Soil Gas Transport in Multiphase Materials for

Prediction of Acid Mine Drainage

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Abstract

To assess the economic viability of a proposed mining project, a cost estimate for its mine waste management systems is required, including design and operations of structures such as waste rock dumps, tailing storage facilities and any associated waste treatment systems. In orebodies with sulfide mineralisation, such as coal and base metals, accurate cost estimates are especially important due to the potential high costs of acid mine drainage (AMD) waste management during mine operations and possibly in perpetuity. AMD is generated when sulfides are exposed to oxygen and moisture and sulfide oxidation occurs, creating acid (H_2SO_4) which can mobilise metals and other toxicants into surface and groundwaters, potentially causing damage to downstream aquatic ecosystems. Currently AMD is assessed and managed using a variety of demand-side, geochemical based testing and modelling techniques, such as humidity cells and leaching columns, which are often expensive, lengthy and complex studies. Due to the limitations of these tests, and the large numbers of parameters involved in geochemical testing and modelling, the results can often still underestimate the effects of AMD, potentially resulting in harm to aquatic ecosystems. The use of a supply-side approach to AMD oxidation, such as oxygen consumption techniques, and soil gas (oxygen) transport, to estimate the potential effects of AMD for mine waste management purposes, has been identified as a useful method that may offer an additional methodology for AMD assessment for geochemical engineers and mine waste managers.

This research project seeks to contribute to a new methodology to mine waste management design for AMD mine materials, targeted at the mine design concept and prefeasibility phases. Its principle is based on the use of 1D or 2D soil gas (oxygen) transport models to provide an estimate of potential AMD mine waste volumes that may be oxidised and hence require stabilisation treatment. The soil gas transport models proposed provides for quick, practical and accurate volume assessments in waste rock dumps and waste tailing storage facilities. The proposed method combines lab testing to collect soil gas diffusion data for specific mine wastes, with soil gas transport modelling to test several soil gas diffusion models in 1D and 2D. Several configurations of soil gas diffusion columns were designed and tested over several iterations to provide fast (<3 hours) and economic soil gas diffusion

estimates. These columns are designed to be built from commonly available UVPC stormwater pipe materials for less than $500 USD. The method is scalable to any size of project and can provide accurate AMD estimations by collecting additional mine materials soil and rock data for i) soil water characteristic curves (SWCC), ii) soil gas diffusion testing, and iii) soil oxygen penetration column tests.

The thesis consists of 8 Chapters: Chapter 1 provides an overview of the problem and the research questions for this project. Chapter 2 presents a critical review of the available literature and Chapter 3 identifies the key knowledge gaps and summarises the research program objectives and work plan. The following three Chapters present results in the form of three journal Papers (two published, one under review) to document the research findings of the project.

Chapter 4 presents (Paper i) an introductory Paper to describe the potential pitfalls and impacts of the methodology used for geochemical based AMD mine materials testing and matrix particle size on conceptual mine waste treatment costs. Chapter 5 (Paper ii) presents a comparative assessment of the existing soil gas diffusion coefficient estimation models available in the literature and Chapter 6 (Paper iii) explains the development of a 1D soil gas transport model and testing methodology for AMD mine waste volume determination.

Chapter 7 details further development of the 1D model into a 2D finite difference model and demonstrates the additional accuracy of the 2D approach when applied to complex geometries such as sloped or cracked materials and mine waste structures such as tailing storage facilities and waste rock dumps. Chapter 8 presents the key findings and contributions from the research and identifies the key limitations of the work and future research directions.

The findings of Paper i highlight the potential for exponential levels of multiplicative error when undertaking geochemical based assessment of AMD materials for treatment and mine closure purposes alone. The use of soil gas diffusion transport models to assess AMD material volumes can potentially contribute to reducing this error by providing additional material volume estimations for comparison, with lower rates of experimental error. Soil gas diffusion testing and related soil gas

diffusion models can be compared and checked for potential error across soil and rock matrix types using literature-based diffusion testing results and matrix particle size analysis approaches.

The importance of measurement of soil gas diffusion coefficients and the derivation of soil moisture vs soil gas diffusion responses for use in soil gas transport modelling of AMD material response in the mining sector was demonstrated and discussed in Paper ii. Reliance on single material diffusion coefficients, or diffusion coefficient estimation models in the literature was found to be problematic, due to the agricultural basis for these models. The soil gas diffusion risks for agriculture are opposite to that of the mining sector, drying soils with high diffusion coefficients are a risk for mining, while wetting soils with low diffusion coefficients are a risk for agriculture and crop production, and all diffusion coefficient models found in the literature were based on agricultural risk profiles. All commercial soil gas transport models evaluated during the project were found to include either single value diffusion coefficient-based functions, or agriculture-based diffusion coefficient estimation functions.

A 1D soil gas diffusion model and methodology for assessing AMD impacted mine materials is presented in Paper iii. The Paper builds on the soil gas diffusion column method shown in Paper ii by adding an oxygen penetration column test to derive the boundary conditions required for the 1D model. The 1D model is used to evaluate the performance of several diffusion coefficient estimation models available in the literature. The discussion highlights the potential limitations and agricultural bias for several existing diffusion coefficient estimation models, analysis of possible dual diffusion functions based on soil matrix geometry and particle size and proposes the use of safety factors to ensure AMD material volume assessments are suitably conservative.

The development of a simple spreadsheet based, finite difference 2D soil gas transport model derived from the 1D model is documented in Chapter 7. The 2D model was designed to work with measured soil moisture/diffusion coefficient models, single value diffusion coefficients, or diffusion coefficient models from the literature. Statistical 2D model performance evaluation was undertaken, and the results demonstrate the additional capability of the 2D model to provide accurate volume

assessments of potentially AMD affected mine waste materials with complex geometries such as cracks and fractures, when using the soil gas diffusion transport method provided by this research project. The 2D model results again highlighted the importance of measurement of soil gas diffusion coefficient at several material moisture levels to provide a realistic soil gas diffusion model result for accurate geochemical and waste management design with AMD materials.

The overall conclusion of the research project is that the use of the proposed soil gas diffusion measurement and modelling methodology provides a potential fast, economic and more accurate alternative to the complex suite of geochemical assessment methods currently used to estimate the rate of sulfide oxidation. The method is useful for assessing concept and prefeasibility mine design estimates of volumes of AMD mine materials and waste potentially requiring treatment. Testing the AMD mine materials for soil gas diffusion behaviour at a range of moisture levels provides the most accurate results, as many diffusion coefficient models available in the literature may underestimate AMD oxidation. The soil gas diffusion method is presented with an accuracy hierarchy, and the use of safety factors is explored to replace diffusion testing if use of the complete soil diffusion and oxygen penetration testing method presented in this thesis is not possible.

When combined with detailed level geochemical assessments, the method offers a complimentary data source, suitable for detailed and final design of AMD waste management and treatment systems.

Declaration

This is to certify that:

i.   the thesis comprises only my original work towards the PhD except where indicated in the Preface,

ii.   acknowledgement has been made in the text to all other material used,

iii.   the thesis is fewer than 100 000 words in length, exclusive of tables, illustrations, references and appendices.

David Dettrick

8th July 2020

Preface

This thesis summarises the research I performed while working at the Department of Infrastructure Engineering at the University of Melbourne and Earth Systems Pty Ltd between 2016 and 2020. The research work was undertaken using both the support and resources of Infrastructure Engineering and in-kind support from Earth Systems. The research program and concepts referred to in Chapter 3 were originally conceived by myself with support from my supervisors Dr. Sam Yuen, Dr Justin Costelloe and Dr Meenakshi Arora. The issues of particle size, geochemical reactivity, soil matrix and potential errors in geochemical neutralisation of AMD materials presented in Chapter 4 (Paper i) arose from initial ideas and discussion with Nic Bourgeot during an oxygen penetration test series at Earth Systems. Soil gas diffusion column experiments were undertaken at the University of Melbourne and the Earth Systems laboratories and various iterations of diffusion column equipment design and manufacture was undertaken in my home workshop in Altona. This thesis is structured around three multi-author Papers that provide context and analysis for the independent research conducted to address the gaps in knowledge identified in chapter 2 of this thesis.

Chapter 4 (Paper i) of this thesis has been published in the Journal *Mine Water and Environment* as D. Dettrick, N. Bourgeot, J. Costelloe, S. Yuen, and M. Arora, "The Effect of Particle Size on Mine Waste Sulfide Oxidation Rates and Conceptual Treatment Costs", Mine Water and the Environment (3 Nov 2019) 38:735–745. Chapter 5 (Paper ii) was published in the *Journal of Environmental Management* on the 2nd of August 2019 as D. Dettrick, J. Costelloe, M. Arora and S. Yuen, "A comparison of measured and predicted diffusion coefficients applied to sand and silt sized acid mine drainage materials" Journal of Environmental Management 231 (2019) 1106–1116.

Chapter 6 (Paper iii) is currently in the review process at Engineers Australia Technical Journals (Australian Journal of Multi-disciplinary Engineering) as D. Dettrick, J. Costelloe, M. Arora, and S Yuen, "A 1D soil gas diffusion model for estimating oxidation rates of AMD mine materials", AJMDE: Australian Journal of Multi-Disciplinary Engineering.

In all of the publications, I undertook the equipment design and build, data collection, analysis, model development and was responsible for manuscript composition. My supervisors Dr. Sam Yuen, Dr Justin Costelloe and Dr Meenakshi Arora, all contributed to manuscript edits and concepts formation.

Acknowledgements

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List of Abbreviations and Definitions

Acronym or abbreviation	Meaning
1D	One -dimensional
2D	Two -dimensional
ADE	Advection-dispersion equation
AMD	Acid and Metalliferous Drainage -previously Acid Mine Drainage
ARD	Acid Rock Drainage -used in the USA and North America, equivalent to AMD
ASTM	American Society for Testing and Materials
BET	Brunauer-Emmett-Teller matrix surface area determination
BS	British Standard
C_g	Oxygen concentration in soil matrix at depth z
C_o	Atmospheric oxygen concentration
D_p	Diffusion coefficient of soil media "P"
D_o	Diffusion coefficient in free air
δ	Constrictivity – a soil matrix complexity fitting term for transport
demand side	Testing or modelling of AMD by-products e.g. leachate generation
ε	Air filled or effective porosity
FS	Safety factor or Factor of Safety
GMER	Geometric mean error ratio
GWT	Groundwater table, top of the saturated zone.
H	Henry's law constant
IP	Intellectual property
K_{rw}	Relative hydraulic conductivity for the unsaturated water phase in a soil matrix
L	Soil oxygen depletion depth
MD	Mean difference
θ_R	Residual soil moisture
θ_w	Saturated soil moisture
OPT	Oxygen penetration test
OxCon	ES Analytical Pty Ltd (2016) proprietary "Rapid Oxygen 122 Consumption Cell test (KT-01)"

Acronym or abbreviation	Meaning
$\varnothing$	Total porosity of soil media
PASS	Potential acid sulfate soils
PHREEQC	PH (pH), RE (redox), EQ (equilibrium), C (program written in C) -USGS Model
POR	Pyrite Oxidation Rate
PSD	Particle size distribution
QA	Quality assurance
QC	Quality control
R^2	Coefficient of variation
RMSE	Root mean square error
S	Relative soil moisture
supply side	Testing or modelling of conditions required for AMD processes to occur e.g. O_2 supply
SWCC	Soil Water Characteristic Curve
SWLR	Structure dependent water induced linear reduction model
τ	Tortuosity – a soil matrix complexity fitting term for transport
TOUGH2	Transport Of Unsaturated Groundwater and Heat -Lawrence Berkeley Model
TSF	Tailings storage facility
WRD	Waste rock dump
XRD	X-ray diffraction to determine material mineralogical content

1 Introduction

1.1 Background

The increasing regulatory and environmental focus on mine closure and waste management has required the development of new analysis techniques and methodologies for AMD risk assessment and management over the last 30 years. Previous standardised geochemical assessment methods had limitations which have often resulted in underestimates of predicted AMD materials reactivity, loads and volumes. Consequently, acidic water and associated dissolved metals, has reached groundwater and surface waters downstream of mining activities, causing harm to aquatic ecosystems (DITR 2016).

Currently, new kinetic AMD assessment methods, such as oxygen consumption-based techniques, and oxygen penetration techniques, measure oxygen consumption of AMD materials over time and offer more information on the rate of acidity production (Davis et al. 2014). These techniques offer potential new information, which when combined with accurate information on soil oxygen transport processes, forms the keys to management of AMD mine materials (Amos et al. 2014). Testing the effectiveness of the integration of oxygen consumption, supply and AMD reaction kinetics into existing soil and rock moisture models, is a first step towards developing a new generation of soil gas transport models designed to help predict AMD processes for geochemical stabilisation and geotechnical design purposes. Soil gas transport models will help with active AMD management during mine design, operations and closure by identifying potential volumes of AMD materials impacted based on the results of soil gas diffusion testing, for concept and prefeasibility design (Kuo and Ritchie 1999).

For the detailed mine design phase, the results of physical soil gas transport modelling can be combined and integrated with geochemical testing programs, to provide accurate and reliable measurements of affected mine material volume and reactivity. These are the two key parameters for geochemical stability and the required waste treatment systems capable of preventing AMD-based environmental impacts post-mining in perpetuity.

1.2 Research Questions and Directions

The overall aim of this thesis is to develop a methodology and associated technologies to support existing and derived soil gas transport models to simulate oxygen consumption of sulfide materials and that these models can be used to predict potential volumes of AMD mine waste requiring treatment at a concept or prefeasibility design level. When integrated with the results of standard AMD geochemical kinetic testing, or advanced kinetic testing, such as oxygen consumption techniques, the level of treatment design certainty is potentially increased to final, or detailed design level. The hypothesis is that relatively simple, 1D or 2D soil gas transport models, can be used to predict AMD risk based on the measured diffusion behaviour and soil matrix properties of complex AMD mine materials. This thesis will achieve this aim by answering the following questions:

- What are the limitations of current testing protocols for AMD mine materials and their potential effects on mine waste management and treatment cost estimation?
- Are the currently available soil gas transport diffusion models able to be used to accurately predict the volumes of AMD affected materials and hence increase the reliability of estimating AMD mine material volumes?
- What is the most effective/accurate soil gas transport-based methodology for estimation of AMD material volumes?

The overall research direction followed during the project is summarised below in Figure 1-1. The figure also shows the research decision framework, and the general location of the information within the thesis document Chapter by Chapter. The project included the development of economic soil gas diffusion testing apparatus and soil gas transport models. Geochemical models were investigated, but not included in the final scope of this thesis (see Appendix 2 below), as geochemical models were identified as additional complexity and cost without a contribution towards achieving the project modelling goals of simplicity and ease of use for AMD waste managers. This approach is discussed further in Chapter 3 below.

At a prefeasibility and concept mine design level, the key issue for mine waste management systems design, is the estimation of probable volumes of AMD waste materials generated during waste oxidation processes, and this can be evaluated with the soil gas (oxygen) transport models and methods presented in this thesis.
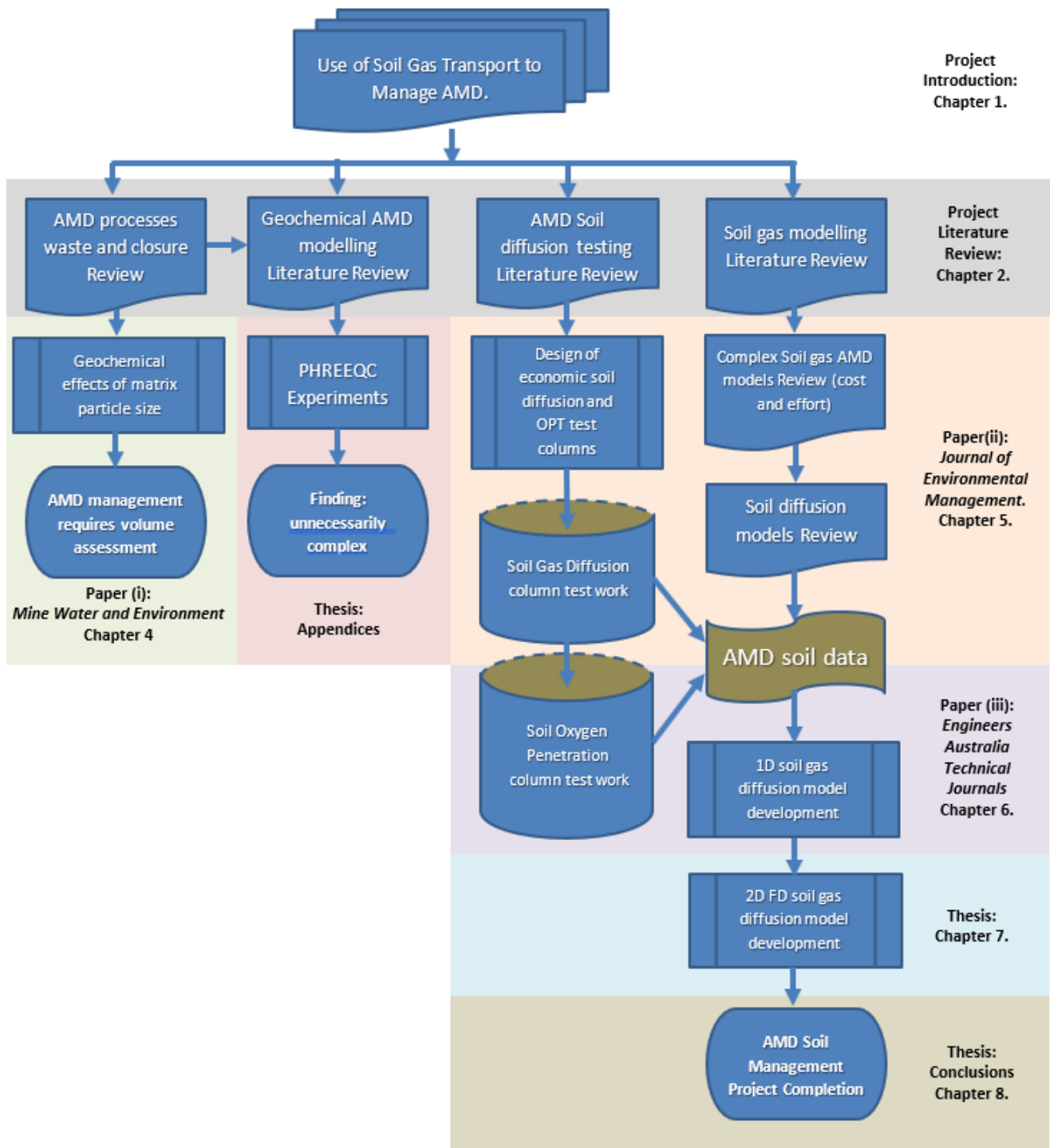
Figure 1-1: Overview of Research Project Directions, Decisions and Thesis Document Structure.

1.3 Thesis Organisation

The thesis document is structured as follows:

- Chapter 2 provides an overall project literature review and general background information on AMD process and conceptual models that demonstrate why soil gas (oxygen) transport is a key to not just the management of AMD but also the measurement of its rate of production. It also examines the key testing methods that are currently used to measure AMD potential in mine materials. The development of unsaturated zone modelling with respect to soil gas diffusion is then discussed with a short history of developments and foundational papers, building up to some recent developments in multiphase, multi-porosity and geochemical modelling. The potential for error, uncertainty, availability, and cost of available geochemical and multiphase models is presented, with a sensitivity analysis of two key currently available models. The Chapter then outlines the current knowledge gaps in the research topic identified by the literature review and the research questions proposed to be answered by this thesis.

- Chapter 3 outlines the general approach of the research project and links the identified knowledge gaps to the project objectives, equipment design, data collection and modelling approach. An overview of the research process and methods used to gather data required to answer the key research questions is provided.

- Chapter 4 is reproduced from Paper i titled "The Effect of Particle Size on Acid Mine Drainage Soils Sulfide Oxidation Rates" (Dettrick et al. 2019a). The Paper is a part of my PhD research work and was originally written by me. The co-authors are my work colleague Nic Bourgeot who assisted with provision of crushed AMD materials for testing purposes and my supervisors in this thesis who provided guidance during my research, J. Costelloe, S. Yuen, and Arora, M. The Paper evaluates the potential for soil matrix particle size effects to impact on AMD testing methodologies and likely

impacts on conceptual mine waste volume assessments and closure costs as AMD material neutralisation/geochemical stabilisation. The issues for potential multiplicative error are demonstrated in the exponential functions derived for AMD production based on geochemical testing methods. It is published in Mine Water and Environment Journal of International Mine Water Association in November 2019.

- Chapter 5 is reproduced from Paper ii titled "A Comparison of Measured and Predicted Diffusion in AMD Materials" (Dettrick et al. 2019b). The Paper is a part of my PhD research work and was originally written by me. The co-authors are my supervisors in this thesis who provided guidance during my research, Costelloe J.F., Arora, M, 2017, Yuen, S. Along with the comparison of measured and modelled diffusion coefficients, the Paper presents the design of an economic diffusion column design for under $500 USD, aimed at geochemical engineers in the mining sector. The Paper also demonstrates the importance of measuring soil gas diffusion response, rather than relying on diffusion coefficient estimation models currently available in the literature, using statistical error assessment of estimation models versus the measured diffusion methodology proposed in this thesis. The limitations and errors of diffusion coefficient estimation models are explored and an additional method of possibly using a safety factor to reduce risk is presented. This Paper was published in Journal of Environmental Management in January 2019.

- Chapter 6 is reproduced from Paper iii titled "A 1D soil gas diffusion model for estimating oxidation rates of AMD mine materials" The Paper is a part of my PhD research work and was originally written by me. The co-authors are my supervisors in this thesis who provided guidance during my research, Costelloe J.F., Arora, M, Yuen, S.. Along with the discussion of the 1D soil gas diffusion model development, this Chapter outlines the design of the oxygen penetration column, which was built for the project diffusion test program, to determine oxygen depletion boundary conditions. The overall proposed testing methodology and example AMD soil data for using soil gas diffusion to estimate volumes of mine materials potentially affected by AMD

oxidation processes is presented. The statistical performance of the 1D model is then evaluated using the proposed measured variable diffusion approach, a fixed diffusion coefficient approach, and several diffusion coefficient models from the literature. This Paper has been submitted to the Engineers Australia Technical Journal: Australian Journal of Multi-disciplinary Engineering and is under review at the time when this thesis is being examined.

- Chapter 7 Details the development of a 2D finite difference adaptation of the 1D soil gas diffusion model discussed in Chapter 6. Several 2D model results are presented and compared with discussion, further highlighting the need for soil gas diffusion testing on AMD mine materials to improve soil gas diffusion model accuracy for the assessment of AMD material volumes. An assessment of the improved accuracy of AMD material volume prediction when applying the 2D model to mine materials of wastes with complex geometries such as cracks, fractures and slopes is presented. The improved accuracy and simplicity of the derived 2D finite difference soil gas diffusion model when used with the methods proposed in this study are highlighted.

- Chapter 8 provides a project summary, key contributions and conclusion to the thesis. Additional areas of potential further research and limitations of this research are highlighted to help progression in the field.

- Appendices 1 and 2: additional project data including; design information for the economic diffusion column designed and built for the project diffusion test program, physical and chemical data for the test soils, PHREEQC code developed for the project examining the potential effects of AMD reactions with air/soil gas, and AMD particle surfaces. The Appendices also contain an outline the methodologies developed and required to obtained relevant data for soil gas transport analysis that is not described in the Papers. The methods include soil properties such as soil water characteristic determination, standard porosity and bulk density tests, measurement and calculation of effective air-filled porosity, the plans and testing methods for the new cost-effective diffusion column and advection column design and constructed as part of this research

project. Oxygen consumption techniques and Oxygen penetration testing (OPT) techniques are summarised and data from these tests is collected from representative projects with target soil characteristics identified as desirable for the development of soil gas transport models.

1.4 References

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Davis, B., Bourgeot N, Taylor, J., (2014), "Using Kinetic Geochemical Testwork to Assist with Mine Planning, Operations and Post Closure", in Proceedings of the Eighth Australian Workshop on Acid and Metalliferous Drainage (Eds H Miller and L Preuss) pp.281-294.

Dettrick. D, Bourgeot, N, Costelloe, J., Arora, M., and Yuen, S., 2019a, "The Effect of Particle Size on Mine Waste Sulfide Oxidation Rates and Conceptual Treatment Costs", Mine Water and the Environment, 38:735–745. This is referenced as paper i in this thesis, and forms Chapter 4.

Dettrick, D, Costello, J., Arora, M., Yuen, S., 2019b, "A Comparison of Measured and Predicted Diffusion Coefficients Applied to Sand and Silt sized AMD Materials", in Journal of Environmental Management, Vol 231, pp1106-1116, Elsevier, Amsterdam. This is referenced as paper ii in this thesis, and forms Chapter 5.

Dettrick. D, Costelloe, J., Arora, M., and Yuen, S. in review, expected 2020, "A 1D soil gas diffusion model for estimating oxidation rates of AMD mine materials", Engineers Australia Technical Journals, AJMDE: Australian Journal of Multi-Disciplinary Engineering. This is referenced as paper iii in this thesis, and forms Chapter 6.

DITR 2016, Preventing Acid and Metalliferous Drainage - Leading Practice Sustainable Development Program for the Mining Industry, Department of Industry, Science, Energy and Resources, Australian Government, Canberra.

Kuo, E.Y., Ritchie, A.I.M., 1999, Enhanced Oxygen Transport by Convection in Sulfidic Rock Piles: The influence of the form of the Sulfide Oxidation Rate. Mine Water and Environment, IMWA Proceedings, p455-460.

2 Literature Review

2.1 General Background to the problem of Acid Mine Drainage

Sulfide minerals are present throughout the earth's crust and are often encountered during the process of mining or excavation of soils and rock containing sulfidic materials (DITR 2007). Sulfur ranks 14th in Earth crustal abundance terms at 0.052% making it a reasonably abundant element for environmental chemistry (Manahan 2005). Some common sulfide minerals include pyrite FeS_2, pyrrhotite FeS, marcasite FeS_2, chalcopyrite $CuFeS_2$ and arsenopyrite $FeAsS$ and these minerals are likely to be present at coal, quarry, and mineral mine sites in varying amounts (DITR 2007).

Due to the reactivity of sulfide with oxygen, materials containing sulfide have generally had little contact with oxygen, by being located under the groundwater table, or contained within oxygen and water inhibiting layers, such as clays and non-fractured rock. The location of the sulfide material can be quite shallow, such as with sulfides found in mangrove swamps, so long as the natural process of sulfide oxidation by the earth's atmosphere has been inhibited. Along with sulfide minerals formed from vulcanism and other geological processes, potentially acid sulfate soils (PASS) are often found in areas subject to long periods of inundation with seawater, or saline groundwater, which is common in Australia. Sulfate ions contained in saline water are converted to sulfides by anaerobic bacterial action in the presence of organic material, such as in many marine mangrove swamps, and freshwater wetlands (EA 1997).

The primary environmental impact associated with exposed sulfidic materials arises as a result of oxidation which can be of both chemical and biochemical (assisted by bacteria) origin. Acid and metalliferous drainage (AMD) may result from the oxidation of sulfide after the exposure to oxygen and water. AMD is particularly problematic when rapid oxidation of sulfide materials occurs (DITR 2016, Ferguson and Erickson 1988) over large areas and there is sufficient contact with oxygen to allow AMD chemical reactions to complete.

Many historic or legacy mines have not been designed for geochemical stability and generate AMD. The AMD/PASS oxidation process has two main by-products that can impact the environment:

i) Acidity, via acid drainage which may dissolve and release toxic metals into sensitive surface and groundwater ecosystems; and

ii) Sulfate, via neutral drainage (ND) processes which may elevate the salinity of freshwater, causing toxicity to many freshwater ecosystem species (DITR 2007).

Additionally, in anaerobic conditions with sufficient organic carbon and microbial action, discharged sulfate can reduce to toxic hydrogen sulfide, particularly in sediments, or potentially trigger eutrophication by phosphorus in sediments when ferric hydroxide converts to iron sulfide phases (LDSDP 2016).

AMD/PASS impacts on the built environment include:

i) Acidic erosion of subsurface layers and subsidence leading to structural damage to roads, bridges and buildings; and

ii) Acid corrosion of metal and concrete, bricks and mortar, buried metal and concrete pipes (DOE 2014).

A conceptual model for mine pit AMD production during operation and closure has been developed by INAP (2009) and is shown below in Figure 2-1.
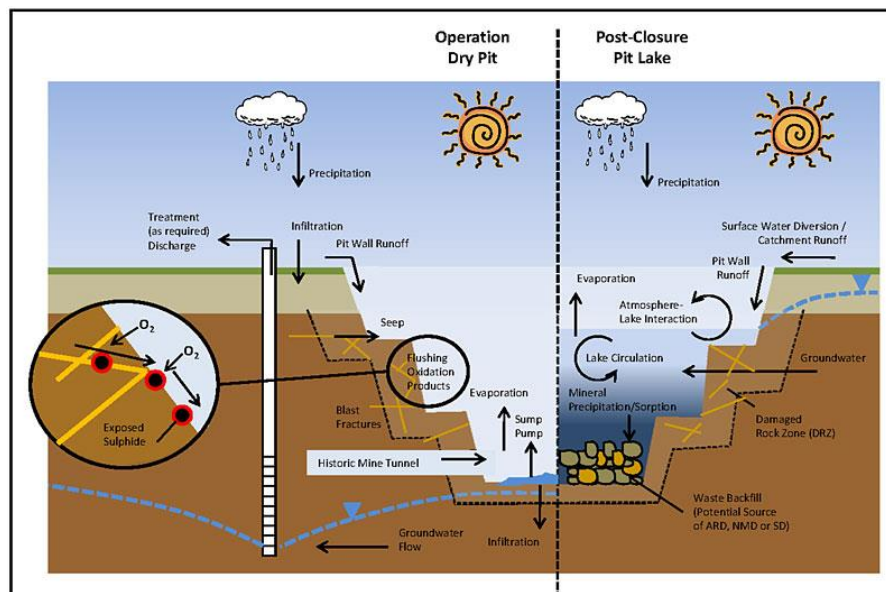
Figure 2-1: Conceptual Model of AMD in a dry and wet mine pit, including influence of oxygen supply through fractures and sulfidic material (from INAP, 2009).

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In the conceptual mine pit model, the importance of oxygen supply to the sulfidic materials is shown for both surface and unsaturated zone materials, in particular, the influence and effects of fracture and seam flow of air (oxygen) and water is emphasised. During operations groundwater seepage into the pit, and rainfall washing the pit walls, are some of the key sources of water that will be affected by AMD acidification processes. Oxygen supply will be approaching zero in saturated groundwater conditions, but soil gas (oxygen) transport may take place in the unsaturated zone above the groundwater table, contributing to AMD conditions in large zones based on seasonal groundwater level changes. During closure, pit lakes are often formed in mine pits and pit wall runoff can produce AMD by-products (INAP 2009). This is particularly concerning as large volumes of low pH pit lake water constitutes an environmental hazard if released, or if contacted by wildlife, stock or people. The low pH water is expensive to treat and difficult to dispose of due to the creation of salinity during the acid neutralisation process. Large pit lakes comprised of low PH water can effectively prevent the resource from being re-mined in the future when extraction technologies are likely to have improved. This is referred to as resource sterilization in the mining sector, as the high cost of treating low pH water prevents the mining project from being profitable (DITR 2016).

2.1.1 Global Environmental Problem

AMD is a legacy problem affecting abandoned mine sites, and PASS affects development sites, such as reclaimed mangroves swamps, urban areas and new mines. The extent of these problems are in part related to the large amount of sulfidic material contained within the earth's crust as discussed above, which can potentially affect many projects, from coal mines, to mining of sulfidic ores, to land development via reclamation.

PASS sites are considered to exist in Australia (and probably globally) at sites lower in elevation than 5 m AHD (DOE 2014). CSIRO (1999) estimate 30,000 km^2 of PASS soil exists in Australia alone.

AMD legacy mine sites that are no longer operational, are emitting acidity but closed before the development of modern environmental standards, have affected large areas of rivers globally, with

more than 20,000 km in the USA from previous and ongoing coal mining operations. Some global statistics on AMD include:

- Australia has an estimated legacy AMD repair bill of $1-3 billion AUD and approximately 50 mine sites actively managing high level AMD risks, with another 50 -70 mine sites managing lower level AMD risks (SSD 1997).

- The annual costs of AMD management at operating sites in Australia have been estimated as US$100 million (DITR 2016).

- Canada has an estimated AMD damage bill of $2-5 billion CAD (MEND 2014).

- USA has between 20,000 and 50,000 legacy mines currently generating AMD, with around 20,000 km of streams and rivers affected (Skousen et al 2018). Acid mobilisation of metals arsenic, cadmium, copper, silver and zinc is of greater concern than the acidity itself in the aquatic ecosystem. The total liability is estimated to be $20 billion USD (US EPA 1994).

- The Coal Authority (2019) in the UK has an annual budget of £80 million for AMD legacy projects and prevents over 4000 tonnes per annum of AMD derived iron floc entering watercourses and operates more than 68 mine water treatment schemes to prevent acidity and mobilisation of metals.

- Former East Germany uranium/coal mines have an estimated AMD liability of €7 billion Euros, and 50% of an existing 219 lignite mine pit lakes have a pH of less than 4 (Geller et al. 1998).

- Heavy metal pollution from rock and soil minerals dissolved by AMD is the biggest environmental issue in the mining sector, with impacts predicted to continue for more than 2000 years into the future if left unmitigated. The worldwide economic impact of AMD is considered to be greater than $10 billion USD (Taylor 2012).

Example pathways for AMD to enter the environment from tailings waste are shown below on Figure 2-2.
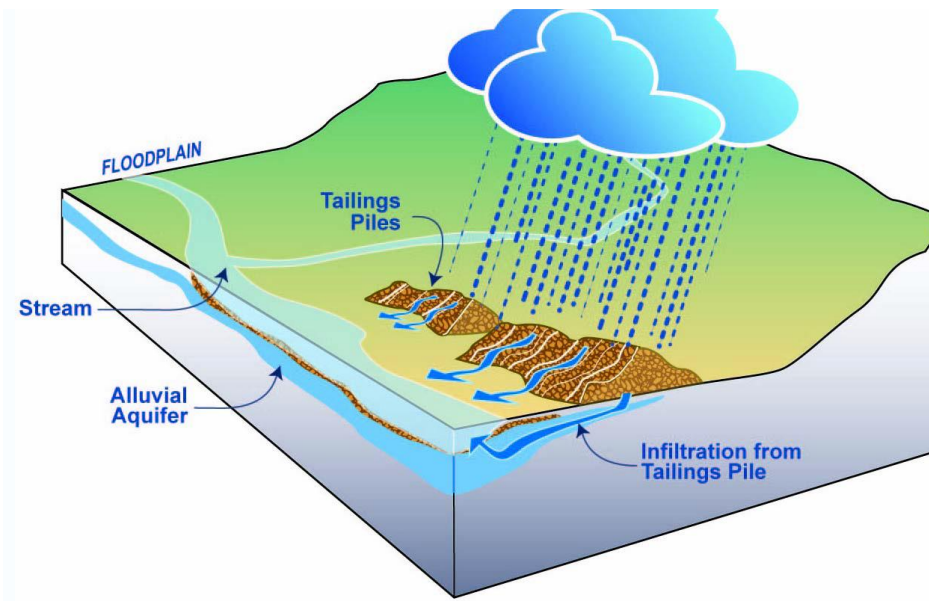
Figure 2-2: Transport pathways for contaminants in a hypothetical tailings pile (Maest and Kuipers 2005).

2.1.2   AMD Chemical Processes

The three key stages of chemical reactions describing the AMD process for pyrite are shown on Figure 2-3 below:

$$FeS_{2(s)} + 3O_{2(g)} + H_2O_{(l)} \Leftrightarrow Fe^{2+}_{(aq)} + 2SO_4^{2-}_{(aq)} + 2H^+_{(aq)}$$

Iron sulfide + Oxygen + Water   Ferrous iron + Sulfate   + 2 x Acid

$$4Fe^{2+}_{(aq)} + O_{2(g)} + 4H^+_{(aq)} \Leftrightarrow 4Fe^{3+}_{(aq)} + 2H_2O_{(l)}$$

Ferrous iron + Oxygen + Acid   Ferric iron   +   Water

$$FeS_{2(s)} + 14Fe^{3+}_{(aq)} + 8H_2O_{(l)} \Leftrightarrow 15Fe^{2+}_{(aq)} + 2SO_4^{2-}_{(aq)} + 16H^+_{(aq)}$$

Iron sulfide + Ferric iron + Water   Ferrous iron + Sulfate + 16 x Acid
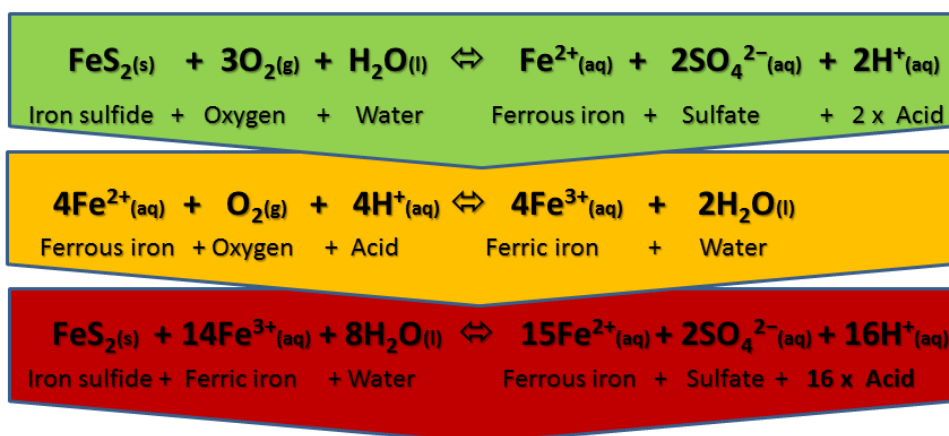
Figure 2-3: Typical AMD reactions (adapted from DITR 2007).

These reactions can occur spontaneously or can be catalysed by microorganisms that derive energy from the oxidation reaction. There are many forms of sulfide in addition to pyrite, but pyrite is often the most common form of sulfide. The presence of acidophilic and/or iron-oxidising bacteria can

substantially affect the rate of AMD production in the environment. In the second stage reaction, acidity is required in addition to oxygen to complete the reaction. As the process develops into the second and third stage the ferric cations and water produced in the second stage, can also combine with sulfide, ferric cations and water to produce a great deal more acidity. The presence of oxygen is not required in third stage AMD reactions, as water is hydrolysed into ferrous iron, sulfate and acid H^+ ions.

As shown in Figure 2-3, both water and oxygen are required to create initial conditions for AMD to develop. Limiting oxygen supply to minimise AMD reactions has been successfully applied to management of sulfidic soils and rocks in the mining sector (DITR 2016). Some examples of reducing AMD material exposure to oxygen include; covering waste rock with saturated clay layers, flooding closed mine pits to the groundwater table, establishing water layers above tailings storage facilities, burying sulfidic wastes under the water table by either backfilling old mining pits or in underground mine workings. Alkaline minerals such as carbonates have naturally high acid neutralising capacity and at some mine sites can be mixed with sulfidic materials and encapsulated to prevent AMD generated acidity reaching the environment. Barritt et al. (2016) gives examples of non-acid forming in-situ mine materials used to encapsulate potential acid forming mine materials at several mine sites.

Examination of oxygen supply as the key limiting factor of AMD production and its potential use for mine waste management assessment is the key theme in this research project.

2.1.3   Multiphase modelling of AMD

As can be seen from the chemical equations in Figure 2-3 above, AMD process are multiphase processes including gas, liquids and reactive geo(bio)chemistry and mineralogy. The AMD reaction requires both oxygen and water (as soil moisture) to complete, if either is missing the oxidation reaction will not take place or will be substantially reduced. Models developed to predict AMD processes may benefit from multiphase and particularly soil gas (oxygen) transport predictive capability. Predicting oxygen supply conditions is important to the early phase of AMD production, as it is the prevention of this first AMD process that can ultimately prevent the second and third processes from occurring. Soil

gas transport modelling is therefore clearly identified as an important tool for predicting AMD behaviour and identifying potential volumes of mine waste affected (Binning et al. 2007).

2.1.4 Control and Management of AMD

The management of AMD processes has become central to the initial design and operation of mine sites, quarries and land developments to prevent environmental harm occurring from these activities when they disturb fresh sulfidic mineralogy. The infrastructure particularly affected includes:

- Excavations: mine pits, quarry pits, underground mines (UGM), soil mining, residential development, and agriculture.

- Waste management infrastructure: waste rock dumps (WRD), tailings storage facilities (TSF), ore stockpiles, run of mine (ROM) pads, heap leach piles (US EPA 1994).

Two main options exist for management of AMD materials:

i) Geochemical neutralisation by mixing sulfidic AMD material with neutralising materials, or

ii) Prevention and controlled minimisation of AMD production by limiting oxygen supply (DITR 2007).

Minimisation of water, which is the other key AMD reactant, cannot be achieved due to the low masses of water required, which can often be obtained from the natural, steady state moisture content of the AMD materials themselves.

This thesis provides a methodology for AMD material volume assessment for both treatment processes and is aimed towards developing new and existing models to examine the effects of oxygen supply through soil gas transport processes. The method is aimed towards concept and prefeasibility design stages of a mining project to predict volumes of AMD materials potentially requiring treatment, enabling a cost estimation of the treatment systems required to prevent the development of AMD in sulfidic soil and rock materials.

2.1.5   AMD Monitoring and Assessment

Currently, effective management of AMD equates with robust geochemical based characterisation of AMD risk potential. The reactivity of AMD materials are the subject of a wide range of demand and supply side, geochemical, static and kinetic testing procedures. Static testing, such as sulfur and sulfide content, can be used to identify a range of reactive materials for further Kinetic testing (Karlsson et al 2018). Kinetic testing is required to establish the geochemical behaviour of sulfidic soil and rock materials when exposed to leaching by rainfall and other climate processes. Standard demand-side geochemical kinetic testing processes test outputs from AMD processes and include the i) humidity cell, ii) the leaching column test, and iii) field test materials piles. There are a number of limitations with respect to each of the existing demand-side kinetic testing techniques when applied to AMD geochemical characterisation. These limitations are listed below for each technique (Maest and Kuipers 2005) in Table 2-1.

One of the major limitations for all of the standard demand-side geochemical kinetic testing techniques, when applied to AMD characterisation, is the inability of these methods to separate sulfate produced from ongoing sulfide oxidation from sulfate already contained within the materials being tested. This means that at best, overall loads of acidity and salinity can be predicted, although often not with complete certainty, but no rate of reaction-based information can be reliably determined (Davis et al. 2014).

Table 2-1: Limitations of existing kinetic testing techniques (Maest and Kuipers 2005)

Kinetic Technique	Limitation for AMD characterisation
Humidity Cell	Cannot simulate field leaching conditions, Additional size reduction, if used, causes discrepancies between laboratory results and field conditions; not appropriate for saturated mined materials (e.g., submerged tailings); if neutralisation potential > acidity potential, acid generation lag time for metal/acid production may be longer than test, no rate of reaction.

