxes in leachate to re-equilibrate.

If the water residence time is of the same order as, or is longer than, periodic variations in a system, such as in test piles which are subject to seasonal temperature and infiltration rate changes, the sulfate flux can never be in equilibrium with conditions in the whole system. In such cases therefore, sulfate fluxes cannot be used to quantify any time-dependence of periodic variations in oxidation rate which occur with a period less than the water residence time. The best that could be done would be to integrate sulfate loads over at least one residence time and estimate an average oxidation rate, assuming that sulfate precipitation is not significant during the period. This was the approach taken with the Duluth Complex test piles where there was a sufficiently long time series of data. In the Red Mountain field measurement program however, where the residence times were longer than one year, no useful information could be obtained on oxidation rates in the bulk samples because data were only collected for three months.

6.4 Particle Size

A conclusion which can be drawn from the results presented here is that particle size distribution is not a significant factor in determining the oxidation rate of particular material types over the one to two year time-scales for which the measurements were carried out. This was most clearly demonstrated in the results presented in Case 4 (see Figure 7 for example).

Davis and Ritchie (1987) have provided an explanation for this observation. They applied their model of oxidation of pyritic mine wastes to compare the effect of different descriptions of particle size distribution on sulfate production rate (among other parameters). They found that a realistic description of particle size distribution in a full-size dump was needed to describe behaviour in the long term. In the model the smaller the particle the higher the oxidation rate. In the earlier stages of dump evolution it is the oxidation of the smaller particles which dominate. As time passes however the smaller particles have fully oxidised and it is only larger particles which contribute to the (lower) oxidation rate in the longer term.

A consequence of the foregoing discussion is that for a given material, any measurement of oxidation rate will give approximately the same value at early times, irrespective of the upper cutoff diameter in the particle size distribution in the sample, due to the dominance of the contribution from the smallest particles. The Cinola Project results have provided supporting evidence. Both the humidity cells and test piles were initially oxidising at close to the same rate. In the humidity cells, where there was a small range of particle sizes in the samples, up to 2 mm diameter, it was found that the oxidation rates fell by about two orders of magnitude in 3 years (Figure 4). In the test piles containing run-of-mine material, however, the oxidation rates after 4 years were higher than seen in the humidity cells after 3 years (Figure 5), due to the continuing contribution of the larger particles in the piles.

It can be seen, therefore, that humidity cells provide a simple means of determining the maximum rate at which a particular material can oxidise. Because they contain only small particles, however, rates measured in humidity cells as a function of time cannot be taken to represent field behaviour.

Davis and Ritchie (1987) and Frostad (1999) measured the particle size distribution in two samples from run-of-mine waste rock. They found that greater than 90% of the mass was made up of particles less than 200 mm in diameter. Since the contribution to the overall oxidation rate by particles larger than 200 mm will be very low, even after hundreds of years (Davis and Ritchie 1987), and since the mass fraction of these particles is also low, it is reasonable to follow the example of Davis and Ritchie and exclude particles greater than 200 mm from consideration. As a consequence, laboratory measurements of the oxidation rate of samples containing a particle size distribution up to 200 mm can be taken to be representative of the oxidation rate of the material in full-sized dumps. The Aitik laboratory columns contained the appropriate particle size distribution. Although changes in oxidation rate over time measured in such columns can also be taken to be representative of field behaviour, the time-scales would be the same as in the field and are therefore of little practical interest.

There is clearly a need to run some experiments using columns containing particle size distributions up to 200 mm for long enough to determine the dependence of intrinsic oxidation rate on sulfide sulfur content as the particles oxidise. The resulting sets of data from such measurements on a range of material types should be used to test and, if necessary, modify the functional dependence of the intrinsic oxidation rate on sulfide sulfur content currently used in models which are to be applied to full-scale dumps.

6.5 Temperature

In comparing oxidation rates measured in the laboratory and the field, a source of difference can be differing temperatures in the two systems. Oxidation rates in the field may also vary due to seasonal temperature variations. In the discussion of the Duluth Complex data in Section 4.3.1, reference was made to the use of the Arrhenius equation to account for temperature differences, using activation energies measured in the laboratory for different sulfide minerals. An obvious assumption in this approach is that these activation energies can be applied to bulk materials. Whilst the assumption seems reasonable for fine grained materials, where the sulfides may be largely liberated from the host materials, it seems less reasonable for run-of-mine material.

In many situations, however, it may be judged that temperature differences or seasonal variations are small enough that their affect on oxidation rates may be neglected. If it can be demonstrated that there are circumstances where it is important to take more accurate account of the dependence of oxidation rate on temperature than is afforded by the current approach, it is recommended that a program of work be undertaken to establish the validity of the Arrhenius equation for bulk materials and to find more appropriate values of the activation energy of dominant sulfides.

6.6 Scale-Up

The term ‘scale-up’ can be used to describe measurements made at increasing scales of particle size. The measurements presented in this report have covered a wide range of particle size distributions, from samples containing particles less than 0.149 mm to run-of-mine samples. It has been shown that laboratory columns can be used to measure oxidation rates in material with particle sizes up to a diameter of around 0.2 m, as in the Aitik columns.

Fundamental questions must be asked however when test piles are constructed at mine sites with the stated aim of ‘scaling up’ from the laboratory to the field. The principal ones concern the quality of information which can be obtained from test piles and whether any information comes from test piles which could not be obtained from suitably-designed columns. The latter issue requires a clear statement of which particular parameters governing the oxidation of sulfidic wastes are to be assessed in such experiments.

In addition to oxidation rates, there are other parameters which need to be considered in describing the behaviour of full-scale test piles. Such parameters include acid consumption rates, rates of dissolution of acid consuming materials, and rates of formation and dissolution of secondary minerals. These too can be determined in well-designed laboratory experiments. In order to be able to develop models which can be reliably used to answer questions such as if and when effluent from a pile will become acidic and/or contain dissolved metals, how long these conditions will pertain and how piles can be constructed to control effluent composition, information needs to be know at length scales and timescales appropriate to full-sized dumps. Such information includes the spatial distribution of different material types in a dump and an adequate understanding of the hydrology of unsaturated waste rock. Whilst a further consideration of these issues is beyond the scope of this work, it is apparent that measurements need to be made on full-sized dumps to obtain the required information, rather than test piles.

It is not necessarily the case that test piles which are exposed to the weather behave in ways which are characteristic of full-sized dumps. This is because of the important length scales and time scales associated with oxidation in waste rock dumps. A discussion of these scales can be found in Ritchie (1994b), and a brief explanation is given below.

As an example of the relevance of length scales, a length scale associated with temperature variations is the depth in a waste rock dump to which seasonal temperature variations have an effect (Ritchie 1994c). This length has been shown to be around 7 to 10 m. Below this depth the temperature of a dump which is not oxidising will be constant and equal to the annual average temperature at the site, assuming there is no remnant heat at depth from previous oxidation (Bennett and Timms 1999). In a dump which is oxidising at depth, the temperature below 7 m will be determined by the heat source distribution in the dump. From the point of view of temperature then, a test pile which is of the order of 3 to 5 m high is only representative of the near surface layer of a waste rock dump.

Another length scale is associated with the transport of oxygen by diffusion. Depending on the intrinsic oxidation rate of the dump material, the depth to which oxygen can penetrate by diffusion in a newly-constructed dump could be of the order of a metre or tens of metres. This depth of oxygen penetration will determine the region in which the primary oxidation reaction products are generated at early times (typically years to tens of years). The chemical composition of leachate from the base of a dump in which the depth of oxidation is governed by the oxygen supply will depend also on the geochemical reactions between the pore water and the waste rock minerals below the oxidising zone, as the leachate percolates through the dump. Given the relatively small size of test piles, it is clear that the chemical composition of drainage from them will not be the same as from full-sized dumps.

Leachate composition from full-sized dumps will be determined by a combination of parameters which will vary in space and time. These parameters include:

- the acid generation rate in the oxidising material (which is governed by the intrinsic oxidation rate of the material and which has been found to vary over several orders of magnitude);
- the spatial distribution of oxidising material in the dump;
- the rate of neutralisation of the acid by gangue minerals (ranging from carbonates to silicates);
- the distribution of the acid consuming minerals in the dump;
- the evolution of oxidation in the dump as a function of space and time (for example, as described by Gibson et al. 1994)
- the time it takes to completely oxidise sulfidic materials in the dump (years to hundreds of years);
- the functional form of the intrinsic oxidation rate (which depends on temperature, oxygen concentration etc); and
- the hydrology of waste rock dumps, including infiltration, residence times and flow paths.

This list is far from comprehensive but serves to illustrate that a test pile cannot represent a full-sized dump any better than a column when it comes to predicting the chemical composition of effluent as a function of time or providing information such as the time for effluent from a dump to become acidic and the time over which pollutants will be generated.

The principal reason for operating test piles seems to be to provide additional data on the effect of particle size on oxidation rates, since this parameter is the only one which has actually been 'scaled up'. It has already been stated in Section 2.2 that it is only necessary to know oxidation rates to within an order of magnitude for key decisions to be made about the management of sulfidic wastes. The cases presented in this report have shown that there has been good agreement between oxidation rates measured in humidity cells, columns and test piles where measurements have been made using the same materials at different size scales. This was true of data from Case 2, the Cinola Project (compare Figures 4 and 5), and Case 4 (Figure 9). In Case 3, the Red Mountain Project, there was reasonable agreement at two size scales (Figure 6) and it could be expected that after some time, depending on the relative residence time of water in the different columns, the agreement between the rates would improve.

