



QUANTIFYING TEXTURE FOR ACID ROCK DRAINAGE CHARACTERISATION AND PREDICTION

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Synopsis

Minerals, metals and mining are the cornerstone of technological development and play an essential role in achieving the United Nations Sustainable Development Goals. Mining, however, is not a waste-free process, with mine wastes being a source of a host of environmental problems. One of these is acid rock drainage (ARD), which forms through a complex series of acid formation (mainly via sulfide oxidation), neutralisation (primarily by carbonates) and gangue mineral dissolution reactions in waste rock and tailings storage piles. The resulting drainage waters are often acidic, highly saline and may contain elevated levels of deleterious elements.

Effective ARD mitigation requires accurate ARD characterisation and prediction strategies. To date, standard guidelines recommend a suite of geochemical static (characterisation) and kinetic (prediction) tests. Characterisation tests such as acid-base accounting (ABA) and net acid generation (NAG) tests provide a quick and relatively inexpensive estimate of the “worst case” scenario for acid formation and neutralisation, while kinetic tests (commonly humidity or column leach tests) aim to predict the long-term weathering potential of waste material. The UCT biokinetic test (not currently industry standard practice) was developed to address the effect of microorganisms on ARD formation and allow for the collection of relative kinetic data on neutralisation and acidification within a shortened time period. None of these tests, however, account for the additional layer of complexity introduced by mineral texture, which describes the interrelationship of mineral grains to one another, their shapes and sizes, with some frequently studied textural parameters including mineral liberation, association, grain size distribution and particle size. Mineralogical and textural analyses are infrequently practiced in the context of ARD assessment due to the difficulty in obtaining statistically sound quantitative textural data, high costs of measurement, and standard ARD assessment protocols recommending (rather than necessitating) these assessments. An ARD assessment approach that includes static, kinetic, mineralogical and textural assessments has nonetheless been suggested by several researchers.

This project assessed the dominating textural parameters on the scales of kinetic (humidity cell) test (HCT) feed material (meso-scale) and characterisation (static and UCT batch biokinetic) test (SCT) feed material (micro-scale) using four waste rock samples (A, B, C and D) from a greenstone belt gold deposit as a case study. More specifically, the study aimed to assess the role of mineralogy and texture in the ARD assessment “toolbox” and to investigate the role of coarse material sampling for ARD assessment. Data sets collected included the PSD of the micro- and meso-scale material, sample chemistry data obtained from XRF spectrometry and LECO total sulfur, bulk mineralogy data from QXRD and QEMSCAN, as well as textural and mineralogical data from QEMSCAN for sized and unsized micro- and meso-scale material. ARD-specific data sets included results of geochemical characterisation tests such as ANC and single-addition NAG tests, the UCT batch biokinetic test with and without pH control for samples C and D, as well as prediction test data from water-fed and acid-fed humidity cell tests.

The geochemical static tests performed on samples A, B, C and D classified them as PAF, PAF, uncertain and NAF, respectively. Non-pH-controlled UCT batch biokinetic tests remained circumneutral for samples B, C and D over the duration of 90 days, while for sample A the pH became acidic over time. The pH-controlled tests demonstrated a steady depletion of neutralisation potential over the first 30 days. Humidity cell test results demonstrated no acidic leachate formation for water-

fed tests over 40 weeks, while acid-fed tests showed a decreasing pH over time as the neutralisation capacity was reduced.