Kinetic Technique	Limitation for AMD characterisation
Leaching Column Test	Channelling of leachate along preferential flow paths or sides of column; must examine mineralogy before and after tests for estimation of weathering rates of primary minerals, complex sulfate analysis (existing versus produced), test to completion, no rate of reaction possible.
Field test piles	Requires consideration of sampling and sample handling for proper scaling to full scale system, requires large amounts of time and earth moving materials handling, incomplete reactions, insufficient climate extremes

Figure 2-4 below shows kinetic testing layouts for humidity cells and columns. As can be seen from Figure 2-4, leachate analysis is the key for determining AMD oxidation rates and hence acidity production rates, but the sulfate separation issue limits the predictive power of the techniques. These traditional, (non-oxygen) methods for AMD risk measurement therefore are indicative only and do not provide a comprehensive picture of AMD reaction rates (Maest and Kuipers 2005).
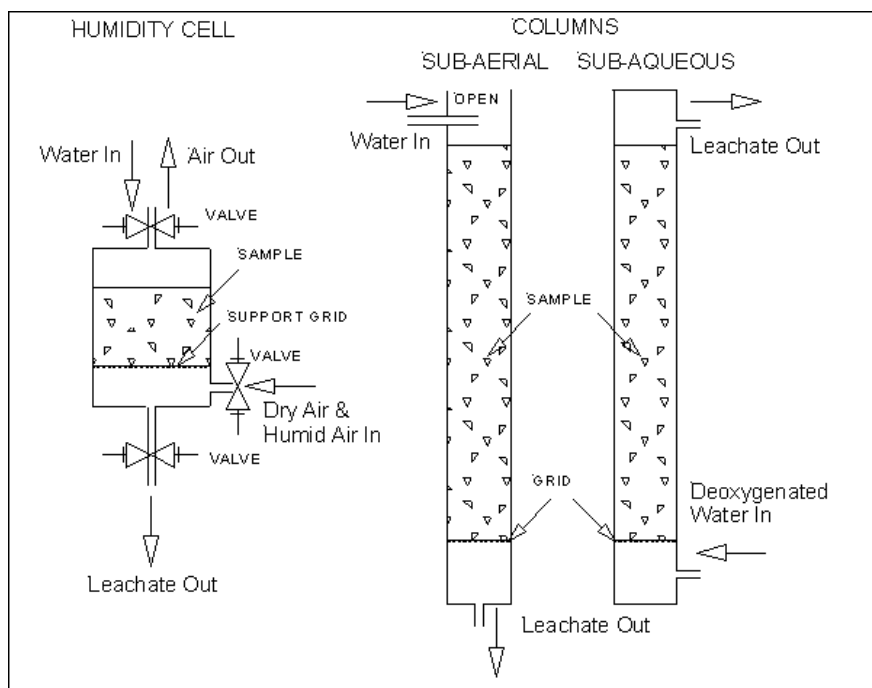
Figure 2-4: Kinetic test rigs for humidity cells and columns (Robertson and Shaw 2006).

The focus is on a lumped or spatially aggregated approach as the results are limited to the entire cell or column. Advances on these kinetic techniques are required to develop reaction rate dynamics

that accurately predict the amount of actual acidity produced as AMD and the reaction rate for an overall assessment of AMD management risk. Materials that oxidise quickly have different management requirements to those that oxidise slowly, which is a reaction dynamics issue. In all cases the total volume of AMD material present is the ultimate measure of the AMD management task, at a particular mine site, and can be therefore related to a cost. These non-oxygen based kinetic techniques are not able to provide accurate rate or volume information.

2.1.6   AMD Materials Oxygen Consumption Tests

New supply-side methods for determining AMD reaction rates, such as oxygen consumption testing (Schmieder et al. 2012, Davis et al. 2014), and the oxygen penetration test or OPT (Elberling 1994) build on the existing demand-side, humidity cell technique by using oxygen consumption within the AMD material as it oxidises as a direct indicator of the oxidation reaction. Oxygen consumption methods effectively measure soil gas oxygen diffusion-based oxidation of the AMD target material in the sealed cell, offers robust results such as pyrite oxidation rate (POR) in kg (H_2SO_4)/week. The research and development of the oxygen consumption method has been undertaken by several firms including Earth Systems (2012, & Schmieder et al. 2012) and Universities (Elberling 1994, Tibble and Nicholson 1997) and the complex geochemical modelling procedures and associated intellectual property required to calculate POR, are closely guarded and confidential proprietary laboratory procedures.

OPT column testing additionally can provide a measure of oxygen consumption in each soil layer, providing potential boundary conditions for soils gas transport models. The results from these methods offer the opportunity for use as soil gas transport model boundary condition data and/or calibration data for a linked gas transport and geochemical model or AMD risk predictive model. This research project seeks to avoid the relative complexity and uncertainty of geochemical testing and modelling, through the development of a new and simpler AMD material volume assessment methodology including the use of both soil gas diffusion behaviour testing and OPT columns.

After the proposed AMD volume assessment methodology is undertaken, if standard kinetic or oxygen consumption testing results are available in sufficient detail and statistical confidence, then these results can be used in combination with the soil gas transport modelling method proposed to further refine the likely cost of treatment for the identified volume of AMD material requiring treatment, potentially to a detailed or final design level.

2.1.7   Review of developments in multiphase flow modelling in porous media

While there are a great many solute contaminant transport models available in the form of first principles dispersion or empirical 'decay-constant' models, there are few that incorporate geochemical reaction equilibria and thermodynamic principals. Fewer models still can simulate geochemical reactions limited by soil gas transport. Most models are focused on a specific solution such as saturated flow, unsaturated flow, or the geochemistry of aqueous solutions. A literature review has been undertaken to gain an understanding of the history of the key developments in multiphase flow modelling and to determine the state of play and modelling capability in current practice.

Gas and water flow through soil is of central concern in many industries including petrochemical, oil and gas, contaminated site management and in the mining sector -at AMD susceptible sites. It is important to chart the development of foundational and contemporary models for groundwater and soil gas flow (solids, water and gas -multiphase) within complex mine soils and rock, such as sandy clay and fractured rock, materials frequently struck during the mining process.

2.1.8   Historical background to flow through porous media

Henry Darcy (1856) is generally credited with establishing the first laws of saturated flow through porous media, during his design of the water supply systems of Dijon from the Rosoir Spring. Darcy undertook experiments on the flow of water through vertical homogeneous sand filter columns used for water purification and derived the famous Darcy formula or law, equation (2-1):

$$Q = K \, A \, (h_1 - h_2)/L \qquad\qquad \text{equation (2-1)}$$

where

Q is fluid flow

K is the hydraulic conductivity

A is the area of flow

h_1 , h_2 is the water height (head) between two points, and

L is the length of flow

The Darcy equation allows for the estimation of saturated flow of liquids through porous media. While saturated flow is easier to model and study experimentally, especially in isotropic media such as sands, unsaturated flow models require a nonlinear approach due to the complex interactions of pore pressure on water and the inverse porosity relationship for gas and water. In simple terms, as the soil pore spaces fill with water, there is less area for gas flow, and the converse as pore spaces fill with gas also.

Figure 2-5 illustrates this phenomenon and shows the inverse relationship between relative permeability of steam, water and the capillary pressure (Mahiya 1999). In the figure it can be seen that as the pore space in the media saturates, the volume available for gas movement decreases reducing gas permeability (k_{rs}) while permeability of water (k_{rw}) increases with a cross over point of around 60% saturation.
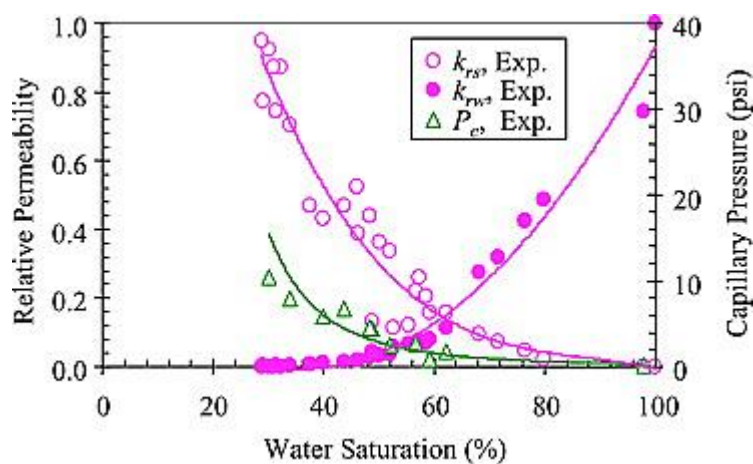
Figure 2-5: Relative permeability of steam (k_{rs}) and water (k_{rw}) and capillary pressure (P_c) after Mahiya (1999)

Buckingham (1907) was one of the first to recognise the application of Darcy's law to unsaturated flow in porous media and realised that instead of water pressure as head being the driving force, it became matric potential or capillary or pore pressure.

Richards (1931, 1936) developed a non-linear partial differential equation for movement of water in unsaturated soils, but this is difficult to use as it does not have a closed form analytical solution, see equation (2-2):

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(\theta)\left(\frac{\partial \varphi}{\partial x} + 1\right)\right]$$ **equation (2-2)**

where

K is the hydraulic conductivity

φ is the pressure head

z is the elevation above a vertical datum

θ is the soil water content, and

t is time

This equation relies on the collection of soil water content data, which is both complex to undertake, time consuming and extensively variable in field results (Van Genuchten 1980).

Brooks and Corey (1964) used an analytical expression for conductivity based on the Burdine (1953) approach. Mualem (1976) refined the Brooks and Carey (1964) approach by developing an analytic model which predicted the unsaturated hydraulic conductivity of a soil media by using the moisture content-capillary head curve and the measured value of the hydraulic conductivity at soil saturation. The model is built upon Burdine (1953) with a modified assumption concerning the hydraulic conductivity of the pore sequence in order to take into account the effect of pore size variation

on the soil profile. A computational method was then derived for the determination of the residual water content and for the extrapolation of the water content-capillary head curve as measured in a limited range.

2.2 Developmental Papers for variably saturated, multiphase, multiporosity flow

Several foundational papers are identified as relevant to developing the origins of contemporary multiphase and single/dual/multi porosity models for saturated and unsaturated soil conditions. Multiphase and single/dual/multi porosity models have been developed extensively in the petrochemical industry, possibly due to current increased demand and reduced supply of the 21st century, the oil reservoir supply shortages in the 1970's and the current movement to use increasing amounts of petrochemical reservoirs containing unconventional oil and gas resources that would not have been used when oil and gas was in plentiful supply in the 20th century. Technology advances in multiphase (gas and liquid) pump design from the petrochemical sector have also driven model development in the contaminated site rehabilitation sector, with soil vapour modelling and multiphase groundwater pump and treat systems being developed. The additional multiphase modelling capabilities have also allowed steps to be taken towards modelling soil gas and moisture supply to oxidation of sulfidic materials in mines with AMD issues.

2.2.1 Unsaturated zone models

As the proposed research area is focused on mining waste management, waste dump design and closure landforms to prevent AMD, unsaturated zone models are central issues and the foundational papers have been selected with this focus. The papers reviewed are Brooks and Corey (1964), Van Genuchten (1980).

Brooks and Corey (1964) is a long paper and contributes to a major improved understanding of multiphase flow in the unsaturated zone. They relate the problems associated with bringing petrochemical and physics soil models into an agricultural soil setting due to complex and conflicting

terminology, and focus on developing the multiphase air/water permeability relationship with only two parameters –pore pressure and pore size distribution index –a combination of the Richard's equation and the Burdine's (1958) approach. The paper presents both methods for measuring pore size distribution and bubbling (pore) pressure. The concept is presented as "two immiscible fluids as the non-wetting and wetting phases" (Brooks and Corey 1964:9) –air and water. This opening is confusing in current terms and probably should just have discussed the performance of the separate phases, but it is likely that the understanding at this point was developmental. Brooks and Corey's assumption is that Darcy's law holds for both phases in a porous media is presented along with the concept of effective permeability. Hysteresis is also presented –the difference between starting with dry media and wet media. The paper does not explain the reason for hysteresis –which is surface tension in the water phase, an effect that doesn't occur in gas phases (Doughty 2013). Surface tension is presented as "curved interfaces" and then they outline the problems with this assumption rather than highlighting its strengths. They relate the capillary pressure formula (equation (2 3),

$$P_c = P_{gas} - P_{liquid} \qquad \text{equation (2 3)}$$

which begins to develop the inversely proportional multiphase concept of soil pore space.

The Brooks and Corey paper is focused on soil drainage, so effectively does not focus on hysteresis. Burdine's theory is presented in an Appendix and dual porosity is discussed as "primary and secondary porosity" but then developed to a tortuosity analogy as a method to simplify the problem of an averaged K value giving an incorrect result. Brooks and Corey admit that using an averaged hydraulic radius is the same assumption as an averaged K. In this they show the gap in their theory, which is that for higher moisture contents, an averaged hydraulic radius, rather than simulation of dual or multi porosity, yields a discontinuity in the pore pressure. They show that several previously determined experimental approximations of relative permeability are only valid for particular soil matrix pore size distributions.

Corey's effective saturation concept is for residual saturation to be related to saturation, and the non-linear and dual asymptotic relationship between residual saturation and saturation is developed.

They then build their key formula by relating effective saturation to the inverse of pore pressure and the maximum size of pores within the media to the power of lambda (λ), which is an index that characterises pore size distribution. From this they develop their signature formula (equation 2 4):

$$K_{rw} = \left(\frac{P_b}{P_c}\right)^{\eta} \qquad \text{equation (2-4)}$$

where

$\eta = 2 + 3\lambda$

K_{rw} the relative conductivity (effective permeability) for the water phase

λ is the pore size distribution index for the media

P_b is the largest pore pressure of the media

P_c is the capillary (pore) pressure

The Brooks and Corey (1964:12) graphs of the relationships between capillary pressure as a function of saturation were a great step forward in the understanding of unsaturated soil behaviour, see Figure 2-6 below.
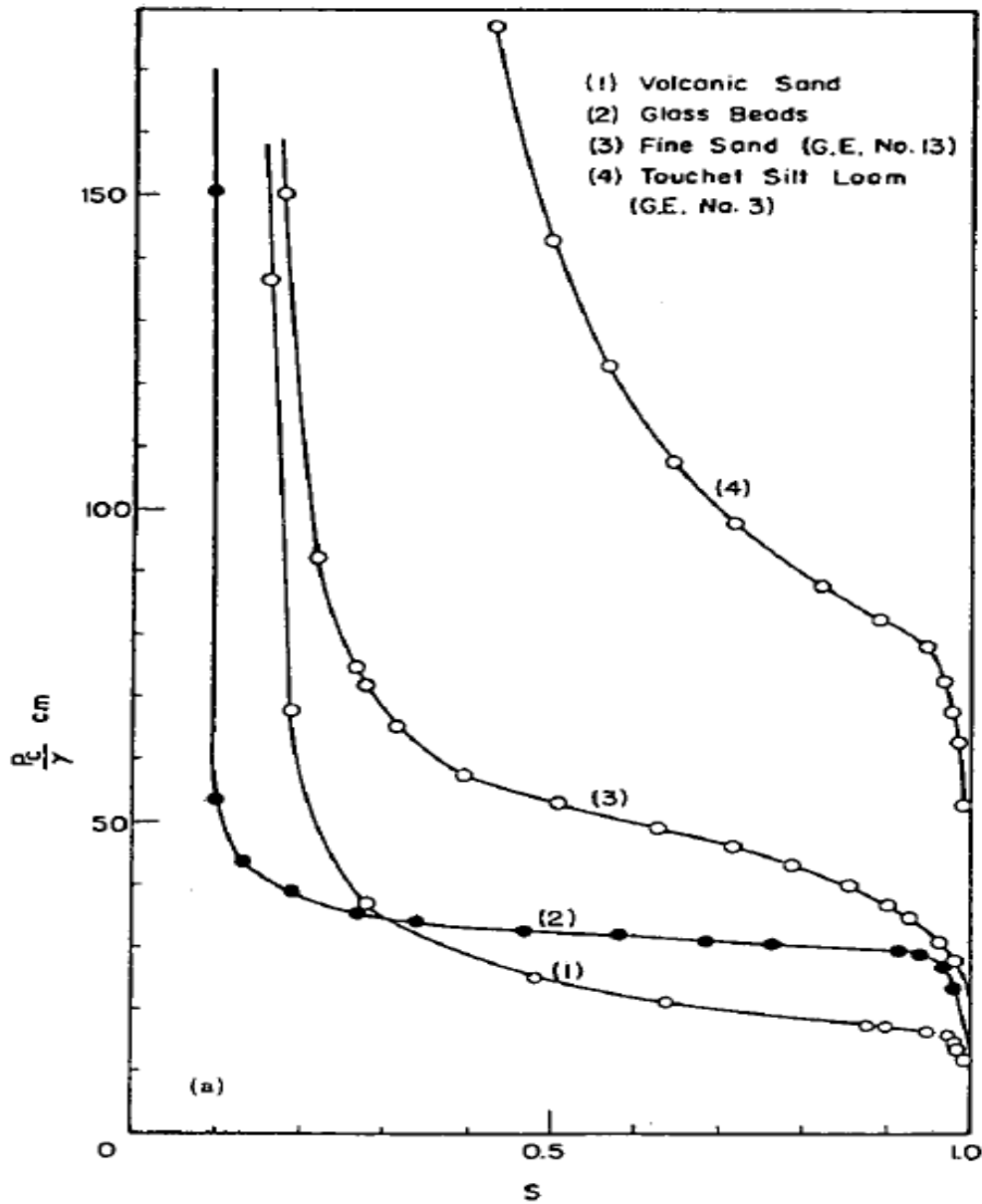
Figure 2-6: Capillary pressure vs soil saturation (Brooks and Corey 1964)

Van Genuchten (1980) fine-tuned the open form multi-parametric equations of Brooks and Carey (1964) approach with the Mualem (1976) approach. He also used the Burdine (1953) pore size distribution theory to reduce the unknown parameters and developed his famous and widely used closed form equation for predicting hydraulic conductivity in unsaturated soils (equation 2 5):

$$K_r(h) = \frac{1-(\alpha h)^{n-2}[1+(\alpha h)^n]^{-m}}{[1+(\alpha h)^n]^{2m}} \qquad \text{equation (2-5)}$$

where

K_r is the relative hydraulic conductivity

h is the pressure head

α, n and m are equation parameters.

Perhaps the greatest step forward of Van Genuchten's (1980), was in presenting the pore pressure against moisture content which is now a very familiar concept to civil engineers and soil scientists, see Figure 2-7:
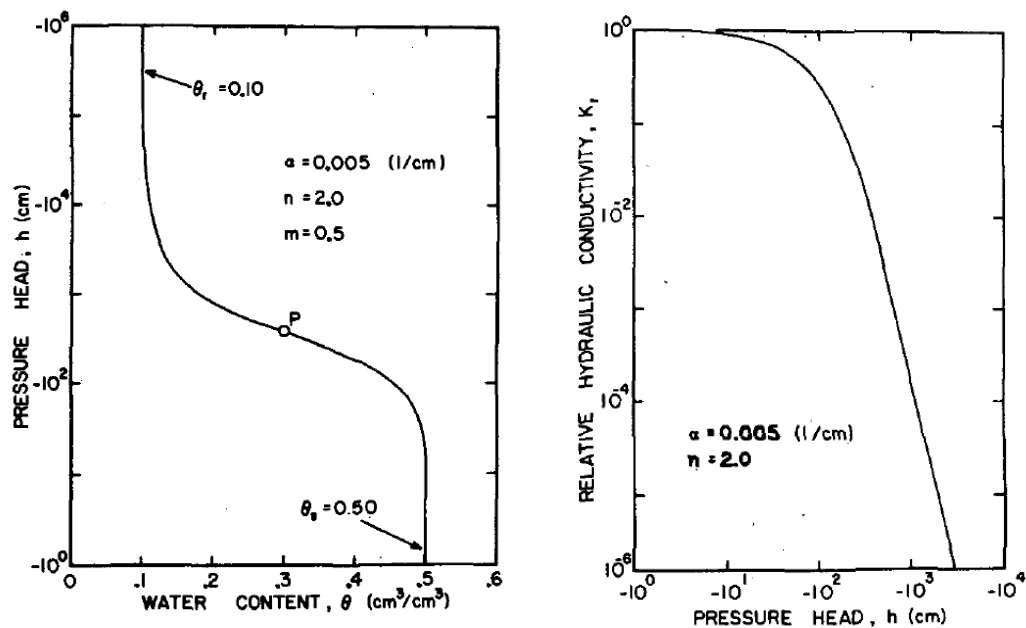
Figure 2-7: Typical plots of capillary pressure vs moisture and Kr vs pore pressure (Van Genuchten 1980)

The asymptotic relationship derived as moisture approaches minimum residual moisture θr and saturation θs was correlated to logical soil media behaviour with good theoretical and field based correlation (Van Genuchten 1980). The relative hydraulic conductivity derived also displayed the required inverse relationship to capillary pressure. The Van Genuchten equation model is still in wide use today for unsaturated soil moisture modelling in models such as TOUGH2 (Preuss et. al. 2012), FEFLOW (DHI-WASY 2014), COMSOL (2013) but the experimental process to obtain field scale data is difficult, costly and time consuming to undertake. Laboratory testing for soil water characteristic curves (SWCC) is also difficult, time consuming and costly. It is often difficult to find commercial soil laboratories that undertake specialised SWCC testing. Proprietary models such as those listed above

are expensive and are often beyond the reach of mining sector based companies exploring AMD processes (where unlike the petrochemical industry, multiphase flow through porous media is not usually directly related to mine production) in terms of licence and training costs, and implementation time.

2.2.2   Dual/Multi Porosity Models

Dual and multiple porosity models have been emerging since the 1960's as practitioners recognised that in some saturated and unsaturated systems, multiple transport conditions may exist. Fractured rock aquifers are the classic case where fast flow can take place through fractures and gaps in the rock matrix, and slow flow through the rock media itself. Other examples of dual porosity systems include sandy clays.

Barenblatt et al. (1960), Warren and Root (1963) both suggested early frameworks for dual porosity systems which featured consideration of i) primary porosity, the small pores and intergranules in rock matrix and ii) secondary porosity, the fracture and joints in the rock system. These dual porosity systems can be applied for liquid and gas transport in the target soil matrix.

The modelling of interporosity, which is the interaction between primary and secondary porosity flow, is an important feature of the dual porosity system. Interporosity modelling efforts can be categorised into one of the following approaches, listed in order of increasing computational power and complexity:

i)   ignoring the matrix media flow in favour of fractured flow (single porosity models eg Millington and Quirk (1961));

ii) computationally separating the two systems of flow (Gerke and Van Genuchten (1993), Samardzioska and Popov (2005), Kristensen et al. (2012), Berisso et al. (2012));

iii) averaging the conductivity of the media and the fractured zone (Samardzioska and Popov 2005);

iv) models with average pressure difference determining the switch between matrix and fracture flow (Pruess (1991) and Gerke and Van Genuchten (1993));

v) discrete fracture and matrix modelling (Samardzioska and Popov 2005).

Discrete fracture and matrix modelling require large amounts of fracturing data, some of which is impossible to collect in-situ, and is computationally complex, which has restricted its use to small scale subjects such as laboratory scale rock cores or triaxial test samples (Samardzioska and Popov 2005).

Pruess (1983) developed the multiple interacting continua (MINC) dual porosity approach as a progenitor for the TOUGH and TOUGH2 (Pruess et al. 2012) model series. Pruess believed that accurate description of interporosity flow requires a resolution of the pressure- and temperature-gradients at the matrix/fracture interface. In the numerical approaches mentioned above this was achieved by explicit partitioning of the flow domain into "small" simply connected grid blocks, as in conventional porous medium simulators. This type of approach is unsuitable for naturally fractured reservoirs with ubiquitous fractures, where it would lead to excessively large numbers of grid blocks.

Gerke and Van Genuchten (1993) developed a one dimensional dual-porosity model for the movement of water in structured porous media. Within this dual porosity approach, the Richards (1931) equation is used for variably saturated flow in the media matrix and the fracture systems, and solute transport is handled with the advection-dispersion equation. By their own assessment the system of equations produced good results as a one-dimensional model without requiring more complex multidimensional diffusion-based transport models. The contribution of the matrix media to the overall soil water was substantial even compared to the fractured flow systems in the simulation, an important finding; despite the highly nonlinear and transient nature of the flow processes in the fracture system (flow occurs from the matrix to the fracture based on relative pressure between the two systems).

2.2.3   Recent Multiphase Publications

Samardzioska and Popov (2005) built on Gerke and Van Genuchten (1993) by comparing the three major model types for modelling of flow and solute transport in fractured porous media, i) equivalent continuum (averaging entire media conductivity properties), ii) dual porosity (as per Gerke and Van Genuchten (1993)), and iii) discrete fracture. The models were compared in two media with

different fracture fields. The discrete fracture model becomes unworkable with large numbers of fractures due to analysis and computer processing time. The equivalent continuum model cannot provide reliable estimates of head or concentration as it is based on processing the whole domain. The limitation of the dual porosity model in unsaturated systems is the averaging of pressure head to determine K_a, which is the hydraulic conductivity at the fracture matrix interface. Samardzioska and Popov avoided this problem by considering a fully saturated media avoiding the need for a K_a that depends on hydraulic head. Overall the discrete fracture model performed most reliably and accurately, while the dual porosity model was next most accurate but found to be sensitive to matrix block size and volume estimation of the fractures and the equivalent continuum model provided acceptable results but was least accurate. See figure xx below for a comparison of analytical and modelled dual porosity model

The scale of the model domain only included three fractures developed from a single core sample, which made the complexity of the discrete fracture model realistic for data processing purposes. Samardzioska and Popov (2005) admit that the discrete fracture model would require vast amounts of data to attempt in a real world, large model domain, and that developing an accurate fracture dataset over a continuous and large area is not possible using current technology.
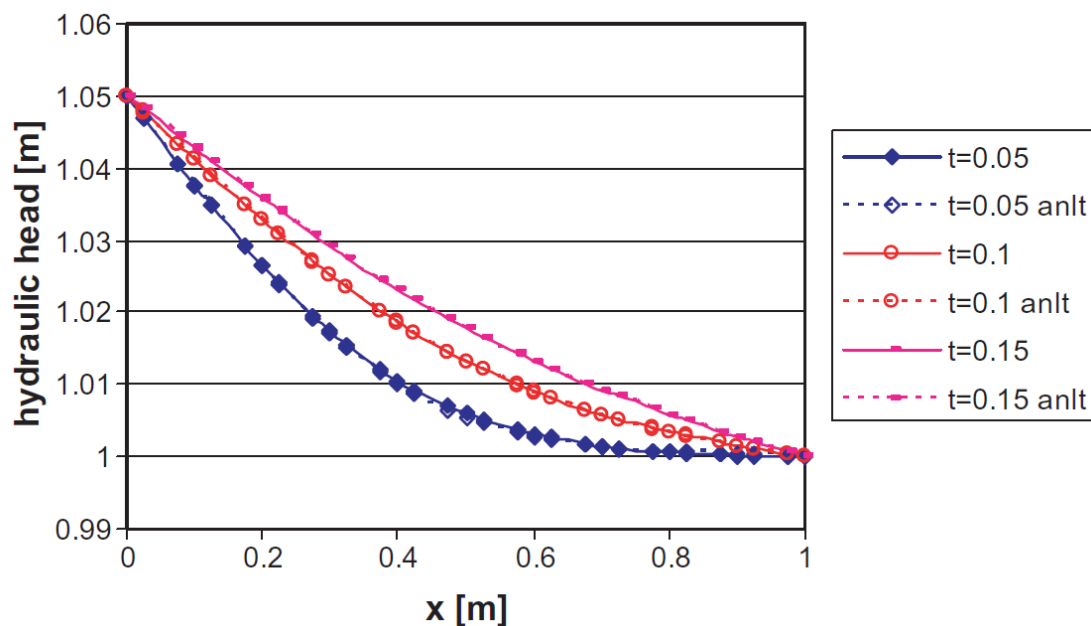
Figure 2-8: Comparison of the dual porosity code for flow with analytical solution; K = 10 m/day, C = 1 m-1 Samardzioska and Popov (2005).

Schwartz et al. (2000) attempted to calibrate dual porosity models using the advection dispersion equation (ADE) and field tracer results. The findings were similar to Samardzioska and Popov's (2005) work in that estimates of the fracture and matrix media dispersion coefficients are important but difficult to determine analytically prior to inclusion in the model. The main criticism of the paper is that during the building of the dual porosity ADE insufficient references were given of equation sources, making it difficult to know the source assumptions of the modelling.

Buchgraber et al. (2012) took a novel approach to developing petrochemical dual porosity models for enhancing oil recovery, by developing a physical micro-model creation etched into 2D silicon wafers to simulate the characteristics of dual porosity systems found in carbonate reservoir rocks (see example in Figure 2-9). The benefits of this technique were the ability to directly observe the effects of the dual porosity system on the multiphase reservoir oil and water fluids. Multiple replicates are possible with exact duplicate physical models. Porosity, permeability and other variables, were able to be measured with the model. The model was created by photographing carbonate thin sections and using photolithography to create the exact physical models. The microporosity regions retained oil and at higher pressures small amounts were released, better results were obtained from using injected surfactants. The advantage of the physical model is being able to observe the effects of different porosities and different phases in real time.
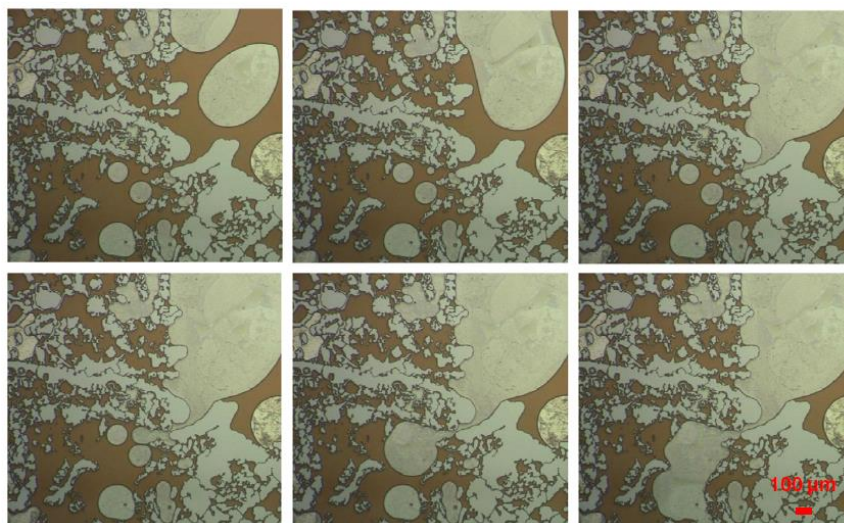
Figure 2-9: Time lapse photography of clear water entering oil in the dual porosity matrix over 190 seconds (from Buchgraber et al. 2012).

The disadvantage of the physical model method is the small area of sample able to be simulated (less than 50 μm), and the requirement to be able to photograph the dual porosity system with liquid indicator through the microscope, which is likely to not replicate soil gas transport behaviour. As a result of these limitations, this method has not been considered as useful for this study.

Kristensen et al. (2012) examined gas-phase diffusivity with dual porosity models and compared the results to Millington and Quirck (1961) multiphase models. The dual porosity model was additive and included (i) a "wet region" in which transport occurs only in drained and isolated fractures with a low tortuosity and a gas diffusivity increasing linearly with air-filled porosity (similarly to the Penman Model) and (ii) a "dry" region in which some small and tortuous matrix pores are drained and contribute non-linearly to the gas diffusivity (similarly to the Millington and Quirck (1961) and Moldrup (2001) relationships). Applied to glacial clay till and limestone, two classic media displaying dual porosity behaviour, the results showed dual porosity models have the potential to be an order of magnitude more accurate than classical modelling approaches for multiphase scenarios including subsoil gas diffusion processes. Figure 2-10 shows the improvement in result offered by the dual porosity model compared to single porosity approaches using the Millington and Quirk (1961) model.
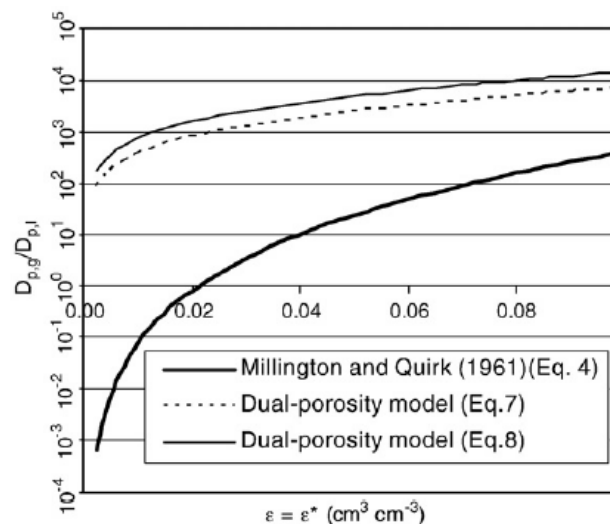
Figure 2-10: Diffusion coefficient of trichloroethane at varying fracture porosity (Kristensen et al. 2012)

Saxena et al. (1994) assessed preferential flow (dual porosity) systems in sand and clay soils for potential agricultural applications using the MACRO model. In MACRO, single porosity sand

systems become reduced to Richard's equation and advection dispersion solutions. In clay soils with macropores, a dual porosity model was created for MACRO. The models showed good results with observed seepage in lysimeters, apart from winter months, where freezing of the soil and snowpack was found to not be able to be simulated by the model. Macropore flow was clearly demonstrated in the modelled clay soil by comparison with tracer transport. Preferential flow was indicated in sand and modelled acceptably. The single porosity model for the clay soil failed to predict the tracer breakthrough with any accuracy at early phases and towards the end of experiments. The dual porosity models were considered improved estimates compared to the simpler advection dispersion models.

Berisso et al. (2012) undertook a study to examine sub soil compaction by heavy tractors, measuring in-situ soil parameters, air permeability, and gas diffusivity at four depths up to 1 m in agricultural loamy soils. The Double Exponential model used in the study, lends itself to dual porosity modelling and was fitted to the soil parameters to estimate soil aeration successfully. The results found that soil anoxia takes place to at least 1m depth and lasts up to 14 years, affecting several potential soil nutrient and water retention properties in the compacted soils.

Dai et al. (2011) developed dual porosity geochemical reactive transport models for fractured rock media to study the behaviour of uranium and neptunium movement through the strata. Several different conceptual models of the system lead to the development of seven dual porosity, multi-component reactive transport models. The parameters for the models were provided by stepwise multi-tracer information from transport experiments, including tritium to estimate non-reactive components residence time in fracture, fracture size, and matrix tortuosity. Dai concluded the models provided useful results for the prediction of transport in dual porosity system.

Figure 2-11 shows the predictive accuracy offered in modelling U breakthrough curves using dual porosity models.
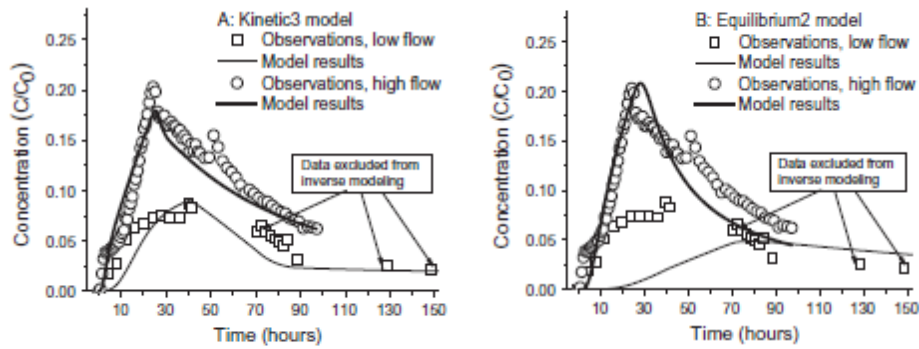
Figure 2-11: Example Uranium Breakthrough Curves from Modelled and Observed Results (Dai et al. 2011).

2.2.4   Soil Gas Diffusion Advection Models

As discussed previously, prediction and modelling of Fickian soil gas diffusion is a complex modelling subject due to the inversely proportional relationship of gas diffusion to soil moisture content, and the behaviour of soil moisture and pore pressure based on soil structure. The soil gas diffusion coefficient D_p (often related as D_p/D_o and D_o is the gas diffusion coefficient in free air) is the central requirement to successful and accurate modelling of soil gas diffusion. A wide range of predictive models available in the literature for D_p/D_o are presented by Moldrup (2013).

Soil gas diffusion is important for soil geochemical and ecosystem processes including soil bacterial growth, soil evaporation and drying (Jury and Horton 2014). Examples of industries affected by soil gas diffusion include agriculture and cropping, hydrocarbon contaminated sites, gas and petrochemical industries, and waste landform design, such as municipal landfill and mining waste rock dump capping systems. Since Buckingham (1904) and Richards (1931) soil moisture and soil gas diffusion has been the subject of much enquiry due to the lack of closed form equations for predicting soil moisture. As a result, soil gas and moisture modelling has relied upon complex and time-consuming laboratory and field-based measurements of soil moisture to determine D_p. Debate has continued about the importance of the difference between in-situ, intact and remoulded soil samples in lab testing and the potential influence this has on predicting D_p.

The "extreme complexity of soil architecture" highlighted by Moldrup et al. (2013) of soil physics, and especially unsaturated soil physics, necessitates new approaches to improve the prediction of soil gas and moisture transport processes.

Previously the differences between intact or remoulded soil samples have either been ignored or developed into a quasi-dichotomous system of results and modelling based on separating the intact and remoulded soil data and predictions. This has led to problems with consistency and reproducibility in soil gas permeability results –major issues for the reliability of the soil gas diffusion predictions (Moldrup et al. 2013).

Moldrup et al. (2013) compares historical and contemporary soil gas diffusivity models, including Anderson (2000), Millington and Quirk (1960, 1961), Buckingham (1904), and Deepagoda et al. (2012). Moldrup et al. (2013) then collected soil data from sieved, remoulded soils, porous materials and 290 intact soil samples from the literature. The data in the literature came from one or two chamber soil gas testing methods using O_2 or CO_2 as the test gas.

The data collected are shown below in Figure 2-12 for dry porous media ($\varepsilon = \phi$). The figure shows the total field of the data used for the modelling and an overall sense of the applicability of the various predictive models and demonstrates the structure dependent water induced linear reduction (SWLR) model has reasonable coverage across soil types. The testing of model accuracy and prediction was undertaken using root mean square error (RMSE) and bias, and the results were shown on graphs for each existing soil gas diffusivity model used, including the new SWLR approach. The data was broken into media types and testing types (remoulded/in situ) for the purposes of providing further analysis of the applicability of the various models to the media, with a range of soil moisture conditions from dry to near saturation.

The new SWLR model was shown for three values of C_m, which showed that the new SWLR model also has limitations if not applied with the correct parameters based on observed porous media type. The model shows good results for fines and clay minerals and one of the target mine materials for this research project is sulfidic mineral sandy clay and silts.
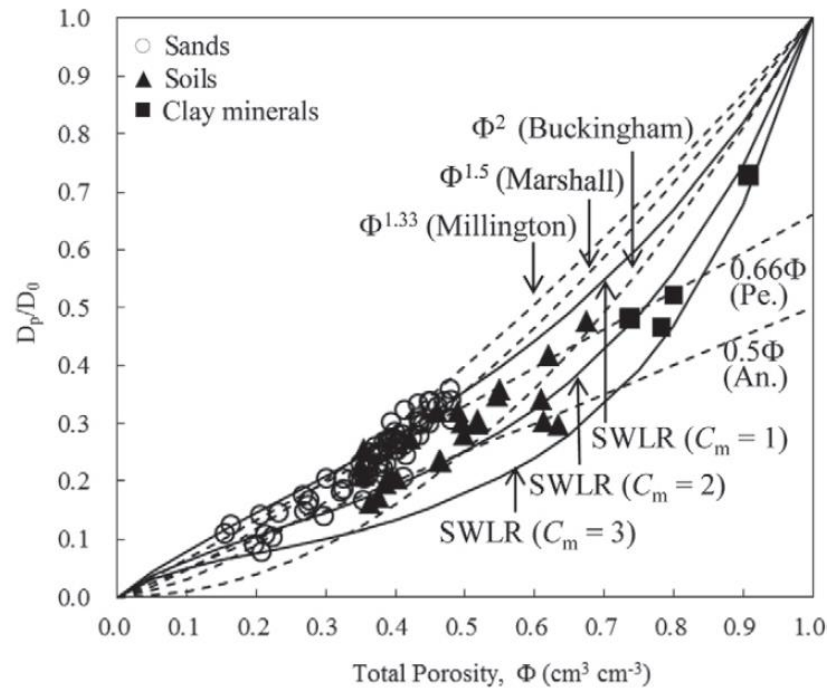
Figure 2-12: Gas diffusivity data for dry porous media and predictions from existing models (Moldrup 2013)

The Moldrup et al. (2013) diffusion coefficient function has therefore been selected for inclusion and further research as a potential candidate for estimating soil gas diffusion coefficient in the developed soil gas transport model. This diffusion coefficient estimating function is further evaluated in Chapter 5. To use this model successfully, soil physical properties including porosity, soil water characteristics and dry bulk density were determined in the laboratory for the target AMD soils being examined.

To avoid any inaccuracy derived from relying on literature-based, soil gas diffusion coefficient estimation models in this Phd study, a new soil gas diffusion testing column and method was designed over several iterations. The final diffusion column is used to provide soil gas diffusion behaviour of AMD mine materials at multiple moisture contents, to allow for the development of a moisture vs soil gas diffusion coefficient model based on actual soil matrix gas diffusion behaviour in the test soils. This diffusion column apparatus, and method is described in detail in Chapter 5. The design of the diffusion column is also presented in Appendix 1 as Supplementary material from Chapter 5 (Paper ii). The column was designed to fabricated in a mine site workshop from commonly available UPVC and stormwater fittings and be highly economic at <$500 USD.

2.2.5 Geochemical models for oxidation processes

Geochemical models for oxidation processes include mass load models based on molar chemistry, lumped parameter models, chemical equilibrium models to combined chemical thermodynamic and chemical kinetic models. An example geochemical model is the Debye-Huckel (1923) equations for ionic solutions see equation (2-6):

$$ln(\gamma_i) = -\frac{z_i^2 q^2 K}{8\pi\varepsilon_r\varepsilon_0 k_B T} = -\frac{z_i^2 q^2 N_A^{1/2}}{4\pi(\varepsilon_r\varepsilon_0 k_B T)^{3/2}}\sqrt{\frac{I}{2}} = -Az_i^2\sqrt{I} \qquad \text{equation (2-3)}$$

where

z_i is the charge number of ion species i

q is the elementary charge

K is the inverse of the Debye screening length

ε_r is the relative permittivity of the solvent

ε_0 is the permittivity of free space

k_B is Boltzmann's constant

T is the temperature of the solution

N_A is Avogadro's number

I is the ionic strength of the solution

A is a constant that depends on temperature.

Mathematical complexity, trained specialist modellers and relatively large numbers of parameters are a feature of current geochemical modelling. Helgeson (1968) is generally credited with generating the earliest computer models for geochemical reactions and beginning with irreversible

reactions, it was proved that thermodynamics data can be used to calculate reactions for multicomponent systems -if sufficient data exists. With the development of more powerful computers in the 1980's and 1990's a series of geochemical speciation codes emerged, with capabilities well documented by Maest et al. (2005).