Test piles as a means of obtaining data have a number of disadvantages over laboratory columns, primarily due to lack of control over the test conditions. Whereas laboratory columns can be run at particular temperatures, irrigation rates and can be aerated, test piles are subject to climatic variations. If the oxidation rate is strongly dependent on temperature then the interpretation of data from test piles in regions where there is a large seasonal temperature swing becomes difficult. It has been seen how some test piles have remained frozen for half the year or more, or the water infiltration rate has been so low that the residence time for water in parts of the system can be longer than one year. Piles can be considered to be unconstrained columns, in which the geometry of the system adds further complication to the interpretation of data where oxygen supply by diffusion and water flow path lengths need to be taken into account.

On the basis of the foregoing discussion, no justification has been found for running test piles for determining oxidation rates. No evidence has been found that test piles provide any information on oxidation rates which cannot be measured in well-designed laboratory columns under controlled conditions.

7 SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

The conclusions made here are based on the available data. Few measurements had been made using the same material types across the scales being considered. Good data were particularly lacking at the field scale. One recommendation of the work reported here is that better experiments need to be designed and carried out to address issues of scale-up.

The primary objective of the work has been achieved, in that it can be concluded from the information presented in this report that laboratory-scale measurements of oxidation rates of sulfidic mine wastes have been shown to be sufficiently close to field measurements that the laboratory rates could be used with confidence in predictive models of full scale waste piles.

The validity of the previous conclusion has been found to be independent of particle size distribution in the materials measured, particularly where oxidation rates only need to be known to within an order of magnitude. In general, measurements of oxidation rate will produce the same results, irrespective of whether they are made according to standardised humidity cell procedures or in columns, as long as all the material is supplied with oxygen, the water infiltration rate is high enough to keep the water residence time reasonably short and there is not a significant loss of sulfate in the material through precipitation of secondary minerals. This is not to say, however, that particle size is not an important determinant of oxidation rate. The apparent insensitivity to particle size distribution is because the techniques are in effect measuring the maximum value of the intrinsic oxidation rate which is dominated by small particles. It needs to be stressed that the particle size distribution will affect the change in the intrinsic oxidation rate over time as sulfide is consumed, but none of the techniques described here set out to measured such a dependency.

Because humidity cells contain only small particles, they provide a useful means to measure the maximum oxidation rate of a particular material. However, in order to provide data on the time-dependent behaviour of oxidation rates which can be taken to be representative of the material in full-sized dumps, laboratory measurements need to be made on samples with a particle size distribution up to about 200 mm. Consequently, it is recommended that such a measurement program be run for long enough to determine the dependence of intrinsic oxidation rate on sulfide sulfur content as the particles oxidise. The resulting data should be used to test and, if necessary, modify the functional dependence of the intrinsic oxidation rate currently used in models which are to be applied to full-scale dumps.

The most significant shortcomings of the measurement procedures reported here were:

- the lack of recognition of the need to keep the residence time of water in a system short, compared with the expected rate of change of oxidation rate and associated processes (particularly seasonal changes), and
- the failure in most cases to quantify the likelihood of secondary mineralisation in a system and the effect that this may have on the interpretation of measurements.

An attempt has been made in this report to provide sufficient information on each of these matters to be of assistance in the design of any future measurement programs.

Early in the process of compiling data for use in this work, it became clear that there was a dearth of well-designed measurements which could be used to compare oxidation rates of materials at different size scales. Many previous programs have focussed on measuring the concentration of chemical species in effluent, without also recording the effluent flow rates which are also necessary to determine chemical fluxes. It is recommended that a minimum set of parameters to be measured in any laboratory or field test should include direct measurements of effluent flow and concentrations of sufficient chemical species to check for secondary mineralisation in the system.

It is recommended that measurement programs using large columns, test piles or full sized dumps include instrumentation to enable pore gas oxygen concentrations to be determined throughout the system. This information can be used either to assure that all the material is free to oxidise or to determine the region of the system which is oxidising.

If it can be demonstrated that there are circumstances where it is important to take more accurate account of the dependence of oxidation rate on temperature than is afforded by the current approach, it is recommended that a program of work be undertaken to establish the validity of the Arrhenius equation for bulk materials and to find more appropriate values of the activation energy of dominant sulfides.

In considering questions of scale-up, it has been concluded that test piles do not provide any information on oxidation rates which cannot be measured in well-designed laboratory columns under controlled conditions.

There should now be discussions between modellers, experimental scientists and the mining industry to ensure that the remaining scientific questions related to the management of sulfidic mine wastes are well-posed and that the required information is identified. Appropriate measurement programs should then be instigated to provide the information and supply data to enable predictive models to be tested.

8 ACKNOWLEDGEMENTS

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Figures

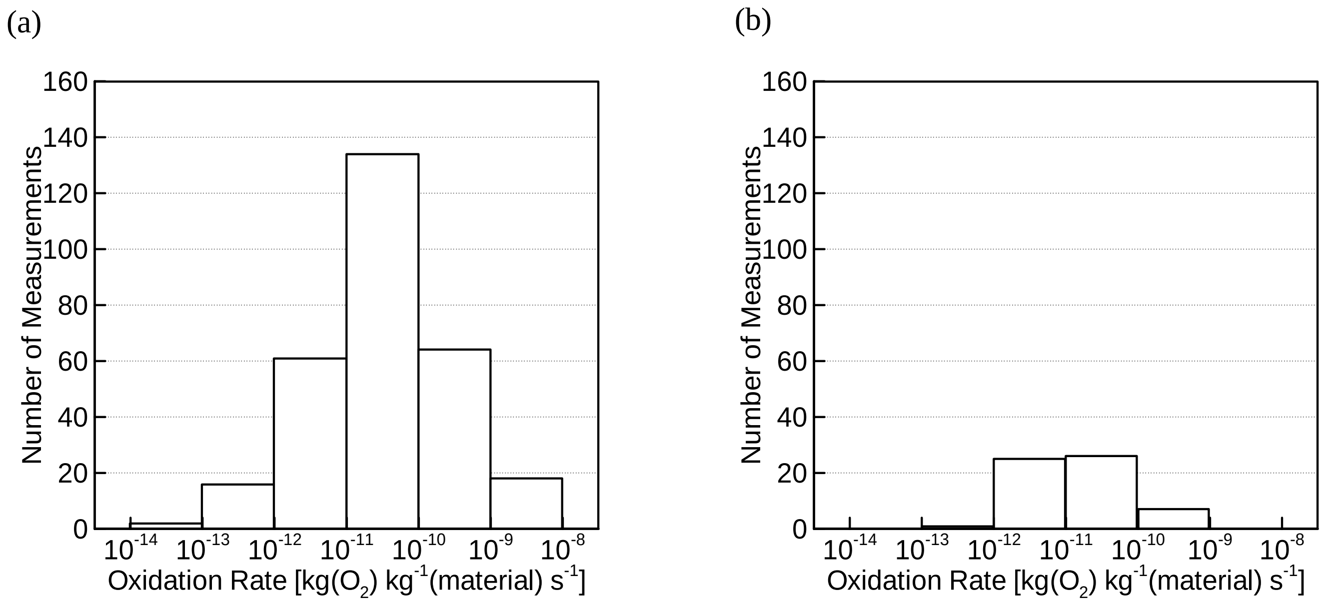

Figure 1 Oxidation rates measured in waste rock by (a) humidity cells and (b) columns. Data obtained from International Kinetic Database (Morin et al., 1995).

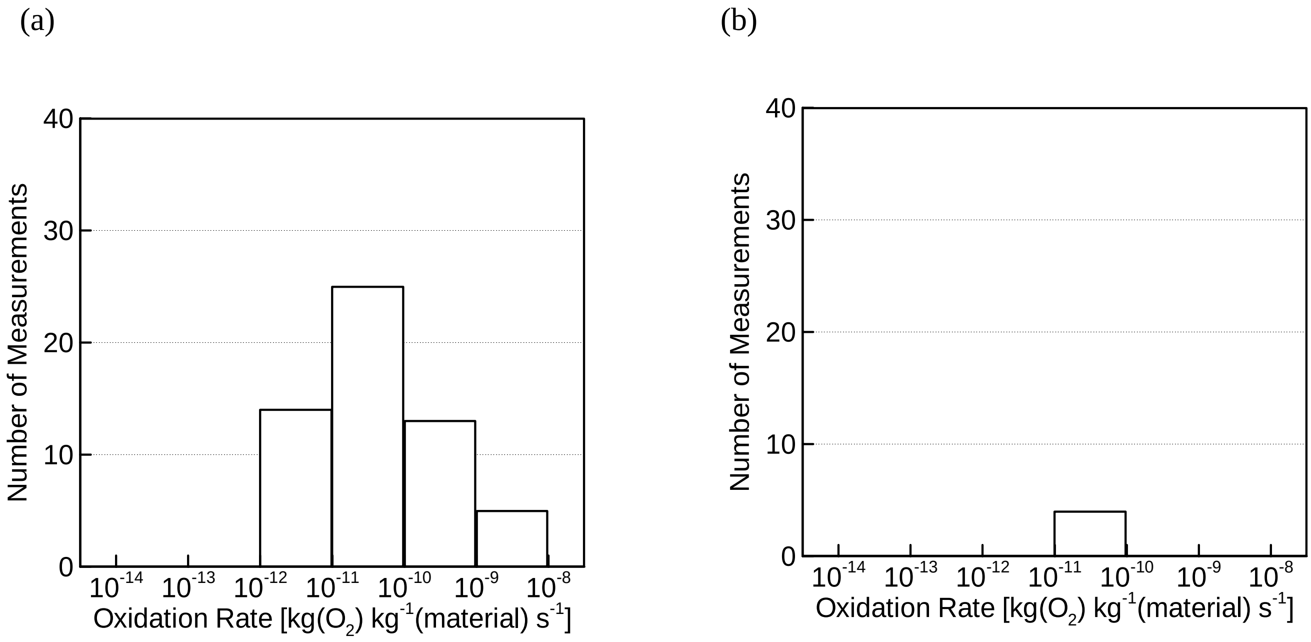

Figure 2 Oxidation rates measured in tailings by (a) humidity cells and (b) columns. Data obtained from the International Kinetic Database (Morin et al., 1995).