The mineralogy was important for the interpretation of test results on both the micro-and meso-scales and was assessed in terms of both discrete minerals and reactivity groupings (Fe-Sulfide, other sulfide, dissolving (carbonate), fast weathering, intermediate weathering, slow weathering, inert and other). For sample A the mineralogy was dominated by the inert (quartz), slow weathering (magnetite, plagioclase-albite) and intermediate weathering (Fe-amphibole) categories, with lesser contributions from the Fe-Sulfide (pyrrhotite), dissolving (calcite) and fast weathering (epidote) groups. The main groups contributing to the sample B mineralogy were the slow weathering (plagioclase-albite, magnetite, K-feldspar), inert (quartz) and intermediate weathering (Fe-mica, chlorite) groups, followed by Fe-Sulfide (pyrite), dissolving (calcite) and fast weathering (epidote) mineral groups. Sample C mineralogy comprised predominantly inert (quartz, titanite), Fe-Sulfide (pyrrhotite), dissolving (calcite) and intermediate weathering (Fe-mica, chlorite) minerals, with lesser contributions from slow weathering (K-feldspar) and fast weathering (epidote) minerals. Sample D comprised intermediate weathering (Fe-amphibole, chlorite, Fe-mica) and slow weathering minerals, with lesser contributions from slow weathering (magnetite), dissolving (calcite) and Fe-Sulfide (pyrrhotite) minerals. Textural parameters (liberation and association, grain size distribution and liberation spectrum) were evaluated for the Fe-Sulfide and dissolving minerals. On the micro-scale, a large portion of the Fe-Sulfide and dissolving minerals in the samples was found in the liberated category (<90% exposure to the atmosphere). On the micro-scale, samples A, B, C and D were found to contain 73%, 94%, 71% and 48% liberated Fe-Sulfide material and sample B, C and D to contain 84%, 69% and 50% liberated dissolving minerals. On the meso-scale the Fe-Sulfide liberation was limited for all samples (12%, 14%, 25% and 6% for samples A, B, C and D, respectively), which was also observed for the dissolving minerals (11%, 16% and 6% liberation for samples B, C and D respectively). The low amount of liberated material was thought to be due to the mass contribution (>50%) of the texturally significant size fractions (>1mm), which comprised predominantly locked Fe-Sulfide and dissolving minerals. Evidence of a bimodal distribution was, however, found for sample C via the liberation spectrum and grain size distribution (early liberation size of 8mm), which accounted for the larger degree of liberation observed in the >1mm size fractions, and a larger degree of liberation for the sample overall. The association of Fe-Sulfide and dissolving minerals for all samples was found to be primarily to inert, intermediate weathering and slow weathering minerals, with a larger degree of association of Fe-Sulfide to dissolving minerals observed in sample C.

On the micro-scale the mineralogy helped inform the placement of the samples on the geochemical classification plot based on the Fe-Sulfide, dissolving and intermediate weathering mineral contents. For the non-pH-controlled UCT batch biokinetic test, the presence and abundance of calcite was thought to dictate the PAF/NAF nature of the test, as even relatively low amounts of calcite rendered the pH circumneutral for the duration of the test (sample B). For pH-controlled tests, however, the calcite was depleted over time, which led to a favourable acidic environment for the acidophilic bacteria used in the batch biokinetic test. For both the geochemical characterisation and the pH-controlled UCT batch biokinetic tests there was evidence to suggest the contribution of intermediate weathering (Fe-amphibole, Fe-mica, chlorite) and slow weathering (magnetite) minerals to the neutralisation potential in the sample. On the meso-scale the effects of mineralogy were most prominent for the acid-fed humidity cell tests, which showed some pH fluctuations and a steady depletion of the primary

neutralisation potential. The pH fluctuation after the depletion of the dissolving minerals was attributed to the dissolution of intermediate weathering minerals over the 40 weeks of the tests. These effects were not observed during the 40 weeks of the water-fed experiments. Given sufficient time for the latter test, however, it would be expected that upon the onset of acidification, similar effects of the mineralogy on the leachate quality would be observed as in the acid-fed tests. Knowledge of the Fe-sulfide and dissolving mineral texture yielded several insights. On the micro-scale, the liberation and grain size distribution data provided an indication that a sample-customised grinding size should be established to ensure adequate “worst case” scenario determination via characterisation tests, as material with fine Fe-Sulfide or dissolving mineral grains may not be fully liberated at the recommended 75µm top size. On the meso-scale, the texture yielded insight into the circumneutral behaviour of the water-fed HCT, as most of the acid-forming minerals were contained in size fractions where the liberation was either limited or negligible, with predominant association to slow weathering, intermediate weathering and inert minerals. These findings highlighted the importance of considering mineralogy, texture and the PSD of the material for HCT result interpretation.