The geochemical models included in this review have advanced well past first principal, empirical 'die off' models, such as the Monod reaction, or purely linear equations used in many contaminant transport models. Most geochemical models feature equilibrium and thermodynamic models, most feature iterative solutions of the Debye-Huckel equations for ionic solutions. The multiphase (gas and liquid interactions) component of geochemical modelling is the least developed component at present, with many models currently in use being limited by solid phase or gas phase predictive capacity. PHREEQC (Parkhurst and Appelo, 1999) is an example of a popular "freeware" geochemical model that is limited to solid and liquid multiphase prediction, even though the model features dual porosity capability.

The major geochemical modelling capable codes available are summarised from the literature and Maest et al. (2005) and are shown in Table 2-2 below.

In summary of the geochemical codes discussed, the integration of soil moisture and soil gas models, and solutions mixing geochemical models has been slow, with perhaps only two of the major models capable of representing soil gas/moisture multiphase reactions directly. It is possible to link soil gas transport data from unsaturated zone models to transport models and this has been achieved by several researchers.

Table 2-2: Geochemical models for AMD prediction (including Maest et al. 2005)

Model	Strengths/Capabilities	Weaknesses/Gaps
WATEQ4F v.2 (Ball and Nordstrom, 1991)	Most complete mineral database for acid drainage, redox species; database updates for uranium, chromium, and arsenic redox species.	No gas phase model, mass transfer module only
MINEQL (Schecher and McAvoy, 1991); MINEQL+ v. 4.5 (Environmental Research Software, 2005)	Basis for MINTEQ (along with WATEQ); v. 4.5 is windows MINTEQA2 with a user interface for relational databases; temp = 0-50oC, ionic strength <0.5M.	No gas phase model
MINTEQ (Allison et al.,1991)	Most complete ion exchange and sorption, supported/approved by US EPA, with PHREEQE, most often applied to acid drainage problems.	No gas phase model
HYDRAQL (Papelis et al.,1988)	Speciation, adsorption, organic ligands.	No gas phase model
Geochemist's Workbench (Bethke, 1994; 1996 - REACT is mass transfer module)	Can include bacteria, Pitzer formulation, evaporation, mass transfer, isotopic calculations, temperature dependence for 0- 300oC, sorption, complex kinetics and decoupled redox reactions.	No gas phase model, mass transfer module only. Proprietary model.
PHREEQC v. 2 & PHAST (Parkhurst and Appelo, 1999)	Most often applied to acid drainage problems, can define kinetic reactions, mass transfer, reaction path, ion exchange fluid mixing, sorption, solid solution equilibria, PHAST provides 3D transport, inverse modelling, carbon isotope compositions. PHREEQC is Freeware.	No gas phase model, fixed volume gases.
SOLMINEQ.88 (Kharaka et al., 1988);	Most user-friendly, Pitzer, organic ligands, covers temperature range from 0- 350oC and 1-1,000 bar pressure, mass transfer options (fluid mixing, mineral precipitation/dissolution, ion exchange, sorption).	No gas phase model Proprietary model
PATHARC (Alberta Research Council; Bill Gunter and Ernie Perkins)	Most user-friendly reaction path program, dissolution/ precipitation kinetics and equilibrium reactions, gases, evaporation; isothermal, does not include solid solution	No soil gas diffusion or advection Proprietary model
TOUGH Series (Pruess et al., 2012)	Designed specifically for waste rock and heap leach systems, includes heat generation by acid production and oxygen convection, no attenuation mechanisms. Soil gas diffusion through unsaturated soil equations.	Limited geochemical model. Single diffusion coefficient. Proprietary model
SULFIDOX (based on Ritchie 1994)	Uses soil gas as limitation for oxidation rates, 2D model, Monod or linear reaction rates.	Simple Monod reactions, Proprietary model –not available for purchase or research
OGS_GEMS (Kolditz 2012, Kosakowski and Watanabe 2014, Wang and Kolditz 2006)	GUI based Gibbs Energy based system useful for solid solutions. OGS is the 1-3D transport model linked to the GEMS geochemical model. Freeware	Gas phase transport appears limited to advection processes. GEMS can be coupled with physical models.

The major strength in current geochemical models is the solid and aquaeous phase, where the bulk of modelling effort has been undertaken to date. The major weakness in most geochemical models is the gas phase. PHREEQC (Parkhurst and Appelo 1999) for example, only includes a fixed volume gas model. The TOUGH2 (Pruess et al., 2012) code series appears to have a complete gas flow model, but only based around a single material diffusion coefficient and TOUGHREACT has the ability to predict AMD based on oxygen supply. The OGS-GEMS systems (Kolditz 2012, Kosakowski and Watanabe 2014, Wang and Kolditz 2006) may also be able to model gas flow and model the AMD reaction (some mineral phases may be missing for both TOUGHREACT and OGS-GEMS) and is similar in complexity to the TOUGH2 series.

Kuo and Ritchie (1999) prove that convective/advective oxygen supply processes can be up to four times higher than traditional diffusive soil oxygen supply in waste rock dumps, using simple linear or Monod transport simulation equations for intrinsic sulphide oxidation rate. Binning et al. (2007) contradict Kuo and Ritchie, with a combined advection diffusion and Maxwell-Stefan approach determining that advection can be up to 25% of the advective diffusive soil gas transport regime. Diffusive and convective/advective gas transport processes and their interrelationship have been identified by several authors including Binning, as requiring further research, and are a key component of this research project.

Candidate models investigated for potential use in this research project included spread sheet 1D gas transport models, dual/multi porosity models, and several complex multiphase models such as the frequently used PHREEQC. PHREEQC has not implemented gas phase reactions to the level required for this soil gas transport modelling at this stage in its development, although this will occur in the future according to PHREEQC developers (Parkhurst and Appelo 1999). Details of PHREEQC experiments in AMD modelling during this project are included in Appendix 2 below.

Many of the models evaluated were not available, as they were either proprietary models or subject to the intellectual property rights of private consulting companies. The TOUGH code series was rejected for use due to the high cost, complexity and impact on the limited research project budget

(TOUGH2 is $34,500 source + $8,500 executable = $43,000 $USD -based on 2016 pricing). Additional costs of training personnel to use TOUGH2 in the mining sector are also considerable, so it is likely this code will remain the specialist domain of consultants and academic researchers. Additionally, analysis of the TOUGH2 code manual shows the single diffusion function also includes a tortuosity component, which cannot be readily measured, and no ability to insert a laboratory or field measured soil gas diffusion function for multiple soil moisture points.

Sensitivity analysis of key variables likely to affect AMD conditions in a soil matrix are presented in Figure 2-13 below. Within the figure, the overlap of the key geochemical model PHREEQC and complex multiphase model TOUGH2 are shown in relation to the 1D and 2D soil gas diffusion models developed in this study. From Figure 2-13, PHREEQC provides good coverage of geochemical modelling issues, including the problems with reactive surfaces and determination of these within an AMD soil matrix. TOUGH2 REACT provides a larger coverage, up to and including soil gas diffusion, although with limited diffusion coefficient functionality, as TOUGH2 cannot currently use multiple diffusion coefficients, or measured moisture vs diffusion coefficient functions, such as those presented in Chapter 5 and 6. TOUGH2 REACT is also prohibitively expensive for the mining sector at approximately $75 K USD (based on 2016 prices), without costs of training, or external specialist geochemistry and unsaturated zone research support.
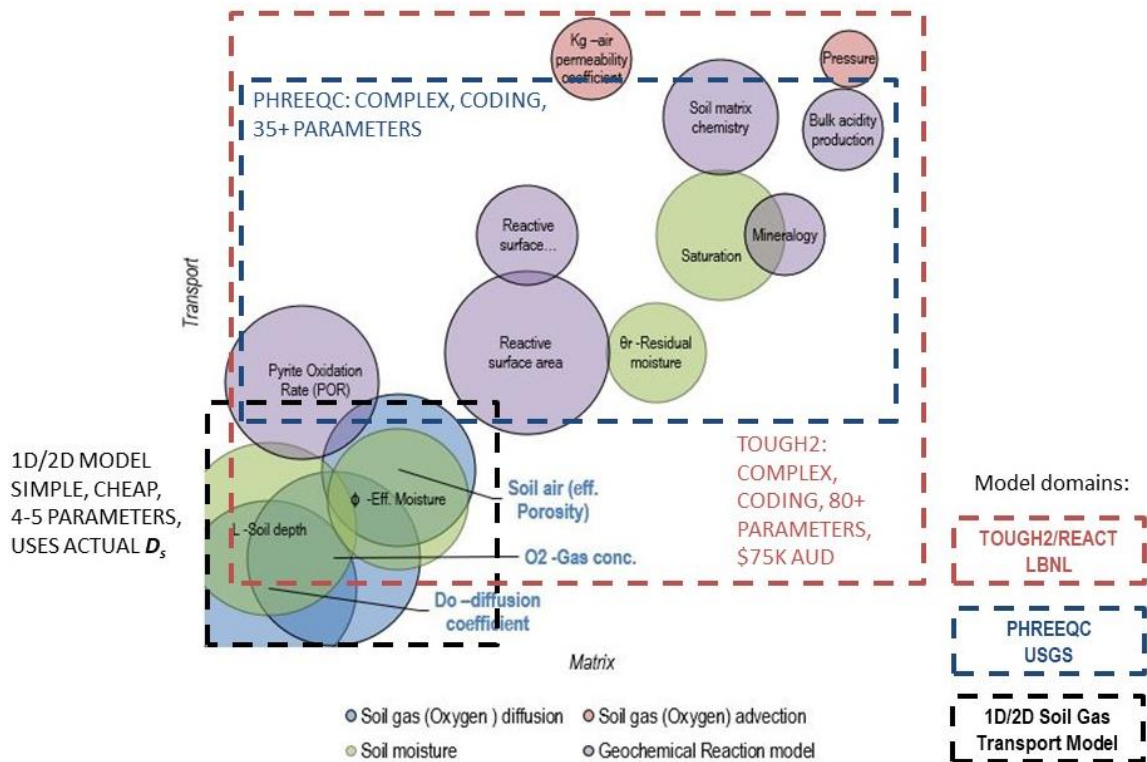
Figure 2-13: Sensitivity Analysis of some soil gas transport and AMD relevant parameters, PHREEQC, TOUGH2 and 1D/2D Model.

It is worth noting the number of parameters in a model and therefore either i) the multiplicative cost of extensive field data collection or ii) without field data, the parameter-based assumptions not based on actual field conditions that are required in complex models. Pilkey et al. (2007) builds on the analysis of Maest et al. (2005) by noting that the number of uncertainties in complex models are quite serious and "highly likely to be insurmountable". PHREEQC has assumptions in reactive surfaces, in addition to this, TOUGH2 also assumes values for tortuosity and constrictivity, amongst several assumed parameters discussed previously, both of which cannot currently be measured and are considered fitting parameters. Doherty (2020) discusses "over fitting" in models with large numbers of parameters, such as groundwater models, and makes the point that the larger the number of parameters, the simpler the fitting potential, and that this then puts pressure back on the initial modelling assumptions and field data quantity and quality, an issue not often able to be dealt with in totality by the modeller, especially in the concept phase of mine design, when detailed data is often scarce.

2.3 Literature Review Conclusion and Knowledge Gaps

In the past 10 years a great deal of progress has been made in developing models to simulate behaviour in multi-porosity media and multi-phase materials. Dual porosity and discrete fracture models offer increased accuracy over traditional media averaging models but require additional work to determine appropriate parameters. They should therefore be used in appropriate situations and with adequate data sets. Dual porosity systems are adopted to simulate strong differences in soil behaviour that are discontinuous and are not well simulated by single porosity or diffusion coefficient systems. Developing models which allow for measured variable diffusion behaviour can potentially also provide excellent results. The development of economical and practical soil gas transport diffusion testing equipment and associated soil gas transport diffusion models aimed at the mining sector for AMD management, are a key gap in current research and this is one of the key subjects of this research project.

Simple soil gas diffusion modelling has also been improved from Richards (1936), Millington and Quirk (1961) through to Moldrup's (2013) approach, which has enabled laboratory intact and remoulded samples to be modelled accurately.

Geochemical reaction rate and thermodynamic models have advanced considerably and there are several used regularly to predict acid mine drainage based on mass load and reaction rates. (Parkhurst et al. 1999, 2010). As is evidenced by Table 2-2 above, however, the major gap in current geochemical and AMD assessment models appears to be soil gas supply-side based oxidation models, the major area examined in this project. Geochemical multiphase models exist that are capable of prediction of sulfide oxidation rates for determination of AMD risk, but they are proprietary models and are most likely too expensive in terms of cost, support and training to be used as regular tools in the mining sector. Additionally, as discussed in detail in Chapter 4 (Paper i), geochemical model assumptions can present exponential levels of multiplicative error to model results, particularly in an AMD material volume assessment context. This is primarily due to the effect of particle size and associated reactive surface area, the determination of which is an issue which has not been completely resolved and is complex to test for. For more on this matrix complexity/reactive surface issue, refer to

Chapter 6 (Paper iii) which utilises Brunauer-Emmett-Teller Surface area determination (BS 148 4359-1:1996 standard method).

Simple soil gas diffusion, and complex multi-porosity, multiphase models have been applied to a range of soil gas and reactive transport systems successfully. They are therefore worthy of consideration for modelling tools to predict AMD sulfide oxidation effects for waste storage and mine pit operations in the mining sector.

In conclusion, the major knowledge gaps in current modelling of AMD and sulfide oxidation processes are as follows:

1. Soil gas transport processes, particularly with respect to geochemical models and diffusive dominated soil gas transport processes (Amos et al. 2014).

2. The interrelationship of diffusive soil gas transport behaviour with AMD processes, and in particular, the use of measured boundary conditions to help develop a modelling approach for soil gas transport and oxygen supply to the AMD reaction process.

3. The development of cost-effective soil gas diffusion columns and experimental method to measure the soil gas diffusion coefficient in mine materials.

4. Investigating the use and modification of previous soil gas transport models derived primarily for agricultural soil research, which tend to focus on soil gas transport during wetting rather than drying conditions.

5. The development of a cost-effective modelling methodology to integrate with advanced kinetic tests, such as oxygen consumption and oxygen penetration column tests, to achieve more accurate 1D soil gas transport models derived for conditions existing in the actual AMD mine materials.

6. Relatively simple, cost-effective and practical modelling of soil gas transport approaches, such as spread sheet style approaches to modelling soil gas diffusion processes for AMD management and assessment.

This research project, by focusing on the physical soil gas (oxygen) diffusion component of AMD mine materials, attempts to avoid a great deal of model complexity, potential source of error, and uncertainty in developing the proposed soil gas diffusion method to assess potential volumes of materials affected by AMD.

The key conclusions arising from this literature review are that:

- More research on modelling soil gas diffusion processes is required for effective AMD management;

- There is a lack of simple, freely available, soil gas transport diffusion models for specific use in AMD material management;

- Soil gas diffusion parameters and matrix behaviour are currently poorly covered for AMD mine materials; and

- Current, commercially available, soil laboratory testing equipment for soil gas transport by diffusion is costly and usually based on agricultural soil investigations, which have opposing and different risks and drivers to AMD materials management.

This research project has been framed to develop a new, cost effective, concept design level, AMD soil volume estimation method and associated soil diffusion testing support technology, and to develop simple spread sheet style 1D and 2D models to assist the mining sector with AMD materials volume estimation, treatment and management.

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3 General Approach and Areas of Research

This Chapter details the overall approach and methodology adopted to achieve the objective stated in Chapter 1. The general approach for this project has been to:

- Determine the state of the art in soil gas transport modelling that would be likely to assist with mining sector assessment of AMD volumes and management of AMD wastes such as mine tailings and waste rock;

- Identify and collect AMD soil data from new kinetic processes relevant to soil gas transport, including oxygen consumption methods and oxygen penetration methods;

- Design and construction of economic soil gas diffusion test columns and oxygen penetration columns to assist with determination of variable soil gas diffusion properties of AMD materials and measurement of boundary conditions. For example, oxygen penetration columns can be used to measure the oxygen extinction depth boundary condition in AMD mine materials.

- Develop, validate and test 1D and 2D soil gas transport models to evaluate their potential usefulness for use in the mining sector for AMD volume assessment and waste management.

Specific research focus areas undertaken to address the gaps identified during the literature review and through the course of this project are shown in table form in the next section.

The research focus subject areas required and actions undertaken in order to fill the research gaps identified in the project literature review, are shown in Table 3-1 below.

The research components covered by the 3 related publications forming the core of this thesis are also referenced in Table 3-1.

Table 3-1: Identified Knowledge Gaps and Associated Project Research

Identified Knowledge Gap	Associated Project Research
Soil gas transport processes, particularly with respect to geochemical models and diffusive dominated soil gas transport processes (Amos 2014).	Investigate Potential Soil Gas Transport Geochemical Modelling with PHREEQC Investigate AMD soil matrix properties (Dettrick 2019a) Investigate existing soil laboratory testing methodologies and requirements for soil gas diffusion and relevant parameter measurement
The interrelationship of diffusive soil gas transport behaviour with AMD processes and in particular use of measured boundary conditions to help develop a modelling approach for soil gas transport and oxygen supply to the AMD reaction process	Investigate effects of AMD mine material geochemical properties on relevant soil gas diffusion soil behaviour properties during laboratory measurement processes (Dettrick 2019a) Determine relevant soil gas transport monitoring technology for measurement of boundary conditions for the purposes of soil gas transport model development
The development of low cost soil gas diffusion column and experimental method to measure the soil gas diffusion coefficient in mine materials.	Review of soil gas transport (oxygen) diffusion testing methodologies Design and construction of an economic soil diffusion test column (Dettrick et al. 2019b) Identification of a soil gas penetration column design and construction of the test column (Elberling et al. 1994) Development of factor of Safety approaches for situations with little or no available soil gas diffusion data (Dettrick et al. 2019b)
Investigation of the use and modification of soil gas transport models and their associated key parameters identified in the literature review.	Review of soil gas transport (oxygen) diffusion measurement and estimation methodologies (Dettrick et al. 2019b) Modelling and testing of literature-based soil gas transport (oxygen) diffusion estimation models (Dettrick et al. 2019b)
The development of a cost-effective model and testing methodology to build on advanced kinetic tests to achieve simple and accurate 1D and 2D soil gas transport models derived for simulating conditions existing in actual AMD reactive mine materials.	Modelling and testing of literature-based soil gas transport (oxygen) diffusion estimation models (Dettrick et al. 2019b) Development and testing of 1D model (under review Dettrick et al. Engineers Australia Technical Journals exp. 2020) Comparison with other 1D soil gas transport models Development and testing of 2D model
Affordable, efficient and simple modelling approaches such as spread sheet style approaches to modelling soil gas diffusion processes for AMD management and assessment.	Development and testing of 1D spread sheet-based model (under review Dettrick et al. Engineers Australia Technical Journals, exp 2020) and associated testing methodology and required soil parameter testing Development of soil gas diffusion testing hierarchy for best accuracy (under review Dettrick et al. Engineers Australia Technical Journals, exp 2020) Development and testing of 2D model

3.1.1 Methodology

The key steps for the work program of this research and design project are summarised below:

1. Select and/or develop candidate models for possible use as soil gas transport and geochemical models suitable for AMD materials.

2. Select candidate AMD soils for laboratory testing for diffusion properties relating to soil gas (oxygen) transport processes, and for comparison and calibration.

3. Design several options for and build cost-effective soil gas diffusion and oxygen penetration columns.

4. Undertake the required soil laboratory testing program for mine waste material soil parameters, soil gas diffusion coefficient and oxygen penetration depth.

5. Develop three research Papers from the results of the research, column design and laboratory program:

    i. The effect of mine material matrix and particle size on AMD reactions and geochemistry on mine waste management.

    ii. A comparison of measured and modelled soil gas diffusion using available soil gas diffusion estimation models.

    iii. A 1D soil gas diffusion model for estimating volumes of potentially oxidised materials and oxidation rates of AMD mine materials.

6. Develop a 2D finite difference soil gas diffusion model for estimating volumes of potentially oxidised materials of AMD mine materials.

7. Compare calibrated model results against approximated and modelled soil gas diffusion models, and soil gas diffusion coefficient results from the soil laboratory testing program.

8. Publish the research Papers on these findings and document diffusion column and oxygen penetration column designs, additional materials and result of research in the thesis.

3.2 Modelling Approaches

The strategic approach to modelling used within this project adopted aspects of the modelling guidelines produced by Hill and Tiedeman (2007) for modelling parsimony (simplicity) and calibration. Refsgaard and Henirkson (2004) – see Figure 3-1, were used for modelling terminology and strategic model development process For a detailed overall modelling method and approach, including model results evaluation, Barnett et al. (2012) was applied. The Refsgaard and Henirkson (2004) and Barnett et al. (2012), approaches are iterative, and both are illustrated below for reference.
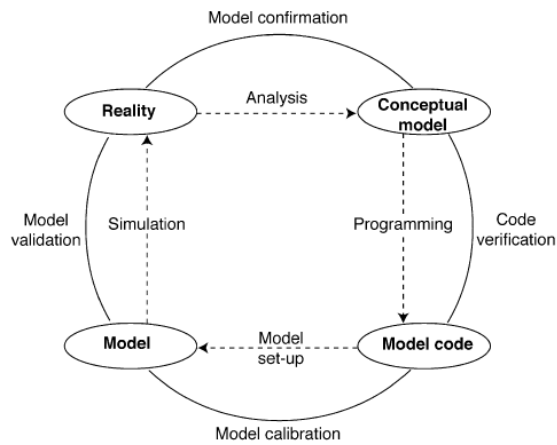
Figure 3-1: Elements of strategic modelling terminology (Refsgaard and Henrikson 2004)

Barnett et al. (2012) propose the following modelling process which uses some slightly differing terminology to that of Refsgaard and Henrikson (2004) and is shown in Figure 3-2.

(continued in right hand pane)
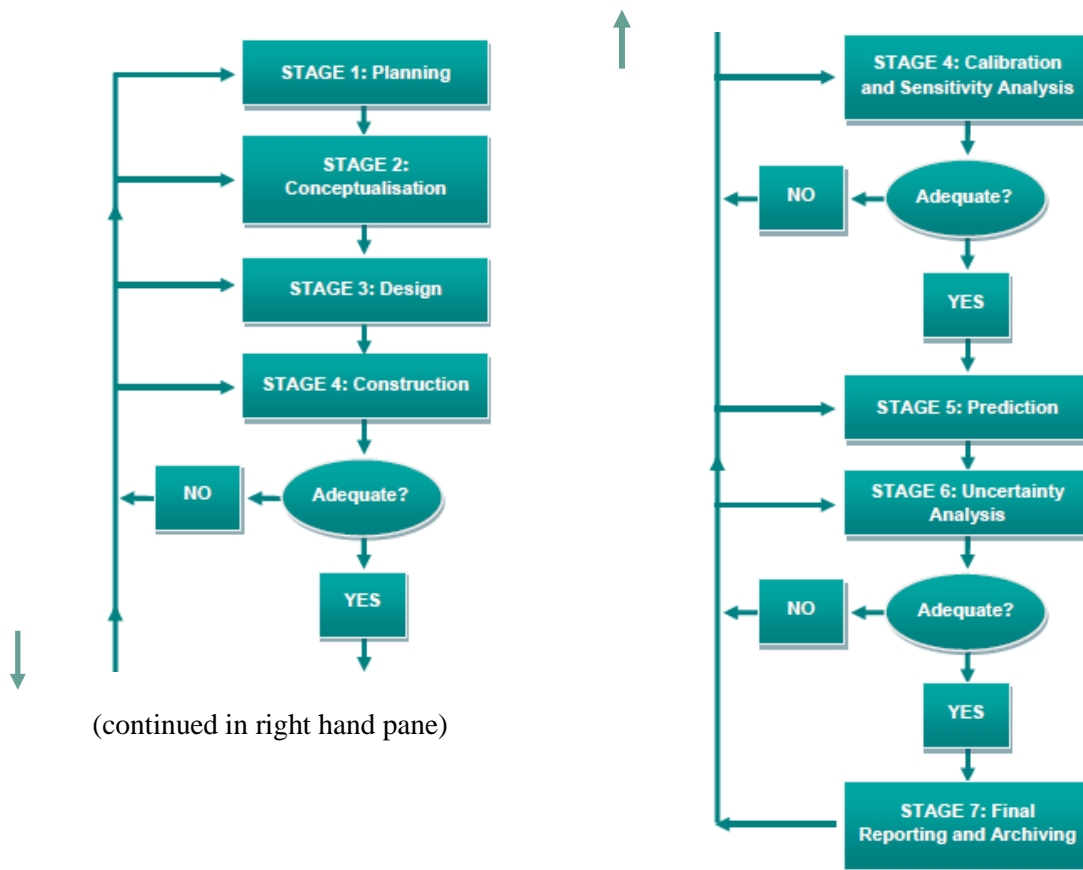
Figure 3-2: Groundwater modelling process (Barnett et al. 2012).

To enable the ease of use and improve industry adoption of the models derived in this study, the following approaches were undertaken:

- Modelling parsimony -keep models as simple and understandable as possible.

- Use of commonly available software such as Microsoft Excel.

- Use of economic and easily fabricated, soil gas transport testing equipment to determine soil gas diffusion parameters and material oxygen penetration depth boundary conditions for soil gas transport modelling.

In the next Chapter the relationship between soil matrix, particle size and AMD material geochemical reactivity will be examined with an emphasis on mine waste management, particularly during closure, or to achieve long term AMD waste geochemical stability.

3.3 References

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Dettrick. D, Costelloe, J., Arora, M., and Yuen, S. in review, expected 2020, "A 1D soil gas diffusion model for estimating oxidation rates of AMD mine materials", Engineers Australia Technical Journals, AJMDE: Australian Journal of Multi-Disciplinary Engineering. This is referenced as Paper iii in this thesis, and forms Chapter 6.

Hill, M.C., Tiedeman, C.R., 2007, Effective Groundwater Model Calibration: With Analysis of Data, Sensitivities, Predictions, and Uncertainty, John Wiley and Sons, New Jersey.

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4 The Effect of particle Size on Acid Mine Drainage Soils Sulfide Oxidation Rates (Paper i: Published)

This Chapter investigates issues in geochemical reactivity assessment and introduces a new kinetic AMD assessment tool - oxygen consumption techniques. AMD material matrix issues are discussed and evaluated through an assessment of the differing reactive potentials of reactive surface area and soil matrix particle size. The testing of a variety of particle sizes of AMD reactive materials, yields an exponential effect for reactivity versus decreasing particle size. This raises an important issue for geochemical modelling of AMD materials and waste treatment -the effect of potential exponential effects on multiplicative error. This Chapter was published as: D. Dettrick, N. Bourgeot, J. Costelloe, S. Yuen, and M. Arora, 2019a, "The Effect of Particle Size on Mine Waste Sulfide Oxidation Rates and Conceptual Treatment Costs", Mine Water and the Environment, 38:735–745.

4.1 Abstract

Acid and metalliferous drainage (AMD) oxidation reaction rates were determined using oxygen consumption rates in a high sulfur overburden rock from the Australian Latrobe Valley coal provinces, and a mid to low range sulfur waste rock from a porphyry copper deposit in Papua, New Guinea. Nine grain sizes were tested, ranging from material retained by a 0.038 mm sieve through to a 40 mm sieve. Oxygen consumption rates in sealed cells were measured to establish pyrite oxidation rates (POR) in each sample. The oxygen consumption rates displayed a strong exponential reaction correlation with particle size for the material. The POR was found to range from 0.28 to 10.90 wt%/year FeS_2 for the materials tested. A relationship between particle size and POR was established for comparative purposes. The smaller grind sizes included in this study extend the AMD/POR particle size data set available in the literature and will assist with geochemical engineering for designing tailings storage facilities. The potential economic and mine design ramifications of additional reactivity of fine mine materials is assessed and discussed using a unit cost framework for applying neutralizing materials.

4.2 Introduction

The optimum particle size to adopt for mineral processing, particularly for sulfidic ores, is a complex question for the mining and resources sector (Runge et al. 2013). Mine profitability requires optimization modelling of many variables during the feasibility stage of mine design, based on balancing the cost of operations against the cost of mine closure. Interacting variables include: the current and future value of mined minerals and metals, recovery rates of processing technology, the geochemical interactions between the host rock geochemistry and the target mineral or metal during processing and closure, the cost of mining, crushing and milling technology, the transport of milled product and waste rock, the cost of environmental containment of waste rock and mine tailings, and providing ease of access to waste products for potential future re-mining (Chadwick 2009). The focus of this Paper is on sulfide geochemical interactions and the influence of mineral processing, tailings, and waste rock particle size on the final reactivity of mining waste.

Acid and metalliferous drainage (AMD), or acid rock drainage (ARD) develops when sulfide materials, such as iron pyrite (FeS_2), oxidize when exposed to the atmosphere (EA 1997). The acidity dissolves the metals in soil/rock, which can create toxic conditions for fish and aquatic ecosystems and can potentially damage corporate reputations (DITR 2007). There is a need to better understand, predict, and control the rates of AMD production at both existing and legacy mine sites (US EPA 1994). Information on particle size and AMD reactivity is particularly important for long term geochemical stability of mining wastes post closure, and for minimalizing cost transfer from mine waste management during operations to the closure phase. Future environmental liability is related to particle size, as increases in reactive area can contribute to AMD production in the waste materials that remain. Therefore, there is a trade-off between the particle size generated by mineral processing that optimizes product recovery and the potential for AMD from the waste tailings. Designer tailings are therefore created by balancing returns on processing of the milled ore bearing rock against the increased reactivity and long-term management requirements of the more reactive milled pastes.

It is well-established that solubility (Stumm and Morgan 1981) and sulfide oxidation rates (Hollings et al. 2000) increase with decreasing particle size due to increases in reactive surface area. This effect was described by Apello and Postma (2007), who illustrated the relationship between surface area and particle size for a range of soils and theoretical smooth spheres indicated as Geometric surface area on Figure 4-1. An increase in available surface area increases the molecular amount of reactive chemical available for reaction to gases and liquids coming in contact with the surfaces.Therefore, reactive surface area and particle size are key parameters for geochemical modelling.
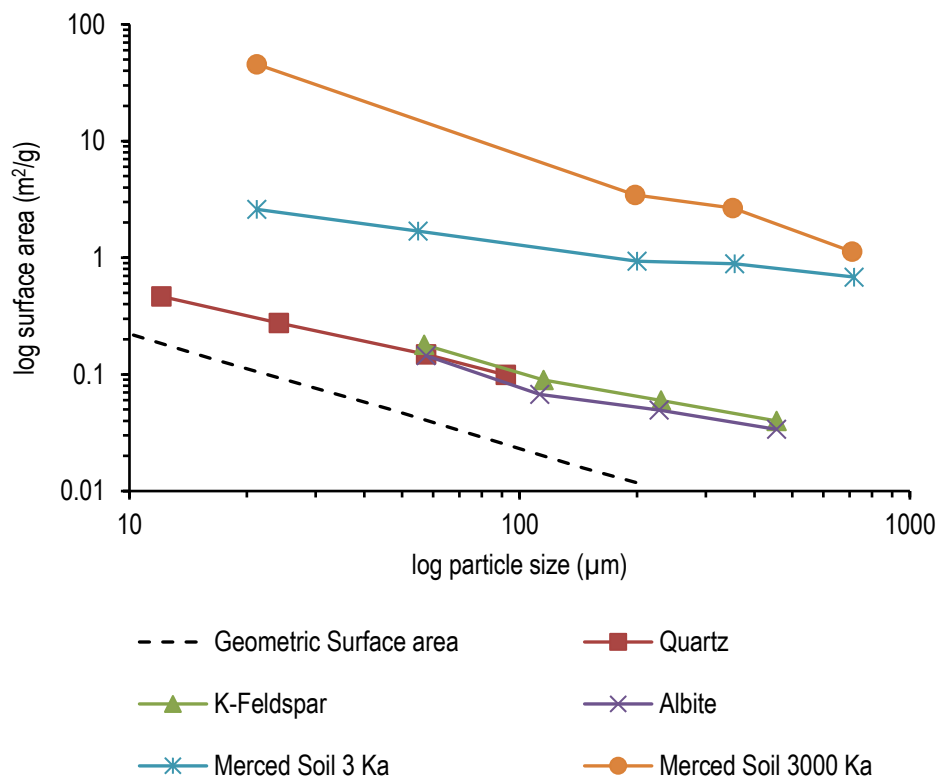
Figure 4-1: Relationship between surface area and particle size (after Apello and Postma 2007)

Measurement of reactive surface area has increased greatly in the last 10 years. Measurement methods, primarily to support geochemical modelling, include the Brunauer–Emmett–Teller surface area determination (BS 4359-1) and temperature-programmed desorption (Schroeder and Gottfried 2002). These methods are expensive and are presently only capable of testing silt sized materials in amounts of approximately 2 grams. However, the effect of particle size on the AMD reaction is complex and requires further examination.

Studying the effects of particle size on AMD reaction rates requires the careful selection of geochemical testing methodology. Most current static and kinetic geochemical AMD tests, such as humidity cells, are based on measuring the maximum potential acidity generation (Maest et al. 2005; US EPA 1994). These methods typically rely on sulfate production to report oxidation, which may confound results if sulfate within the rock or soil sample is released during kinetic testing procedures (US EPA 1994). Advanced rate-based AMD kinetic testing based on oxygen consumption measurement was identified as a potential way to examine sulfide oxidation reaction rates while not requiring the use of sulfate as an indicator. This method has recently been deployed successfully in AMD risk studies (Anderson et al 1999, Hollings et al. 2000; Schmieder et al. 2012). A great deal of work has been undertaken on AMD geochemical characterization, but few studies have focused on AMD and particle size relationships using oxygen consumption techniques (Davis et al. 2014; Hollings et al. 2000) Several studies have also examined particle size relationships using conventional column leach and/or humidity cell analysis (Brough et al. 2017; Elghali et al. 2018, 2019; Erguler et al. 2014; Erguler and Erguler 2015; Lapakko et al. 2003, 2006). 2015; Lapakko et al. 2003, 2006).

The limited number of published particle size studies with AMD materials is perhaps due to the confidential nature of many mining activities, and possibly slow uptake of the new kinetic AMD characterization techniques, such as oxygen consumption testing. Current methods use geochemical characterization of exploratory drill core rock samples crushed to 15 mm, primarily for process metallurgy requirements, and is based on a process that includes minor amounts of fines, but insufficient to fully represent tailings particle size ranges after mineral processing (Runge et al. 2013). The AMRIA (2002) guideline suggests a sample grind size of 4 mm and < 0.75 mm. A review of published studies including AMD and particle size relationships showed limits to material particle sizes from 25 to 0.1 mm, including Erguler and Erguler (2015) and Erguler et al. (2014). Lapakko's (2013) study examined < 0.053 mm for two mine materials. Runge et al. (2013) suggested that for many process metallurgy requirements, the tailings sizes are indeed much smaller than 15 mm, with several common grind sizes below 0.1 mm (Figure 4-2).

The new oxygen consumption techniques for measuring AMD production rates offers accurate results, but the current dataset for oxygen consumption-based pyrite oxidation rate (POR) analysis needs to be extended across a wide range of geochemical conditions and parameters (Hollings et al. 2000). The smaller grind sizes included in this study extend the current AMD/POR particle size data set available in the literature and will assist with geochemical engineering for tailings storage facility (TSF) design.
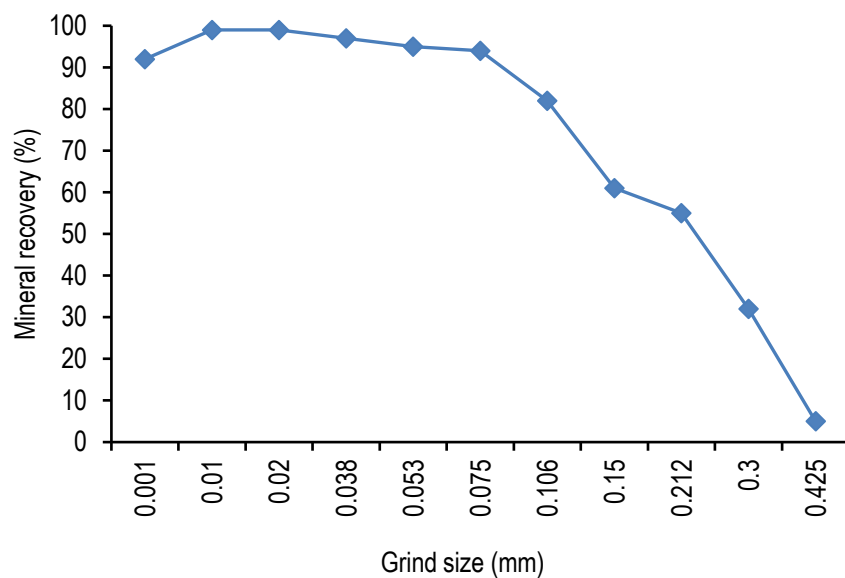
Figure 4-2: Example grind size and expected mineral recovery for copper flotation process

(Runge et al. 2013)

The main objective of this study was to understand the dependency of reaction rate of AMD mine materials on particle size to assist environmental managers such as mining companies and regulators with focused information to manage risk after sulfidic material oxidizes, such as when exposed to the atmosphere for the first time. Identification of chronological phases of AMD management requirements are seen as being beneficial to mine design and cost minimization (DITR 2007; US EPA 1994). We also sought to model conceptual cost variations based on a more accurate assessment of AMD risk.

4.3 Methodology

4.3.1 Sample Collection and Particle Size Fractionation

20 kg of sulfidic rock samples were collected as broken rock pieces (100 – 250mm length) from both an open cut brown coal mine in the Latrobe Valley, Australia (OB) and a porphyry copper deposit in Papua New Guinea (WR). The Latrobe Valley sample was a "brassy top" marcasitic rock, similar to that associated with the Greta seam of the Sydney basin, where marine incursions during the Late Permian allowed bacterial hydrogen sulfide to combine with dissolved iron in the seawater to form pyrite (Blewitt 2012). The Latrobe Valley coal is overlain in many places by a marine succession that formed brassy top between the coal seams. The Papua New Guinea waste rock porphyry consists of hydrothermally altered deposits of magnetite and sulfide in Cu-Au skarn formed in sedimentary mudstone. The porphyry consists of complex layering of alteration and mineralization derived from multiple hydrothermal events developing magnetite and Cu-Au (among other minerals) within quartz veins to form quartz-magnetite-sulfide veins (Corbett 2009). Both the brassy top and Cu-Au porphyry derived waste rock contain sulfides. A Gold float process tailings material was also used as an additional particle size distribution to show the impact of similar grind size materials, based on data from Runge et al. (2013).

The rock samples were then representatively sub-sampled via coning and quartering, ground, and separated into particle size fractions. Sieve sizes included 0.038, 0.075, 0.106, 0.425, 1, 2, 4.75, 19, and 40 mm to provide a range of smaller grain sizes similar to that created by grinding circuits for flotation recovery of porphyry copper (Figure 4-2, Runge et al. 2013). The OB material was ground to < 0.038 mm, < 0.106 mm, and < 1 mm, while the WR was ground to < 0.075 mm, < 0.425 mm, < 2 mm, and < 40 mm. To extend our understanding of the relationship between particle size and reaction rates over a wider range of particle sizes than currently available in the literature, the samples were sieved to two sizes below 0.1 mm, including 0.075 mm and 0.038 mm sieves.

4.3.2 Oxygen Consumption Rates

The Earth Systems Ltd. OxCon testing technique (Davis et al. 2014; Schmieder et al. 2012) was used on each of the particle size samples to determine oxygen consumption rates, which were then used to estimate POR. The oxygen consumption technique has been successfully used by several studies (Anderson et al. 1999; Bourgeot et al. 2011; Davis et al. 2014; Elberling and Nicholson 1996; Elberling et al. 1994; Schmieder et al. 2012; Tibble and Nicholson 1997). The technique involves oven drying the specific grain size sample at 105 °C for 24 h, wetting until the required gravimetric moisture content of 10–15% is attained, and then reweighing and placing the sample in a sealed OxCon cell (Figure 4-3). The oxygen meter was calibrated for accuracy against atmospheric O_2 and using a calibration gas with 10% O_2, and 99.99% N_2. Oxygen consumption of the ground rock sample was then measured for 72 h to determine the POR. Sulfide oxidation rates were then evaluated by normalizing the observed oxidation rate against the sulfide content of the samples. This was undertaken using the pyrite equivalent content, which assumes all sulfide is present as pyrite, and was expressed as POR in units of weight percent of remaining pyrite (equivalent) that will oxidize to form sulfuric acid (equivalent) acidity per year (wt% Py/year). Additional Bureau of Metrology (2017) atmospheric pressure data was collected during the test and compared to chamber pressure to verify acceptable chamber leakage rates (Figure 4-3). Pressure in the chamber did not vary with atmospheric pressure, which indicates minimal leakage. Temperature was kept relatively constant (from 25.0 to 25.8 °C) over the 26 day test. These test conditions were maintained for each OxCon apparatus is shown in Figure 4-4.

4.3.3 Sulfur Content in Samples

Sulfur content in the samples was examined to determine if reactivity is related to sulfur content. Three representative sub samples of each grain size batch were analyzed for total sulfur (S) and extractable S as per ASTM E1915-13 (2013). Total S was determined using a Leco sulfur analyzer. The Leco process involves heating the sub sample in an induction furnace while passing a stream of oxygen through the sample.
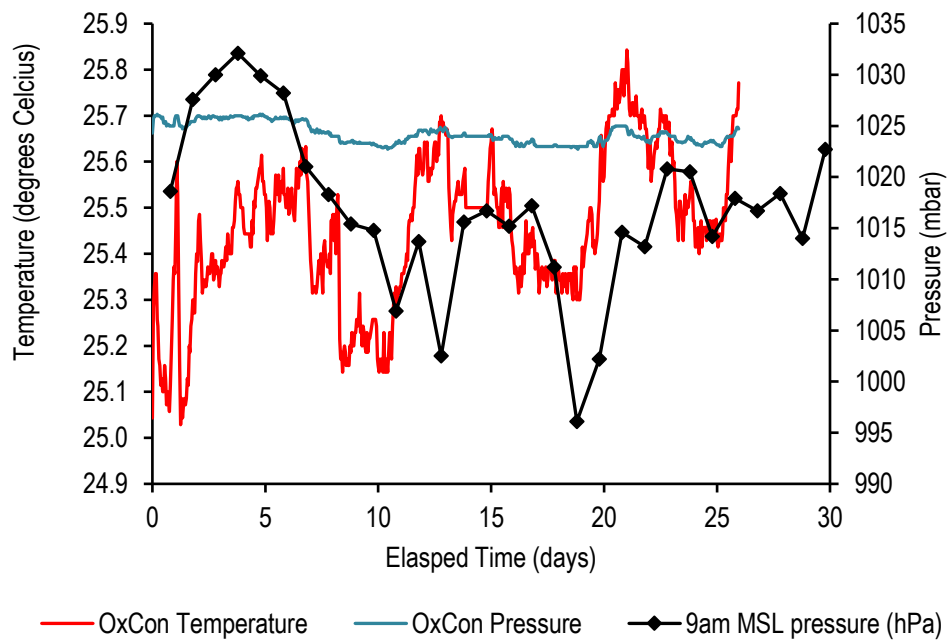
Figure 4-3: WR 4.75–40 mm example Ox Con chamber error checking data.
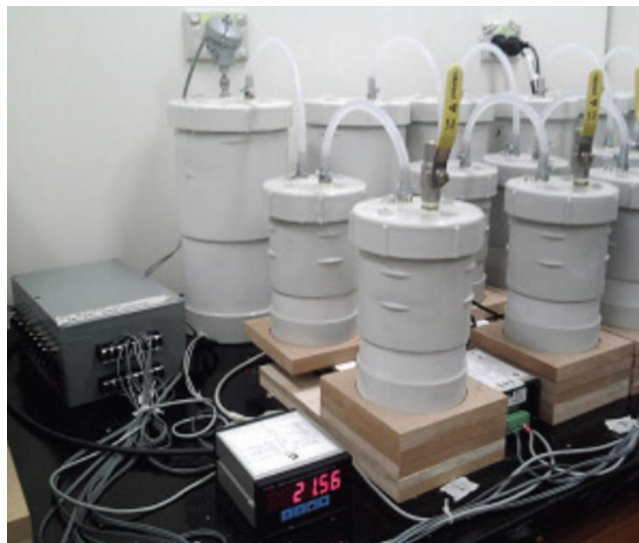
Figure 4-4: Earth Systems OxCon Apparatus in action for kinetic POR determination

(Schmieder et al. 2012)

Sulfur dioxide released from the sample is then measured by an infrared detection system, which yields the total sulfur content. The HCl extractable S results were determined by heating the prepared sub-sample with dilute HCl for 30 min. Silica and any acid-insoluble materials were removed by filtration and ferric iron was reduced to ferrous iron by the addition of hydroxylamine hydrochloride.