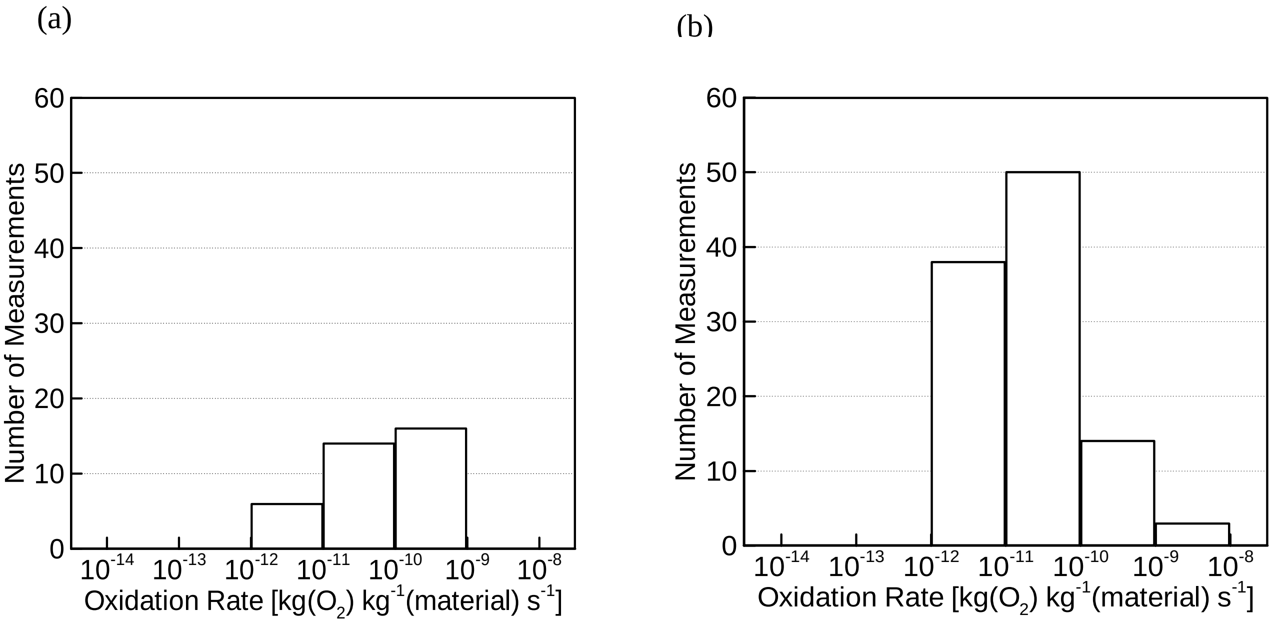

Figure 3 Oxidation rates measured by EGi in columns containing (a) tailings and (b) waste rock, overburden or coal reject.

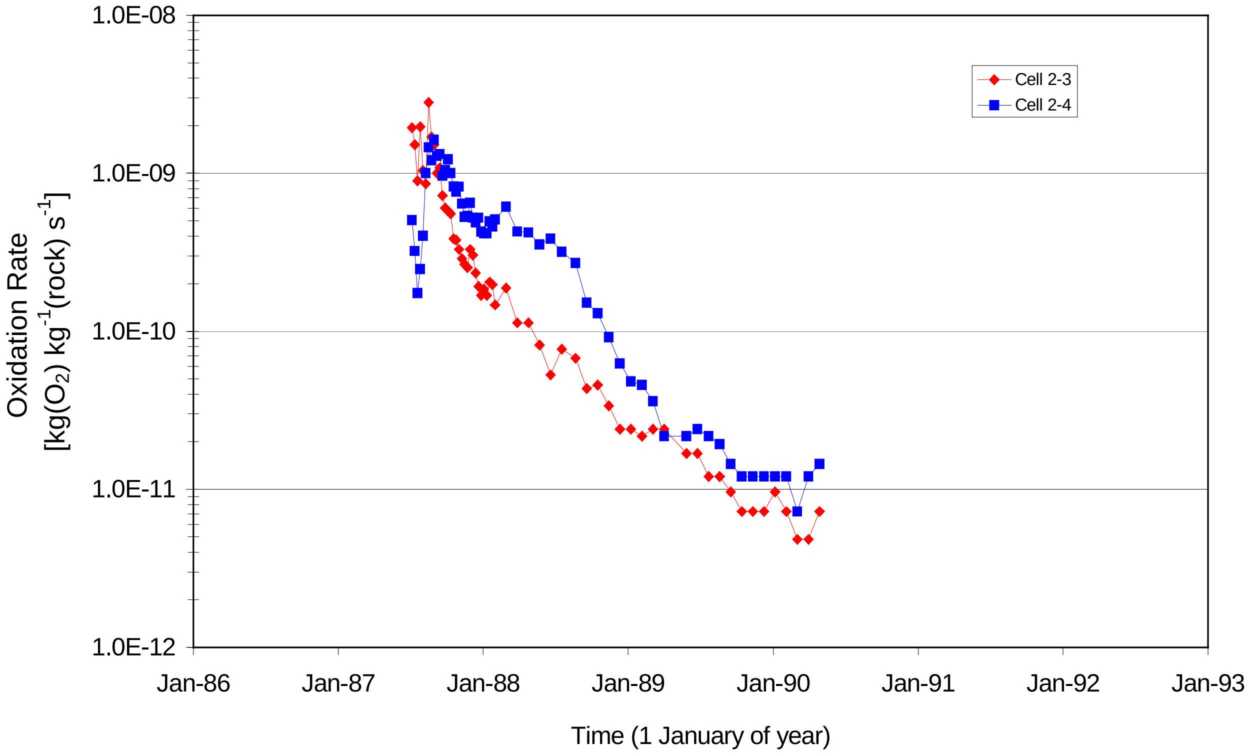

Figure 4 Estimated oxidation rates in Cinola Project humidity cells, derived from sulfate release rates.

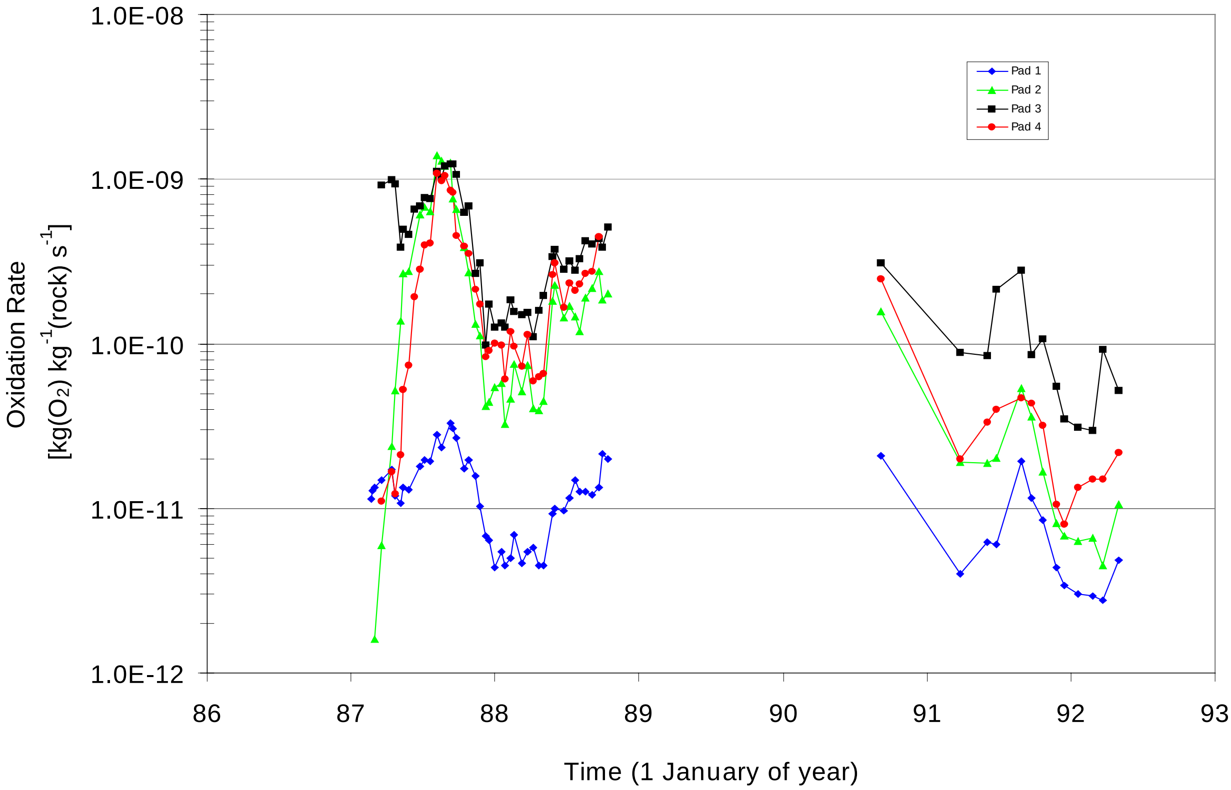

Figure 5 Estimated oxidation rates in Cinola Project waste rock pads, derived from sulfate release rates, assuming constant rainfall rate.