When considering texture as a parameter for ARD assessment, the potential for sampling and mineralogical errors arose due to the coarse material size (specifically on the meso-scale) and the limitations on the number of particles that could be assessed. Quantitative mineralogy and texture data allowed for the quantitative assessment of the sampling and mineralogical errors, which were investigated through Pierre Gy’s fundamental sampling error (FSE) equation, the binomial distribution approximation and the plotting of confidence intervals over the Fe-Sulfide liberation data. The results showed that although tools such as Gy’s “safety line” provide a useful quick means of sampling error assessment, this approach may yield excessively large sample mass requirements for coarse material. Calculating the sampling error from the textural and mineralogical data provided a useful tool to estimate sample representativeness. Additionally, the estimation of sampling errors may help in the planning of an appropriate sampling approach, which may ultimately provide a means to relate data sets to one another across scales based on how representative samples are of one another, and therefore of the parent lot.

The current study showed how mineralogy and texture are not simply “tools” in the ARD assessment “toolbox”, but rather a key means for interpreting characterisation and prediction test data. Additionally, the quantitative assessment of mineralogy and texture provided the opportunity to assess the material-specific sampling error, which, in turn, may allow for the correlation of data sets across various scales and for the planning of appropriate sampling strategies. Recommendations for future work include: the quantitative assessment of the ARDI for meso-scale material; the assessment of detailed characterisation and prediction test leachate chemistry; trace element assessment and deportment throughout UCT batch biokinetic and humidity cell testing; mineralogical and textural assessment on characterisation and prediction test residues during and after tests; an in-depth analysis of the minimal/optimal sample block/sub-sample mass required for minimal error; the assessment of samples using X-ray microcomputed tomography to assess and decrease the effects of stereological bias prevalent in 2D measurements; and the application of a similar texture and mineralogy assessment to additional waste types (such as coal wastes, or waste material containing non-Fe-bearing sulfides).

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List of presentations and publications

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Glossary

a	In the sampling equation – average concentration of the lot
ABA	Acid-base accounting
Ae	Artefact element
ANC	Acid neutralisation capacity
ARD	Acid rock drainage
Association	Textural parameter that describes the way and extent to which minerals are contacting one another in a sample
Critical component/analyte	The component of interest in the sampled material, such as pyrite for acid rock drainage potential
c	In the sampling equation – mineralogical composition factor or the “constitution” factor
C	In the sampling equation – sampling constant
d ₅₀	For a particle size distribution, the size of the particles at which 50% of all the material is at this size or smaller
d ₉₀	For a particle size distribution, the size of the particles at which 90% of all the material is at this size or smaller
d _l	In the sampling equation – liberation size of the mineral of interest
Deleterious elements/metals	Elements harmful to living organisms
EDS	Energy dispersive spectrometry
EPMA	Electron probe microanalysis
f	In the sampling equation – shape factor
Fe-Sulfide	Mineral consisting of iron and sulfur. In the context of this study these are generally pyrite, pyrrhotite or a combination of the two
Fragment	A particle or other physically separable unit of the lot such as a mineral, grain or molecule
g	In the sampling equation – granulometric/grain size distribution factor
GOF	Goodness of fit (statistical indicator associated with QXRD data)
Grade	For the analyte it may be described as its ratio to the total mass
Grain	A single-mineral entity