The sulfate in the resulting filtrate was then precipitated with barium chloride in a dilute HCl medium. The barium sulfate precipitate was then filtered, ignited, weighed, and calculated as %S (of the HCl-leachable sulfate) in the original sample.

4.4 Results

4.4.1 Particle Size

This study extends the particle size data below < 0.1 mm by providing data on < 0.075 mm and < 0.038 mm grain size materials, to provide additional oxygen consumption derived AMD reaction rates for the smaller particles expected in a TSF. The sieve sizes used to create consecutively smaller particle sizes are shown in Figure 4-5, along with the sieve sizes used by Hollings et al. (2000).
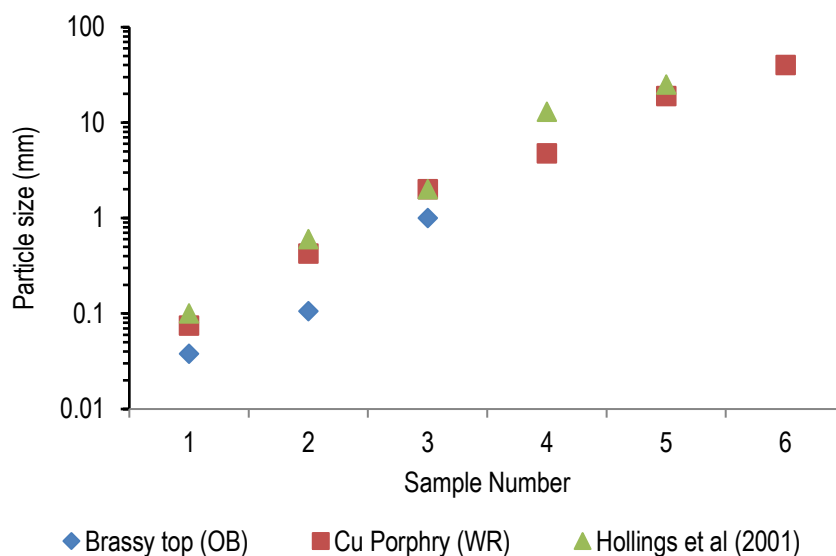
Figure 4-5: Particle sizes used for particle size separation in this study and that of Hollings et al. (2000)

4.4.2 Confirmation of Optimal Oxidation Conditions using Target Material

Oxygen consumption testing was completed on the OB and WR materials passing a 2 mm sieve, for a range of adjusted moisture contents to determine the effect of moisture on POR. The range of moisture was adjusted from residual moisture, where absorbed moisture is dominant and effective porosity is large, through to approaching saturation. These tests were used to confirm optimal median

moisture content to provide high rates of AMD/POR sulfide oxidation. These optimal oxidation conditions (10-15% moisture content) were maintained to ensure high POR rates and less variability, so these factors would have minimal influence on the study, as suggested by Hollings et al. (2000). Figure 4-6 shows that POR was sharply reduced at low moisture contents (< 4 wt%) due to a lack of available moisture for pyrite oxidation, and also at high moisture contents (> 16 wt%) due to low effective porosity and associated low soil gas (oxygen) diffusion rates.
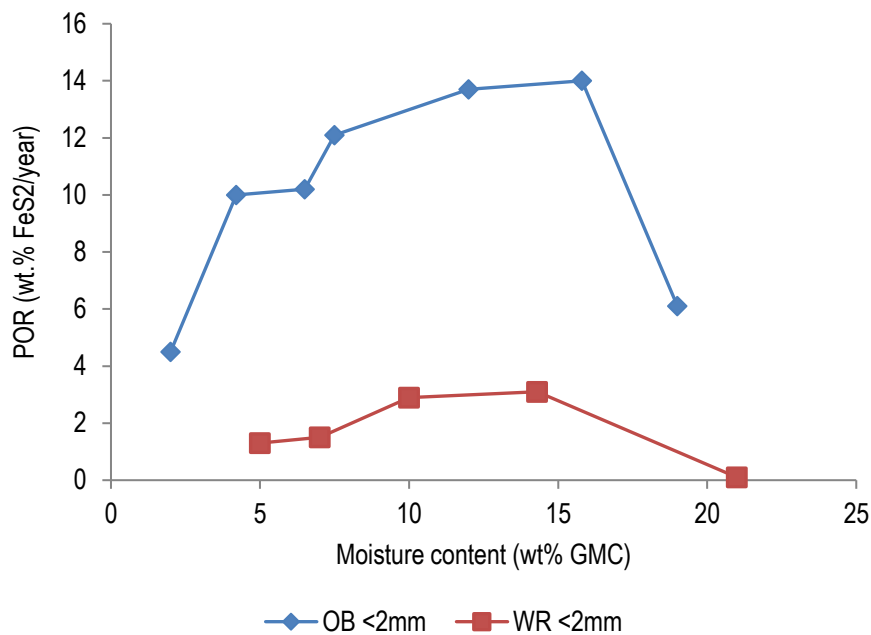
Figure 4-6: OB POR vs. gravimetric moisture content (GMC).

The median moisture contents (10-15 wt%) were identified for both the OB and WR material as having high and relatively stable POR rates. These optimal moisture content values (10–15%), temperature (20–21 °C), and atmospheric pressure were maintained for subsequent oxygen consumption testing on sieved material, as per Hollings et al. (2000) for optimal oxidation of both the OB and WR samples.

The OB samples were oven dried prior to wetting to the target moisture content to minimalize biological activity during the testing period, and the oxygen consumption chamber was gas sealed to prevent oxygen leakage during testing.

4.4.3 Sulfur Content

Results for total S (%) in the WR and OB sieved samples are shown in Figure 4-7, with the total S content in OB rock (25–35%) being significantly greater than in the WR (0.5–5%). The data for total S shows the increased variability of sulfide content in the largest particle size sample (WR <40), and the converse, which is a much smaller difference in total S content as particle size decreases.
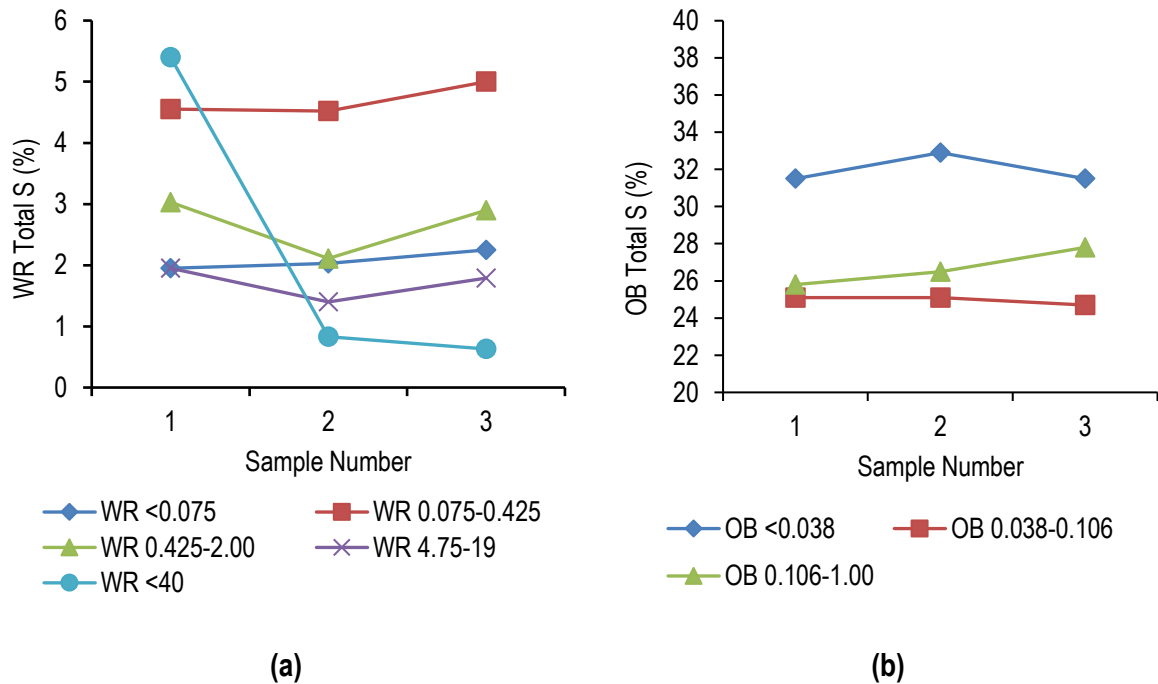
Figure 4-7: Total S (%) results for the WR (a) and OB (b) samples

The WR sample with the large particle size of > 19 mm supports this trend, showing the most variation with one sample with more than 5% total S and the other two sub samples yielding less than 1% total S. In the WR sample, the highest total sulfur content was found in the 0.075–0.425 mm sample rather than in the finer < 0.075 mm. This may be due to the natural crystallization size of the sulfide materials, since this effect did not occur in the OB sample. The HCl extractable sulfur is an indicator of completed sulfide oxidation and was useful for normalizing the oxygen consumption data to show a relationship between reaction rate and grain size (Figure 4-8).

(a)

(b)
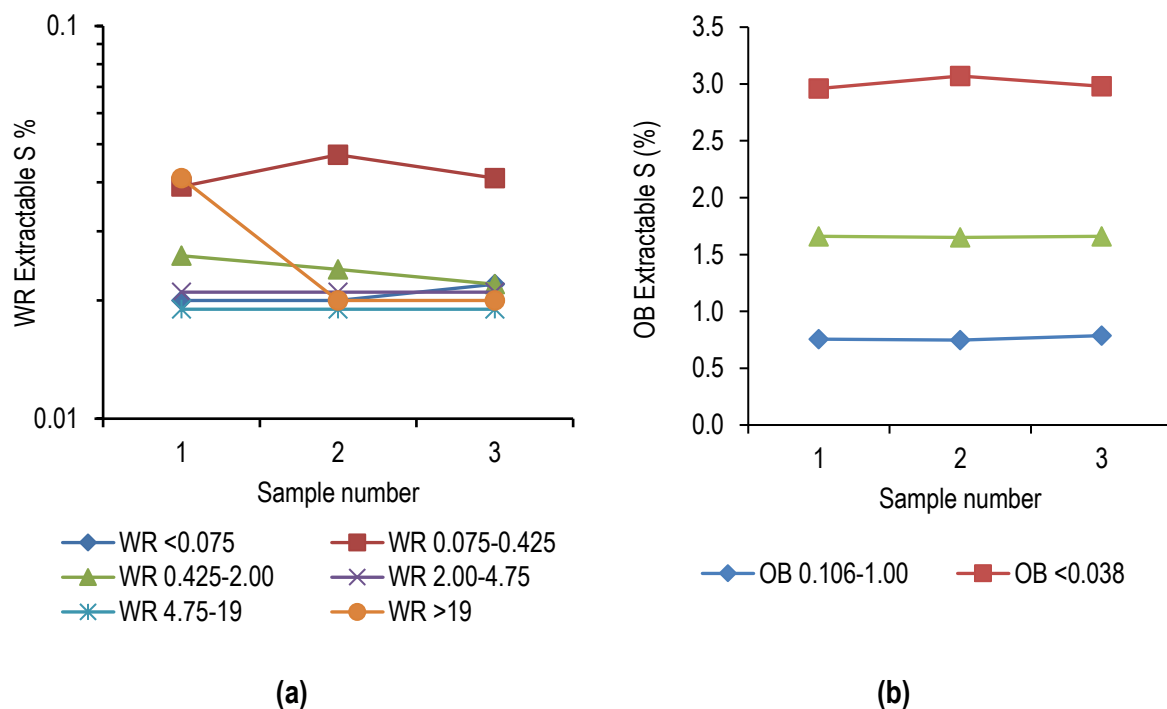
Figure 4-8: HCl Extractable S (%) results for the WR (a) and OB (b) samples.

The WR samples were low in extractible sulfur, which may indicate that less prior oxidation occurred in these materials, while the OB samples were higher in extractible sulfur, but with more total sulfur, which may have remaining oxidizing potential. This was investigated in further analyzes of particle size and total and extractible sulfur below. The WR and OB samples were plotted for grain size against total and extractible HCl sulfur content. Figure 4-9 shows that the WR samples contained less extractible sulfur and were less variable in content than the OB samples.

While the WR samples showed a slight (1–2.5%) change in the fraction of extractible S compared to total S, the OB samples showed a large increase in the fraction of extractible S with decreasing particle size, again demonstrating potential reactivity and particle size effects. The OB samples contain relatively high total S (25–30%) and higher extractible S (0.75–3%), compared to the WR sample, which had less total S (0.5–4.5%) and less extractable S ($\approx$ 0.05–0.1%).

(a)   **(b)**
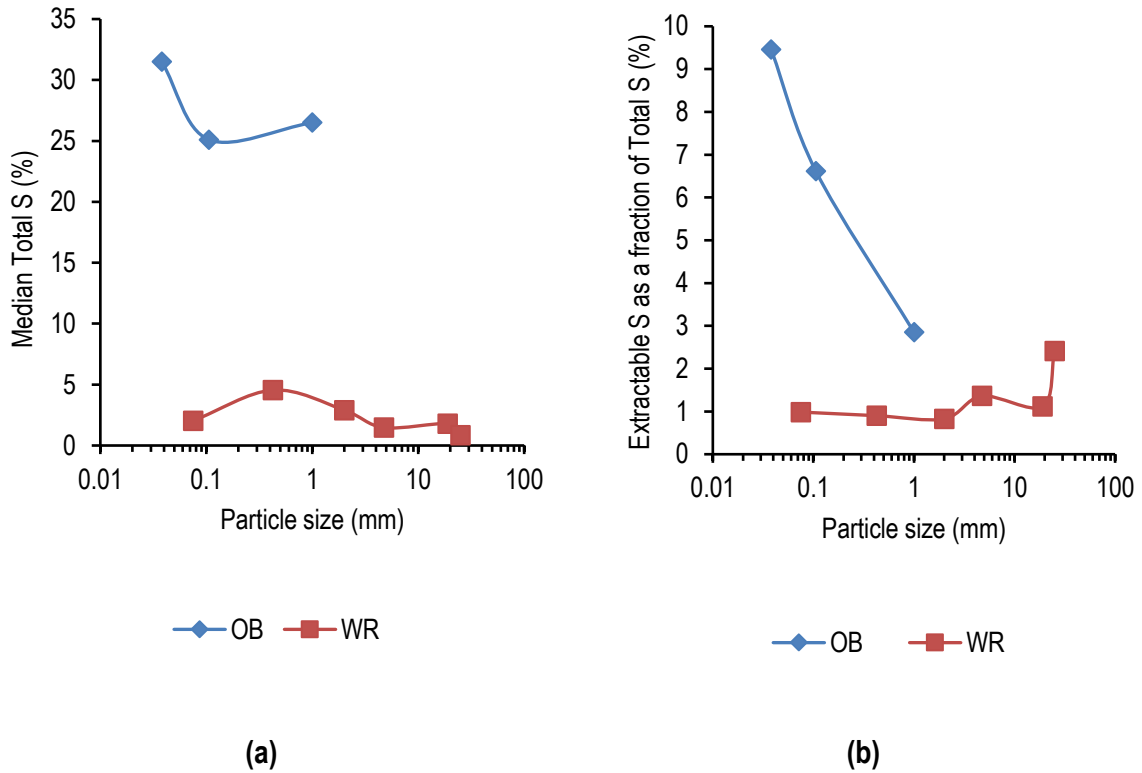
Figure 4-9: Particle size vs. median total S (%) and particle size vs. median extractable S as a fraction of median total S (%)

4.4.4   Oxygen Consumption and Pyrite Oxidation Rates

The oxygen consumption results were used to predict the POR, which was used as the indicator of the AMD reaction rate in this study. The POR were sample size adjusted (as wt%/year FeS2) for each grain size sample and median total and extractable S (Table 4-1). The oxygen consumption results for the WR 4.75–40 mm particle size are highlighted to show the influence of particle size for the larger particles, with relatively little oxygen consumption over 30 days due to few available sulfide oxidation sites. Oxygen concentration (%) reaction trace for each of the sieved WR and OB materials in the OxCon cell over the testing period is shown in Figure 4-10.

Comparing the oxygen consumption of the various size grades of the OB and WR material, it can be seen immediately that the OB material was more reactive, with each size grade consuming all of the available oxygen in the cell in less than 14 days.

Table 4-1: Particle size, Total and extractable S and POR results.

Material	Particle/grain size (mm)	Median total S (%)	Median extractable S (%)	POR (wt%/yr FeS2)
OB	<0.038	31.5	2.98	117.02
	<0.106	25.1	1.66	71.16
	<1	26.5	0.756	14.01
WR	<0.075	2.03	0.02	10.51
	<0.425	4.55	0.041	4.42
	<2	2.9	0.024	2.12
	<4.75	1.47	0.02	1.09
	<19	1.79	0.02	0.26
	<40	0.83	0.02	-

(a)   **(b)**
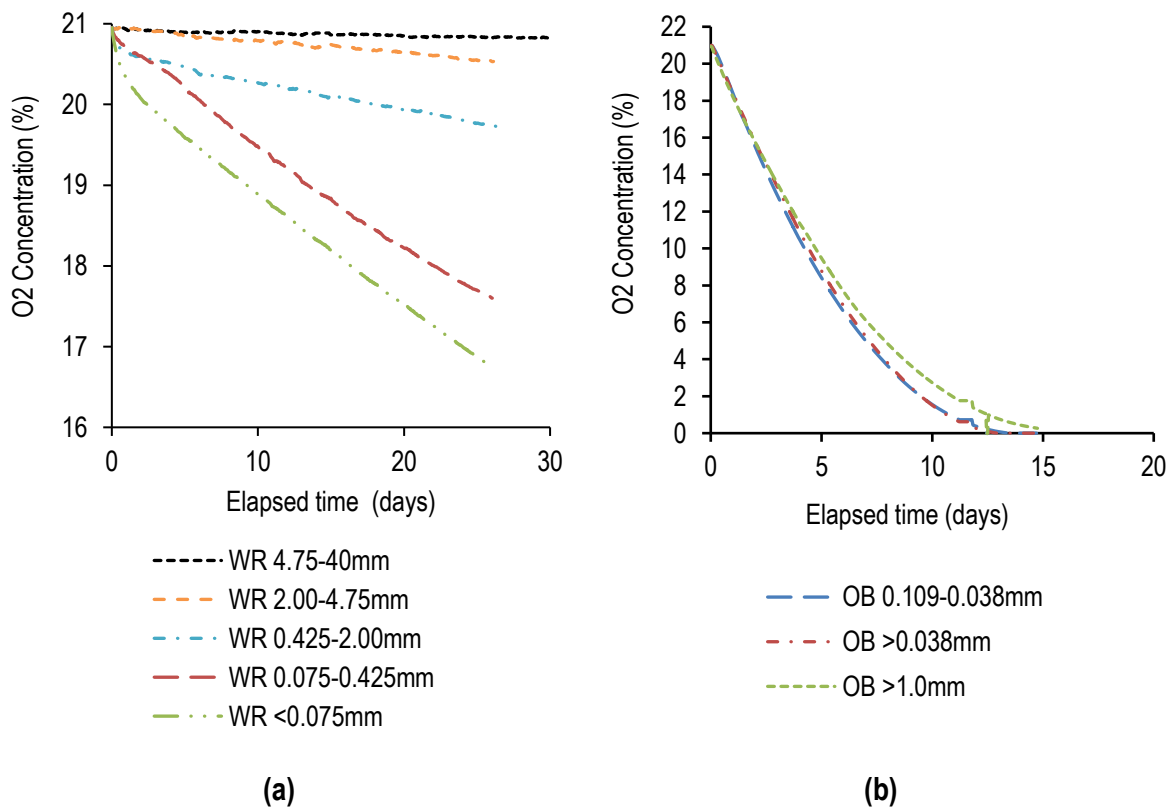
Figure 4-10: Ox Con O$_2$ (%) concentration in WR (a) and OB (b) samples over time

The WR material showed a strong reaction gradient with smaller particles being more reactive than larger particles, as one would expect. However, the WR material was less reactive than the OB material with only a 4% reduction in O2 concentration over 25 days.

Finally, the results of the POR were then graphed against particle size to demonstrate the relationship between particle size and reactivity (Figure 4-11). For both materials, the relationship was exponential: as particle size decreased, reactivity increased exponentially, confirming that particle size influences reaction rate.

(a)　　　　　　　　　　　　　　　**(b)**
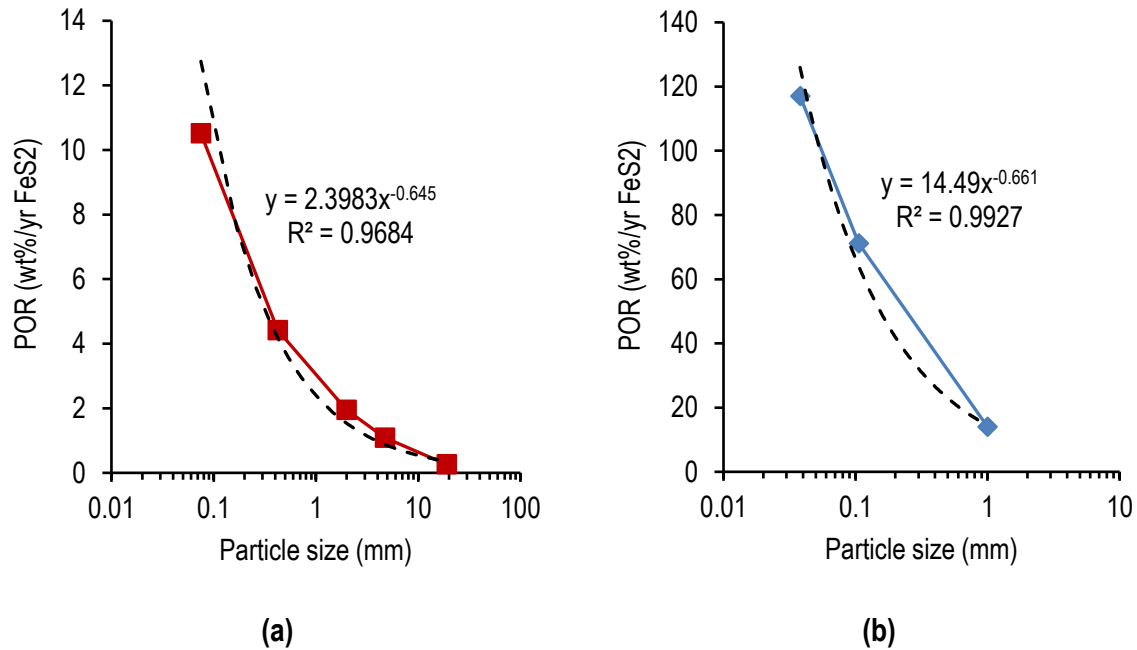
Figure 4-11: Pyrite oxidation rate and particle size in the WR (a) and OB (b) samples

The OB and WR data fit to a power relationship shows an R2 of 0.99 and 0.97, respectively. The highly exponential behavior of POR compared to particle size, particularly in material below 1 mm in size, confirms that decreasing particle size increases reactivity. Comparing the strength of this reactivity effect between the low total S (WR) and the high total S (OB) material, it can be seen that the OB material displays a more strongly exponential behavior. Particle size increases acidity generation exponentially and this effect is likely to increase further with greater sulfur content. In the next section, the particle size and reactivity functions derived in Figure 4-11 will be used to derive treatment costs for a geochemically stable mine closure.

4.5　Mine Rehabilitation Costs for Three Different Mine Wastes

A conceptual calculation of mine rehabilitation costs was conducted to illustrate the AMD management costs to provide geochemical stability for three different mining wastes: (1) the WR

material, (2) the OB material and (3) a gold float tailings material. Particle size data for similar mine wastes types was applied to the material POR data to provide three AMD management scenarios, including a copper float tailings particle size analysis (PSA) for the OB, a heap leach grind size for the WR, and a gold float PSA for the gold float tailings material.

The conceptual costing model developed below represents simplified case where all of the particles sizes in the bulk material are fully exposed to oxygen and thus are oxidising at maximum potential rates. In reality this is unlikely occur because moisture gradients within the material will tend limit soil gas transport and hence sulfide oxidation with depth. Each mine waste management system will also vary based on geometry (for example valley fill tailings storage, compared to bunded above ground level tailing storage) with the actual extent of exposure being very system dependent. However, these comparisons do indicate the need to factor in time of exposure into a TSF geochemical risk and cost management framework in the context of likely POR, as time of exposure could have major implications for sizing and costing of water treatment that may be needed to mitigate potential adverse impacts on both the environment and/or process water circuit quality.

The assumptions of the modelling include:

- Rehabilitation requires addition of neutralizing materials to achieve geochemical stability for closure. materials.
- The same unit price and reactivity (neutralizing potential) for neutralizing materials at each mine site. materials.

Table 4-2 illustrates a simple methodology showing how PSA-based AMD costs can be calculated conceptually using the PSA/POR data from this study. The geochemical engineer undertaking the neutralization process design in tailings or waste rock will need to conduct some further studies to investigate the reactive surface area/particle size relationship of the neutralizing material to determine the ultimate neutralizing potential per unit of material.

Table 4-2:Example PSA based AMD load -concept cost calculation for OB mine material.

Particle Size (mm)	POR (wt%/yr FeS2)	PSA Percentage (wt%)	Neutralising material (units)	Concept Cost (per unit)
<0.038	117	10	12	59
<0.106	71	60	43	213
<1	14	30	4	21
			Total	**293**
Unmilled ore	14	100	14	70
			Total	**70**

The calculated cost of geochemical treatment for the three mine materials are presented in Figure 4-12. Figure 4-12(a) shows the reactivity of each particle size group for each mine material, with fine materials displaying more reactivity, even in the least reactive WR material. Figure 4-12(b) provides data on the relative mass of each material based on the PSA; most of the OB material (60%) is grind size 0.106 mm, the more reactive 0.038 mm material is only 10% by weight, while the unmilled material is all the same material (100%). Most of the WR material is 1 mm in size, while the gold float process tailings is at the other end of size spectrum, with most (70%) being less than 0.038 mm.

Figure 4 12(c shows the relative amounts of neutralizing material required by mass for each material and grind size and a comparison to the unmilled ore. While the 1 mm component is greater by mass, its lower reactivity requires less neutralizing material, while the 0.038 mm material requires more. The final AMD treatment cost is shown in Figure 4 12d, which illustrates the possible potential error of basing a conceptual mine design on the unmilled ore geochemistry alone. Treatment costs based on a PSA/POR-based reactivity analysis is about four times greater for OB material than predicted by simple POR testing of the unmilled ore sample. The gold float tailings treatment cost was about seven times greater than the unmilled ore. On the cost saving side of the balance sheet, the WR materials cost less to treat than the unmilled ore materials, indicating that all materials should be tested for POR prior to commencing geochemical stabilization design work as a potential cost saving.

Ore reactivity as POR (a)

Particle size analysis (wt%) (b)

Neutralising material required (c)

AMD treatment cost (d)
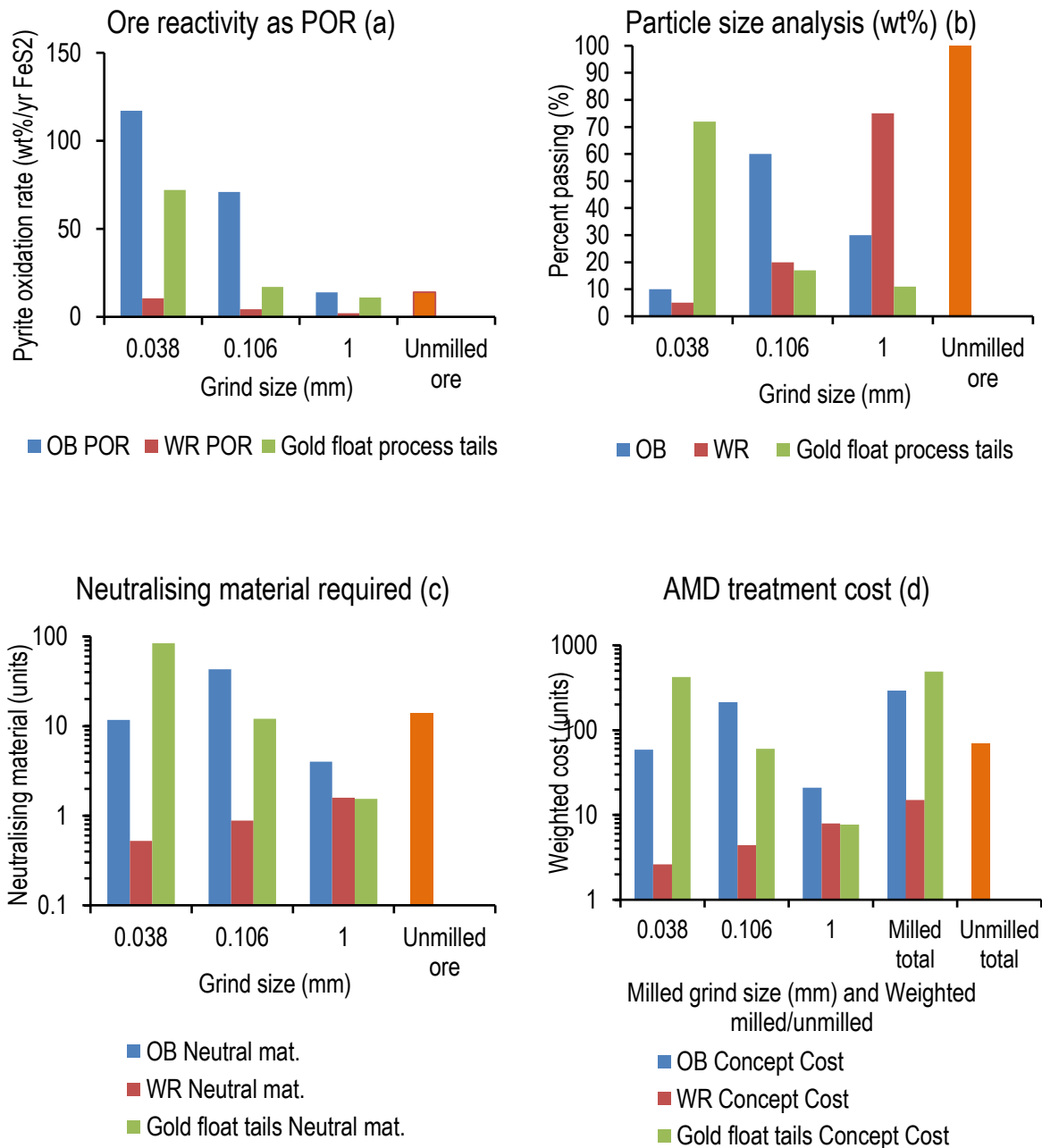
Figure 4-12: Conceptual geochemical stabilization cost of considering unmilled ore compared to PSA/POR method for OB, WR, and gold process float tailings

Similarly, all potential neutralising materials available at the mine site should be evaluated for their effectiveness for use as potential treatment material. Detailed neutralising material data studies will allow detailed analysis of the required volumes and specific requirements; this can represent a major cost saving to mine design when enough neutralizing materials are available at the mine site.

4.6 Discussion

The results show that particle size distribution can strongly influence total mine tailings processing costs. The ramifications of this for practitioners designing mine waste storage facilities, such as a TSF with particles in the silt to sand range, should be obvious. Modelling of mine rehabilitation costs shows that to accurately predict AMD generation during operations and closure phases, mine designers must estimate the sulfide reactivity rate for each representative mill grind size. Undertaking the PSA/POR test detailed in this study for five grind sizes is estimated to cost less than $50,000 (US) commercially, which is insignificant relative to total processing or mine development costs.

It is important to note that Erguler et al. (2014) found that reducing particle size can reduce hydraulic conductivity for some situations and materials, which may reduce AMD development, but this is likely site specific and applies to undisturbed mine wastes. There is also a possibility that reducing hydraulic conductivity will reduce the rate of oxidation but will not prevent the completion of the process. When mine wastes are moved (for rehabilitation or uncontrolled placement), it is thought that a decrease in particle size and increased reaction is likely. Careful modelling of available neutralizing material and soil gas transport is required to pursue treatment savings that may be derived from reducing hydraulic conductivity (AMIRA 2002).

The greater variation in total S in the larger WR particles illustrates why mine ore is crushed and milled prior to processing, not just to provide for greater ore recovery but to ensure reliable extraction rates. Well mixed, fine grained materials will generally display less variation in content from the same source materials.

Total acid load has to be calculated over the period of mining life and after closure for inclusion in acid–base accounting calculations (DITR 2007). In this study, for the materials tested, the volume of particles below 1 and 0.1 mm in size were capable of delivering 6–10+ times the acidity load by mass of the larger materials in the waste rock and ore materials after blasting and crushing.

The mine process designer should estimate the return in ore from the milled product and compare that to the long-term cost of ensuring geochemical stability of the tailings before deciding on an optimal particle size. Developing similar particle size to POR relationships is recommended during geochemical assessment of the ore in the exploration phase to help determine the final reactivity and POR of the anticipated wastes (tailings and waste rock).

The results of this study indicate strongly that very fine grained materials may increase the cost of maintaining geochemical stability of the processed mine wastes in AMD mine materials. Oxygen diffusion inhibiting covers may reduce the rates of pyrite oxidation, but unless the mine is in a high rainfall area, this oxidation cannot be prevented during closure. Geochemical stabilization of waste rock and tailings will very likely require additional neutralizing materials. The neutralization material or treatment required should be calculated based on the volumes of various grain size fractions stored in the TSF/WRD to correctly account for exponential acidity production by the finer grain sizes.

While this sounds like a case for permanent water covers, wet clay-GCL caps, pit backfilling and other oxygen diffusion limiting technologies, there are at least three potential issues that require investigation before these technologies can be an acceptable solution: (1) weathering and natural soil heaving and slumping may cause wet clay-GCL caps to become permeable within 4–5 years of commissioning (Benson 2014); (2) very fine grained materials can become mobile in the porous media of the TSF/WRD liner, seepage groundwater, and surrounding geology, especially if pyrite oxidation and acidity changes the porosity of the liner system (Naka et al. 2014); and (3) seismicity of the TSF location may limit the design life of the TSF structure (and many existing TSFs are built to have a short design life due to planned landform redesign during closure) and require geochemical stabilization to prevent environmental harm in the case of structural failure (Zardari 2011).

These three issues virtually mandate the creation of geochemically stable mine tailings and waste rock at least at closure, but preferably during operations. These issues should be dealt with at an early phase by mine designers and geochemical engineers, for instance by adding sufficient neutralizing material to deal with all of the potential acidity before final deposition in the TSF. Government EIA/EIS

procedures and guidelines for the mining sector should be updated to include similar procedures for evaluation of reactivity risk to increase the likelihood of sustainable outcomes for the mining sector.

4.7 Conclusion

The study demonstrated that grain size is a principle factor affecting POR and reactivity within AMD materials in waste rock and tailings materials generated from mining processes, using materials from a highly sulfidic overburden from the Latrobe Valley coal provinces, and a moderate-to low sulfidic rock material from a porphyry copper deposit in Papua, New Guinea. The AMD POR reactivity was found to exponentially increase as grain size decreased, with the effects particularly marked for materials less than 1 mm in size. This exponential reaction relationship for small particles is important to understand if a mine waste structure, such as a TSF or waste rock dump, is to achieve environmentally sustainable mine closure requirements.

This study extends previous geochemical reaction rate studies using oxygen consumption techniques on AMD/ PSA-based reactive materials and shows that particle size is a clearly an important mine design parameter that needs to be considered, along with its associated geochemical reactivity. Mine waste managers seeking designer tailings with greatly reduced environmental risk, are advised to undertake geochemical reactivity testing on all mine site materials, at several moisture contents and grain sizes representing the proposed milled material grain size for mineral processing. The results of the grain size reactivity analysis should be included in the mine's acid base accounting assessment so that a fair and reasonable assessment of risk can be apportioned for both mining bonds and mine closure costs. Some mine site materials will be determined to have neutralizing capacity, which is an important potential cost saving for the geochemical stabilization mine waste management system.

The implications for AMD material treatment effects on a theoretical closure costs have been carefully evaluated for three different mine wastes. The scenarios demonstrate both underestimation and overestimation of the closure cost, when insufficient kinetic testing results are available. Final theoretical AMD treatment costs were shown along with the potential error in basing concept mine design on geochemistry results from unmilled ore geochemistry alone. Conceptual treatment costs

based on PSA/POR based reactivity analysis was between 4 and 7 times higher for the ground ore materials than for the same conceptual design cost to treat unmilled ore.

The cost of the studies to undertake this work and the geochemical engineering design required should have a negligible effect on project profitability and represents project insurance for companies facing the risk of an AMD legacy. Long term costs will be dramatically reduced, especially during closure, when treatment and mitigation costs without suitable geochemical analysis is likely to be ten times higher, and ore is no longer available to help pay for water treatment.

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5 A Comparison of Measured and Predicted Diffusion Coefficients Applied to Sand and Silt sized AMD Materials (Paper ii: Published)

This Chapter investigates issues in measurement of soil gas diffusion coefficients in AMD mining derived materials in the laboratory, presents an economic diffusion column design, and evaluates the performance of several diffusion coefficient estimation models available in the literature, when compared to laboratory measured values. The discussion includes analysis of possible limitations and agricultural basis for many existing diffusion coefficient estimation models, and analysis of possible dual diffusion functions based on soil matrix geometry and particle size and proposes the use of safety factors to provide AMD material volume assessments that are conservative. The content of this Chapter is reproduced from the research Paper published as: Dettrick, D, Costello, J., Arora, M., Yuen, S., 2019b, "A Comparison of Measured and Predicted Diffusion Coefficients Applied to Sand and Silt sized AMD Materials", in Journal of Environmental Management (JEM), Vol 231, pp1106-1116, Elsevier, Amsterdam. Additional data for this Paper was provided as supplementary material in the JEM and is attached in Appendix 1. The supplementary materials include:

- The Economic Diffusion Column Design based on readily available stormwater and gas grade UPVC and stainless-steel materials.

- Diffusion column leakage testing results.

- AMD material matrix moisture behaviour data including:

  o Soil water characteristic testing results.

  o Parameter fitting to derive Van Genuchten (1980) unsaturated zone equation parameters for soil moisture estimation.

  o Predicted soil moisture contents at depth above the groundwater table.

5.1 Abstract

Determining the rate at which Acid Mine Drainage (AMD) sulfide oxidation occurs in mining waste products is a central requirement for safe and sustainable long term design of storages, including

tailings storage facilities, ore stockpiles and waste rock dumps. Inappropriate design can result in AMD acidification, mobilisation of heavy metals and pollution of ground and surface waters. The use of soil gas (oxygen) transport modelling to model AMD based sulfide oxidation and potential acidity loads is widespread, but diffusion coefficients used for modelling are based on existing diffusion coefficient models derived for natural and agricultural soils. Mining wastes are often well sorted due to mineral processing, and differences in material structure and porosity can impact on diffusion coefficient behaviour compared to natural soils.

This study compares a variety of approaches to estimate the diffusion coefficient and compare these results to measured values for comparison and analysis. A diffusion column apparatus is used to compare diffusion coefficient models from the literature with test results from the laboratory in several mining derived AMD materials. The results of the comparison indicate that laboratory testing of diffusion provides more accurate estimation of soil gas diffusion coefficients in mine materials. The use of diffusion coefficient safety factor approaches are explored as possible alternatives, if measurement of mine material matrix soil gas diffusion coefficient is not possible.

5.2 Introduction

Geochemical engineering is required to ensure the ongoing chemical stability of mine waste products, such as process tailings, stockpiled ore materials and waste rock. The production of acid mine or acid rock drainage (AMD) and associated acidity is caused by oxidation of sulfides contained within mine wastes and ores (US EPA, 1994). Acidity generated by AMD processes has the potential to mobilise heavy metals in surface and groundwater systems, causing harm to sensitive aquatic ecosystems (EA, 1997). Globally it is estimated over 100,000 km of river and stream systems are impacted by AMD and resultant poor water quality (EA, 1997; US EPA, 1994). USEPA has recently included AMD mine sites on the Superfund list for the first time, and the estimated cost of cleaning up a shortlist of 156 mines would be $7–24 billion USD (Tuffnel, 2017).

Reducing oxygen diffusion rates into mining wastes is a key geochemical engineering strategy to reduce acidity production (Hollings et al., 2000; Kuipers et al., 2006; Maest et al., 2005). The

provision of adequate neutralising capacity is another key AMD management strategy (EA, 1997). Mine waste facility design for mine operations and particularly mine closure, therefore, requires accurate oxygen transport modelling through saturated and unsaturated material layers that comprise the waste facility structure, to enable selection of materials for oxygen limitation systems or neutralising chemical supply.

Many mine waste facility designers apply rules of thumb and literature values for soil gas transport variables, such as diffusion and advection (e.g. Moldrup et al., 2000a). Sulfide oxidation rates, and hence acid generation rates, are crucial to determining required neutralisation capacity to build on the traditional acid base accounting undertaken by mining companies (Kuipers et al., 2006; DITR, 2007). Modelling of sulfide oxidation and acidity generation is therefore a key component to successful geochemical design of mine waste facilities, such as tailings storage facilities (TSF) and dams. Soil gas diffusion is likely to be the dominant process for oxygen transport in TSF materials without cracks, as the air velocity required to substantially increase soil gas advection processes is infrequent (Jury and Horton, 2004).