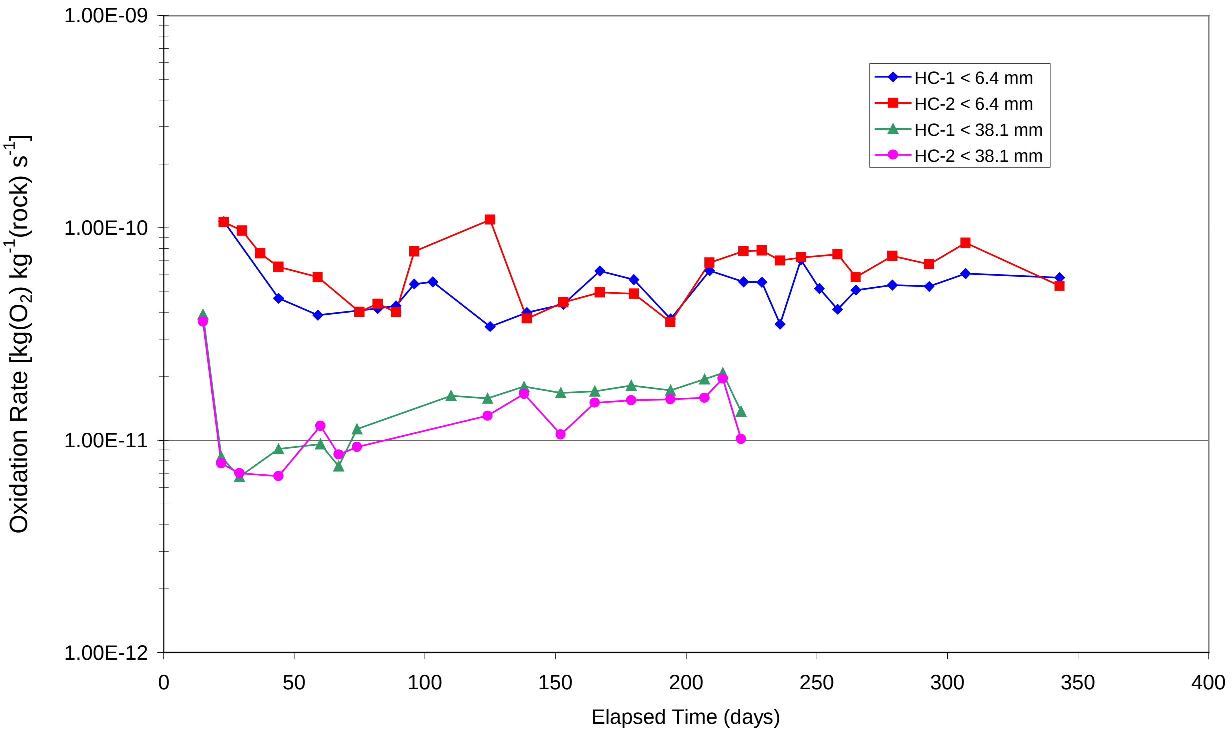

Figure 6 Estimated oxidation rates of Red Mountain Project rock types HC-1 and HC-2 in 1 kg humidity cells (particle size diameter < 6.4 mm) and 50 kg columns (particle size diameter < 38.1 mm).

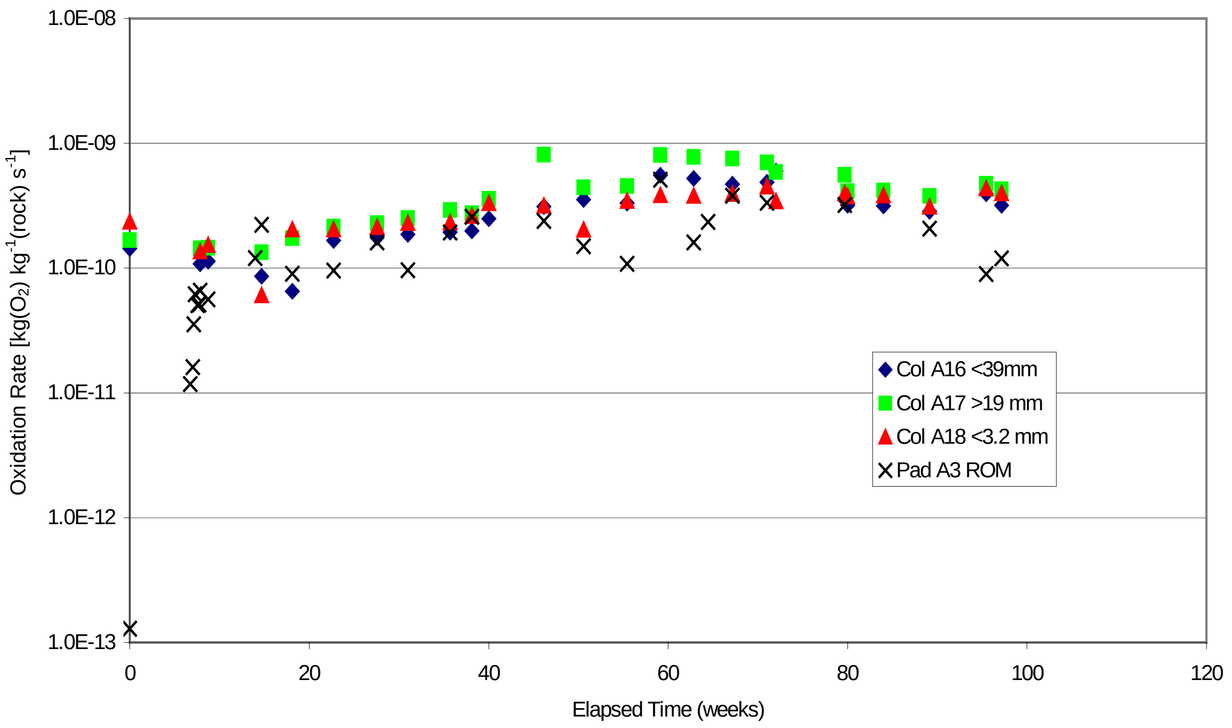

Figure 7 Oxidation rate versus time for PAF-HC material from Site A at different size scales in columns and a test pile.

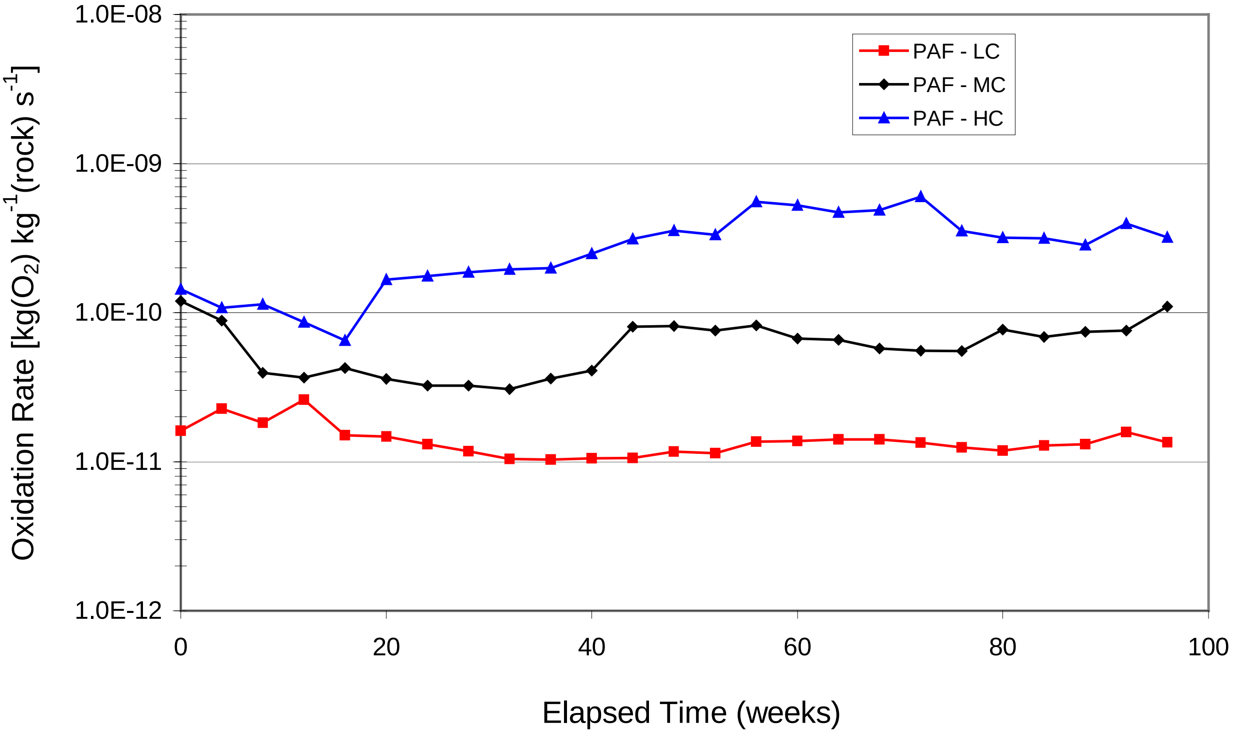

Figure 8 Oxidation rates in columns containing different material types from Site A, all with particle sizes < 39 mm diameter.

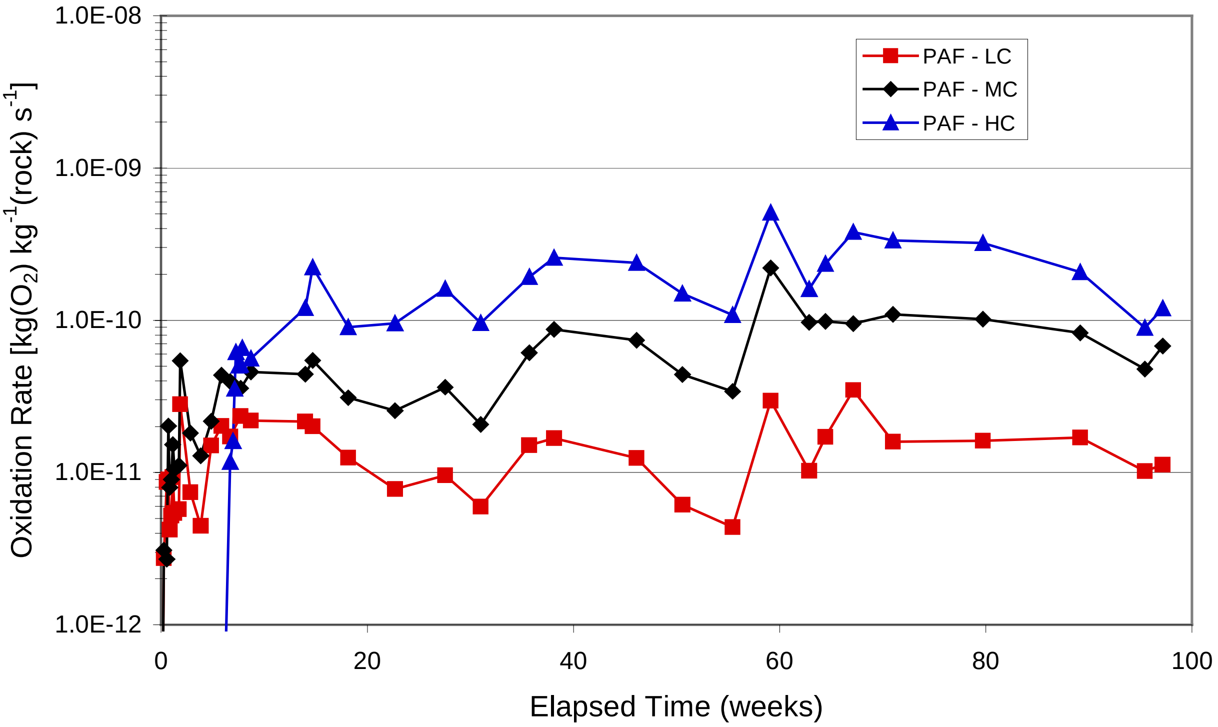

Figure 9 Oxidation rates in test piles containing different material types from Site A, all with run-of-mine material.

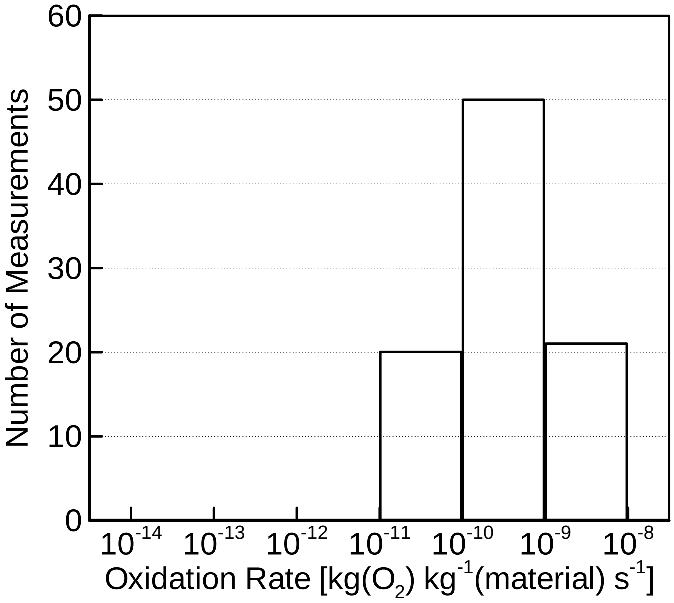

Figure 10 Oxidation rates determined from field measurements at Site A.

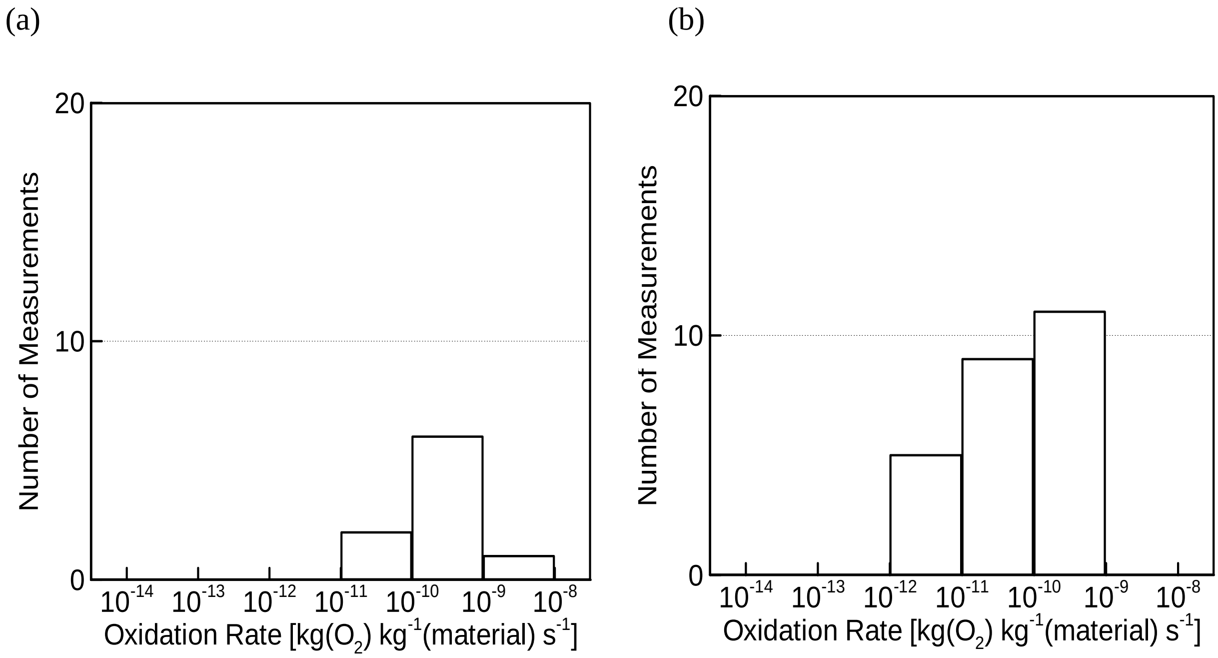

Figure 11. Oxidation rates of material from Site B measured (a) in columns and (b) in the field