Sandy–silty agricultural soils have been studied extensively for soil gas diffusion (Deepagoda et al., 2012; Moldrup et al., 2000a, Mahiya 1999; Gerke and Van Genuchten 1993; Van Genuchten, 1980, Millington and Quirk, 1961, Millington, 1959, Marshall, 1959, Fatt and Klikoff, 1959, Penman, 1940, Buckingham, 1904). Sand–silt grain size materials are important to the mining sector as many mining wastes, including tailings, are ground to this size range to maximise process metallurgy recovery rates (Runge et al 2013). While little work has been undertaken examining soil gas diffusion characteristics of these mining wastes, studies have been undertaken developing models for AMD based on existing natural and agricultural soil models (e.g. Kuo and Ritchie, 1999; Pruess et al., 2012). Natural and agricultural soils differ to mining wastes due to mineral processing which creates materials of well sorted, poorly distributed particle size, compared to good agricultural soil which often displays a well distributed particle size distribution. Fick and author anonymous (1855) related diffusion in liquids to Fourier's (1822) equations for heat conduction, which are also based on random molecular movement, to develop the partial derivative of concentration over distance based on the diffusion coefficient

determining the concentration gradient. Fick's law can also be used for gas diffusion and is shown in equation (1):

$$J_d = -D \frac{\partial C}{\partial z} \qquad (1)$$

where J_d is the rate of transfer per unit area, D is the diffusion coefficient, C is the concentration of the diffusing substance and z is the depth of the material media normal to the surface. Crank (1975) noted that Fick's equation is only correct in isotropic materials and dilute (trace) solutions where concentration is normal to the flow direction, and that in other materials the diffusion coefficient is strongly related to concentration. In porous sand–silt materials, such as those found in TSF, the diffusion coefficient becomes strongly dependant on moisture content, as the air filled porosity fills up and the volume available for gas transport decreases. To deal with this many researchers have applied a simple moisture controlled tortuosity component, see equation (2) (Jury and Horton, 2004):

$$J_d = -\frac{\varepsilon}{\tau} D \frac{\partial C}{\partial z} \qquad (2)$$

where ε is the media porosity and τ is the tortuosity variable, all other variables are the same as equation (1). Some authors have defined tortuosity as the ratio of the actual distance travelled to the distance of separation of the two concentrations of an element, such as a gas (Comsol, 2013). The main problem with this approach is the addition of yet another unknown variable without a precise method for in-situ or laboratory measurement and would most likely be different in all porous media. Values for tortuosity are difficult to find in the literature but emerging visual tortuosity assessment methods may exist for a limited list of soil types. For example, Deepagoda et al. (2012) provide a potential technique by linking gas diffusivity and air phase tortuosity to soil matric potential in common agricultural soils, but the error of the technique increases as D_p/D_o decreases, and the lowest value was 1.0×10^{-5}. In this case D_p is the gas diffusion coefficient in the material matrix, while D_o is the gas diffusion coefficient in free air. One of the key physical characteristics of mining tailings waste is the milling of the waste to produce optimal particle sizes for mineral/ metallurgical processing plant circuits (Runge et al., 2013). Additionally, the deposition of mine tailings into a TSF further sorts the tailings materials. Heavier and larger particles remaining deposited closer to TSF spigots, and fine materials

being transported further from the spigot. Paste style tailings materials may not display the same particle sorting behaviour. Processed mine materials often display strongly spatially sorted characteristic particle size distribution curves with large percentages of sand followed by silt materials, and relatively small amounts of clay grain size, this feature of tailings and its impact on soil gas diffusion coefficient is investigated in this Paper. This characteristic may influence the use of diffusion coefficients and functions derived in soil science for agronomics, as those agricultural soils are often comprised of a large and even distribution of all particle sizes.

This study compares a variety of approaches to estimate and model the diffusion coefficient, to laboratory measured values of soil gas diffusion for comparison and analysis. A series of accepted diffusion coefficient estimation models available in the literature are applied to several AMD reactive materials and compared to laboratory measured values for the same AMD material. The potential for negative impacts on geochemical design of mine waste facilities based on modelling using these literature based diffusion coefficients and models is then examined.

5.3 Materials and methods

The following methods were undertaken to achieve the above objectives:

5.3.1 Material selection

Two sets of sandy-silt AMD material samples were selected for study based on their grain size and high reactivity due to sulphide content. These two AMD materials were physically compared to four different mine derived tailings and to several natural soils to characterise potential differences in soil gas transport behaviour. The two sandy silt materials sourced from mine exploration sites, SS and SC, and a non-reactive silty sand control material, SSS, were used for diffusion column testing. The materials were selected for their very low clay sized particle content (<1%), to avoid potential compaction issues arising within the diffusion test column, which was also managed by using diffusion sample depths of 15 mm and 60 mm. The target materials (SS, SC) were sieved for particle size analysis and to assign soil classification types to help understand the physical characteristic and structure of the

material matrix, for the purposes of conceptualising soil gas transport, and analysing diffusion behaviour. The non-reactive silty sand control (SSS) was prepared with quartz washed river sand, sieved into the required particle size groups and then mixed by percentage to simulate similar material to the AMD mine materials. The non-reactive material was then subject to diffusion testing to attempt to confirm the AMD reaction was not affecting the diffusion results in the time period of the diffusion column tests. Unfortunately, the SSS material displayed differing diffusion characteristics and BET surface area and volumes (see Chapter 6), despite several attempts to create a viable control, and so was not considered in the results.

5.3.2 SWCC testing for moisture response

To provide data for the literature based diffusion coefficient estimation models, the three test materials required additional soil laboratory data to be collected, the most complex of which was the soil water characteristic curve (SWCC) response using the method of ASTM D6836 (2008). The SWCC soil testing was required to provide data for the Moldrup et al. (2000a) function ($\varepsilon 100$ = effective porosity at matric suction 100 kPa), the David (1993) relative diffusion function and to provide information in relation to soil moisture content. Details of SWCC testing results are included the Supplementary Material in Appendix 1 below.

5.3.3 Selection of diffusion coefficient estimation functions for comparison

A literature review was undertaken to determine commonly used soil gas diffusion coefficient estimation functions. Historical significance of the estimation functions was also considered a criterion for inclusion. All diffusion coefficient $\left(\frac{D_p}{D_o}\right)$ estimation functions selected for testing are presented in Table 5-1 along with the required parameters.

5.3.4 Soil gas diffusion apparatus

The two test AMD materials, SS and SC, were tested to determine the diffusion coefficient D_p, for a range of moisture contents. The atmospheric diffusion (Oxygen) coefficient D_o, was measured in

the diffusion chamber designed and built for this project, for apparatus design details, see the Supplementary Material section in Appendix 1. For each material tested at a set moisture content, the diffusion chamber was purged with industrial Nitrogen (99.9% N_2) to an O_2 concentration of less than 0.5% and then the diffusion chamber was opened, allowing oxygen to diffuse through the material sample from the atmosphere. O_2 concentration (%) results were collected from a GD2528 analogue O_2 (%) meter via data logger every minute for the duration of the test.

Table 5-1: Diffusion coefficient estimation functions and data requirements.

Diffusion reference	Model equation	Data requirements
Effective diffusion (Fick 1855)	$\dfrac{D_p}{D_o} = \dfrac{\varepsilon_t . \delta}{\tau}$	D is the diffusion coefficient ε_t is the effective porosity δ is the constrictivity τ is the tortuosity
Buckingham (1904)	$\dfrac{D_p}{D_o} = \varepsilon^2$	Air filled porosity, $\varepsilon = \emptyset - \theta_w$
Penman (1940)	$\dfrac{D_p}{D_o} = 0.66\varepsilon$	Air filled porosity, $\varepsilon = \emptyset - \theta_w$
Millington - Quirk (1961)	$\dfrac{D_p}{D_o} = \varepsilon^{\frac{10}{3}} \Big/ \emptyset^2$	ε = air filled or effective porosity $\emptyset$ = total porosity
David (1993)	$D_{eff} = \tau . D_a^o . (1 - S)^\alpha + \dfrac{\tau . S . D_w}{H}$	S is relative soil moisture D_a is diffusion in air D_w is diffusion in water H is Henry's law constant τ, α are fitting constants
Moldrup (2000a)	$\dfrac{D_p}{D_o} = 2.\varepsilon_{100}{}^3 + 0.04\varepsilon 100$	$\varepsilon_{100}= \phi - \theta_{100}$ $\emptyset$ = total porosity θ_{100} = moisture at suction 100 kPa ε_{100} = effective porosity at suction 100 kpa
Moldrup et al. (2000b)	$\dfrac{D_p}{D_o} = \emptyset^{1.5} \left(\dfrac{\varepsilon}{\emptyset}\right)^{2.5}$	ε = air filled or effective porosity $\emptyset$ = total porosity
Moldrup (2013)	$\dfrac{D_p}{D_o} = P\varepsilon^X \left[\dfrac{\varepsilon}{\phi}\right]^{T_a}$	ε is soil air content ϕ is soil total porosity P, X and T_a are model parameters.

The O_2 meter was checked for calibration before undertaking each diffusion test by filling the diffusion chamber with atmospheric (21.9%) O_2 levels, with industrial N_2 (99.9%) containing less than 0.1% O_2, and with calibration gas at 10% O_2. Finally, to achieve accurate results that minimise the volume effect of the porosity of the test material, there must be maintained at least 5:1 of diffusion chamber volume to sample volume (Rolston, 1986; Rolston et al., 2002).

5.4 Results

5.4.1 Diffusion column testing for D_o

Two sets of quality control tests were performed to evaluate the accuracy of the diffusion column apparatus, i) a test for D_o (see below) and ii) a chamber leakage test (see Supplementary Material in Appendix 1 below). The diffusion chamber was used to test O_2−N_2 diffusion to check for potential fluctuations in results compared to literature values using four repeat tests.

After Test 1 the inlet valve was tightened, and Tests 2, 3, 4 yielded extremely stable and reproducible diffusion results in the chamber (Figure 5-1a). The results of the diffusion testing for the N_2-air diffusion coefficient are shown in Table 5-2. The diffusion behaviour of the gases in the diffusion column produced a reasonable linear fit for ln $(C-C_S)/(C_O-C_S)$, with Test 1 showing the predicted variable behaviour due to initial setup diffusion column leakage as discussed above (see Figure 5-1b), where C is the current oxygen concentration, C_O is the initial oxygen concentration of the diffusion chamber, and C_S is the final concentration of oxygen and usually approaches atmospheric oxygen concentration of 20.9%

Table 5-2:Results of $D_{N2\text{-}air}$ diffusion column testing

Test	R^2	slope	$D_{N2\text{-}air}$
N_2-air test 1	0.992	-2.877	0.230
N_2-air test 2	0.983	-2.197	0.176
N_2-air test 3	0.969	-2.193	0.175
N_2-air test 4	0.994	-1.926	0.154
		median	0.176

There are very few D_{N2}-air results published in the literature, but the results compare well with Winter's (1950) results for D_{N2}-air of 0.172 cm^2/s, and the upper limit (N$_2$-air test 1) with Richard's (1996) $D_{O2\text{-}N2}$ results of 0.219 cm2/s (see Table 5-2). The result also compares well with $D_{O2\text{-}AIR}$ (open air D_O) results from Cussler (1997) of 0.176 cm^2/s, showing the similarity in behaviour between N$_2$ and Air for diffusion of O$_2$ is not unexpected as Air is comprised approximately 80% N$_2$. These results also confirm the minimal effect of the filter mesh used to retain the material sample (see Figure 5-1).

(a)   **(b)**
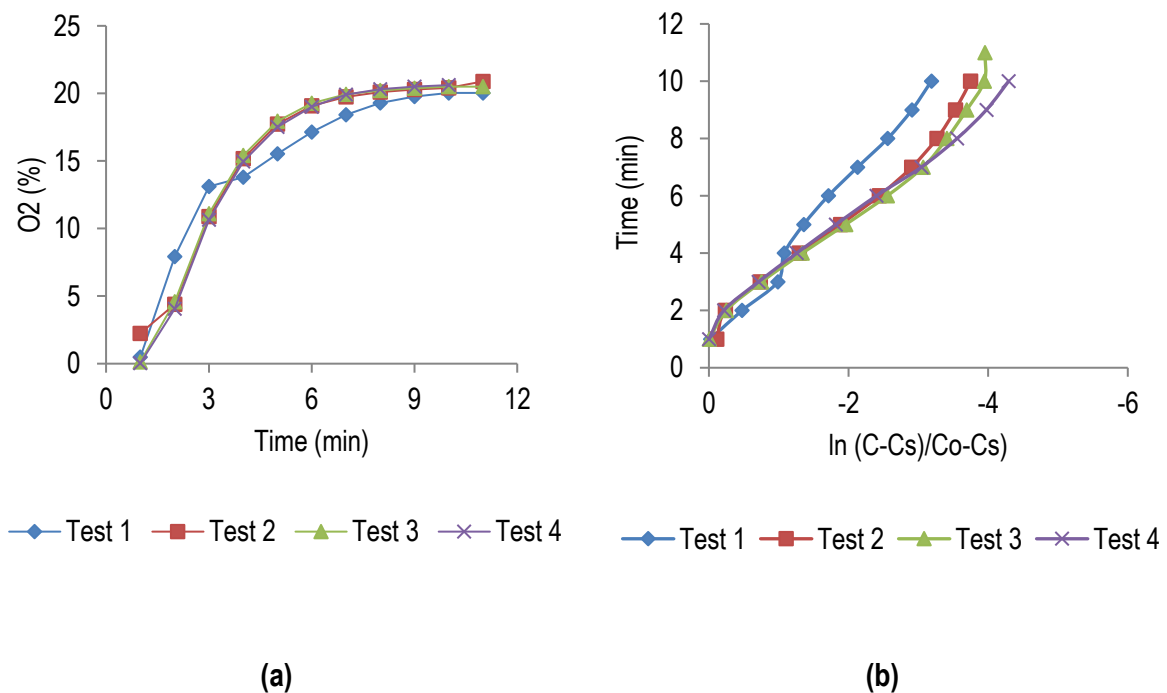
Figure 5-1: Diffusion column O2−N2-air diffusion testing (a), and diffusion gradient (b) using four repeat tests. The inlet valve was tightened following Test 1.

5.4.2   Soil characteristics

The particle size distributions (PSD) for the target materials (SC, SS, see Table 5-3) are compared to several mine tailings materials and natural soils from the literature (Figure 5-2) (see Table 5-4). Lines for the No. 4 (4.76 mm) and No. 200 (0.074 mm) sieves are shown for soil classification purposes (USCS 2016). The natural soils, including lateritic (Amadi 2010), river clay sand (Bazant 1979), and silt loam (Brady and Weil 1999), are generally well graded with silt loam possessing greater silt fines, and river clay sand having more clay and sand as expected. The lateritic soil forms the middle ground of the natural soils and was well graded across all material sizes. These soils display generally

higher levels of clays and fine silts than mine tailings that have been derived from crushed rock or mineral sand mining and have little clay content as a result.

Tailings 1–4 are all derived from copper processing activities from undisclosed mine sites and are similarly graded to the natural soils, apart from the tendency for the tailings to have little material

Table 5-3: Soils classification with USCS (2016)

Soil/Tails Sample		Mine tailings					Target materials		Natural soils		
		Tails 1	Tails 2	Tails 3	Tails 4	Gold float process	SC	SS	Lateritic Soil	River Clay Sand Soil	Silt Loam Soil
Hazen Coefficient of uniformity ($Cu=D_{60}/D_{10}$)		50.0	48.0	30.0	5.0	3.6	2.9	2.3	128.6	115.0	9.0
Coefficient of curvature ($Cc= D_{30}^2/D_{10}xD_{60}$)		1.8	3.0	1.3	0.3	2.5	1.2	1.1	1.1	5.4	0.9
Gravel soil $D_{50}>2.36$ mm		No	No	No	No	No	No	No	No	No	No
Well-graded gravel	GW	No	No	No	No	No	No	No	No	No	No
Poorly graded gravel	GP	No	No	No	No	No	No	No	No	No	No
Sand soil $D_{50}<2.36$ mm		Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Well-graded sand	SW	Yes	No	Yes	No	No	No	No	Yes	No	No
Poorly-graded sand	SP	No	Yes	No	Yes	Yes	Yes	Yes	No	Yes	Yes

above 0.5 mm in size. The gold float process tailings, also from an undisclosed mine site, were examples of a more processed material, well sorted and dominated by material from 0.01 to 0.1 mm in size. The target SS and SC materials were well sorted, dominated by material from 0.1 to 0.3 mm in size, a lower clay silt component than the natural soils and most of the tailings material. The particle sizeresults were then classified using the Unified Soil Classification System (USCS, 2016) for coarse grain soil to further examine the soil matrix structure and implications for the porosity of the soils (Table 5-3). The soils are all classified as sands with $D_{100} < 2$ mm. Tailings 1 and 3 satisfy the classification for well graded sand. Tailings 2 and 4, the gold float process tailings, and target materials SS and SC are classified as poorly graded sands.

The three natural soils included show the upper and lower grain size variation expected in natural soils, from the middle range Lateritic soil –a well graded sand soil, silt loam soil - poorly graded silt soil (low coefficient of curvature) and river clay sand -poorly graded sand soil (high coefficient of curvature). The SC, SS, Gold float process tailings, and Tailings 4 have very low Hazen coefficient of uniformity as expected < 5, while natural soils are far more uniform with Hazen coefficients of up to 128.

Table 5-4: Literature values for natural soils and parameter estimation for target materials.

Soil material	α	n	m	θ_r	θ_s	λ	RSS error
Tails 3/Sand	0.15	2.68	0.63	0.05	0.43	1.68	n/a
Lateritic Soil	0.02	1.37	0.27	0.03	0.46	0.37	n/a
Clay	0.01	1.09	0.08	0.07	0.38	0.09	n/a
SC	0.03	3.01	0.67	0.01	0.26	2.01	0.03
SS	0.04	3.01	0.67	0.01	0.27	2.01	0.04

Note: examples soils based on data from UNSODA (2017) Soil Data Base and using Van Genuchten (1980).

The soil water characteristic curves for the AMD mine materials tested in the study (SS and SC) are shown in Figure 5-3, along with literature values for sand (Tailings 3), Lateritic soil/silt and clay soil for comparison.
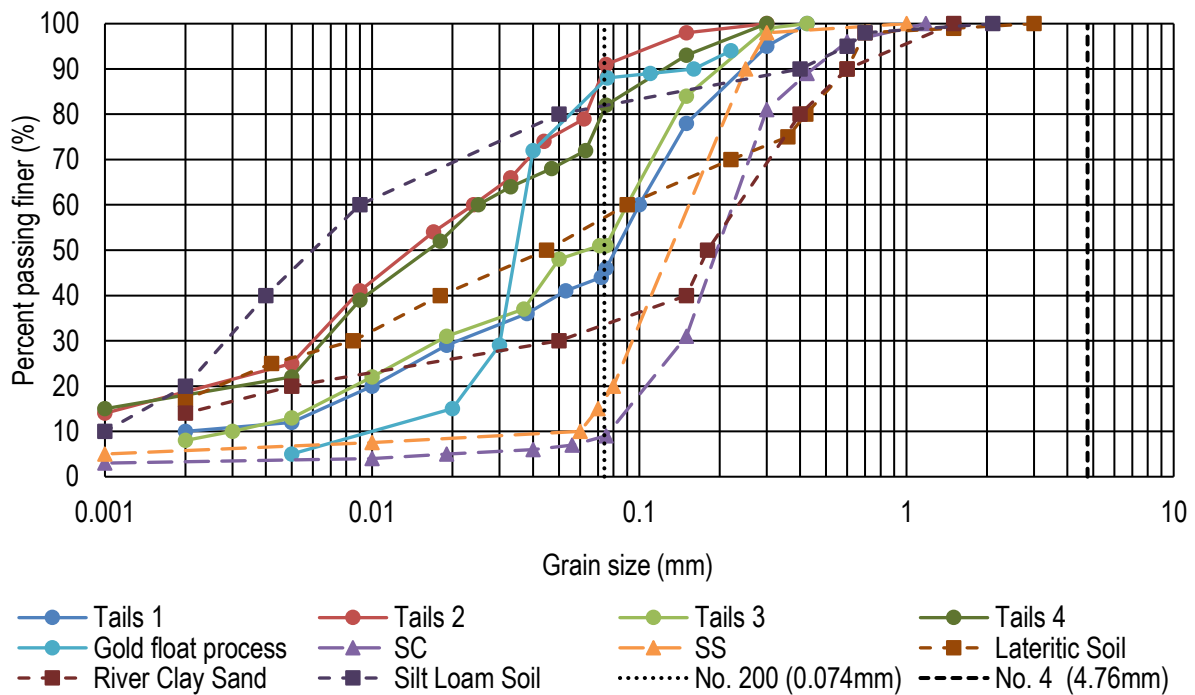
Figure 5-2: Particle size analysis of target materials SS, SC, and comparison to four mine tailings materials, Gold float process tailings and three natural soils (see text for data references).

SS and SC display similar pore pressure response to well graded sand (and to sandy mine tailings) but due to their lower content of silt and clay (Figure 5-2), have a lower saturated moisture (θ_s), a lower residual moisture (θ_r) and air entry value of 200 kPa matrix suction.

When inspecting the PSD (Figure 5-2) and SWCC in Figure 5-3, the key drivers of soil moisture response appear to be fines content, particularly clay materials, and coarse sand content. The Tailings 3/Sand, SS and SC materials are low in clay and comprised primarily of sand and silt. These types of materials may be suitable for a dual porosity model approach for diffusion coefficient, similar to Gerke and Van Genuchten (1993), or multi-porosity approaches such as Moldrup et al. (2004). The SWCC results were fitted to the Van Genuchten (1980) equations and the results are shown below in Table 5-4, including the predicted moisture content for SS and SC materials at matric suction of 100 kPA for use in modelling the Moldrup et al. (2000a) diffusion coefficient function. Further details of SWCC results are provided in the Supplementary Material section.
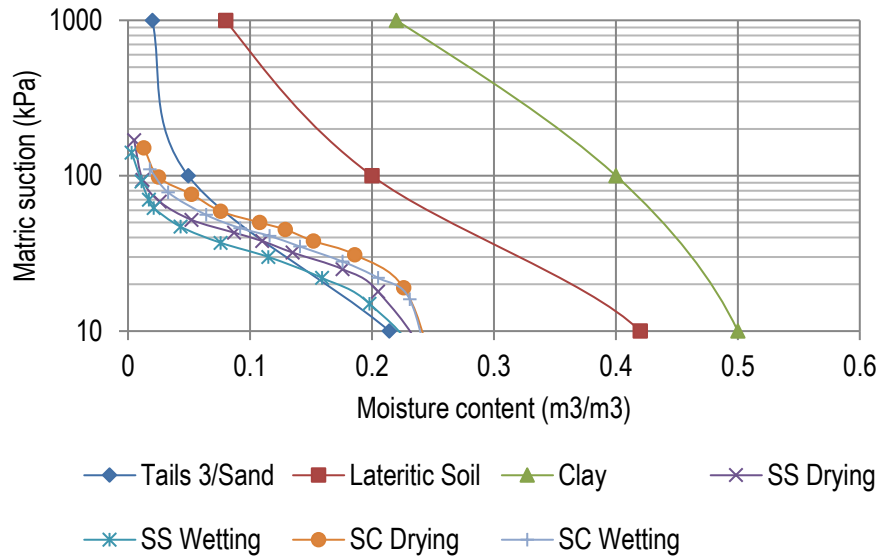
Figure 5-3: SWCC for the target materials SS, SC and sand, silt and clay.

5.4.3   Diffusion testing

Diffusion testing was undertaken using the diffusion column apparatus on the target AMD materials, SS and SC. Two sample depths were used for testing the materials in the diffusion column (Dettrick 2019b and see Appendix 1 below), 15mm and 60 mm, and moisture contents were varied at 4% intervals to examine effective porosity effects on the measured diffusion coefficient. The diffusion coefficient results were found to be within 1% difference at both depths tested, and soil moisture based effects were strongly evident. The diffusion test column results for the SS and SC materials are shown in Figure 5-4.
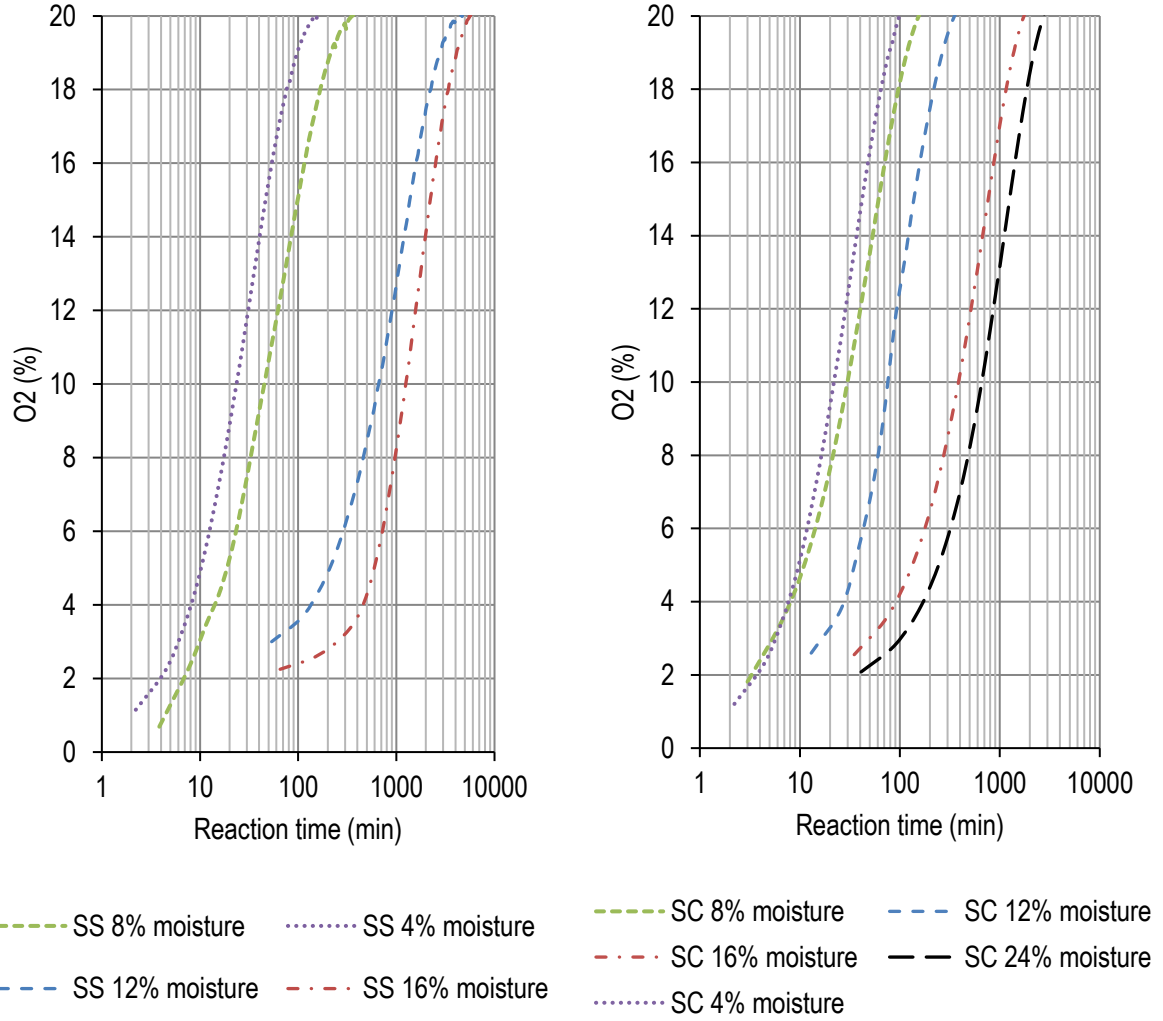
Figure 5-4: Diffusion column test results and volumetric soil moisture content (a) SS, (b) SC material.

The diffusion coefficient for each material was then determined using Rolston (1986) and the results are shown as a diffusion coefficient plotted against soil moisture to provide a diffusion function for both SS and SC materials for further analysis.

The Rolston method uses equation (3) for determining D_P:

$$\frac{C-C_s}{C_0-C_s} = \frac{2hexp\left(-D_p\alpha_1^2 t/\epsilon\right)}{l\left(\alpha_1^2+h^2\right)+h} \quad (3)$$

where the plot of ln [(C–C$_S$)/(C$_o$–C$_S$)] versus time (t) becomes linear with a slope of $D_p\alpha_1^2/\epsilon$ for an appropriate test period. Rolston provides tables for determining α_1^2 , h and l values, to

remove error for soil storage of gas when concentration changes, where l is sample length, h is a soil air chamber volume function and α_n is the positive root of $\alpha l\ \tan\alpha l=hl$. The measured diffusion coefficient vs soil moisture content results are shown in Figure 5-5.
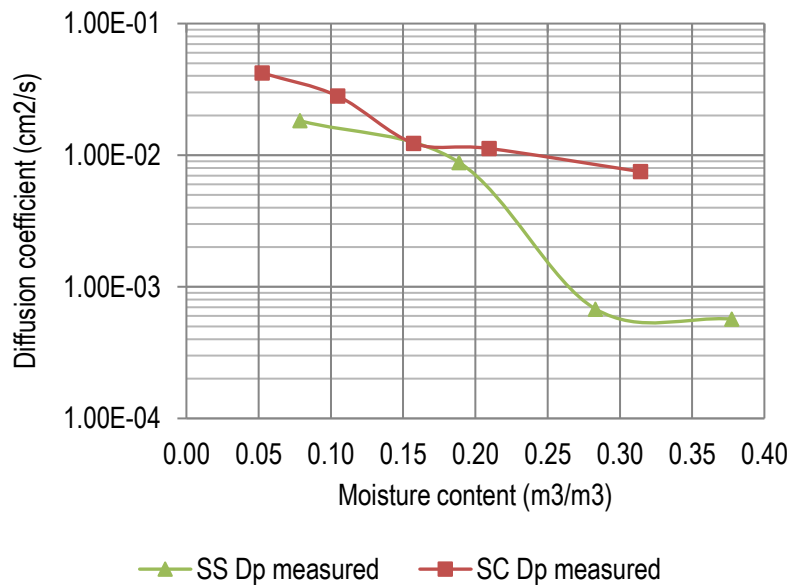
Figure 5-5: Mine material measured diffusion coefficient vs soil moisture.

Examining the diffusion behaviour of the two mine materials in Figure 5-5, it can be seen that the SC material has a generally faster diffusion behaviour over the whole range of soil moisture due to its coarser grain size than the SS material (Figure 5-2). The focus of this study is on the moisture range 0.05–0.25 to represent the zone of interest for potential high oxidation rates based on increased soil gas supply, with changing soil moisture as likely found in a dry TSF, or waste rock dump. Diffusion response in the SC and SS can change by nearly two orders of magnitude in only 4m of TSF or mine waste depth, based on steady state unsaturated soil moisture behaviour, see Supplementary Material in Appendix 1 . From Figure 5-5 the general trend of the diffusion function as the air-filled porosity fills up with moisture, is for the diffusion function to slowly approach its asymptotic moisture influenced value. As the materials dry and approach field capacity, the diffusion function starts to increase exponentially as connected gas flow volumes increase. Gas conductivity values are exponential based on experimental testing (Jury and Horton, 2004) so similar change in diffusion values is not unrealistic. As soil matric potential starts to approach residual soil moisture, diffusion also becomes asymptotic.

5.4.4 Comparison with diffusion coefficient models

The diffusion coefficient D_o for nitrogen –air was measured for the testing apparatus and determined to be 0.176 cm/s (see Supplementary Material in Appendix 1 below for more details on this test). To maximise the potential for accuracy, all literature based (see Table 5-1) diffusion coefficient model parameters, including δ, τ, τ, α, and C_m were fitted to measured diffusion column data from Figure 5-5. Air filled or effective porosity (ε) has been estimated as total porosity (Φ) – soil moisture content (θ_w), due to the low clay content of the SS, SC materials, see equation (4).

$$\varepsilon = \Phi - \theta_w \qquad\qquad (4)$$

The measured diffusion results for the SS, SC materials were then compared to the predicted values from the literature based on the diffusion coefficient models presented in Table 5-1 and Figure 5-6. Figure 5-6 shows the measured SC material diffusion coefficient data for visual comparison of fit. The SC diffusion results (D_p term as D_{SC}) demonstrate that as soil moisture drops below 0.1 m^3/m^3, the D_{SC} increases rapidly, which is an important reason to keep tailings material wet, or under water if containing AMD sulfide materials. The D_{SC} response behaviour exhibits a strong dual diffusion response around 0.1 m^3/m^3 compared to the literature diffusion functions, The D_{SS} response potentially also demonstrated a dual diffusion response around 0.3 m^3/m^3, this will be investigated further in the discussion section below.

Comparison with other diffusion function models shows that the closest fit for D_{SC} visually are i) Moldrup et al. (2013), ii) the Effective Diffusivity linear function, and iii) Moldrup et al. (2000b). Several of the other functions are close but consistently underestimate D_{SC}, which is a concern for potential use with AMD models of oxidation.
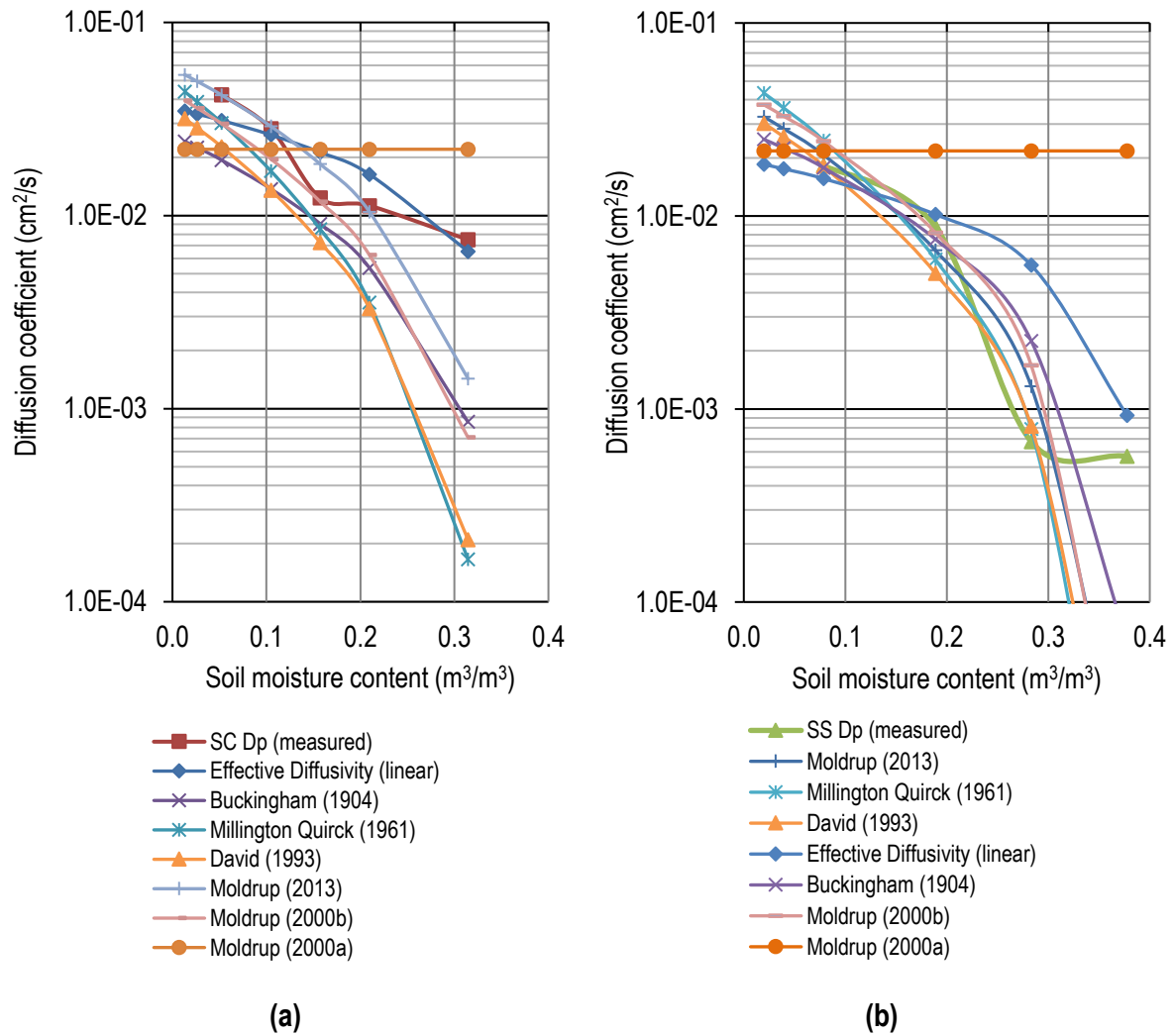
Figure 5-6: SC and SS mine material -measured diffusion coefficient compared to literature diffusion coefficient models.

5.4.5   Assessment of error

Model error is used to identify the best candidate models for accurately assessing the diffusion coefficient in the target AMD materials. The assessment of model error is undertaken using the following statistical measures selected for determining goodness of fit, noting that underestimation of diffusion coefficient is of some environmental concern in the mining sector, due to possible underestimation of acidity generated from oxidation of AMD mine materials. Error models used in this study include; mean difference (MD), root mean square error (RMSE), geometric mean error ratio (GMER), R^2, and gradient of observed versus predicted comparative data sets. The relevant equations for each error formula are shown below as formulas (5) – (8).

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$$MD = \frac{1}{N} \sum_{i=1}^{N} (P_i - O_i) \tag{5}$$

$$RMSE = \left[\frac{1}{N} \sum_{i=1}^{N} (P_i - O_i)^2\right]^{0.5} \tag{6}$$

$$R^2 = \frac{\left[\sum_{i=1}^{N}(O_i - O_m)(P_i - P_m)\right]^2}{\sum_{i=1}^{N}(O_i - O_m)^2 \sum_{i=1}^{N}(P_i - P_m)^2} \tag{7}$$

$$GMER = exp\left[\frac{1}{N}\sum_{i=1}^{N} ln\left(\frac{P_i}{O_i}\right)\right] \tag{8}$$

-where N is the number of data points, O is observed data, and P is predicted data, i is the count of the current data point, and m is the mean data point.

GMER, MD and to some extent observed versus predicted gradient is particularly useful for unsaturated AMD material properties as it helps to assess whether a function or model under or overestimates the particular diffusion function being examined, an important assessment for mining applications. The relationships between observed and predicted for the diffusion functions used in the study are shown in Figure 5-7 for the purposes of visual assessment of fit. A y = x perfect fit line has been included for convenience to visually assess over prediction and under prediction.

After processing the observed versus predicted data results for the error assessment functions (5) – (8), the results of the statistical error assessment have been summarised in Table 5-5. To further develop each R^2 and gradient result, the observed versus predicted data were subjected to a linear regression model for each tested diffusion estimation function. Moldrup et al. (2000a) is intended to be a single value diffusion function designed to give a quick estimate of diffusion coefficient for checking calculations, therefore gradient and R^2 error are not relevant.

(a)

(b)
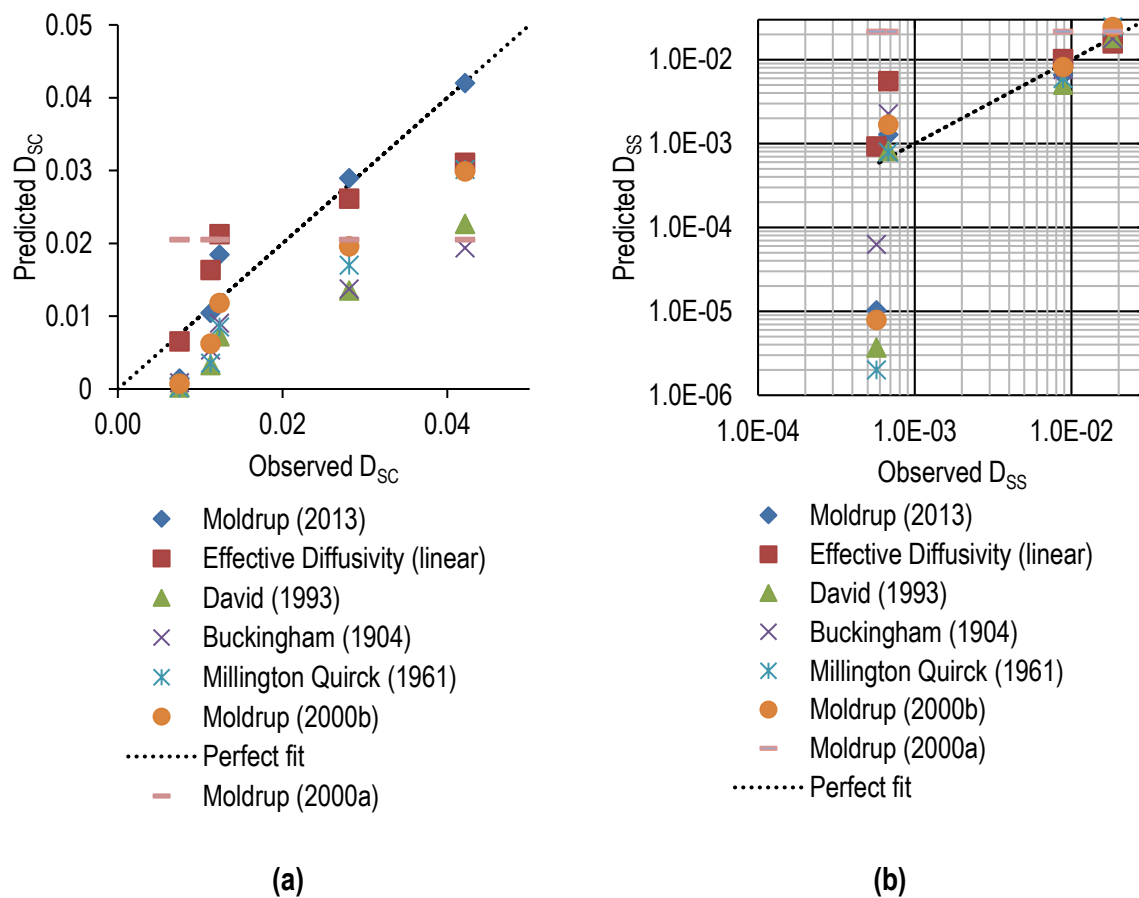
Figure 5-7: SC and SS mine material predicted versus observed for all diffusion coefficient functions used in this study.

From Table 5-5 it can be seen that for the SC AMD tailings material, Moldrup et al. (2013) and the Effective diffusivity linear function describes more of the variation in diffusion coefficient over the range of soil moisture tested than the other functions. Both Moldrup et al. (2013) and Effective diffusivity are approaching zero (but negative) MD, indicating a good fit, but also underestimation. RMSE for both functions are also low compared to the other functions tested. GMER suggests that Effective diffusivity is a better fit to the SC results than Moldrup et al. (2013) and also with a tendency to over predict diffusion results very slightly. Returning to the model results in Figure 5-6, Moldrup et al. (2013) matches the SC measured diffusion well for the dry soil conditions result approaching θ_R, overestimates for midrange moisture values (0.1–0.2 m^3/m^3), and then underestimates wet soil diffusion (measured 0.0075 cm^2/s compared to predicted 0.0014 cm^2/s, a relative error of ~80%). For mining tailings management in particular, this would be considered poor performance that would substantially under predict the rate of sulfide oxidation and hence acidity production.

Table 5-5: Error Assessment Table of diffusion coefficient functions applied to SC and SS target materials.

D_p Model	Moldrup (2013)	Effective Diffusivity (linear)	David (1993)	Buckingham (1904)	Millington Quirck (1961)	Moldrup (2000b)	Moldrup (2000a)
Error test	SC material						
Gradient	1.0137	0.8751	0.5046	0.4756	0.6526	0.7003	n/a
R2	0.925	0.4729	0.9316	0.9124	0.9209	0.9363	n/a
MD	-7.27E-13	-2.94E-10	-1.09E-02	-1.06E-02	-8.40E-03	-6.62E-03	2.53E-04
RMSE	3.89E-03	6.83E-03	1.21E-02	1.28E-02	8.90E-03	7.67E-03	1.30E-02
RMSElog	3.31E-01	3.14E-01	7.64E-01	4.95E-01	7.86E-01	4.82E-01	2.91E-01
GMER	7.71E-01	1.08E+00	2.63E-01	3.89E-01	2.91E-01	4.78E-01	1.24E+00
Error test	SS material						
Gradient	1.0503	0.92	1.2183	0.9538	1.2183	1.2607	n/a
R2	0.9631	0.7441	0.9272	0.9807	0.9272	0.9689	n/a
MD	-6.48E-14	7.92E-04	-8.66E-04	-1.29E-04	6.01E-04	1.20E-03	1.17E-02
RMSE	1.47E-03	2.57E-03	1.70E-03	9.48E-04	3.11E-03	2.81E-03	1.46E-02
RMSElog	7.91E-01	9.25E-01	9.85E-01	4.89E-01	1.10E+00	8.52E-01	9.93E-01
GMER	4.91E-01	1.68E+00	3.38E-01	7.90E-01	3.27E-01	5.32E-01	5.14E+00

Note: Dark to light green indicates best performance, yellow to orange indicates reasonable performance, red is poor performance.

The SS material error assessment in Table 5-5 highlights the performance of Moldrup et al. (2000b) and Buckingham (1904) as models with the highest fit to the measured data variation. Moldrup et al. (2013), David (1993) and Millington and Quirk (1961) models also perform well for variation with $R^2 > 0.9$. MD indicates close fits but with under prediction of diffusion for David (1993), Moldrup et al. (2013) and Buckingham (1904).

Examination of GMER results suggests the performance of Buckingham (1904), Effective diffusivity and Moldrup et al. (2000b) is good, with Effective diffusivity over predicting and Buckingham (1904) and Moldrup et al. (2000b) under predicting diffusion. Figure 5-6 shows that Effective diffusivity is under predicting gas diffusion in dry conditions but usefully over predicting in wet conditions, while Buckingham (1904) and Moldrup et al. (2000b) functions are over predicting in dry conditions, under and over predicting moderate moisture conditions, and then under predicting near saturation conditions, again a concern for modelling of TSF or waste dump conditions which may rely on moisture to reduce oxidation rates. Buckingham (1904) and Moldrup et al. (2000b) appear to perform best overall, which is problematic as this result for SS material does not agree with the previous findings for SC material. It appears each material may be modelled with differing performance by the

models, so this represents a difficult potential choice for modellers –particularly if little material data exists.

5.5 Discussion

Why the literature diffusion functions are not performing well at predicting diffusion coefficient in the target AMD mine materials is the central question of this study. Most soil gas diffusion studies (Buckingham, 1904; Penman, 1940; Marshall, 1959; Rolston and Moldrup, 2002; Rolston, 1986; Moldrup et al., 2013; Millington and Quirk, 1960, 1961; Gerke and Van Genuchten, 1993) have been undertaken on natural and agricultural soils that would be composed of well graded grain sizes and similar to the loam and lateritic materials used in this study. Mine materials such as tailings, however, are often well sorted into specific grain sizes for processing by the crushing and grinding involved in mineral processing required for many ore recovery processes (Runge et al., 2013).

The influence of the soil moisture response in Figure 5-4 and Figure 5-5 for SS and SC indicate a non-linear likelihood for a two stage soil gas diffusion result, probably due to the combination of small amounts of clay sized material, mixed silt and coarse sand found in these materials. From θ_s to 0.1 m^3/m^3 moisture content, a low rate of diffusion is predicted as the change in matrix suction generates lower rates of reducing soil moisture, keeping effective porosity (matrix air space) low. From 0.1 m^3/m^3 moisture content to θ_r, the change in suction generates a large change in soil moisture, lowering effective porosity quickly and rapidly increasing diffusion. There is also a non-linear change in diffusion between 4-8% moisture and 12–16% moisture for both SC and SS materials. A similar non-linear diffusion behaviour was observed in natural sandy soils modelled by Moldrup et al (2013).

At the extremes of soil moisture, approaching θ_R and θ_S, the literature diffusion estimation functions appear to only approximate the measured diffusion coefficient and are spreading even on the log scale shown for diffusion coefficient in Figure 5-6. Potential error from the designed diffusion column will be discussed followed by an examination of the accuracy of the diffusion functions available in the literature, when compared to the measured diffusion coefficient results.

5.5.1 Diffusion column design

Testing of the diffusion column design used for this work, shows that minimal leakage does occur (0.0375% O_2 at 250 minutes), see Appendix 1 s9.3 for details. Kempton and Atkins (2009) shows field measurements of oxidation can also potentially suffer from chamber leakage, making results inaccurate. The SS diffusion tests were all less than 250 min, while the SC tests were all less than 2800 min, which represents a maximum error of <0.25% O_2 or 1.2% error. This compares well to the mid moisture range of both SS and SC diffusion coefficient estimation models from the literature, which display a relative error approaching 50% ranging across the various model predictions.

The drying out of the soils during the period of the test was also identified during diffusion column testing as also potentially problematic. Assouline et al. (2014) predicts with modelling that for column lengths less than 340 mm, evaporation is in the order of 0.9 cm/day, peaking at approximately 2.5 cm after 10 days for a column of 62.5mm –similar to the diffusion column 60mm test. Han and Zhou (2013) presents measured data showing an approximate 13% reduction in moisture content (m^3/m^3) over 36 hr for a 50mm column. This error may be minimal within a 250 min test, but diffusion tests requiring over 24 hr may require humidity controls. Potential alternative approaches to the use of humidity controls adopted in this study to minimise humidity and oxidation effects are suggested by Rolston (1986) including i) using the linear section of the ln $(C-C_S)/(C_O-C_S)$ diffusion column result as a sub sample of the total diffusion test to avoid excessive moisture loss effects, or ii) use of shorter material sample column lengths which can be used to achieve shorter test times. The use of these techniques generated sample times for D_p of < 250 minutes.

Soil structural change due to AMD related geochemical effects can most likely also be eliminated as a potential error source due to the fast nature of the diffusion column test relative to the rate of material oxidation. By using the linear section of the diffusion test results, all diffusion column test data were collected within 24 hr to minimise the possibility of AMD oxidation to influence material structure. This may be a potential issue for longer period tests such as humidity cell geochemical tests

which may run over several months or years. One of the key strengths of the diffusion test, is the ability for the test to be conducted within a few hours.

5.5.2   Diffusion coefficient estimation functions

Most of the literature diffusion coefficient estimation functions tested (see Table 5-1) were designed to represent conditions in natural agricultural soils and to be used for investigations such as root zone oxygen supply and CO_2 production. The mining materials SC and SC focused on in this study displayed well sorted particle size rather than the well distributed particle sizes found in most agricultural soils. The effect of sorted particle distributions versus non-sorted particle distributions in the material matrix is considered one of the key potential reasons for the literature diffusion functions not providing an effective simple estimate for soil diffusion behaviour.

The measured diffusion was likely taking place in the effective and total porosity and this was illustrated by extending the diffusion testing beyond the SWCC predicted saturated moisture point. The SWCC technique is focused on water transport, while diffusion techniques are based on gas transport. Effective porosity is generally a fluid flow concept that may not apply directly to gas flow, and several other forms of porosity have been suggested such as macroporosity and mesoporosity (Ezekwe, 2010). To illustrate the key effects of the differences between well sorted and well distributed soil, the particle size and SWCC data for an example Lateritic soil and the SC and SS materials were used to calculate the theoretical pore radius at each soil moisture point on Figure 5-8. The theoretical pore radius can be calculated using equation (9).

$$R = - \frac{2\sigma}{\rho_w g h} \qquad (9)$$

where R is pore radius (m), σ is surface tension at 20 °C in (J/m), ρ_w is the density of liquid water, g is gravitational acceleration (m^2/s) and h is the change in matric head (m).
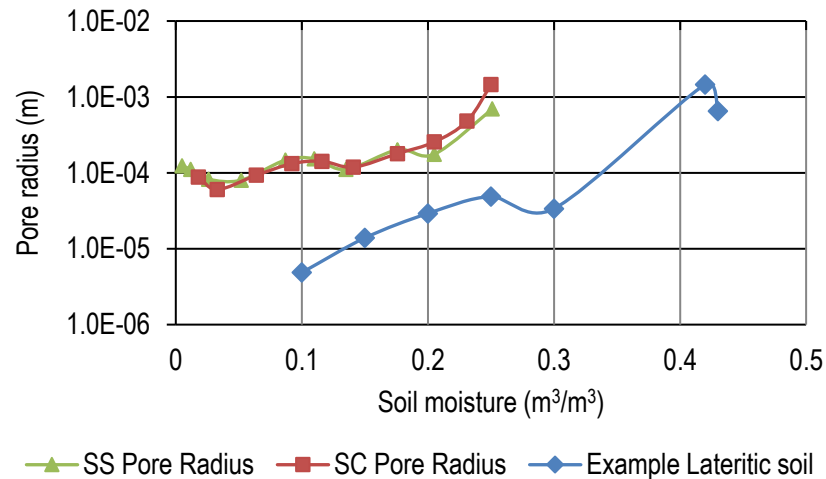
Figure 5-8: SC and SS theoretical (calculated) mine material pore radius compared to an example Lateritic soil.

The sorted mine materials SS and SC do not have the same range of fine pore radius displayed by the natural agricultural lateritic soil. This is believed to be pivotal to soil gas transport parameters such as effective porosity and residual and saturated moisture levels. Moldrup et al. (2000a) shows that there are problems for his models for low D_P/D_O ratios of < 0.1 or an adjusted D_p of < 0.0176. The available mine tailings materials data used in this study display D_P from $4 \times 10-2$ to $5.5 \times 10-4$ cm^2/s, which may therefore be problematic for some soil diffusion functions. Hamamoto et al. (2009) showed that average particle size D_{50} could influence connectivity and tortuosity relationships in soil media, and that increasing porosity increased error in many literature based diffusion coefficient prediction functions.

The SC and SS mine materials studied had relatively high total porosity levels compared to the SWCC saturated moisture predictions. Moldrup et al. (2013) recommends the SWLR diffusion model can be used with a range of media complexity (where $X = 1+ CM\phi$ - see Table 5-1) values from 1 to 3 to avoid over predicting soil gas diffusion in the root zone –a completely opposite risk to AMD oxidation modelling, where under prediction is most often experienced and problematic for geochemical stability. The fitted values of Moldrup's et al. (2013) matrix complexity parameter, CM, were 0.43 and 1.72 for the SC and SS materials respectively, which also indicate a simpler soil structure than the natural agricultural soils that Moldrup found to generally have a CM approaching 3.

The various diffusion coefficient functions are based on Fick's law, and so therefore are reliant on the existence of a concentration gradient boundary condition to be effective, but it has been shown that diffusion coefficient changes relative to the relative concentrations of the diffusing materials. Richard (1996) shows a 6% increase in D_O between 2% soil O_2 and 15% soil O_2 concentration in waste management.

5.5.3 Implications of underestimation of soil gas diffusion coefficient

If soil gas diffusion coefficients are underestimated through the use of an insufficiently conservative natural or agricultural soil diffusion coefficient model, then AMD geochemical modelling undertaken to predict sulfide oxidation, will underestimate the rate of generation of acidity in the mine wastes. This is a serious problem that will potentially lead to insufficient treatment of AMD mine wastes, such as use of too little neutralising material, or reduced depth of final encapsulation of mining waste, and other relevant waste dump design dimensions, including depth of liners and capping systems. Kuipers et al. (2006) in their landmark analysis of the reliability of AMD predications for actual water quality at hardrock mines in the USA, shows that only one of the 75 mines studied in detail successfully predicted the AMD potential for future water quality, but this mine predicted low AMD potential, and this has been proven to be a high AMD potential by impacts to surface waters at the site in actuality. Oxygen transport processes and the uncertainty of AMD analysis are regularly cited as the major risks in mine waste management for AMD materials (DITR 2007).

The high cost of sorting, mixing, treatment, encapsulation and capping of Megatonnes of AMD mine waste materials, is substantially increased if the geochemical design for the treatment and containment systems fail, and waste dumps require being rebuilt due to elevated sulfide oxidation rates (EA 1997). In many cases, AMD may emerge many years after the site has been transferred back to government ownership, and if rebuilding waste dump facilities is deemed too expensive for government priorities, which is often the case, further ongoing ground and surface water treatment is required, sometimes in perpetuity (DITR 2007).

5.5.4 Diffusion coefficient AMD safety factors for mining

Each tested mine material was best represented by differing diffusion functions, and even the best of the literature diffusion functions showed areas of under prediction of the measured D_P values. As discussed previously, this is of some concern for mining related applications of diffusion functions in soil gas transport, as underestimation of oxidation will result in under estimation of acidity loads generated by mine materials in TSF or waste rock dumps. If diffusion must be estimated by a diffusion function rather than measured, it is recommended that several models are examined for fit by comparison with similar classes of materials (eg Moldrup 2013), and then an AMD safety factor applied to ensure all underestimated diffusion results are captured by the final diffusion function. Based on Moldrup et al. (2013) results in this study, several potential options for applying an AMD safety factor (FS) are illustrated in Figure 5-9. If measured data are available and a continuous diffusion function is required, a safety factor could be set by goodness of fit using $FS = 1+(1-R^2)$, if no measured data are available then FS = 1.1 (for this case FS = 1.1 is effectively similar to $1+(1-R^2)$) and 1.3 are shown. In this study a FS of 1.3 is recommended for wet soil modelling, a FS of 1.1 is recommended for dry soil modelling. These values will likely not be applicable to other mine materials.
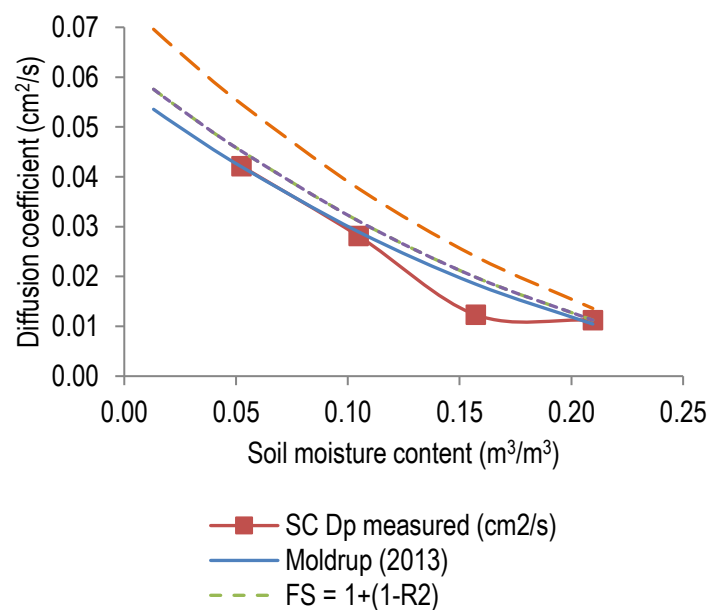
Figure 5-9: SC material with Diffusion Coefficient AMD Safety Factor options: FS = 1+(1-R2), FS = 1.1 and FS = 1.3.

5.6 Conclusion

Measuring soil gas diffusion is potentially an effective, and accurate means to determine transport parameters relevant to the production of AMD in mine materials such as tailing and waste rock. A diffusion chamber with O_2 probe and logger can be built for less than \$500 USD, and diffusion coefficient tests can be completed on AMD materials similar to those tested within hours, particularly if not required to reach complete atmospheric equilibrium O_2 of 20.9%.

The existing diffusion coefficient models from the literature were developed for natural soils that are well distributed or may have higher levels of fines (clays and silts) and therefore smaller pore radii that respond to soil moisture changes with more impact on effective porosity of the material. The resulting higher matric potential of these soils means moisture would be likely to be distributed further through the soil structure, resulting in a broader range of diffusion coefficient values than those found in the mine materials, particularly near saturation.

None of the literature-based diffusion coefficient models evaluated with mine materials were considered accurate for the full range of soil moisture conditions that could be expected in the field, particularly during mine closure when tailings storages may start to dry out, or as water evaporates from the structures, or when approaching saturation, such as underneath designed oxygen limited earth covers. All of the literature-based models also under predicted diffusion coefficient as the soils approached saturation. This is of some concern for soil gas transport model use with AMD materials to predict acidity production, as AMD will be consistently under predicted. This means that soil cover designs for waste rock and tailings storage facilities may not be sufficiently accurate to prevent oxidation of sulfide materials.

Given the limitations of literature-based models for diffusion coefficient estimation in mine materials, using soil gas diffusion apparatus, such as the very economical diffusion column design presented, would appear to be useful tool for predicting oxygen supply potential and associated

oxidation zones of the AMD materials. It is recommended that rather than relying on modelled estimates of D_P, AMD mine waste materials such as tailings and waste rock are subjected to diffusion performance testing to help lower AMD risk in all phases of mine design, operations and closure. If this is not possible, then selected diffusion functions appropriate for available material soil classification data could potentially be adopted with an appropriate safety factor, based on the variation in the available materials diffusion data.

5.7 Acknowledgements

5.8 References

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6 A 1D soil gas diffusion model for estimating oxidation volumes and rates of AMD mine materials. (Paper iii: Under review)

This Chapter describes the development of a 1D soil gas diffusion model and associated methodology for model data collection, when applied to AMD affected mine materials. 1D model performance is evaluated in the context of several diffusion coefficient estimation models available in the literature, which are used to provide the diffusion coefficient function for the 1D model. The discussion includes discussion of the possible limitations and agricultural basis for existing diffusion coefficient estimation models, provides analysis of possible dual diffusion functions based on material matrix geometry and particle size. The content of this Chapter is unpublished and has been submitted for publishing and is in review as: D. Dettrick, J. Costelloe, M. Arora, and S Yuen, in review, expected 2020, "A 1D soil gas diffusion model for estimating oxidation rates of AMD mine materials", Engineers Australia Technical Journals, AJMDE: Australian Journal of Multi-Disciplinary Engineering.

6.1 Abstract

Oxidation of sulfide bearing rock and mine waste material generates acidity via acid mine drainage (AMD) processes. Soil gas (oxygen) transport modelling is a potential methodology to estimate acidity generation in AMD materials. Several attempts have been made in past to theoretically model oxygen consumption and concentration at depth in AMD materials but typically in these studies the oxygen depletion boundary condition was set to 1m depth in the absence of data for development of the theoretical model used in each case. This study undertakes testing to determine the key model boundary conditions including the soil gas diffusion coefficient, soil material oxygen penetration, and then evaluate the performance of a simple 1D diffusion soil gas transport model. A reactive AMD mine material is tested to determine its behaviour with respect to oxygen diffusion with moisture using a soil diffusion column and is also tested for the steady state oxygen depletion depth using an oxygen penetration column technique. Following that, a 1- D soil gas diffusion transport model is derived and evaluated for use in estimating the depth of oxidation to enable the estimation of volumes of AMD affected mine waste materials. Both modelled and measured soil gas diffusion rates are explored using the physical diffusion data and oxygen depletion depth as a boundary condition in an oxidising, reactive

AMD mine waste material. The 1D model accuracy and potential for model error is discussed when used for predicting areas of soil and rock potentially developing AMD and compared with results from diffusion coefficient predictive models available in the literature. It is concluded that in order of accuracy from high to low, the following methods can predict the results of the potential for AMD generation from mine waste oxidising materials i) soil gas diffusion testing and oxygen penetration testing, ii) , modelled diffusion coefficients and oxygen penetration testing, iii) soil diffusion testing and estimated oxygen depletion depth, and least accurate iv) modelled soil diffusion coefficients and estimated oxygen depletion depth.

6.2 Introduction

Globally, oxidation of sulfide bearing rock and soils is one of the leading causes of surface and groundwater pollution and is generically described as acid and metalliferous drainage, acid mine drainage (AMD), or acid rock drainage (ARD) (SSD 1997). Management of AMD requires an estimate of sulfide oxidation rate, to enable accurate acidity load calculations for geochemical stabilisation design work, with waste treatment using waste neutralisation or oxygen inhibition strategies (Maest et al. 2005). Estimation of sulfide oxidation rate is complex and can be undertaken using oxygen consumption testing, or with less accuracy, conventional humidity cell leachate testing (DITR 2016). To complete AMD load calculations, assessment of the volumes that will be subject to oxidation and reaction rates of various AMD materials over the life of projects effected, is required. Target areas for such AMD load calculations and oxidation volume estimated include mining pits, waste rock dumps (WRD) and tailings storage facilities (TSF), and areas of potential acid sulfate soils (PASS) in urban and rural development schemes.

DITR (2016) proposes conceptual implications for cost of management of AMD materials, indicating that costs may be likely to increase the longer management action is deferred. For example, dosing neutralising materials into tailings after process metallurgy operations but prior to final deposition in the TSF, is an option that may be less expensive if designed during the pre-feasibility

mine design, rather than retrofitted later, as there may be volume and water management ramifications of choosing this acidity neutralising method.

An examination of the theoretical AMD reaction (see equation 1) illustrates the significance of air, water and particularly oxygen to the development of acid conditions in rock and soils and by association, ground and surface waters.

$$FeS_2 + \frac{15}{4} O_2 + \frac{7}{2} H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \quad (1)$$
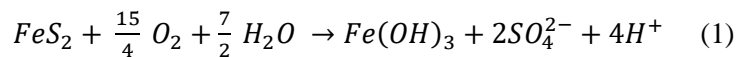
In term 2 of equation (1) above, the requirement for oxygen is shown to be a potential limitation to sulfide oxidation, and therefore control methods that reduce the rate of ingress of oxygen, for example with open water covers, or use of saturated clay covers, is part of the AMD management toolbox (US EPA 1994).

Amos et al, in their 2014 review of developments in mine waste rock hydrology and geochemistry, identified oxygen transport processes as a significant knowledge gap and concluded that AMD soil gas transport modelling required further study to understand the contribution of oxygen ingress to the development of AMD conditions in mine pits and waste management systems such as tailings storage facilities and waste rock dumps. This Paper attempts to address this gap and is focused on the development and testing of a simple 1D soil gas transport model to evaluate oxidation rates and to delineate volumes of low-permeability mine waste rock and tailings as a potential tool to help estimate AMD risk and treatment requirements. To be useful, the 1D soil gas model must predict oxygen transport and depth of oxygen depletion and hence be used for estimated volumes of AMD affected materials. Oxygen diffusion processes often control the rate of reaction due to small particle sizes and fracture diameters, such as TSF wastes and residue storage facilities (DITR 2016). Dettrick et al. (2019b) found the use of measured diffusion more accurate than diffusion coefficient estimation functions reported in the literature which have been developed primarily for agricultural soils and crop growth and may require the use of safety factors when used for AMD modelling in the mining sector. Amos et al. (2014) also found AMD modelling works but requires site specific data for soil gas and materials to be sufficiently accurate. Advection and convection processes, rather than control by

diffusion, may be dominant in systems with large size materials with potential for large airflows and thermal gradients, such as waste rock dumps (Kempton et al. 2009). Within these materials, the limits of advective and diffusive transport will define the areas and volumes that oxidation occurs in. Kempton et al. (2009) also identifies diffusion processes as likely to be dominant over time, in situations where advection processes may require large barometric pressure changes, thermal gradients or subsurface water movement, which are short term phenomena over the life of a mine.

Several new geochemical testing methodologies have been developed to assess kinetics of sulfide reactions that provide benefits over conventional humidity cells (Bourgeot et al. 2011, Schmeider et al. 2012, Davis et al. 2014) that may provide data to support to a simple diffusion Oxygen transport model. These include; i) the oxygen consumption technique (Hollings et al. 2001, Schmieder et al. 2012), ii) soil gas diffusion testing (Moldrup et al. 2013, Dettrick et al. 2019b) and iii) the oxygen penetration column test (Elberling et al. 1994) which offer some additional potential boundary condition data, that allow for the development of a simple soil gas oxygen diffusion model.

Several attempts have been made to theoretically model oxygen consumption and concentration at depth in AMD materials including Elberling et al. (1994), Hollings et al. (2001) and Binning et al. (2007), but in these studies the oxygen depletion boundary condition was set to 1m depth in the absence of data for development of the theoretical model used in each case. Many geochemical based models often including gas, liquid and solid phase reactions have also been developed and trialled using assumptions of saturated conditions as forming the effective oxygen depletion boundary including Romano et al. (2002) and Brookfield et al (2006).

This study seeks to build on these previous attempts by undertaking diffusion testing to determine the key model boundary conditions including, i) the AMD soil gas diffusion coefficient as it varies with soil moisture, and ii) AMD material oxygen penetration depth, and then evaluate the performance of a simple 1D diffusion soil gas transport model. The model will then be tested with well-regarded diffusion coefficient estimation functions available in the literature including Moldrup et al. (2013), Penman (1940) and Buckingham (1904).

To best assist the with AMD management in the early phases of mine development in identified AMD materials, the simple model was developed to meet the following requirements:

- Be economic with model builds of < 30 minutes and work with standard software such as spreadsheets.

- Use steady state rather than transient data, as transient data is unlikely to be available during the early and exploration phases of mining.

- Use standard soil investigation methodologies where possible.

- Benefit from new kinetic geochemical testing procedures.

- Use advanced, cost effective, soil column testing apparatus that can be assembled with commonly available materials including gas plumbing and UPVC pipe for less than $300-500 USD such as proposed by Dettrick et al. (2019b).

6.3 Methodology

Following the soil transport model development methodologies of Buchgraber et al. (2012), Zyvolooski et al. (2007), Brookfield et al (2006), Pantelis et al. (2002), Romano et al. (2002), Larsson and Jarvis (1999), Kuo and Ritchie (1999), Gerke and Van Genuchten (1993) the study results will be presented for one AMD mine material type in order to provide both clarity and substantial detailed AMD material data, to aid understanding of the 1D model development methodology. Natural and other non-target AMD material data is presented for comparative purposes where data was available and relevant. By using this approach, focusing on the methodology and associated required soil testing program and equipment design requirements in detail, the 1D model and method will be more likely to be adopted and used by industry (Pantelis et al. 2002, Refsgaard and Henriksen 2004). Future recommended research arising from this study includes applying the 1D model and method to a larger range of AMD material types and materials for statistical testing of model accuracy, see Identified further research in Chapter 8.6 below.

6.3.1 Test Material Selection:

Sandy–silty agricultural soils have been studied extensively for soil gas diffusion (Deepagoda et al. 2012, Moldrup et al. 2000a, 2000b, 2004, 2013, Van Genuchten 1980, Millington and Quirk 1961, Millington 1959, Marshall 1959, Fatt and Klikoff 1959, Penman 1940, Buckingham 1904). Sand–silt grain size materials are important to the mining sector as many mining wastes, including tailings, are ground to this size range to maximise process metallurgy recovery rates. The sandy-silt AMD material samples were selected for this study based on their grain size and high reactivity due to sulfide content and were verified as reactive for this study with oxygen consumption testing. Sandy silt AMD materials are more likely to be be diffusion dominated with respect to soil gas transport conditions. Of these materials, two sandy silt materials sourced from mineral sand exploration sites and a non-reactive silty sand control material were used for diffusion column testing. The materials were selected to be low in clay content to minimise the potential for matrix change via compaction-based error. The target materials were tested for soil water characteristics curve (SWCC) behaviour using ASTM D6836 (2008) to enable the development of a predictive soil moisture function versus height above saturated soil conditions. The material was also tested for mineralogical content by x-ray diffraction (XRD).

6.3.2 Soil Gas Diffusion Testing

An experimental soil gas diffusion column was built using the method described in Dettrick et al. (2019b), Chapter 5 in this thesis, to measure the soil gas diffusion coefficient in the target AMD material (also see Appendix 1 below). The diffusion coefficients for the target material at different moisture content were determined using Rolston (2002, 1985) and the results have been shown as diffusion coefficients plotted against soil moisture to provide a diffusion function for the materials for further analysis. The Rolston (2002, 1985) method uses equation (2) for determining D_P:

$$\frac{C-C_S}{C_0-C_S} = \frac{2h\,exp\left(-D_p\alpha_1^2 t/\epsilon\right)}{l\left(\alpha_1^2+h^2\right)+h} \qquad (2)$$

and the plot of ln $[(C–C_S)/(C_o–C_S)]$ versus time, t becomes linear with a slope of $–D_P\alpha_1^2/\epsilon$ for an appropriate test period. Rolston provides tables for determining α_1^2 and h, l values, where h is a

chamber volume function. For further details about applying this method to the analysis of test results see Paper i, Dettrick et al. (2019b) which forms Chapter 5.

6.3.3   Oxygen Consumption Testing

Oxygen consumption testing was undertaken using the method outlined by Bourgeot et al. (2011), Taylor (2012) and Davis et al. (2014), a technique which is similar to the method of Hollings et al. (2001). Oxygen consumption testing was undertaken at several soil moisture levels by adding the required gravimetric water content to an oven dried sample. After mixing the make-up water with testing materials for the required moisture content, the AMD target material was placed in a sealed oxygen consumption test chamber and oxygen consumption was logged with an analogue O_2 probe at 5 minute intervals for 72 hours or until less than 1% O_2 was recorded. The physical and geochemical properties of the AMD materials were then used to derive a pyrite oxidation rate (POR) for the material, based on the recorded oxygen consumption rates during the oxygen consumption testing. The KT-01 oxygen consumption test (Taylor 2012) provides rate of reactive sulfide oxidation, and full geochemistry and mineralogy.

6.3.4   Oxygen Penetration Column Testing

An oxygen penetration column test was undertaken to assess the depth of oxygen penetration on the target materials, using the adapted method of Elberling et al. (1994) by adding soil moisture control at the bottom of the soil column apparatus. The oxygen penetration column apparatus is shown in Figure 6-1. The 3m soil column was filled with the target materials at near saturation and allowed to drain for 130 days while saturated soil conditions were maintained at the bottom 25mm of the column using soil moisture probes, collection, and visual observation. O_2 gas probes were fitted to the column at 100mm intervals for the full length of the column to assess depth of oxygen penetration in the AMD materials.
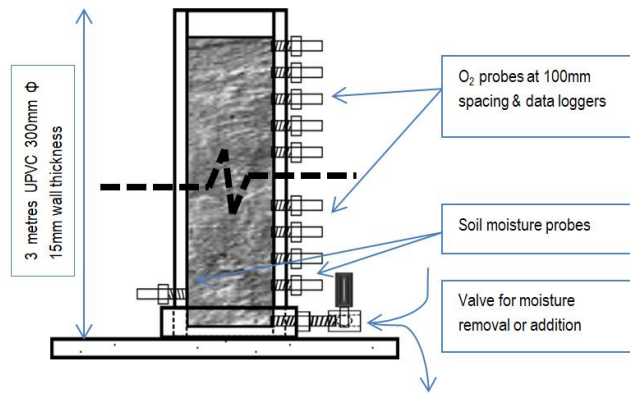
Figure 6-1: Oxygen penetration column apparatus used for this study (modified from Elberling et al. 1994).

The O$_2$ gas probes were data logged and the results for oxygen consumption recorded after 10 days. Results were also collected up to 130 days, by which time the column had reached a steady state moisture profile.

6.3.5   BET Surface Area Testing

Brunauer-Emmett-Teller (BET) Surface area determination was undertaken to determine the surface area, adsorption and desorption area, pore volume and size for the target materials for the purposes of 1D soil gas diffusion modelling. The testing was undertaken by the University of Melbourne, Department of Chemical Engineering using a Micromeritics ASAP 2010 Accelerated Surface Area and Porosimetry System using the BS 4359-1:1996 standard method. A numerical estimate for Moldrup's (2013) media complexity parameter, C_m was then undertaken by comparing material matrix complexity, based on BET test results.

6.3.6   Comparison with diffusion coefficient estimation models

Three most commonly used diffusion coefficient estimation models from the literature were evaluated, to simulate modelling without measured diffusion coefficients, by using the simple 1D model with the estimated value for the diffusion coefficient including:

Buckingham's (1904) equation $\qquad \dfrac{D_p}{D_o} = \varepsilon^2 \qquad$ (3),

Penman's (1940) equation $\qquad \frac{D_p}{D_o} = 0.66\varepsilon \qquad$ (4) and

Moldrup's SWLR model (2013) $\qquad \frac{D_p}{D_o} = P\varepsilon^X \left[\frac{\varepsilon}{\phi}\right]^{Ta} \qquad$ (5).

In the models above, ε is soil air content, ϕ is soil total porosity, P= 1, X=1 + $C_m.\Phi$ and Ta= 1 are model parameters. These estimated diffusion coefficients were used to compare results with the measured variable diffusion model determined from testing soil gas diffusion with the purpose designed column at several moisture contents. To provide these functions with a steady state response for soil moisture and depth, they are modelled using the Van Genuchten (1980) soil moisture model for the material based on laboratory measurements of SWCC for the target AMD material. In Moldrup et al. (2013) C_m is a media complexity measure from 1 to 3, which was evaluated for uncertainty analysis for diffusion coefficient model performance, using $C_m = 1$ and $C_m = 3$. BET surface area data was collected to provide soil matrix complexity data for the purposes of a C_m estimation for the target materials. From Moldrup (2013), a C_m of 3 would represent a lower bound for clay sized materials with porosity up to approximately 0.85, while a a C_m of 1 would represent the upper bound of sand sized materials with a porosity of up to 0.45.

6.3.7   Model Testing

Model statistical error testing was used to identify the best candidate models for estimating soil gas concentration in the target AMD materials. The assessment of model error is undertaken using the following statistical measures selected for determining goodness of fit, noting that underestimation of diffusion coefficient is of significant environmental concern in the mining sector, due to possible underestimation of acidity generated from oxidation of AMD mine materials. Error models used in this study include; mean difference (MD), geometric mean error ratio (GMER), and gradient of observed versus predicted comparative data sets. The relevant equations for each error formula are shown below.

$$MD = \frac{1}{N} \sum_{i=1}^{N}(P_i - O_i) \qquad\qquad (6)$$

$$GMER = exp\left[\frac{1}{N}\sum_{i=1}^{N} ln\left(\frac{P_i}{O_i}\right)\right] \qquad\qquad (7)$$

-where N is the number of data points, O is observed data, and P is predicted data, i is the count of the current data point.

GMER, and MD is particularly useful for unsaturated AMD material properties as it helps to assess whether a function under or overestimates the particular diffusion function being examined, an important assessment for safety in AMD mining applications (see Paper ii Chapter 5).

6.4 Results

6.4.1 Conceptual Model

The soil gas transport conceptual model assumes steady state behaviour. Steady state conditions allow assumptions for moisture gradients based on soil water characteristics in unsaturated mine materials such as tailings and waste rock. The mine materials chosen are fine grained where diffusion becomes the dominant form of soil gas (oxygen) transport. A steady state depth over which oxygen concentration reduces to zero is assumed, due to limitations of soil gas diffusion. The key boundary conditions are the gas reactivity rates, and the oxygen concentration of the atmosphere and the oxygen extinction depth due to the limits of soil gas diffusion and reaction.

The conceptual soil gas (oxygen) transport model is shown below in Figure 6-2. The boundary conditions for the conceptual model include:

- Steady atmospheric concentration of O2.

- Saturated zone at depth below the soil gas diffusion zone.

- Steady state Van Genuchten (1980) unsaturated zone soil moisture conditions will be assumed based on measured SWCC results.

- O2 (%) terminates at depth L from the material surface due to soil diffusion and oxidation processes.

- The material matrix is assumed to be unchanging and at 21 degrees Celsius.
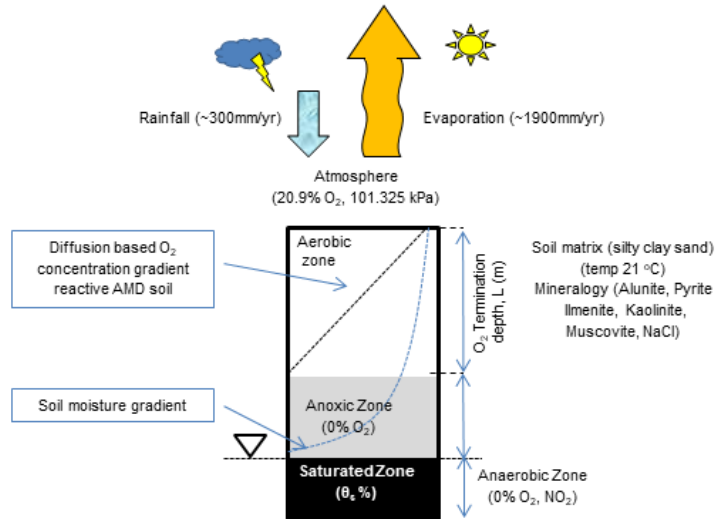
Figure 6-2: Soil gas (oxygen) transport conceptual model

With oxygen content in the atmosphere as a constant, a steady state flow of gas from the atmosphere to material is a key assumption assuming unchanging unsaturated zone moisture, and a zone in which soil gas diffusion effectively limits the available O_2 supply.

6.4.2   1D soil gas diffusion model

Jury et al. (2004) found that in these conditions of steady state as described above, the gas transport equation reduces to:

$$\frac{dJ_g}{d_z} + r_g = 0 \qquad\qquad (8)$$

At the boundary where no gas flow occurs as gas is fully consumed by sulfide, $z = -L$ and therefore

$$J_g(-L) = 0 \qquad\qquad (9)$$

Rearranging (8) and integrating from $z = -L$ to z yields the following (10) which then results in (11)

$$\int_0^{J_g} dJ_g = -r_g \int_{-L}^{z} d_z \qquad\qquad (10)$$

$$J_g(z) = -r_g(z + L) \tag{11}$$

The gas flux equation is in equation (12)

$$J_g = -D_g^s \frac{\partial C_g}{\partial z} \tag{12}$$

Substituting the gas flux equation for $J_g(z)$ in (10) provides

$$J_g = -D_g^s \frac{\partial C_g}{\partial z} = -r_g(z + L) \tag{13}$$

By placing all material depth (z) related terms on one side of the equation and integrating from z=0 to z

$$C_g(z) = C_0 + \frac{r_g}{2D_g^s}(z^2 + 2Lz) \tag{14}$$

In equations (8) to (14), C_g is the oxygen gas concentration at material depth z, C_0 represents the boundary condition of atmospheric oxygen concentration and L equals the oxygen penetration boundary condition depth at which $C_g = 0\%$. D_g^s is the soil gas diffusion coefficient for air–soil, and r_g is the oxygen gas reaction term for sulfide oxidation. To use the model in this study, the L term boundary condition was determined by oxygen penetration column work using the method of Elberling et al. (1994), and the diffusion coefficient D_g^s was measured using a diffusion column using the method of Rolston (2002, 1985), these results are described below.

6.4.3 Target AMD sandy grained material parameters and sulfide oxidation rates

The AMD material used for the soil laboratory test work was an AMD reactive sandy silt (SS) material further described in Dettrick et al. (2019a, 2019b). The material physical and texture parameters, kinetic geochemistry from oxygen consumption testing, and mineralogy data for the SS material is shown in Table 6-1 to 3. The main AMD reaction oxidation activity (as pyrite oxidation rate) in the SS materials is likely from the FeS_2 component which is at approximately 2 wt% POR. Data from several other AMD (sandy clay -SC) and unreactive soils (River sandy silt -SSS, Silt Loam, Illite

Clay) were included for comparative purposes. Figure 6-3 below shows the measured pyrite oxidation rate for corresponding soil moisture.

Table 6-1: Density and particle size distribution SS and SC material

Soil	Particle Density (g/cm3)	Bulk density (dry) (t/m3)	Classification	D10 (μm)	D50 (μm)	D90 (μm)	Clay content (%)
SS	3.37	2.2	Sand and silt	56	131	230	5
SC	2.65	1.8	Sand and silt	62	212	395	3

Table 6-2: Summary of kinetic geochemical data for SS material

Soil	Total sulfur (wt% S)	Sulfide sulfur (wt% S)	MPA (kg H_2SO_4/t)	Moisture %	Pyrite oxidation rate (wt%/week FeS_2)	Acid Generation Rate (kg H2SO4/t/year)
SS	0.96	0.89	29	13.8	2.18	0.64

Table 6-3: Mineralogy of SS material.

Mineral Name	Mineral Formula	Mineral composition (wt%)
Alunite	$KAl3(SO4)_2(OH)_6$	3
Ilmenite	$FeTiO_3$	14
Kaolin	$Al2Si2O5(OH)_4$	1
Monazite	$(Ce,La)PO_4$	<1
Muscovite	$KAl2(Si3Al)O_{10}(F,OH)_2$	<1
Pyrite	FeS_2	2
Quartz	SiO_2	63
Sodium Chloride	NaCl	<1

Qualitative moisture versus POR data for a single oxygen consumption test at each moisture content are presented in Figure 6-3 below to illustrate indicative POR response to soil moisture. The test peak moisture content for POR development is qualitatively estimated to be around 10% GMC. The SS material used in this study shows a typical moisture response to POR (Davis et al. 2014) with low soil moisture content limiting the AMD reaction as predicted by equation (1) and elevated moisture

approaching saturation also reducing oxidation rates by limiting soil gas transport and hence oxygen supply.
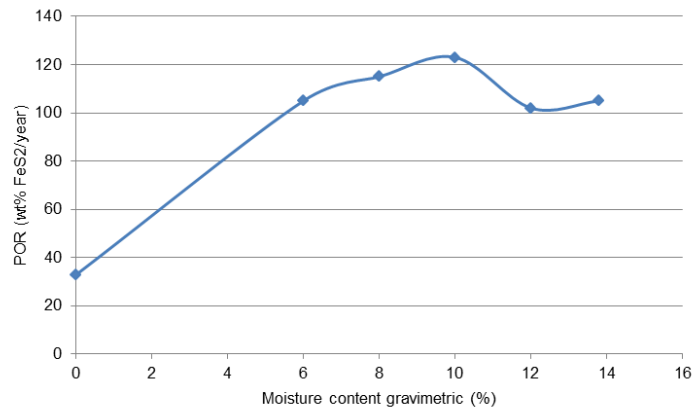
Figure 6-3: Pyrite oxidation rate versus soil moisture for the SS material

Soil water characteristic testing was undertaken on the target material to allow for the modelling of steady state unsaturated zone moisture conditions. The SWCC results were fitted to determine the Van Genuchten (1980) parameters for the soil. The results are shown in Table 6-4 and Figure 6-4 below. The RSS error result for the SS material was low at 0.037.

Table 6-4:   Van Genuchten parameters for SS material with an example Silt Loam (UNSODA 2017) for comparison.

Soil type	α	n	θ_r	θ_s	RSS	m
Silt Loam	0.02	1.41	0.067	0.45	n/a	0.29078
SS	0.0392	3.0066	0	0.269657	0.037	0.667
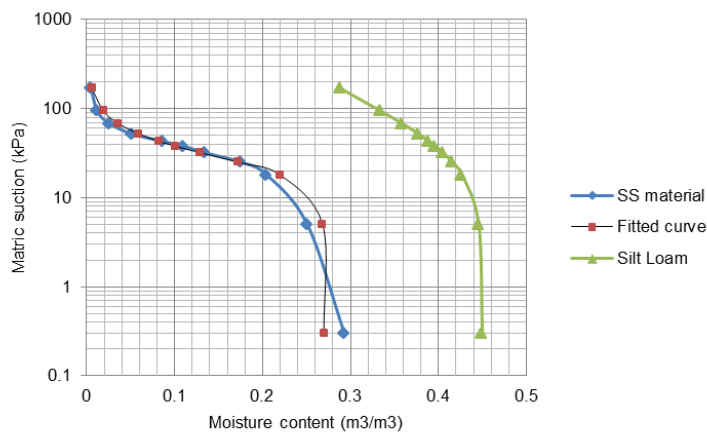
Figure 6-4: SS material SWCC response data compared to standard silt loam soil from UNSODA (2017).