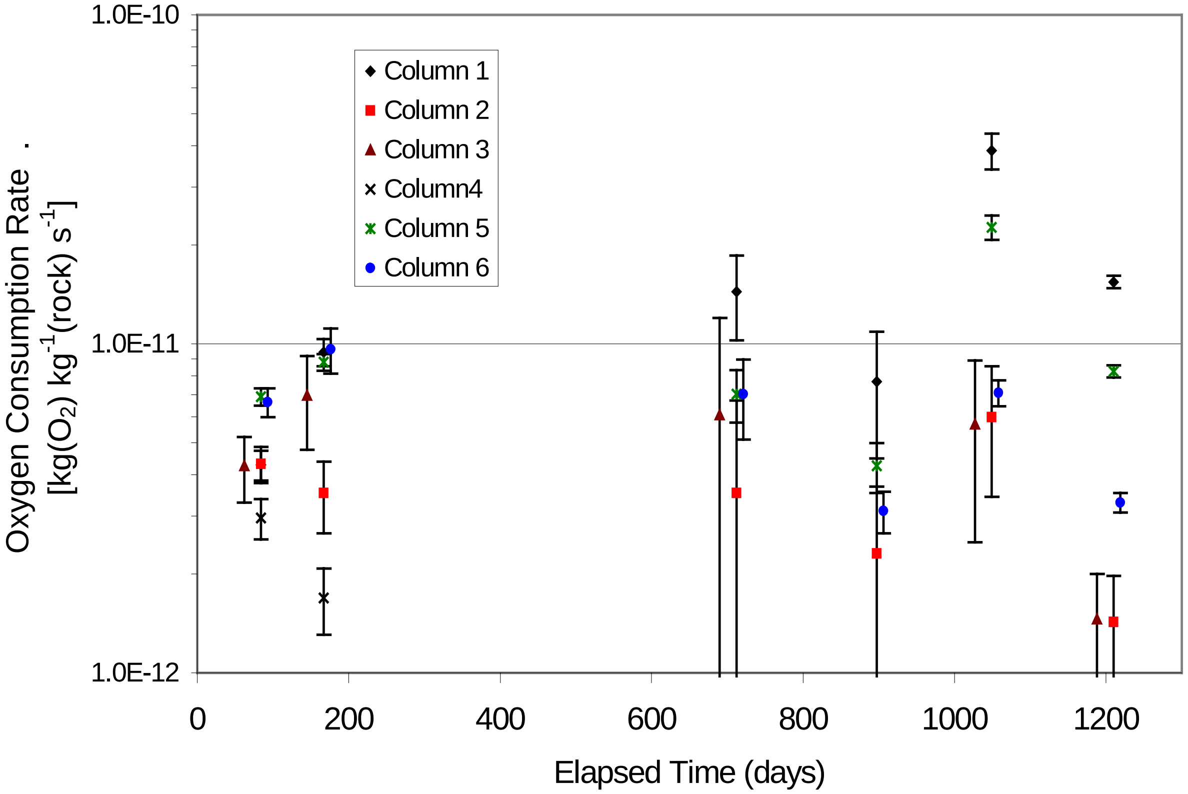

Figure 12 Oxygen consumption rates measured in columns of Aitik waste rock (after Strömberg and Banwart 1999).

Appendix A

PYRITE OXIDATION REACTIONS

Exposure of a pyritic materials to atmospheric conditions, either through excavation of the material or by lowering of the water table, provides greater pyrite-oxygen contact and produces a state in which the pyrite is thermodynamically unstable. When pyrite is exposed to the atmosphere it reacts with oxygen and water according to the following reaction:

$$FeS_2 + 7/2\,O_2 + H_2O \Rightarrow Fe^{2+} + 2\,H^{+} + 2\,SO_4^{2-} \qquad [A.1]$$

The initial products formed by the oxidation process are ferrous sulfate and sulfuric acid, however depending on the pH of the material, these products may be meta-stable and undergo further reaction. For example, in the presence of oxygen, ferrous iron is relatively unstable except under strongly acid conditions, and therefore its presence in solution tends to be transitory. Within an aerobic environment ferrous (+2) iron rapidly oxidises to the ferric (+3) state according to the following:

$$Fe^{2+} + 1/4\,O_2 + H^{+} \Leftrightarrow Fe^{3+} + 1/2\,H_2O \qquad [A.2]$$

Precipitates can also form as a result of secondary reactions. For example, if the material has a pH greater than 4, then ferric ions will tend to precipitate from solution as iron hydroxide, $Fe(OH)_3$. Such precipitates often form as coatings on rock surfaces. Precipitates containing sulfate may also occur under certain conditions. For example, jarosite $KFe_3(SO_4)_2(OH)_6$, is often found under low pH conditions whilst in pyritic materials with a high carbonate content, gypsum $CaSO_4.2H_2O$ commonly occurrs.

Whilst oxygen is an essential ingredient for the initiation of FeS_2 oxidation, once it becomes established, ferric iron may become the dominant oxidant reacting with FeS_2. The reaction describing ferric iron oxidation of FeS_2 is as follows:

$$FeS_2 + 14\,Fe^{3+} + 8\,H_2O \Rightarrow 15\,Fe^{2+} + 16\,H^{+} + 2\,SO_4^{2-} \qquad [A.3]$$

This does not mean that oxygen is no longer required, since ferric iron oxidation of FeS_2 can only continue as long as ferric iron is available. Thus, if reaction [A.3] is to continue, then the ferrous iron that is released from the FeS_2 must be oxidised back to the ferric state. This conversion of ferrous to ferric requires oxygen, as indicated by reaction [A.2].

The amount of oxygen required for pyrite oxidation can be estimated from the reactions described above. For example, from reaction [A.1] it can be estimated that the oxidation of one kg of sulfide occurring as pyrite consumes approximately 0.93 kg of oxygen (O_2). It can also be estimated that for every kg of O_2 consumed, approximately 1.7 kg of sulfate (SO_4) is formed.

It should be noted that not all sulfidic materials are necessarily acid generating, and some materials may need to be exposed to atmospheric conditions for a considerable time before acid conditions occur. The potential for acid conditions to form in a mine waste material depends on the balance between the materials capacity to generate acid via oxidation of sulfides and the inherent capacity to buffer or neutralise the acid as it is formed. The latter characteristic is commonly referred to as the acid neutralising capacity (ANC) and is usually due to the presence of carbonate minerals such as calcite, dolomite and magnesite. Clay minerals may also contribute to the ANC of a mine waste material, but clay minerals generally react at much slower rates than carbonate minerals and therefore may only become important in the longer term once the carbonate content is depleted.

Appendix B

EGi COLUMN LEACH TEST PROCEDURE

During the past 10 years, the column leach set-up and operational test procedures used by EGi have essentially remained the same. There have been some minor variations in the size of the columns to accommodate the particular geochemical and physical characteristics of the test materials, but such changes should not have significantly affected the rates of sulphide oxidation.

Typically, tests were run for a minimum of six-months, often for one year, and sometimes two or more years when there was a particular need to confirm the longer-term behaviour. In most cases the column leach tests were carried out as part of a larger geochemical testing program aimed at fully characterising the mine rock or tailings sample. In most cases, the purpose of the column leach tests was to obtain information on sulfide reactivity, oxidation kinetics and the leaching behaviour of the materials under real-time conditions.

The column configuration typically used by EGi is shown in Figure B.1. The typical column comprises a conventional plastic Buchner funnel with a total capacity of 2.5 litres and internal dimensions of 175 mm diameter and 100 mm height. These funnels typically hold between 2 and 2.5 kg of rock or tailings.

Some tests have also been carried out using larger scale columns, mainly when testing larger particle size material. They include larger Buchner funnels with a capacity of 6.4 litres (260 mm diameter and 120 mm height) which typically hold around 5 kg of rock or tailings, and plastic buckets with a capacity of 28 litre (300 mm diameter and 390 mm height) which typically hold around 35 kg of rock.

The columns are maintained within a temperature controlled laboratory. Each column is supported on wooden frame above a bench so that leachate can be collected in a plastic container located beneath the column outlet. A series of heat lamps are suspended above the columns to accelerate the drying process between waterings and thereby ensure that the samples within the column are exposed to atmospheric conditions for most of the time. These lamps operate on a 12 hours on, 12 hours off cycle. When the heat lamps are operating the temperature at the column surface is typically around 30 to 35 ^{o}C.

The columns are designed to be free-draining and operate on a four-week leach cycle. The aim of the leach cycle is to wet all of the mine rock or tailings within the column once a week and to thoroughly flush the sample once a month. To achieve this, deionised water is applied at a rate of 100 mL/kg of sample to the top of a column once a week for the first three weeks of a 4-week cycle. The water is applied slowly and on each watering occasion the surface of the tailings is initially reworked to remove any cracks that may have developed during the previous week of drying.

At the end of each 4-week period the weight of the column is recorded then the sample is flushed with deionised water at a rate of 400 mL/kg of sample. The sample is allowed to drain for a few days and when leachate flow has slowed, the volume of leachate collected over the four week period is recorded and the leachate sample retained for analysis. Typically, the volume of leachate collected during a four-week cycle is between 150 to 300 mL/kg of sample. The difference in the rates of water application and leaching is due to evaporation, which is promoted by the heat lamps suspended above the columns.

This leaching regime is not intended to simulate the rainfall and leaching conditions at the minesite from which the sample originates. Rather, it is intended to create a condition whereby the availability of water or atmospheric oxygen are not limiting for oxidation of sulfide minerals within the mine rock or tailings sample.

A sub-sample of leachate is analysed for pH, EC and alkalinity/acidity. The remaining leachate is filtered (< 0.45 µm) and acidified to pH < 2 prior to elemental scans being performed. Typically, leachates are analyses for sulphate, Ca, Mg, Fe, and Al. A selection of trace elements (e.g. heavy metals) may also be analysed depending on the composition of the material being tested and whether such elements are present in the solids at concentrations above average crustal abundance values.