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The Van Genuchten (1980) parameters were used to derive the steady state soil moisture in the oxygen penetration soil column with saturation at 3m material depth, see Figure 6-4. Within the 1D model the predicted Van Genuchten (19080) soil moisture level is then used to derive the associated value for the material diffusion coefficient based on the tested soil gas column testing for differing mine material moisture.

6.4.4 Soil Gas Diffusion Column Test Results

Dettrick et al. (2019b) measured the diffusion coefficient for the SS mine material, the results for this are shown in Figure 6-5 and were used to derive a variable diffusion versus material moisture function based on the measured values of diffusion coefficient D_{SS} for the 1D model, and van Genuchten (1980) soil moisture.

(a) SS material measured diffusion coefficient vs moisture

(b) SS material steady state soil moisture vs material depth above GWT

(c) SS material 1D variable material diffusion function
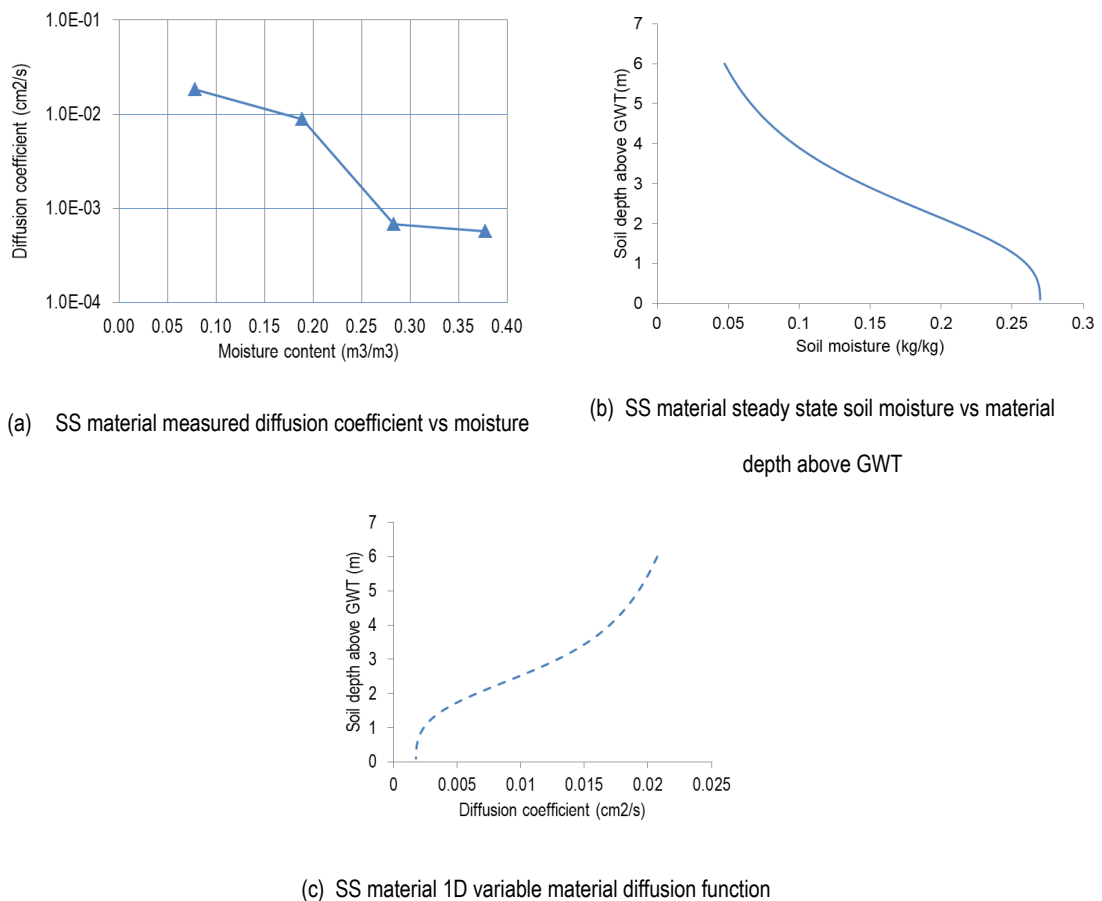
Figure 6-5: Material depth vs moisture function, measured diffusion vs moisture and 1D material depth vs diffusion model.

6.4.5 BET Testing Results

To undertake an assessment of material matrix structure and its influences on soil gas diffusion, BET surface area testing was undertaken on three sandy silty materials for comparison:

- the target AMD material, SS;

- an overburden AMD material from the same mine site, SC; and

- a soil of similar particle size distributions reconstructed of unreactive river sand in the soil laboratory by mass, SSS.

The BET testing results are shown in Table 6-5.

The AMD target SS material, has the highest surface area, followed by the SC material, and then the SSS unreactive river sand, with similar trends across BJH adsorption, desorption, and pore volume. Pore size did not follow this trend, with the SC material having larger pore size, most likely due to a slightly reduced clay content.

Table 6-5: BET surface area testing results for SS material with SC overburden and SSS unreactive soil and several reference BET materials for comparison.

Soil	Surface area				Pore volume		Pore Size	
	Single point surface area (m²/g)	BET Surface area (m²/g)	BJH Adsorption surface area (m²/g)	BJH Desorption surface area (m²/g)	BJH Adsorption volume (m²/g)	BJH Desorption volume (m²/g)	BJH Adsorption pore width (nm)	BJH Desorption pore width (nm)
SS	7.4648	7.7219	5.819	9.2273	0.013582	0.015442	9.3365	6.6942
SC	2.1193	2.1925	1.948	1.6889	0.007583	0.007328	15.5721	17.3549
SSS	0.4595	0.5121	0.566	0.6599	0.001366	0.001426	9.6463	8.6414
Illite Clay*	-	41 ± 3	-	-	-	-	-	-
Glass powder**	-	5.3	-	-	-	-	-	-
Alumina chips**	-	0.46	-	-	-	-	-	-
Quartz***	-	2.50	-	-	-	-	-	-

Note: * results from Macht et al. (2011), ** results from Micrometrics (2020), *** results from Merck (2020).

To assess the potential for material matrix complexity and tortuosity, the Moldrup et al. (2013) SWLR model was used as it provides a material matrix complexity function C_m. C_m was estimated for the SS materials based on the range of C_m proposed by the SWLR model (Moldrup et al. 2013), clay is

approximately C_m = 2-3 while sand (similar to SSS material) is C_m = 1. Macht e tal. (2011) found the surface area of illite clay was 41 m^2/g (Table 6-5). Using illite as an example clay with C_m =3 and SSS as an example sand with C_m =1, and weighting soil type versus BET surface area, a qualitative estimate matrix complexity factor, for the SS material was estimated to be C_m = 1.2. The 1D model was applied to Cm = 1.0, 1.2 and 3.0 to provide a range of soil gas transport diffusion results for comparison to the variable (measured) diffusion model method.

6.4.6   Oxygen Penetration Column Results

A schematic of the oxygen penetration column containing SS AMD mine material is shown in Figure 6-1. The column was allowed to drain from saturation to field capacity and saturated conditions were maintained at 3m depth. The O_2 concentration (%) versus depth of SS mine material was recorded from O_2 sensors located at 100mm intervals on the column (see Figure 6-1). Binning et al. (2007) suggest steady state conditions may be achieved in a 3m column in approximately 10 – 100 days. To ensure both unsteady and steady state conditions were sampled, column O_2 concentration (%) data was collected at regular intervals and the results for the draining 10 day and the steady state 130 day oxygen penetration column are shown on Figure 6-6 below.
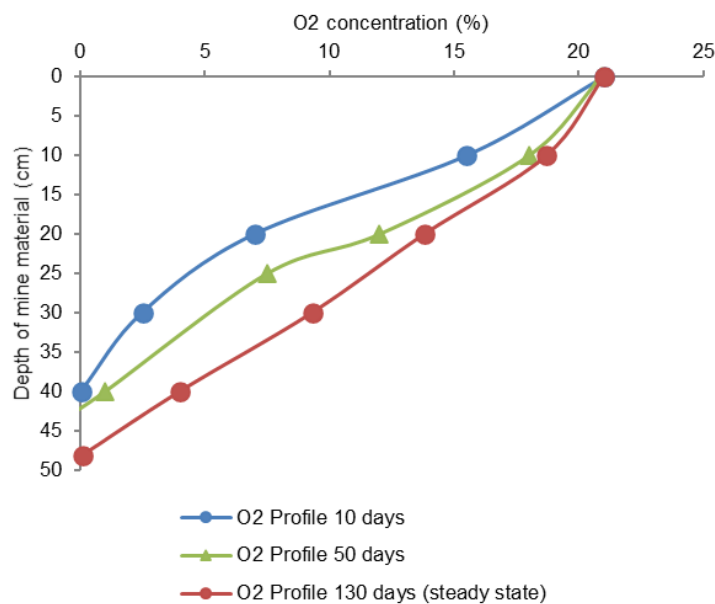
Figure 6-6: Oxygen penetration column data for the SS material draining at 10 days and steady state at 130 days.

Using the boundary condition of oxygen concentration = 0% to determine L, and hence r_g Equation (14) was then used to plot predicted O_2 concentration (%) through the SS material for both the draining column at 10 days and steady state column at 130 days. The scenarios used to test Equation (9) included:

- The variable diffusion model based on measured soil diffusion values shown above in Figure 6-5 (b) was used to provide changing diffusion coefficient based on the predicted material moisture shown in (a).
- The equation was also fitted to the measured OPT data to create a single diffusion coefficient model.

The results of the scenario modelling are shown below for both unsteady state draining (10 days) and steady state conditions (130 days) for the purposes of comparison of model performance. The 10 day unsteady column O_2 concentration data (shown on Figure 6-6) shows the incomplete nature of the oxygen concentration profile in the column, with the non-linear O_2 concentration reducing in the middle profile at 20cm depth and then increasing rapidly from 20cm to the 10 day O_2 depletion depth at approximately 40 cm.

6.4.7   1D 10 day draining column model results

The 1D model results using diffusion estimation models and the measured variable diffusion function are shown in Figure 6-7. With the column in unsteady state, the gas reaction term r_g was calculated for model comparison for an L of 40cm as the $C_g(z)$ term becomes 0 at this point, forming the oxygen depletion boundary condition.

None of the models perform adequately as expected due to the lack of steady state conditions in the oxygen penetration column at 10 days. The 1D variable (measured) diffusion model predicts the O_2 depletion depth accurately, but over predicts O_2 concentration at all other depths from the surface 0 cm to 35cm mine material depth. As discussed in Dettrick et al. (2019a) over prediction of oxidation is safer for AMD waste management than under prediction, which commonly occurs, as can be seen by the Moldrup et al. (2013) $C_m = 3$ model. The fitted fixed diffusion model performs similarly, but

underestimates the O_2 depletion depth by 6 cm, a good result as it safely overestimates O_2 concentration from the material surface to this point.
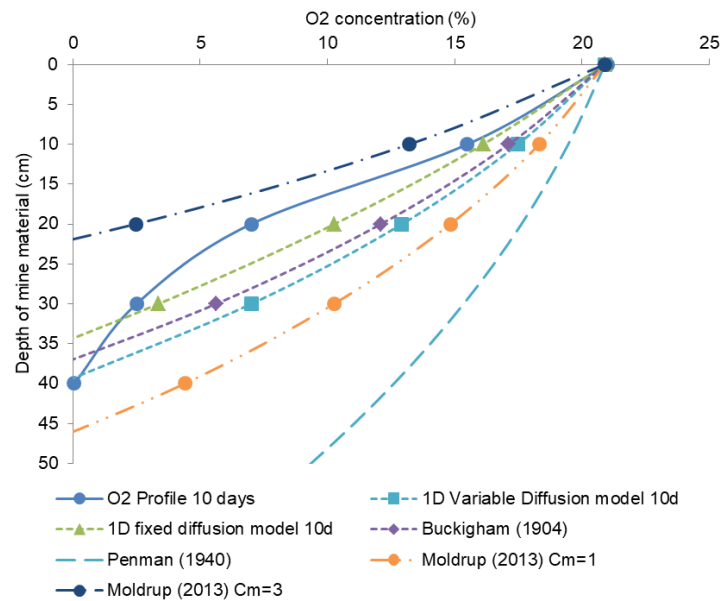
Figure 6-7: 1D soil gas transport model results for material depth versus O_2 (%) in unsteady state column (10 days).

The other models based on estimated diffusion coefficient functions are summarised below in dot point form starting from the best fit to the least best fit.

- The Buckingham (1904) diffusion function does not predict the observed O_2 profile due to the unsteady draining conditions, but is next closest to predicting O_2 depletion depth of 37cm instead the measured 40cm

- The Moldrup et al. (2013) diffusion function with a media complexity factor (C_m) = 1 over-estimates the O_2 profile at all material depths –when compared to the C_m = 3 model this appears to be potentially useful as a safety factor function, which Moldrup discusses in his paper. The predicted O_2 depletion depth is approximately 68 cm which is an over-estimate of 70%, a potentially costly over-estimate for mine site rehabilitation projects, because any neutralant would be added to a greater depth than required.

- The Moldrup et al. (2013) $C_m=3$ model under-estimates all values of O_2 concentration and appears to not be as useful as the above models for the unsteady state approximation. Finding a value for C_m by use of literature diffusion coefficient results, such as those shown in Moldrup (2013), or use of a calculated estimate for C_m via BET testing, cannot be expected to be as accurate as measurement of the diffusion coefficient in the actual target materials.

- The Penman (1940) model performs least well of all the diffusion models used in the 1D model on the unsteady state approximation of O_2 concentration vs depth.

6.4.8   1D 130 day steady state column model results

Binning's (2007) theoretical column modelling results suggests that 130 days should achieve steady state in O_2 flux and moisture conditions in the column material profile. This seems to be confirmed by the near linear O_2 response in the 130 day OPT test column results shown in Figure 6-6. The results for the 1D model performance for each of the diffusion functions, including the measured 1D variable (measured) diffusion and 1D fixed (fitted) diffusion model are shown below in Figure 6-8. The $O_2 = 0\%$, L = 48.1 cm boundary condition was used to calculate r_g for use in all 130 day soil diffusion models.

Reviewing the 1D model performance, it can be seen that the 1D variable diffusion and fixed diffusion function perform the best estimation of O_2 concentration down the column profile with a tendency to slight over estimation of O_2 at depth, which is useful for safe estimation of potential AMD affected mine waste volumes, as underestimation of available O_2 is problematic. The 1D variable diffusion and fixed diffusion models accurately predict the important O_2 depletion depth that is necessary for accurate volume assessments and geochemical stability calculations.
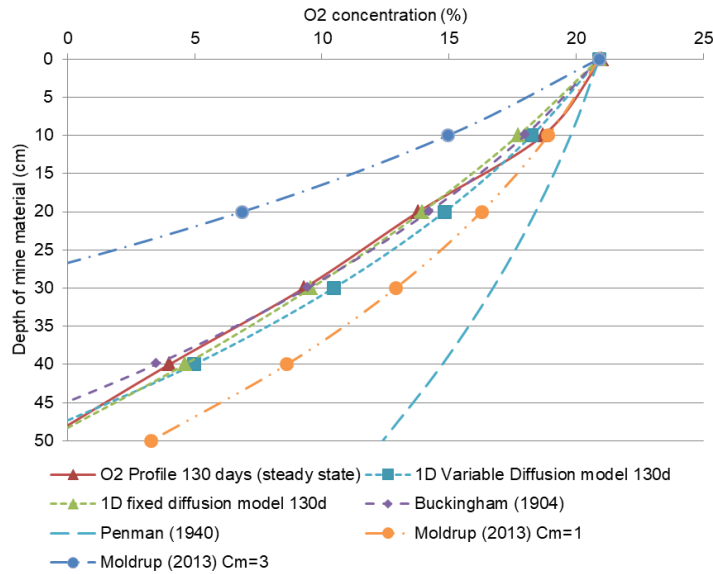
Figure 6-8: 1D soil gas transport model results for material depth versus O₂ (%) in steady state column (130 days).

The Buckingham (1904) model also performs very well at O_2 concentration prediction at depth, but slightly underestimates O_2 depletion depth as 45cm. After the reasonable results shown by the variable diffusion model, the fixed diffusion model and the Buckingham (1904) model, the 1D model results using diffusion estimation models fell into two main classes:

- Over predicting models - Moldrup et al. (2013) Cm = 1 over predicted depletion depth also, while the Penman (1940) diffusion model produced consistently overestimated O_2 concentration for all depths. The Penman diffusion model is simple, based only on a linear factor of soil air content, and if measured soil gas diffusion data is unavailable, maybe a possible useful over-estimator for the diffusion coefficient when used in the 1D diffusion model in equation (7). However, for geochemical waste treatment designers, Penman will result in gross overestimates of AMD material volumes.

- Under predicting models -Moldrup Cm =3 under predicted by the greatest amount. The Moldrop et al. (2013) models may be useful for sensitivity analysis due to the range of results, but Moldrup does not offer much guidance on soil texture and the resultant effect on C_m, especially for mixed soil types such as sand silt type material.

6.4.9   Model Testing

Model statistical error testing was completed for the seven models by comparison of observed and predicted values for soil oxygen concentration. The model test results are shown in Table 6-6 from both the MD and GMER error test functions.

GMER, MD and graphs of observed versus predicted results are useful for unsaturated AMD material properties as these methods help to assess whether a function under or overestimates the particular diffusion function being examined, a particularly important assessment for mining applications, including AMD waste geochemical stabilisation (Dettrick et al. 2019a). For both error tests, results approaching zero indicate a good quality prediction, with negative results for MD indicating under prediction of oxygen depletion depth, the which is a poor result for safety in an AMD waste management context, as amounts of AMD material will be undertreated.

Table 6-6: 1D Model Testing by Error Function MD, GMER.

Error test	Variable Diffusion	Fixed Diffusion	Buckingham (1904)	Penman (1940)	Moldrup (2013) Cm=1	Moldrup (2013) Cm=3	Moldrup (2013) Cm=1.2
10 day model							
MD	2.351	0.000	1.435	7.978	4.530	-10.575	3.670
GMER	2.271	2.851	2.933	5.464	3.897	3.903	3.312
130 day model							
MD	0.303	0.017	-0.594	6.207	2.530	-13.492	1.626
GMER	1.185	1.014	1.222	2.206	1.505	1.731	1.187

The model testing results show that the 10 day results are a poor fit for all models tested. The 1D fixed diffusion model is ranked by MD to be an acceptable model statistically, but this result demonstrates the need for careful statistical result interpretation, as this model also under predicts oxygen depletion depth by approximately 6cm, or 12% of the AMD material volume. Ranked by GMER however, the 1D fixed diffusion model does not score as well and is not considered a good fit. The expected negative result of the Moldrup (2013) Cm =3 model clearly shows the under estimation of oxygen penetration at all depths, showing the upper range of this useful soil texture model.

The 130 day 1D model results show much closer fits to data with the 1D fixed diffusion, followed by the 1D variable model and the Buckingham (1904) model as being the closest fits. The negative value of MD for the Buckingham (1904) indicates a slight tendency to underestimate oxygen depletion, making it less useful for this SS AMD material. Moldrup (2013) Cm =1 shows its potential usefulness as a safe over predication of oxygen penetration and using the BET testing to estimate a Cm of 1.2 shows potential usefulness with low, positive results for both MD and GMER. For both the 10 day and 130 day models, the Penman (1940) approximation overestimates oxygen penetration, but increases the potential volume of AMD material for treatment cost estimations by approximately 66%, which is a potentially expensive overestimate for AMD waste management requirements, particularly in the feasibility phase of mine design.

6.5 Discussion

The 1D variable and fixed diffusion models have limitations which include being steady state, and being developed based on a one-dimensional soil column, assuming oxygen depletion by oxidation processes which create a reaction plane, which may not be complex enough to simulate real diffusion effects (Binning 2007) of soil gas (Oxygen) diffusion. To maintain simplicity, the 1D model currently does not include an advective transport term, but this could be added with little effort and examined for usefulness in future studies. The diffusion measurements used for the 1D model are based on the use of nitrogen and oxygen soil diffusion processes, and other gases such as CO_2, which is a known by product of AMD sulfide oxidation processes, may potentially cause differing effects depending on relative volume. Temperature variation generated by diffusion-based AMD geochemical reactions are likely to be a minor influence on soil diffusion-based gas transport and are not included capability of the simple 1D model that has been developed in this study. However, POR appears to increase exponentially with temperature during advective transport (Davis 2014), which will be an issue for geochemical modelling based only on results from the 1D diffusion model. The 1D model also assumes a uniform material, which is a reasonable assumption for AMD materials that have been highly processed, such as mine tailings materials, but may not apply to waste rock materials, which may vary within the limited diameter of the test column, and the waste rock dump matrix. Larger diameter materials will require a

larger diameter soil diffusion and oxygen penetration column apparatus, and edge effects may potentially generate error if not managed in some way. Dettrick (et al. 2019a) found that particle size is inversely proportional to AMD reactivity, where smaller particle sizes and matrix pores may result in higher rates of AMD production, influencing mine waste management design, and recommended additional testing for geochemistry and diffusion.

Pruess et al. (2012) lists the following additional issues in relation to modelling multiphase soil gas diffusion:

- Non-linear effects of tortuosity;
- Due to variable advective and diffusive streaming effect influences, the Fickian diffusion model has limitations, particularly when the mean free path of gas molecules is comparable to pore sizes.
- Diffusion under conditions where the liquid and gas phase is discontinuous, such as reducing conditions for H2S formation.

6.5.1 Comparison to Other AMD Soil Gas Diffusion Models

Nicholson's (1984) 1D soil gas diffusion model was derived for tailings containing 0.5 and 1% sulfide, which is similar to materials in this study. Nicholson derived a variable diffusion coefficient model for the tailings materials tested, but the 1D soil transport equation derived relies on fixed soil saturation and effective diffusion coefficient, rather than the varying material saturation and diffusion coefficient method developed in this study. The results of the Nicholson (1984) model are shown below for several different fixed material saturation levels and sulfide content in Figure 6-9.

The results of the Nicholson model are from different AMD material to those used in this study, as expected, and cannot be directly compared as the model produces results for one soil moisture point only.
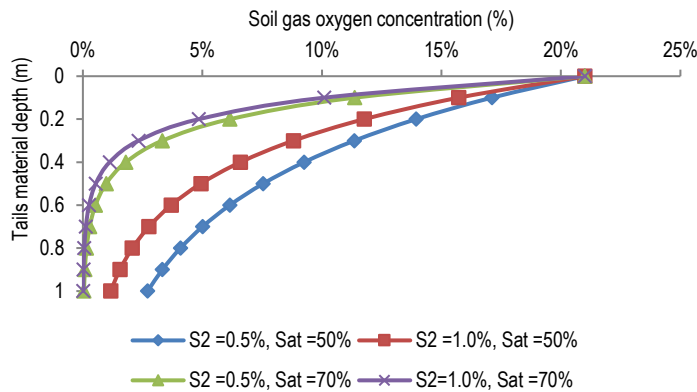
Figure 6-9: Example Nicholson (1984) 1D soil gas diffusion model results.

6.5.2   Summary of model results

In terms of simulating O_2 transport in steady state situations, the 1D variable diffusion model is simple, needing only basic spreadsheet support. It requires commonly and readily available soil testing data and geochemistry information if being used to estimate acidity loads that could be generated by a particular uniform, remouldable mine material such as mine tailings. With adequate methodology and material data, the 1D model can be used to estimate volumes of mine materials potentially affected by AMD at concept design level. The soil gas transport data requirements include:

- Oxygen penetration column data, testing required from 10 -100+ days depending on material, to determine O_2 depletion (0%) depth;

- Soil gas diffusion data for a range of material moistures, 5 tests can be completed with one column in less than 24 hours, more can be completed if multiple diffusion columns are available; and

- Material parameters -porosity, bulk density, effective porosity (calculated) and SWCC parameters.

In addition to the above results, analysis of which method provides the best order of accuracy for the 1D model, yields a hierarchy from highest to lowest, to best predict the results of the potential for oxygen transport and related AMD generation from mine waste oxidising materials. The results of this analysis are shown in Table 6-7 below in terms of decreasing accuracy and testing complexity, to

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help provide guidance on best modelling and testing procedures, as may be required with limited data, resources, or time.

Table 6-7: Relative 1D Model Accuracy based on modelling and testing methodology.

Relative 1D model accuracy	Modelling and Testing Methodology
Higher	Soil gas diffusion testing and oxygen penetration testing
	Modelled diffusion coefficients and oxygen penetration testing
	Soil diffusion testing and estimated oxygen depletion depth
Lower	Modelled soil diffusion coefficients and estimated oxygen depletion depth

Safety factors in soil gas transport modelling of AMD materials have been discussed in Dettrick et al. (2019b) and are a potential solution to poor material data quality, or lack of material data. Moldrup's (2013) diffusion coefficient model also offers the possibility of use for a safety factor style of approach to the amount of AMD materials affected by oxidation processes.

6.5.3 Updated conceptual model

The assumptions in the conceptual model used to develop the 1D soil gas transport model (Figure 6-2) have been improved with the oxygen penetration-based column data. The reactive AMD material column test proved to have a non-linear diffusion function during unsteady moisture states and demonstrated almost linear reduction in O_2 concentration in conditions of steady state moisture. This was supported by the oxygen consumption testing results to some extent which showed that POR can change substantially with soil moisture fluctuations in the material, from saturated to field capacity to near dry conditions. Soil gas diffusion coefficients also respond non-linearly to changing soil moisture levels, further influencing the actual POR at a given soil moisture.

6.5.4 Avoiding underestimation of AMD

Under estimation of AMD and resultant acidity loads is a serious issue that has occurred at many mine sites and land development sites with PASS (Maest 2005). The 1D diffusion model presented seems to be appropriately safe at over estimating O_2 concentration in unsteady conditions - but not the O_2 depletion depth. To ensure a robust result, the use of the model to estimate potential

volumes of material affected by AMD, would require a statistically appropriate material testing regime to properly characterise fluctuations in diffusion behaviour and oxygen penetration depth. The model could perhaps be adapted to be transient using appropriate commercial modelling platforms, but these are most likely unavailable and considered too complex at most mine operations. If using a safety factor to estimate diffusion coefficients with existing diffusion estimation models, such as Buckingham (1904), it must be an inverse function (such as . $F.S^{-1}$) to provide protection against under estimation.

In the simulations undertaken for steady state conditions, if little data are available, the Buckingham (1904) diffusion approximation appears to provide a reasonable under-estimate of O_2 concentration and depletion depth with a small margin for error. This appears to be explained in part by the agricultural focus of many other diffusion coefficient models and functions such as Penman (1940). Moldrup's (2013) diffusion coefficient model provides a C_m factor which can be used to ensure an under estimation of soil gas supply to the root zone for different material types -and is the appropriate safety approach for root zones, but the opposite driver to AMD reactions and risk. These models again may be useful for unsteady and steady state conditions, but Moldrup et al. (2013) does not offer much guidance on soil texture and effect on C_m, especially for mixed material types such as sand silt type material. Therefore, estimating the theoretical C_m parameter would require optimisation, with only accurate values derived through laboratory measurement of diffusion, which eliminates the need for, and reduces the usefulness of the Moldrup et al. (2013) diffusion coefficient model.

Compared to the diffusion coefficient estimation models evaluated, laboratory measurement of the AMD mine material diffusion coefficient and application to the 1D model derived in this study will yield the most accurate results. While the Buckingham (1904) diffusion coefficient model seemed to work well with the target SS materials of the study, Dettrick et al. (2019b) shows this is likely not the case for all materials and recommends laboratory determination of soil gas diffusion coefficients to ensure best accuracy in AMD waste management volume assessments.

Binning (2007) theoretically proved that advective processes may be up to 23% of soil gas air supply, particularly relevant to TSF sites, WRD and mine materials exposed to barometric, temperature

and wind speed fluctuations. Soil gas advection processes potentially represents the greatest limitation in terms of error to deploying the simple diffusion based 1D model that has been derived, but can likely be managed by adding an advective transport term to the model and incorporating into a sensitivity analysis or could also potentially be managed with a safety factor style approach to the use of the 1D diffusion model.

6.6 Conclusion

It is concluded that in order of accuracy from high to low, the following methods can predict the results of the potential for AMD generation from mine waste oxidising materials i) soil gas diffusion testing and oxygen penetration testing, ii) , modelled diffusion coefficients and oxygen penetration testing, iii) material diffusion testing and estimated oxygen depletion depth, and least accurate iv) modelled soil diffusion coefficients and estimated oxygen depletion depth. Given the relatively inexpensive cost of construction of soil gas diffusion and oxygen depletion depth apparatus, method i) offers the best accuracy for concept or prefeasibility level mine waste volume assessments.

At the prefeasibility and operational mine design phase, accurate and simple AMD waste-estimation models are required to help mine designers reduce the cost of minimising environmental harm. The 1D diffusion model presented appears to be an accurate estimator for calculating O_2 depletion at depth, and potentially useful for the calculation of potential total acidity loads and material volumes required for geochemical stability design of AMD mine waste materials. The 1D model has limitations as discussed above but is designed to be cost effective and able to be used on most computers with a simple spreadsheet capability. The simple form of the model, when combined with AMD material oxygen consumption test results, lends itself to reactive mine block models and spatial mine geochemical data calculations with few additional data requirements.

The 1D model achieves best results when applied with soil gas diffusion testing and oxygen penetration column testing of the target AMD materials. Reactive columns such as oxygen penetration columns, theoretically become steady state in 10 to 100 days -which is a risk to modelling schedules if insufficient lead-in testing time is available. The 1D model is highly flexible, can be used with

measured single point diffusion coefficient data, variable diffusion coefficient functions based on laboratory measurement and has been shown to produce reasonable results with estimated (modelled) soil gas diffusion coefficients such as Buckingham (1904) and Moldrup et al. (2013),

In terms of application, the model has been aimed towards, and is most likely suited to the development phase of a mine project, when sufficient mine materials geochemical and soil parameter data is available from geological exploration. It can potentially be applied to TSF and waste dump design, and can assist with materials volume estimates, which can be used to undertake cost estimates for management solutions such as containment, treatment, or neutralisation of the materials during the process of AMD production. Further research is recommended on different material types and conditions to provide more model performance data.

Further research is recommended to develop the 1D model to potentially include advection, and other diffusion coefficient estimation functions, that may be relevant to different materials.

6.7 Acknowledgements

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7   Development of a 2D finite difference soil gas diffusion model for estimating oxidation rates of AMD material.

The 1D model discussed in Chapter 6 Paper iii, is further developed in this Chapter into a 2D steady state, finite difference model with additional boundary condition options for potential modelling of complex faults, cracks and fractures that may be found within in-situ and dumped AMD mine materials. The more complex geometries available in a 2D model provide enhanced options for volume assessments of AMD mining waste materials such as mine tailings and waste rock materials, compared to the 1D model.

The 2D finite difference mesh was created for use in the commonly available Microsoft Excel software, which is an inexpensive modelling option for mine managers and designers involved with mine site operations and design. To undertake 2D finite difference modelling in Excel, the "Options" menu must be opened. In the 'Formula" window the spreadsheet calculation options must be set to manual. Iterative calculations must be enabled, and the desired maximum number of iterations and maximum cell formula change level must be set. Oxygen concentration (%) boundary conditions can then be pasted into the excel cells model mesh at desired locations, along with the 2D model formula.

The 2D finite difference model was derived based on a finite difference application of the 1D model previously derived in Chapter 6, and is shown in equation (7-1) below:

$$\Delta C_{g(i,j)} = \frac{C_{i-1,j} + C_{i+1,j} + C_{i,j-1} + C_{i,j+1}}{4} + \frac{r_g}{-D_g^s}(z + L)\Delta z \quad \text{equation (7-1)}$$

7.1 Tailings Evaporation Cracking Model

To provide more complex boundary conditions for the 2D model, data on surface cracking depth and geometry of an operational mine tailings storage facility was collected. An example section of cracking in tailings storage mud is shown below in Figure 7-1.

Figure 7-1: Cracking in "dry" Tailings Storage Facility mud.

Crack width, depth and separation were measured, oriented around the deepest areas of cracking that was observed and safely accessible. The crack geometry data was then used for the 2D model surface boundary and is shown diagrammatically below on Figure 7-2. Crack width varied from 10 to 50 mm, with wider values usually associated with crack depth and development.
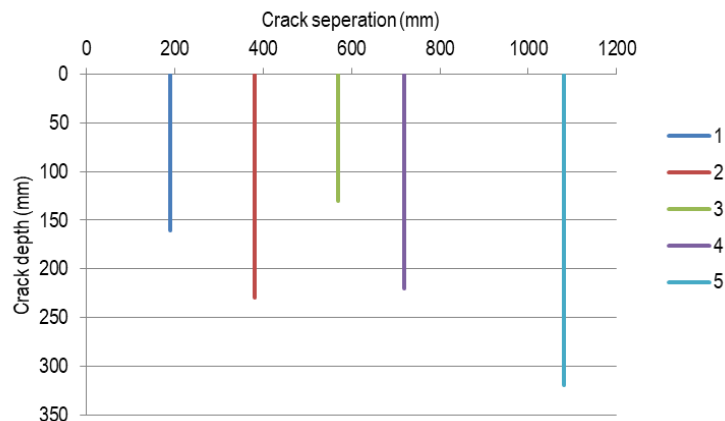

Figure 7-2: Tailings mud crack data used as boundary conditions for 2D model.

The spreadsheet model was developed as a finite element grid/mesh generated assuming a grid cell size of 10 mm for depicting the AMD material matrix geometry in the horizontal and material depth axis. The adoption of a 10mm mesh allowed for inclusion of the observed TSF surface crack geometry and width. Assumptions for the 2D finite difference soil gas diffusion model included:

- Grid for the model $\Delta z = \Delta x = 10$ mm;

- Overall model mesh width 2.0 m, mesh depth from TSF surface of 1.8 m.

- Finite difference calculations were limited to 50 iterations and a maximum change of 0.0001 (%);

- Mine material soil gas diffusion D_g^s and oxygen penetration parameters (L oxygen penetration boundary condition) were based on the measured values for the AMD active SS tailings material (Chapter 6);

- Steady state Van Genuchten (1980) soil moisture conditions based on the measured SWCC parameters for the SS material, calculated from elevation above the groundwater table;

- Saturated mine tailings/groundwater table set to 3m below TSF surface;

- cracks were assumed to be 20.9% O2.

The 2D finite difference grid mesh used for modelling is shown below in Figure 7-3 and is 750 mm in depth and 1500 mm in width and comprised of 11,250 individual mesh cells. Computation time of the finite difference solution is around 10- 30 seconds depending on computer processing speeds.
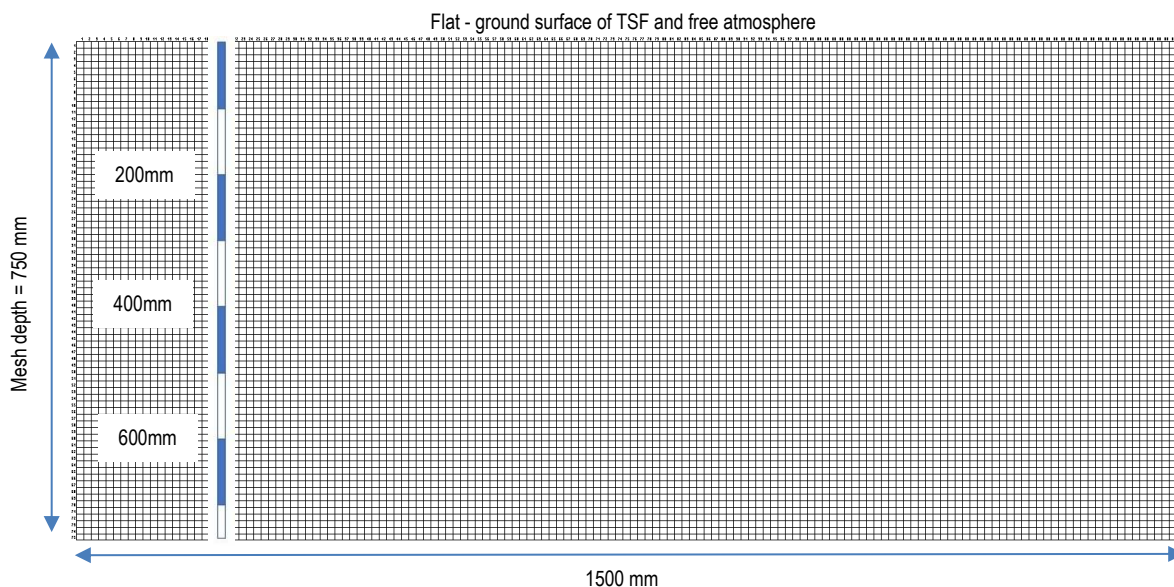
Figure 7-3: The 2D model mesh used for the modelling scenarios and testing.

2D Model Scenarios

The depth to groundwater is an important model boundary condition, as it is used in the variable diffusion model by the Van Genuchten approach to estimate steady state unsaturated soil moisture. In the example TSF mine waste modelling scenarios, saturated TSF seepage conditions are assumed to

exist at 3m metres below the tailings surface. The 2D finite difference models were then set up and run for the following scenarios and assumptions:

- Groundwater/TSF seepage at 3m below the TSF surface and a fixed diffusion coefficient (averaged from Figure 6-5, set to 0.01 cm^2/s);

- Groundwater/TSF seepage at 3m below the TSF surface and fixed diffusion coefficient, with observed/simplified surface cracking development;

- Groundwater/TSF seepage at 3m below the TSF surface and moisture variable (measured) diffusion coefficient, with observed/simplified surface cracking development;

- Soil moisture variation due to pore pressure was assumed to be steady state and follow the Van Genuchten (1984) formulation above a saturated groundwater table.

The 2D steady state model results for each of the above scenarios are shown below.

7.1.1   2D Model Scenario 1

The fixed diffusion coefficient scenario with no crack model is effectively a 1D soil diffusion model and the predicted soil oxygen levels (%) are shown in Figure 7-4 below, refer to Figure 7-3 for model domain

Figure 7-4: 2D Finite Difference Soil Gas Diffusion Model –Fixed Diffusion Coefficient, 3m GWT, no cracks.

The resultant oxygen concentration versus depth relationship is shown on Figure 7-5 to illustrate the 2D model results. The expected gradual non-linear reduction in O_2 concentration is evidenced with an expected asymptotic style O_2 reduction as the concentration approaches zero.
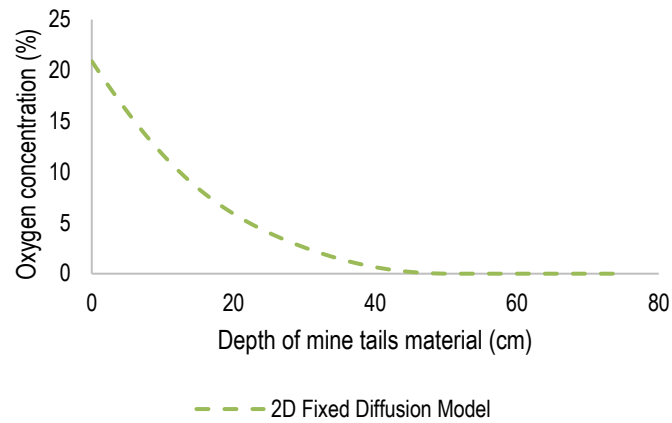
Figure 7-5: 2D model results O2 concentration versus depth of material -Fixed diffusion coefficient.

The boundary conditions for the tailings storage crack model were then inserted in the remaining 2D model meshes, to evaluate the model results for the remaining scenarios.

7.1.2   2D Model Scenario 2

The second scenario includes a 2D model with a fixed diffusion coefficient and the crack model boundary conditions developed previously and is shown below in Figure 7-5, refer to Figure 7-3 for model domain.

The volume of AMD tailings material potentially impacted by oxidation are much greater in the tailings storage facility crack model scenario and show the ability of the 2D model to more accurately represent the potential volumes of AMD mine waste material requiring geochemical stabilisation design and management. Mine materials with complex geometries such as sloping surfaces, fractures and cracking can be simulated using a 2D model mesh to provide a more accurate solution to the AMD waste volume assessment.

Figure 7-6: 2D Finite Difference Soil Gas Diffusion Model –Fixed Diffusion Coefficient, TSF crack model, 3m GWT.

7.1.3   2D Model Scenario 3

The second scenario –Groundwater/TSF seepage at 3m below the TSF surface, and the 2D model set up with a moisture variable (measured) diffusion coefficient based on SS material data from Chapter 6, is shown below in Figure 7-6, refer to Figure 7-3 for model domain

The variable diffusion model depicts a more variable diffusion response, particularly at the oxygen depletion boundary, but also highlighting increased volumes of material throughout the tailings column that are likely to be affected by AMD oxidation conditions.
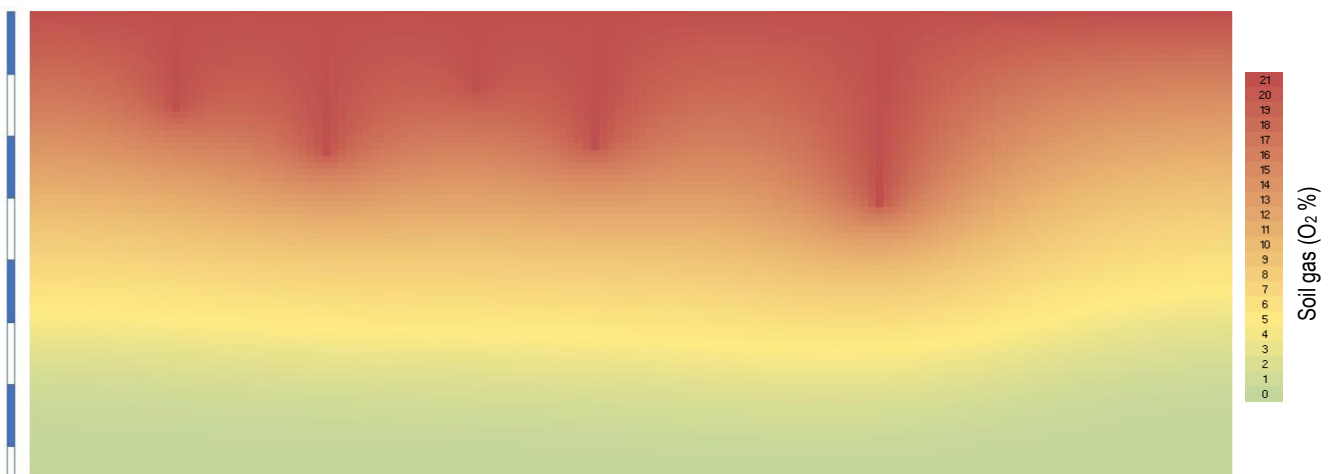
Figure 7-7: 2D Soil Gas Diffusion Model –Variable (Measured) Diffusion Model, TSF Crack Model, 3m GWT.

As can be seen from the figure, the limited accuracy of the fixed diffusion model (Fig 7.6) due to changes in material moisture and diffusion is shown at the oxygen penetration depth at the bottom of the model, and also in the mid-depth area where additional oxygen diffusion is predicted by the variable (measured) diffusion model.

7.2 2D Model Evaluation

To understand the potential impact of this difference in model result on mine waste management, the volumes of the tailings that may require neutralisation have been compared, based on an oxidation AMD status related to the available oxygen in the material matrix, as potential oxidation level x volume, acidity units.