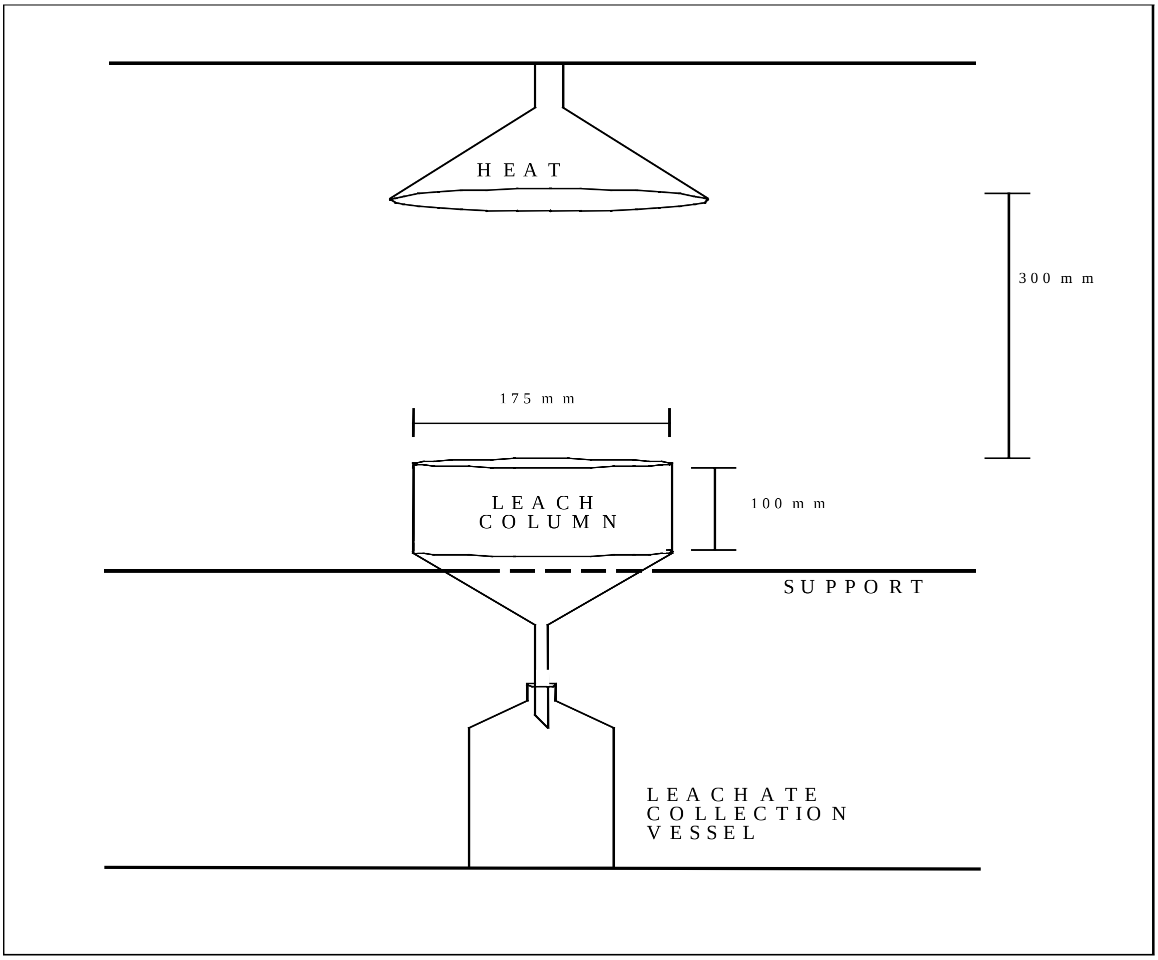

Figure B.1 Leach column configuration typically used by EGi.

Appendix C

SECONDARY MINERALS

Assuming that pyrite is the predominant sulfidic material, the oxidation rate can be determined by consideration of the overall pyrite oxidation reaction as given by the following equation

$$FeS_2 + \tfrac{7}{2}O_2 + H_2O \rightarrow FeSO_4 + H_2SO_4 \qquad \Delta H = -1440 kJmol^{-1} \qquad [C.1]$$

One approach to determine the pyritic oxidation rate is to measure the sulfate production rate and use the stoichiometry of the reaction to calculate the oxidation rate.

The sulfate production rate is estimated according to the following relationship:

$$\text{sulfate production rate (kg sulfate/kg waste/s)} = \frac{\text{sulfate concentration in leachate (kg/L)} \times \text{volume leachate collected (L)}}{\text{mass of waste (kg)} \times \text{leachate collection time (s)}} \qquad [C.2]$$

Based on the stoichiometry of the pyrite oxidation reaction [C.1]:

$$\text{oxygen consumption rate (kg oxygen/kg waste/s)} = 0.583 \times \text{sulfate production rate (kg sulfate/kg waste/s)} \qquad [C.3]$$

This method assumes that the sulfate leaching rate is equivalent to the production rate and also that sulfate is conservative in the system. The former assumption is likely to be true after any accumulated sulfates are flushed from the column during early times. The latter assumption can be checked by monitoring the concentration of major cations in the leachate. This information is used to assess whether secondary sulfate mineralisation (*e.g*. gypsum, jarosite) is likely to be occurring. Precipitation of secondary sulfate minerals within the column will generally lead to an underestimate of the intrinsic oxidation rate.

The formation of secondary minerals will depend on the mineralogy of the wastes, and on temperature, Eh, pH and solute contents of solutions associated with the wastes. Secondary minerals can form during weathering when solubility products are exceeded in the weathering solutions, so that states of mineral saturation or supersaturation are achieved. Precipitation can take place in response to a number of processes including oxidation, dilution, mixing, evaporation and neutralisation (Alpers et al., 1994).

Mineral precipitation or dissolution reactions relate ion activities and solid specific solubility products. For example, for the reaction

$$A_aB_{b(s)} \leftrightarrow aA_{(aq)} + bB_{(aq)} \qquad [C.4]$$

where the subscripts (s) and (aq) refer to solid and aqueous phases respectively, the thermodynamic solubility product for the solid A_aB_b is described by:

$$K_{sp} = [A]^a[B]^b/[A_aB_b] \qquad [C.5]$$

where K_{sp} is the solubility product for the solid described.

Geochemical speciation codes such as MINTEQA2 and PHREEQE can determine whether a mineral will precipitate, or dissolve, by calculating the minerals saturation index (S.I). The saturation index is calculated as follows:

$$\text{S.I.} = \log \text{I.A.P.} / K_{sp} \tag{C.6}$$

where I.A.P is the ion activity product determined from observed solution concentrations following the appropriate activity and speciation calculations, and K_{sp} is the theoretical solubility product adjusted to the observed water temperature. An S.I. less than zero indicates water undersaturated with respect to a mineral phase, an S.I. greater than zero indicates supersaturation and S.I. = 0 indicates equilibrium conditions. Equilibrium conditions with respect to an observed mineral phase suggest that precipitation or dissolution of that phase controls the dissolved concentrations of the components contained in that phase. For a multicomponent solution several minerals may be calculated to be supersaturated at one time. The geochemical speciation code is able to rank the minerals and determine which minera(s) is/are the most likely to precipitate.

For the case of pyrite, the complete oxidation of pyrite in weakly acidic to neutral systems (pH 4-7) can be written as:

$$FeS_2 + 3.75\, O_2 + 3.5\, H_2O \rightarrow Fe\,(OH)_3 + 2SO_4^{2-} + 4H^+ \tag{C.7}$$

In acidic weathering environments, iron-sulfate hydrate minerals can form instead of ferrihydrite [$Fe(OH)_3$]. Gypsum ($CaSO_4.2H_2O$), jarosite ($KFe_3(SO_4)_2(OH)_6$) and alunite ($KAl_3(SO_4)_2(OH)_6$) are possible sinks for sulfate, and it needs to be assessed whether these minerals exhibit solubility control on the effluent concentrations. This can be achieved by considering the saturation index. The extent of gypsum precipitation depends on factors such as water flow rate, which can maintain concentrations below saturation when the columns are rapidly flushed, the sulfide oxidation, which allows sulfate to build up in solution, and the availability of calcite or other calcium containing minerals, which provides Ca^{2+}. Jarosite and alunite can also form when the pore water is acidic and contains high concentrations of sulfate.

Examples 1 and 2 are leachate concentrations obtained from column testwork of a mine waste and mine tailings sample, respectively. To assess whether the precipitation of gypsum is likely to be occurring within the column, the ion activity product can be estimated for both leachate solutions, being the product of the calcium and sulfate concentrations. The solubility product for gypsum at 25 C is 2.5×10^{-5} $mol^2\, L^{-2}$.

Table C.1. Concentration of chemical species in leachate from two columns.

	Example 1	Example 2
pH	6.8	7.6
Na	2.3 mg/L	1.1 mg/L
K	0.9 mg/L	5.2 mg/L
Ca	20.4 mg/L	549 mg/L
Mg	4.6 mg/L	30.5 mg/L
SO_4	51.4 mg/L	649 mg/L

The calculated ion activity product for the leachate solution of Example 1 is 2.7×10^{-7} mol^2 L^{-2}, and therefore, the calculated saturation index is –1.97. Hence, this solution is undersaturated with respect to gypsum. Thus, the precipitation of gypsum in the column is unlikely. The calculated ion activity product for the leachate solution of Example 2, is 9.3×10^{-5} mol^2 L^{-2}, giving a saturated index of 0.57. In this case, the leachate sample is supersaturated with respect to gypsum. This implies that the precipitation of gypsum is likely to occur in the column.

Appendix D

EGI TEST PILE PROCEDURES

The test pile design used by EGi at a number of mine sites is a relatively large-scale pad (up to 500 tonne) which is suitable for investigation of run-of-mine (ROM) size waste rock or spoil materials. Test piles have been used to investigate 'scale-up' factors from laboratory based column tests. Additionally, test piles have been used to evaluate cover design and treatment options (such as material blending) for problematic waste materials.

A schematic plan view and cross-section of a typical test pile are shown on Figures D.1 and D.2, respectively. The pile shown is approximately 10m x 10m at the base and 3m high. Approximately 250 m^3 or 500 tonnes of material is required to load the pad. Run-of-mine (ROM) material can be used to construct the test pile but generally the >300 mm size is screened and excluded.