The fixed diffusion model predicts approximately 643 potential units of acidity/m^3 of tailings, while the variable diffusion model predicts 1010 units/m^3 of tailings. This shows the fixed diffusion model results provides a volume of materials affected by AMD to be underestimated by approximately 36% of the likely true volume. The analysis of model difference between the two results is shown below in 1D Figure 7-8 and in 2D on Figure 7-9, for visual comparison of the model performance.

This finding of underestimation of potential volumes of tailings and mine waste materials susceptible to AMD production, indicates that the variable diffusion model proposed in this research study provides a more accurate and conservative estimate for the purposes of estimation of potential treatment requirements for the AMD wastes.
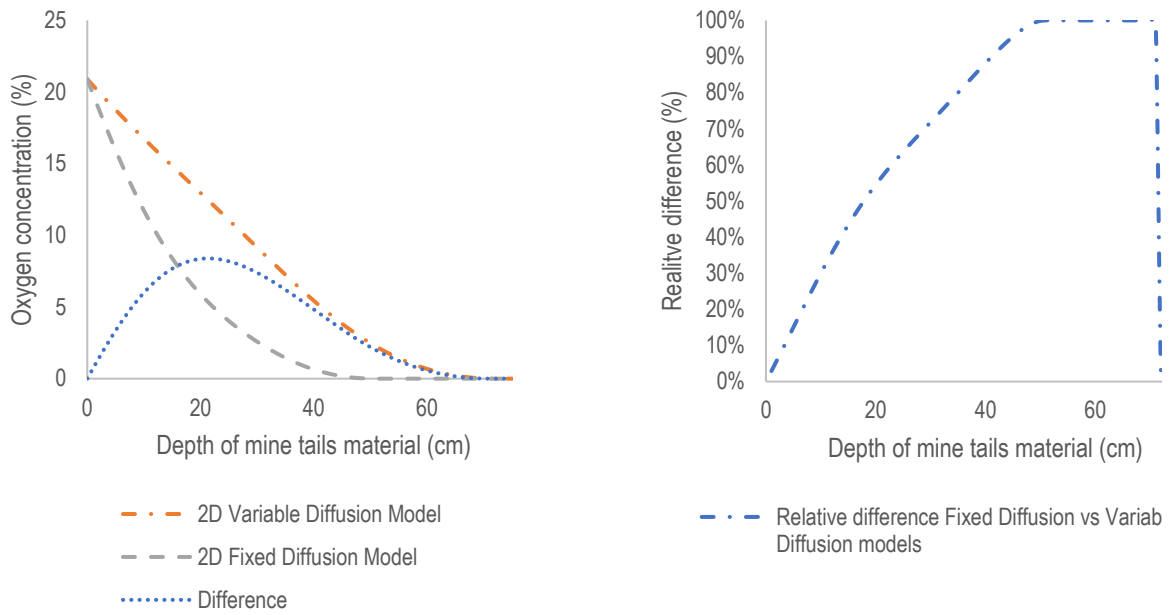
Figure 7-8: Comparison between 2D Variable and Fixed diffusion models and Relative difference (%).

Examining the differences between the 2D variable diffusion and 2D fixed diffusion models in Figure 7-8, highlights the potential differences between the two models, with the 2D fixed diffusion model erroneously predicting much lower levels of O_2 concentration over the depth of the mine tailings materials above the groundwater table. The model mesh domain is shown in Figure 7-3 above.
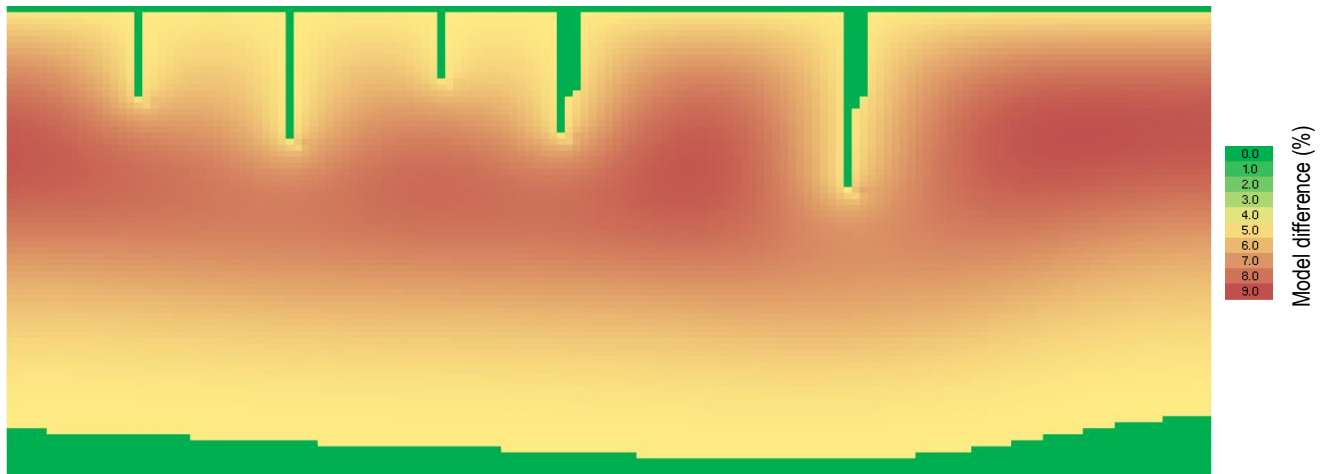
Figure 7-9: 2D Soil Gas Diffusion Model –Difference between Variable and Fixed Diffusion models.

The difference in O_2 concentration predictions between the 2D fixed diffusion and 2D variable diffusion model peaks at around 20 cm in mine tailings material depth, with relative difference increasing rapidly to 100% at 40cm depth. The 2D model difference assessment also highlights the

potential problems for a 2D model using fixed diffusion coefficients, especially in the middle depth regions, which show as red zones peaking at approximately 9% difference on O_2 concentration between the models.

This testing of the 2D model shows that complex geometry requires a more complex model to enable accurate AMD waste volume assessments. The results also indicate that the measured variable diffusion model based on diffusion coefficient testing at several moisture levels, is a more accurate approach than a fixed value for diffusion coefficient. These results support one of the central hypotheses of this thesis, that use of data from measured diffusion coefficients at several moisture levels to form a variable diffusion function for modelling, results in a more accurate simulation of the AMD material gas transport process in the matrix of a target material and therefore provides a more accurate method for volume assessment. Please refer to Chapter 5, 6 and Appendix 1 below for more detail on soil moisture impacts on diffusion. The key conclusion for the development of the 2D soil gas transport diffusion models method is similar to the 1D method in that diffusion behaviour of the target AMD mine material should be subject to diffusion behaviour testing over a range of matrix moisture contents, to avoid under (or over) -estimation) of mine material and waste acidity production.

The value of the 2D model is the ability to produce a more accurate volume assessment of AMD mine materials in complex geometries and conditions than is possible with a 1D soil gas diffusion model. Mine waste materials in slopes, fractures and cracks provide additional pathways for oxygen to enter and create additional AMD in mine material and waste. 1D model results are important to test the results of laboratory based diffusion column tests, but as the effect of the 2D crack model demonstrates, large areas of additional oxidation generate additional volumes of AMD material, compared to the "1D" result of a 2D gird/mesh with no crack model boundary condition as shown in Scenario 1, Figure 7-4.

Mine designers and waste managers can effectively use the 2D model with a range of scenarios for waste geometries, moisture and soil gas diffusion characteristics, to provide an estimate of total AMD mine waste potentially requiring treatment, and across any waste rock dumps or tailings storage facilities proposed for the mine site. To improve the treatment cost estimate, mine material geochemical

oxygen consumption testing can be undertaken, in conjunction with bench top material neutralisation testing, to provide additional accuracy for the treatment cost estimate of neutralisation treatment materials required. Conceptual mine waste treatment cost estimation systems can be based on the approach used in Chapter 4, or other volume and treatment assessment systems, such as spatial GIS assessment systems, based around mine materials, ground models and resource mapping in 3D.

7.3 Recommendations for AMD Waste Geochemical Stabilisation Design

The additional volumetric accuracy of the 2D finite difference modelling approach, combined with the simplicity of the finite difference model and the use of Microsoft Excel, makes this new approach for AMD mine waste volume assessments potentially very attractive for the mining sector, including geochemical engineers and mine designers. The laboratory equipment required to derive the variable soil gas transport diffusion coefficient model are discussed in detail in Chapters 5 and 6 and are fast and cost effective tests that are aimed towards being able to be undertaken at the mine site itself, with the assistance of the mine site engineering workshop, or mine waste managers with access to the required materials. The soil diffusion test column (Dettrick et al. 2019b) and the adapted oxygen penetration column based on Elberling et al. (1994) are both comparatively simple apparatus to build and conduct tests with, compared to conventional humidity cells discussed in detail in Chapter 2, which are both time consuming and complex to operate successfully, and require additional external laboratory leachate testing costs, sometimes for many weeks or months. The use of soil gas transport as a proxy to derive and estimate the volume of AMD affected materials also avoids the potential errors generated when assessing AMD volumes using geochemical techniques alone, based on the potential exponential error effects of particle size and available sulfide reactive oxidation surfaces. When used with robust sampling techniques the 2D model could be used to support geochemical modelling to provide a detailed level of AMD assessment.

Additionally, if time and data limitations exist for the AMD assessment, and the complete testing method proposed in Chapter 6 cannot be used, the 2D finite difference model can be applied

using either the Factor of Safety approach in Chapter 5, or the hierarchy of Model Accuracy based on

available modelling and testing methodology, also presented in Chapter 6.

7.4 References

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8   Summary and Conclusions

The overall conclusion of the research project is that the use of the proposed soil gas diffusion measurement and modelling methodology provides a potential fast, economic and more accurate alternative to the complex suite of geochemical assessment methods currently used to estimate the rate of sulfide oxidation. When combined with detailed level geochemical assessments, the method offers a complimentary data source, suitable for detailed and final design of AMD waste management and treatment systems. The associated research has produced several key outcomes for potential use in the mining sector for assessment and management of AMD mine materials and includes the following key findings:

- Geochemical based AMD assessment procedures are complex and if not undertaken with care, such as testing a range of sufficiently fine particles, may result in the potential for exponential error which can affect mine AMD waste management and treatment design.

- Soil gas oxygen transport with 1D or 2D models, using the methodology suggested in this study, is a useful tool for geochemical engineers and mine waste managers wishing to estimate volumes of mine materials potentially impacted by AMD.

- Literature-based diffusion coefficient estimation models are often based on agricultural models, and used alone without detailed model performance analysis, may not provide sufficiently accurate results or acceptable margins for error in AMD material geochemical stabilisation design and treatment.

- Measurement of soil gas diffusion coefficients in mine materials can be achieved easily with the cost-effective diffusion column design that is included in Chapter 5 (Paper ii) and detailed in Appendix 1.

These findings are summarised in further detail in the sections below.

8.1   Approaches to AMD reactivity assessment.

In Chapter 4 (Paper i) a simple choice of test material grain size is found to be a principal factor affecting measurement of POR and reactivity within AMD materials and can generate high levels of treatment cost estimate inaccuracy. This potential AMD assessment inaccuracy issue is reinforced in industry AMD management guidelines (eg. EPA 1994, Maest et al. 2005). The materials tested in this research both displayed the expected exponential response in reactivity with decreasing particle size, a potential source of multiplicative error in geochemical modelling of AMD materials. The AMD POR reactivity was found to exponentially increase as grain size decreased, with the effects particularly marked for mine materials of less than 1 mm in size.

Hard earned experience (Kuipers et al. 2006) shows that the complex interaction between reaction rate, mineral active surfaces, mineral molecule geometry and composition is difficult to predict or compare to previous cases, because of the large range of possibilities in these parameters. In terms of modelling parsimony (and effort) the 1D/2D variable diffusion model approach requires 4-5 parameters, while geochemical models PHREEQC (Parkhurst and Appelo 1999) requires approximately 35 and has no gas phase, and TOUGH2 (Pruess et al. 2012) requires 80 or more parameters. Ultimately, mine waste management designers relying on geochemical assessment systems alone, will need to manage to manage the many assumptions required, and errors which are potentially exponential in their effects on waste volume estimates and associated treatment cost.

Mine waste managers seeking to minimise the geochemical stability risk of tailings over the long term are advised to undertake detailed geochemical reactivity testing on all mine site materials, including sulfidic materials at the mine site, at several moisture contents and smaller grain sizes representing the proposed milled material grain size for mineral processing. The results of the grain size reactivity analysis should be included in the mine's acid base accounting assessment so that a fair and reasonable assessment of both short-term and long-term risk can be apportioned for both mining bonds and mine closure costs. In a detailed geochemical assessment program, some mine site materials

will likely be determined to provide neutralising capacity, which is an important potential cost saving for the geochemical stabilisation mine waste management system.

8.2 Measuring soil gas diffusion

Measuring soil gas diffusion is an effective, inexpensive and accurate means to determine supply-side, oxygen transport parameters relevant to limiting the production of AMD in mine materials such as tailings and waste rock. It also can potentially avoid exponential multiplicative errors faced by AMD materials assessment using conventional demand-side geochemical testing alone as discussed above, as soil gas diffusion coefficients can be compared and estimated between various materials and matrices using several methods. If a diffusion coefficient is measured inaccurately, the final effects are unlikely to be exponential in effect due to the existence of less potential for multiplicative error than is possible compared to geochemical testing and particle size and reaction surface-based errors as discussed in Chapter 4 and Chapter 2 respectively. Diffusion results can be compared to other measured results for the same material as an initial QA check and sample test duplication or retesting is straight forward and usually able to be completed in less than 3 hours for most mine materials. For very fast reactivity AMD materials, the sample size can be reduced in thickness to reduce the time required for the diffusion test, to minimise any potential impacts of sulfide oxidation on the material matrix structure. Conversely, if the potential impact of oxidation on material matrix structure is of interest, sample depth can be increased to provide for longer diffusion testing periods.

The quick nature of the diffusion testing also allows for timely AMD material volume assessment and avoids some additional geochemical field-based testing errors such as air/oxygen leaks in materials collection containers. Ultimately, to provide a detailed design estimate for AMD treatment cost at any mine site, both an accurate volume and geochemical reactivity assessment, based on appropriate materials representation and sampling methodology, are required.

One of the key findings of Paper ii is that the existing diffusion coefficient models from the literature are likely suited to natural soils that are well distributed but may not be sufficiently accurate for mining derived waste materials. None of the diffusion coefficient estimation models evaluated from

the literature were considered accurate for the full range of soil moisture conditions that could be expected in mine materials, particularly during mine closure when tailings storages may start to dry out, or as water evaporates from the structures, or when approaching saturation, such as underneath designed oxygen limited earth covers. All of the literature diffusion coefficient estimation models evaluated also appeared to under predict diffusion coefficient as the materials approached saturation. This is of some concern for soil gas transport model use with AMD materials to predict acidity production, as AMD will be consistently under predicted.

The use of the soil gas diffusion testing apparatus and methodology presented in this study, will help in conjunction with the models developed in this study, to more accurately estimate the volumes of AMD mine materials likely to be exposed to oxidation processes and therefore be geochemically active. It is recommended that rather than relying on literature based, modelled estimates of D_g^s, for AMD mine waste materials, that these materials are subjected to diffusion coefficient testing at a range of moisture levels. If this is not possible, then selected diffusion functions appropriate for available material data could be adopted with an appropriate safety factor as suggested in Paper ii (Dettrick et al. 2019b).

8.3 1D soil gas transport diffusion model

The 1D diffusion model presented is a cost effective and simple to use estimator for calculating O_2 depletion at depth and is aimed at assisting the calculation of potential total acidity loads requiring treatment in a material, by providing an estimate of material volumes affected, which is required for geochemical stability design of AMD materials. The model has limitations as discussed in Paper iii and summarised below and is designed to be able to be used on most computers with a simple spreadsheet capability. The 1D model achieves best results when applied with soil gas diffusion testing and oxygen penetration column testing of the target material for best accuracy.

The 1D model is flexible and has been shown to produce very good results with measured diffusion coefficients and good results with model estimated soil gas diffusion coefficients in steady state modelling using the Buckingham (1904) and Moldrup (2013) formulations. The 1D model was

not considered to perform well in unsteady conditions, due to a nonlinear soil gas diffusion response and the difficulty of measuring and estimating the soil oxygen depletion depth, L when it is still developing to the steady state. The model works best with steady state conditions, which is also used to derive the fitted reactive gas parameter (r_g) for the test material.

In terms of application, the model has been aimed towards and is most likely suited to the concept and prefeasibility development phase of a mine project, when sufficient mine material volumes and material parameter data is available from exploration geology drill cores and test pits. It is a useful assessment tool to check the performance of literature-based diffusion coefficient estimation models, such as those tested in Paper ii. The 1D model can be applied to TSF and waste dump design, to derive initial volume estimates of AMD materials and potential acidity loads, which can be used to price management solutions such as containment, treatment, or neutralisation of the materials during the process of AMD production.

8.4 2D Soil Gas Transport Model results

The 2D finite difference soil gas transport model derived in Chapter 7 provides an additional level of refinement for AMD material oxidation behaviour and potential treatment volume estimation, when compared to the 1D model. The 2D finite difference model is also designed to be easily used with existing spread sheet software such as Microsoft Excel, to enable more accessibility for mine design and geochemical engineers. The 2D variable diffusion model results highlight the additional flexibility and accuracy for undertaking an AMD waste volume calculation offered by enabling more complex boundary conditions for the 2D mine waste scenario. Tailings mud cracking and many other complex boundary conditions such as fissures, cracking and faulting can be developed for use in the 2D model. Soil gas transport through material slopes and the implications of AMD material moisture and unsaturated zone behaviour can also be simulated within the geometry of stockpiles of mine waste materials.

8.5 Contributions of this Thesis and Limitations

8.5.1 Thesis Contributions

This research has contributed to a new methodology to mine waste management design for AMD mine materials especially suited to the concept and prefeasibility mine design phase. Its principle is based on the use of 1D or 2D soil gas (oxygen) transport models to provide an estimate of potential AMD mine waste volumes requiring treatment. The soil gas transport models proposed provides for quick, practical and relatively accurate volume assessments in waste rock dumps and waste tailing storage facilities. The research project outcomes have included development of new economic laboratory equipment and testing methodology to collect material gas diffusion data with soil gas transport modelling to test several soil gas diffusion models in 1D and 2D. Supporting testing apparatus was designed, including two different soil gas diffusion columns to provide economic soil gas diffusion results. The soil gas diffusion transport method is scalable to any size of project and can provide AMD waste volume estimations of increasing accuracy with increasing data collection of mine materials, soil and rock data for i) soil water characteristic curves (SWCC), ii) soil gas diffusion testing, and iii) soil oxygen penetration column tests. The methodology can also benefit from additional geochemical data and modelling that may be available for the target AMD mine materials, to allow for a detailed level of geochemical stabilisation and engineering design.

8.5.2 Limitations

The limitations of laboratory testing and assumptions of modelling techniques associated with this research project have been discussed in each relevant Chapter section and in the published and unpublished Papers. A summary of key assumptions and limitations is presented below:

Soil gas diffusion testing limitations and assumptions:

- The soil gas diffusion column assumes a uniform, mouldable mine material, which is a reasonable assumption for AMD materials that have been highly processed, such as mine tailings materials, but may not apply to waste rock materials, which may vary within the limited diameter of the test soil column, and the waste rock dump matrix.

- Larger diameter materials may require a larger diameter soil diffusion and oxygen penetration column apparatus, and edge effects may potentially generate error if not managed in some way, such as the use soft wax layers around samples to minimise edge effects.

- Sample drying was also identified during diffusion column testing that took greater than 24 hours to complete as also potentially problematic. Assouline et al. (2014) predicts with modelling that for column lengths less than 340 mm, evaporation is in the order of 0.9 cm/day. This error may be minimal within a 250 min test, but diffusion tests requiring over 24 hr may require humidity controls.

- Alternatively, shorter duration tests could be undertaken using the linear component of the soil diffusion response, which would effectively minimise the effects of material drying, or sample depth can be reduced to decrease the diffusion test time.

1D and 2D Model limitations and assumptions:

- The 1D/2D model presented is steady state, and based on a one-dimensional conceptual model of the material;

- The model development results are based on one testing material type and may differ in other AMD materials;

- Oxygen depletion is assumed to occur by sulfide chemical oxidation processes only (not bacterial activity or AMD based on Fe^{3+} processes) and these reactions create a reaction plane based on Fickian (and author anonymous 1855) soil gas (Oxygen) diffusion assumptions;

- 1D/2D model does not include an advective transport term, as wind velocity related air pressure changes are likely low percentage annual events, and the model is simulating steady state diffusion over a period of less than 24 hours;

- The diffusion measurements used for the 1D/2D model are based on the use of nitrogen and oxygen soil diffusion processes, and other gases such as CO_2, which is a known by product of AMD sulfide oxidation processes, may potentially cause differing effects.

- Temperature variation generated by diffusion-based AMD geochemical reactions are likely to be a minor influence on soil gas transport and are not included capability of the 1D model that has been developed in this study.

- POR appears to increase exponentially with temperature (Davis 2014), which may be an issue for any associated advective, or geochemical modelling based on results from the 1D/2D model

Pruess et al. (2012) lists the following additional issues in relation to modelling multiphase soil gas diffusion:

- Non-linear effects of tortuosity;

- Due to variable advective and diffusive streaming effect influences, the Fickian diffusion model has limitations, particularly when the mean free path of gas molecules is comparable to pore sizes; and

- Diffusion under conditions where the liquid and gas phase may be discontinuous, such as reducing conditions for H_2S formation.

8.6 Identified further research

The field of AMD management and treatment involves a relatively small number of specialist practitioners and similar small budgets as a small sub sector to overall mining sector investment. The reasons for this are many but there are two main reasons: -not all mine sites generate net acidity (any AMD processes are absorbed by local neutralising materials) so it is not always a central focus of mine

design or management; and the relative complexity and newness of suitable testing technology and methods, which have often been developed by individual AMD geochemistry practitioners and companies (Jeff Taylor pers comm 2017).

Several potential areas for future research projects have been identified during this research:

- Further research and testing of the 1D and 2D models across a wider range of AMD material types and conditions to improve the testing and data collection methodology and to test the accuracy of the models.

- Further research is recommended to develop the 1D and 2D models to potentially include advection, and other diffusion coefficient estimation functions, that may be relevant to different mine waste materials with larger particle sizes.

- Further assessment of the potential impact of AMD oxidation processes on diffusion processes in the AMD material matrix, using slow tests ->250mm diffusion samples and quicker tests -<20mm depth diffusion samples

- Additional research could also include developing a detailed safety factor approach for various sulfide bearing mine waste material and rock types, which would be considered a useful contribution to the field, with many potential uses and environmental management benefits.

- Further testing of the developed diffusion column in a wider range of conditions and material types. Developing a sample moisture control system to prevent drying over long testing periods would be an extremely useful development for several fields employing soil gas diffusion. The agricultural sector is particularly interested in soil gas movement at near saturated conditions, in contrast to the mining sector where the focus is often on dry materials, residual moisture or field capacity conditions.

- Development of linked simple spread sheet soil gas models to include effects of climate such as rainfall events, water balances and soil moisture over time, enabling prediction of long-term AMD production rates based on historical and future climate and weather conditions.

- Use of the 2D variable diffusion model and methodology in hydrocarbon-based site contamination assessment for determining volumes of material requiring treatment and also estimation of potential vertical gas diffusion rates.

8.7 References

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9 Appendix 1: Supplementary Material From Paper ii

9.1 A Comparison of Measured and Predicted Diffusion Coefficients Applied to Sand and Silt sized AMD Materials (Dettrick et al. 2019b).

The Soil gas diffusion column used for this study was designed by the author and required four beta test columns before the column design was considered final. The further details of this column design and other laboratory data associated with Chapter 4 are included below.

9.2 Economic Diffusion Column Design

The diffusion column design used for this study was based on the desired outcome of accuracy, ease of use, materials availability and low cost. Four columns were built and progressively improved until the optimal combination of components and geometry was achieved. The final adopted diffusion chamber consisted of uPVC pressure grade PN18 gas rated pipe, welded with gas rated PVC glue and all fittings were of gas quality 316 stainless steel to prevent leakage. The diffusion chamber design incorporates a new stormwater knife valve technology and is shown in Figure 9-1. The total cost of the column components is approximately \$300-500 USD.

The diffusion chamber was designed with modern data logging and collection technology in mind, and the ability to rapidly expose the soil sample to diffusion -one of the key design challenges for soil gas diffusion apparatus. The DN100 knife valve allows for collection of accurate diffusion data within the first several seconds of testing, minimising instability of the O_2 meter readings in the initial period of the diffusion test and increasing the period of accurate soil diffusion data collection. The accuracy, speed and stability of oxygen gas sensors has also improved in the last 5 years allowing for increased accuracy and logging of oxygen concentration.
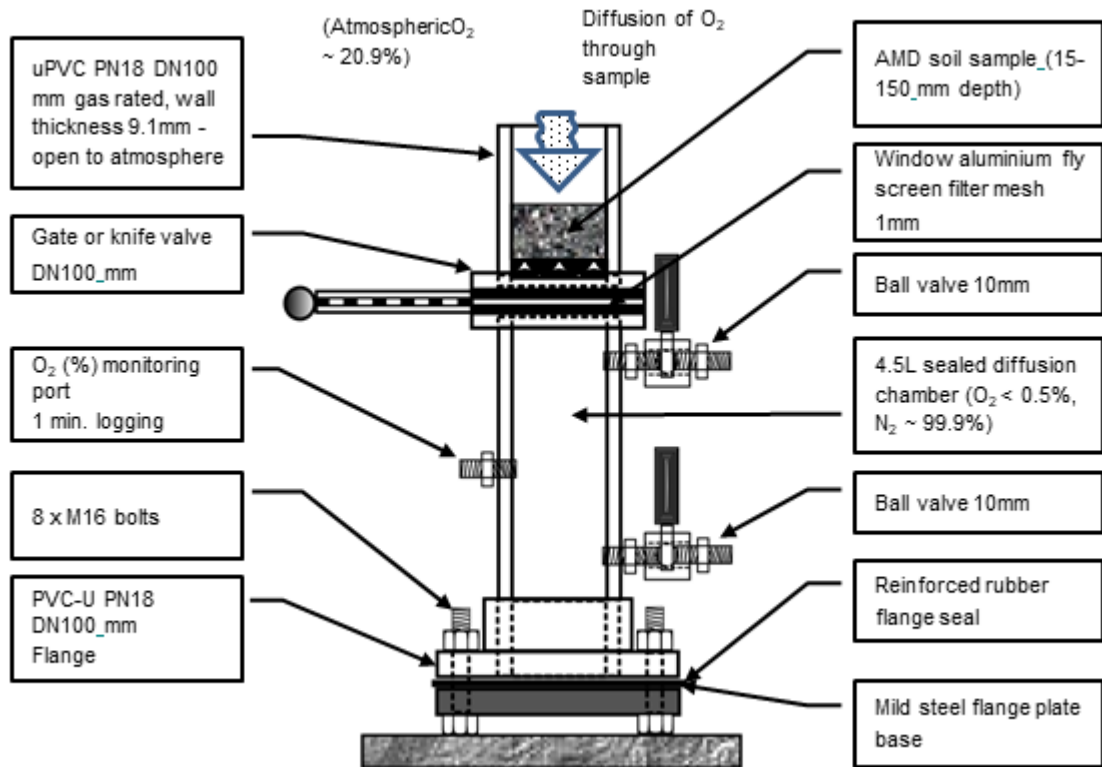
Figure 9-1: Diffusion column design –and conditions at the start of a mine material/O_2 diffusion test (Dettrick et al. 2019b)

9.3 Diffusion column leakage testing

Leakage testing was conducted on the column diffusion chamber fittings and ball and knife valves over approximately 4 weeks, with the knife valve closed and the column diffusion chamber filled with industrial grade N_2 gas (99.9%). The column slowly diffused from 0.1% O_2 to 6.3% O_2 (Figure 9-2). For the longest diffusion test performed (40,000 minutes), this represents a required correction of ~0.6% O_2. For a diffusion test of 250 minutes this represents a correction of -0.0375% O_2, or 0.17% of background. The leakage diffusion trace is linear and displays the effects of barometric pressure change over the period of the test due to the small relative size of the leakage area to the diffusion chamber volume (Crank 1975). The normalised 9am barometric change (Melbourne Airport, Station 086282, BoM 2016) over the test period has been added to demonstrate the relative influence over the test period.
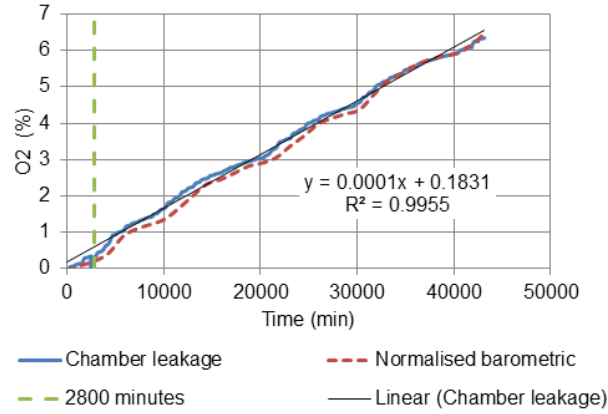
Figure 9-2: Diffusion column chamber leakage over time with normalised barometric as daily 9am data.

9.4 SWCC testing results detail

The SWCC apparatus used in this study was pressure chambers with ceramic porous plates. In this SWCC method, the soil specimen is placed in a ring of known volume and then saturated for 24 hours. The saturated specimen is weighed and then put in a drying oven for 24 hours at 105 °C to determine the soil porosity, wet and dry bulk density. The soil samples and the ceramic porous plate are then re-saturated for 24 hours and placed in SWCC pressure chambers with air pressure set to 0.3 to 150 kPa in regular steps. After water has ceased flowing, or after 24 hours, the soil sample weight is measured, and gravimetric moisture is determined by comparison with the saturated sample soil weight. The overall SWCC testing procedure is described in ASTM D6836-02-2008.

9.4.1 Unsaturated zone soil moisture behaviour and relative hydraulic conductivity

To further understand the physical behaviour of the target soils for moisture and soil gas transport, Van Genuchten (1980) parameterisation was undertaken to develop soil characteristics for use with the soil moisture equation (10).

$$\theta = \theta_r + \frac{(\theta_s - \theta_r)}{[1 + (\alpha h)^n]^m} \qquad (10)$$

Where θ is soil moisture, θ_s is saturated moisture content, θ_r is residual soil moisture due to adsorption, h is pore pressure, α, n, m are fitting parameters. Parameter estimation was undertaken on

the target SS and SC soils to determine α, n, m values. θ_r and θ_s were set to the values provided through SWCC testing.

Results for the parameter estimation are shown in Chapter 6 Paper ii, along with literature values for the natural soils, along the effective porosity for a matric suction of 100 kPa, which is used for the Moldrup 2000(a) diffusion model. The Van Genuchten approach can be used to estimate unsaturated soil moisture above the ground water table (GWT) for the purposes of analysis for in-situ effective porosity relationships. The parameter fitting curves for the SS and SC material are shown in Figure 9-3 & 9-4.
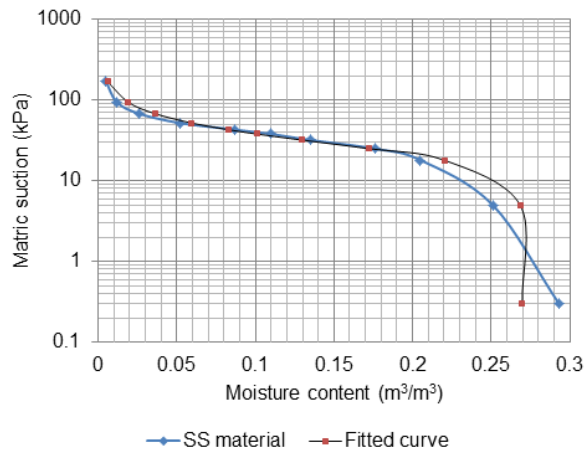
Figure 9-3: SS parameter estimation fitting curve
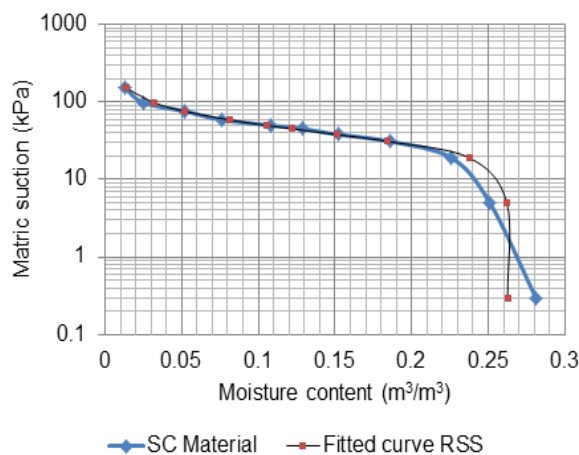
Figure 9-4: SC parameter estimation fitting curve

The relationship between steady state soil moisture content and elevation above a nominal groundwater table is shown in Figure 9-5. The well graded, fine-grained clay and lateritic soils display

significantly less variation in soil moisture, and therefore effective porosity, compared to the subject soils SS and SC. The Tailings 3 material shows a great deal of variation in moisture content near the water table and tends towards θ_r at only 3 m above the GWT. SS and SC mine materials display variation from θ_s to θ_r over 6 m in soil thickness above the GWT. These mine materials can therefore dry to maximum effective porosity for soil gas transport in comparatively small depths of material, which is why reactive AMD tailings are kept under a cover of water to prevent high levels of sulfide oxidation and associated AMD development within the tailings facility (DITR 2007). Conversely if the tailings are dried during closure or at other times, a great deal of potential acidity can be mobilised by oxygen transport and sulfide oxidation of tailings in the poorly sorted tailings material. The importance of having an accurate soil gas diffusion function to estimate oxidation rates is clearly of great import for dry tailings material 3-6 m above the GWT.
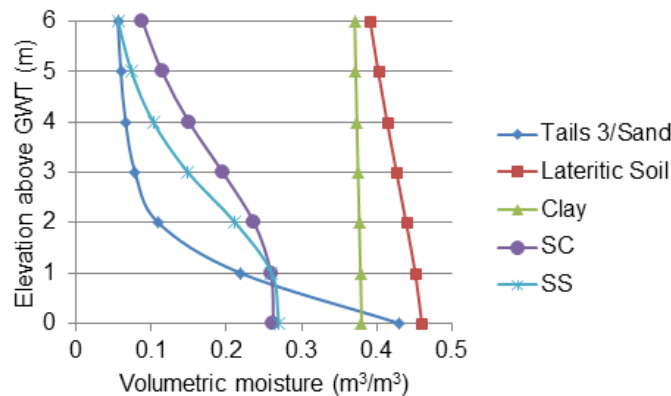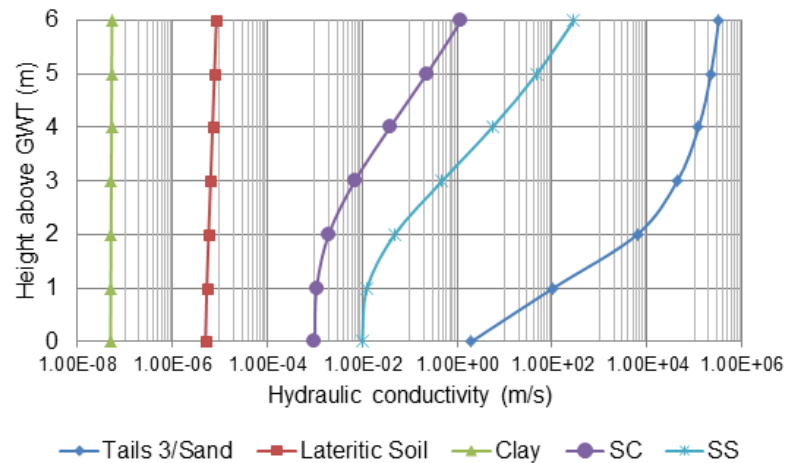

Figure 9-5: Unsaturated zone predicted soil moisture content above a nominal GWT based on Van Genuchten (1980)

The relative conductivity function for unsaturated water transport/diffusion coefficient (K_r) also offers insight to potential soil gas transport behaviour (Figure 9-6) and can be predicted with a further Van Genuchten (1980) formula (11) for the purposes of transport analysis and determining what type of diffusion model may be useful to model diffusion coefficient behaviour based on relative porosity.

$$K_r(\theta) = \theta^{\frac{5}{2}+2\lambda} \quad (11)$$

Where K_r is the relative conductivity function, θ is soil moisture and λ is a fitting parameter.

Figure 9-6: Hydraulic conductivity (K_s/K_r) estimate of study soils based on Van Genuchten (1980).

The predicted unsaturated zone hydraulic conductivity (K_r) for the study soils (Figure 9-6) shows that K_r varies more in the coarse grained material, such as Tailings 3/Sand, than the finer grained material, such as Clay, over a nominal soil depth above the GWT. From Figure 9-6, the tendency is for rainfall excess to infiltrate quickly initially at the soil surface and then slow down as it approaches the saturated zone. Due to the drier conditions, effective porosity will tend to be greater near the surface even following rainfall recharge events, allowing for increased soil gas diffusion compared to deeper parts of the soil profile.

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10 Appendix 2: PHREEQC Experiments and Code Developed for the Project

Geochemical modelling was examined as a potential for modelling soil gas transport but was found to be either i) not implemented by the source code geochemical model, or ii) highly complex and introducing a great deal of additional variables, many of which cannot be tested within the scope of this PhD study, and some of which cannot be tested for at all, such as matrix Tortuosity τ and Constrictivity δ. As a result, geochemical modelling was not further progressed in the research goal of developing a simple physical soil gas transport model for AMD materials.

10.1 Soil Sulfide Oxidation

The key aspect of the development of AMD is sulfide oxidation. In the test soils selected pyrite (FeS_2) is the source for sulfide that oxidised as oxygen is transported through the soil column primarily by diffusion, but likely including advection events over time. The complete geochemistry output for the key test soil are included above in Chapter 6 - A 1D soil gas diffusion model for estimating oxidation rates of AMD mine materials.

Modelling was undertaken with PHREEQC (Parkhurst and Appelo 1999, Appelo, and Postma 2005) to explore the geochemical reactive properties of the sulfide (Pyrite) oxidation of the target soils. A series of "tank" models were built to allow iteration of geochemical properties to simulate the oxidation reactions. The first tank model was designed to illustrate the complete oxidation process and production of acidity and the effect on reaction pH. Assuming a complete oxidation with pyrite in air (as O_2) the model was run with the mineralogy information available on the test soil materials. The key minerals included in the reaction were pyrite, goethite (as a reaction by-product), alunite, and kaolinite, all of which were equilibrated prior to the oxygen reaction which was undertaken in steps. The geochemical tank model results are shown below in Figure 10-1.

As can be seen in the figure the oxidation reaction initially produces $Fe2^+$ as reaction pH drops rapidly from the pure water solution pH of 7 to around pH 1.5. After this $Fe3^+$ replaces the Fe phase

preferentially as pH drops from 1.5 to close to pH 1.0, which can be seen clearly in the results with $Fe3^+$ finishing the reaction at 1e-3 mol and $Fe2^+$ a much lower component at 1e-11 mol.
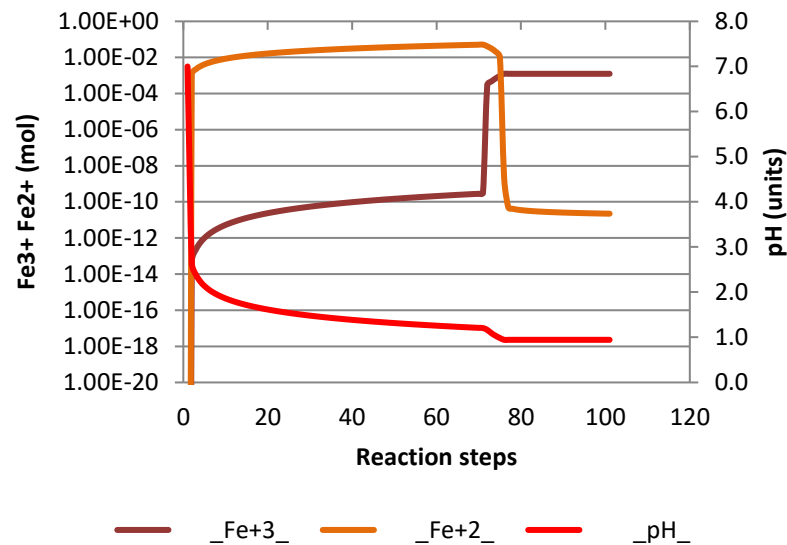
Figure 10-1: Completion reaction of pyrite with O_2 to illustrate acidity potential of AMD reaction

This is considered the extreme case of pyrite oxidation that is possible, assuming perfect conditions of oxidation and no neutralising capacity within the test soils. The second geochemical modelling tank results are based on adding oxy-hydroxide reactive surfaces to the soil matrix as potential neutralising capacity to observe the effects on AMD reaction pH.

The results of the surfaces tank model are shown below in Figure 10-2.
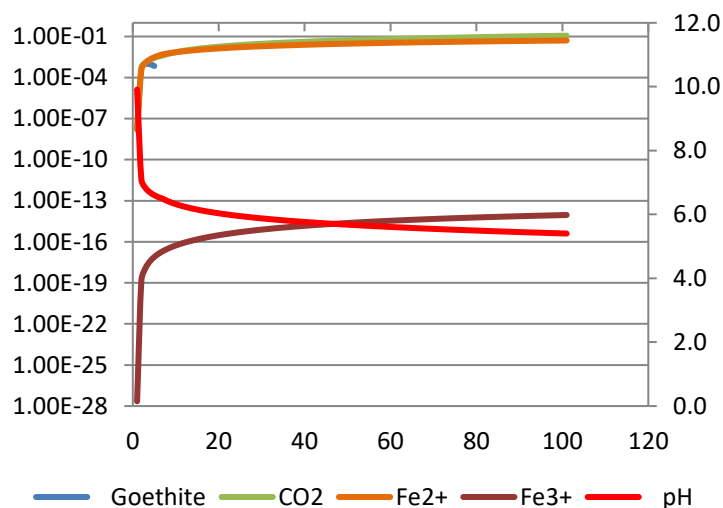
Figure 10-2: Introduction of Reactive Surfaces to illustrate neutralising capacity of AMD soil test material to reaction pH

As can be seen from Figure 10-2 above, the addition of estimated reactive surface areas including potentially neutralising materials, offers a much less aggressive pH result. The problem becomes the estimation of reactive surfaces and associated crystalline structure of FeS_2 within the individual sample on a micro scale. Testing of reactive surface parameters is a relatively expensive emerging technology (eg BET testing, BS 4359) and can only be completed on fine materials of silt size, or crushed samples with total a sample size of less than 2 grams. The results of testing of this small amount of material becomes a potential source exponential error (Dettrick et al. 2019a), and hence difficult to apply to an entire soil column, or a large mine waste site. For more on the potential limitations of micro scale modelling approaches, see the discussion on Buchgraber's (et al. 2012) micro porosity experiment in Chapter 2 above.

Approximately 15 geochemical tank models were developed during this project, but due to the relative complexity of the models and the lack of additional benefits to the identification and estimation of volumes of AMD materials or of zones of oxidation for use in soil gas transport modelling, these models were not utilised in the final 1D variable diffusion model.

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