The base of the pad is lined with HDPE liner to isolate the pad from the underlying material. Berms are also constructed around the perimeter to direct all percolating water through to the water collection system. The leachate is directed from the base of the pad through a filter system and collected in an external container. Flow meters are placed on the inflow or outflow pipe of the collection vessel. Typically in high rainfall environments the flow meter is placed on the outlet pipe and in low rainfall environments the flow meter is placed on the inlet pipe. Leachate samples are taken from the collection vessel or outlet pipe and typically analysed for pH, EC, acidity or alkalinity, SO_4, Ca, Mg, Na, Mn, Fe, Al and selected other elements, as required.

Test piles, like the column and humidity cell tests, operate as a real-time test and therefore needs to be operated for a period of at least six months and possibly a number of years to provide sufficient information for field evaluation.

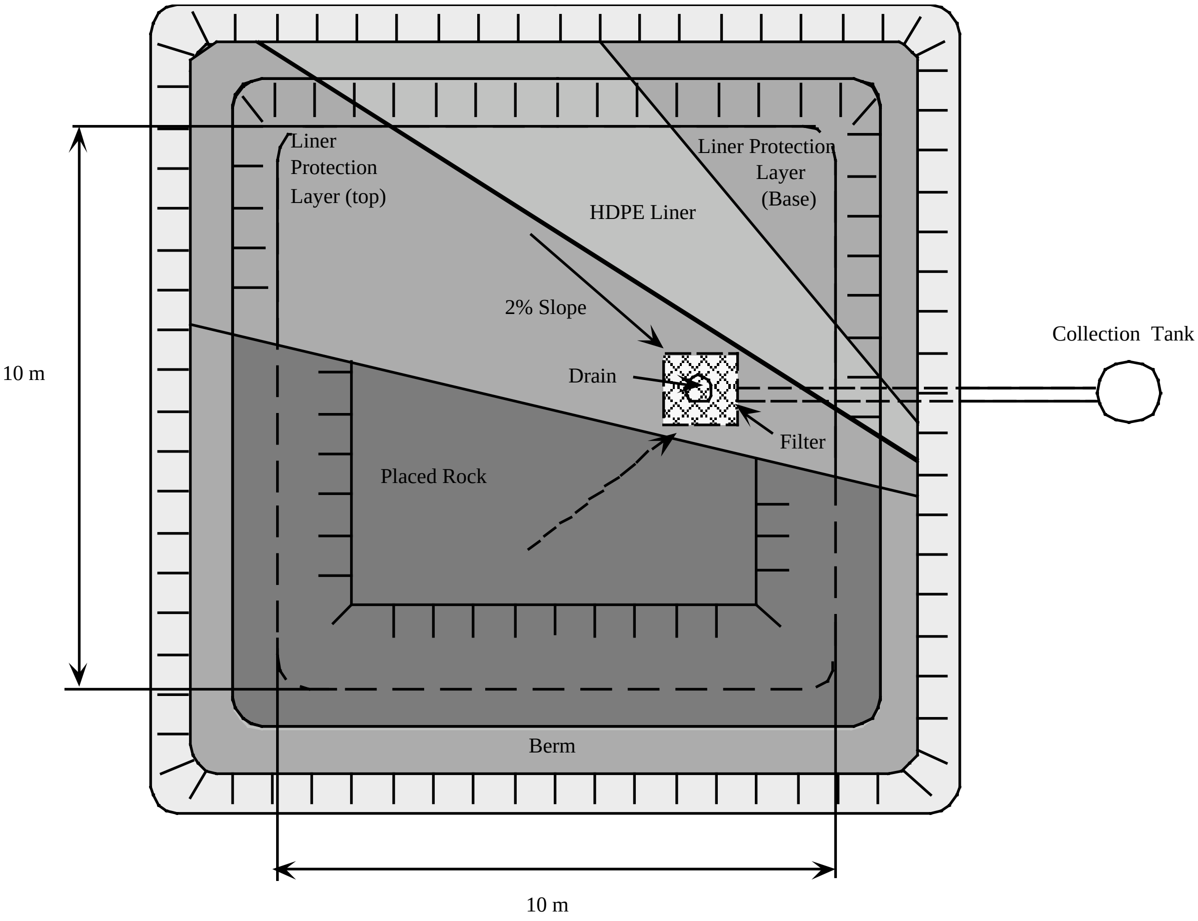

Figure D.1 Typical test pad design – plan view.

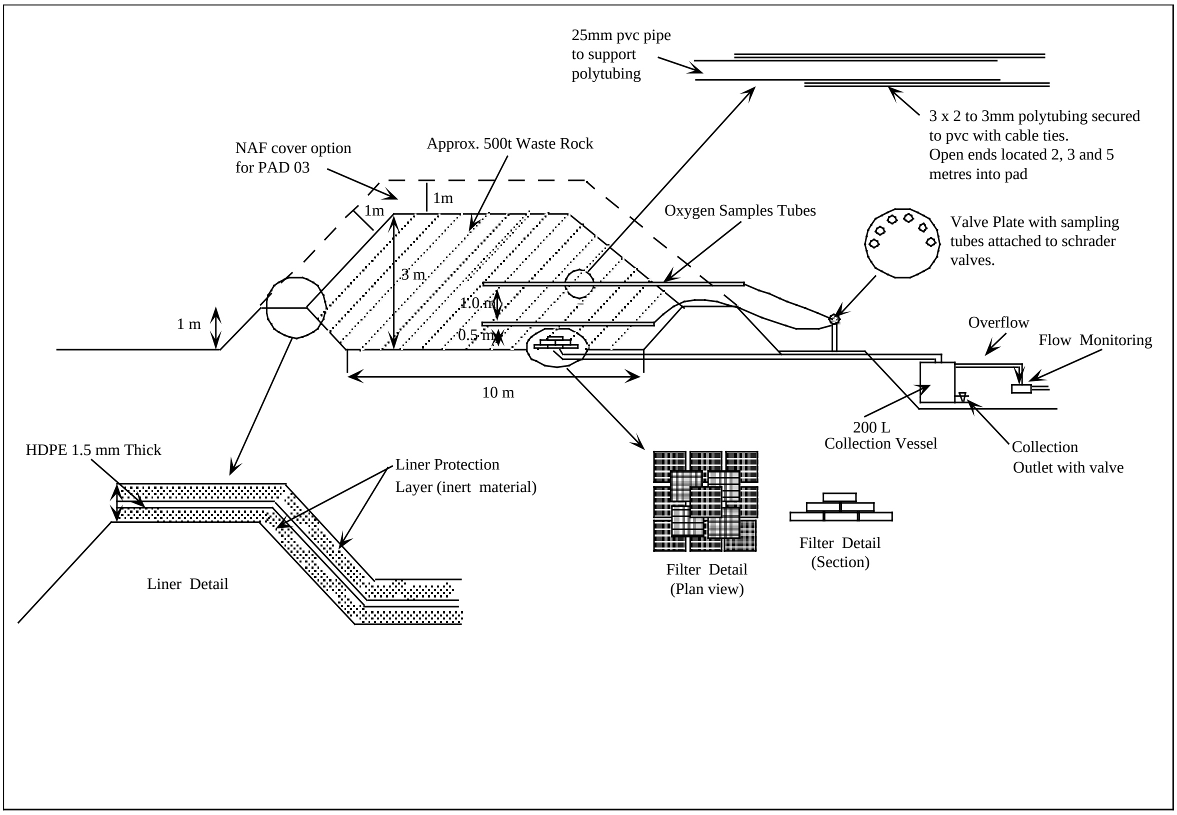

Figure D.2 Typical test pad design – cross section

Appendix E

ANSTO METHOD FOR DETERMINING OXIDATION RATES IN WASTE ROCK DUMPS

During the drilling of the probe holes, large volumes of compressed air are typically injected into the dump pore space. The oxygen concentration in pore gas along a liner has often been observed to decrease with time after a hole has been backfilled, leading to a steady profile usually being established within a couple of days. Oxygen concentration can decrease in this situation both by consumption of oxygen in sulfidic oxidation reactions and by diffusion of oxygen from the aerated region to the surrounding dump. The former mechanism dominates where the consumption rate is high.

Analysis of the rate of change in measured oxygen profiles allows estimates of the oxygen consumption rate to be made as a function of depth. These rates can be equated to the intrinsic oxidation rate (IOR) of the dump material under the conditions pertaining to the material at the time of measurement.

If two measurements of pore gas oxygen concentration are made at a particular depth, C1 and C2 (vol %), spanning time interval Δt (s), then the oxygen consumption rate in the vicinity of that depth can be approximately given by

$$\frac{0.162 \times \varepsilon_g \times (C_2 - C_1)}{20.95 \times \Delta t} \quad \text{kg(O}_2\text{) m}^{-3}\ \text{s}^{-1} \qquad \text{[E.1]}$$

where ε_g is the gas-filled porosity of the dump and the atmospheric oxygen density at standard temperature and pressure is 0.162 kg(O_2) m^{-3}.

It should be noted that because this expression is not rigorous, in that it does not take diffusion into account, values of oxygen consumption rate should be taken as indicative only. Further work needs to be undertaken to establish the range of conditions under which the technique provides a reliable measure of oxygen consumption rate.