Group	The collection of fragments that may act as an independent unit for sampling procedures. The size of the group will also be a function of the sampling process. “In practical sampling terms a group usually denotes the material occupying the extracted volume in the sampling tool”
GSD	Grain size distribution
HCT	Humidity cell test
Deleterious metals	Metals or metalloids of high atomic number that may result in toxicity upon uptake in living tissue and pose negative environmental size effects upon their release into the environment
Increment	A part of the sample (sub-sample) that, when combined with other increments yields a complete sample. An increment may comprise several or a single group of fragments, or a single fragment
l	In the sampling equation – liberation factor for the mineral of interest
l_{50}	For a grain size distribution, the size of the grains at which 50% of all the grains are at this size or smaller
l_{90}	For a grain size distribution, the size of the grains at which 90% of all the grains are at this size or smaller
L_D	Percentage of liberated dissolving minerals in the sample
L_S	Percentage of liberated Fe-Sulfides in the sample
LECO S	Total sulfur determination method using high temperature combustion
Liberated	A particle consisting of a single mineral
Liberation	Liberation is the state of a particle consisting of only one phase, with the quality of liberation being fundamentally based on volume
Lot	The bulk material that is being sampled and can be time-variant (such as a process stream) or time-invariant (such as a stockpile or waste dump)
M_L	In the sampling equation – mass of the lot
M_S	In the sampling equation – mass of the sub-sample
Macro-texture	Description of the overall texture without specific information about the location of individual grains and can be considered on the scale of an outcrop
Meso-scale	A category used to define a sample that contains material that is mostly retained on a 1mm aperture size screen. This material contains the full particle size distribution from parent sub-sample crushing
Meso-texture	Description of the information regarding the grain and phase boundaries

Micro-scale	A category used to define a pulverised sample that contains material that passes through a 1mm aperture size screen. This material contains the full particle size distribution from parent sub-sample pulverisation
Micro-texture	Description of the individual mineral grains and their orientations
Mineral	A natural, solid, crystalline, homogeneous material of inorganic origin with a chemical composition that lies in well-defined limits
Mineralogy	The scientific study of minerals that involves studying their structures, chemical and physical properties, classification, mode of formation and associations
Moi	Mineral of interest
MPA	Maximum potential acidity
N	Number of particles
N _D	Number of dissolving mineral (carbonate)-bearing particles
N _S	Number of Fe-Sulfide-bearing particles
NAF	Non-acid forming
NAG	Net acid generation
NAPP	Net acid producing potential
p	In confidence intervals on mineralogical data – proportion of the mineral of interest
PAF	Potentially acid forming
Particle	An indivisible three-dimensional fragment consisting of one or more mineral phases
ppb	Parts per billion
ppm	Parts per million
PSD	Particle size distribution
QEMSCAN	Quantitative evaluation of minerals using scanning electron microscopy
QXRD	Quantitative X-ray diffraction (with Rietveld refinement)
ρ_m	In the sampling equation – density of the mineral of interest
ρ_g	In the sampling equation – density of the gangue minerals
Re	Real element
RPM	Revolutions per minute
R _{wp}	R-weighted pattern (statistical indicator associated with QXRD data)

Sample	A portion of the lot that has been obtained using correct sampling techniques and guidelines
SCT	Standard characterisation test
SDG	Sustainable development goal
SE	The sampling error arising due to the splitting of samples from a bulk sample (minimal for the micro-scale material due to its top size being in the “safe” zone of Gy’s safety line)
SIP protocol	Species identification protocol used in the QEMSCAN iDiscover software for element information classification
Specimen	A portion of the lot obtained via incorrect sampling technique and which is thus structurally biased
Texture	The description of the shape and size of different mineral grains/constituents and their interrelationship with one another
TOS	Theory of sampling
UC	Uncertain classification from geochemical static test characterisation
UCT	University of Cape Town
UN	United Nations
WDS	Wave dispersive spectrometry
XRF	X-ray fluorescence

References used in the compilation of this Glossary include (Minkkinen, 2004; Petersen et al., 2005; Minnitt et al., 2007a; Becker et al., 2016; Jardine et al., 2018)

1 Introduction

1.1 Background

1.1.1 Minerals, metals and acid rock drainage

Through time the recovery of metals from ores for tools, jewellery, bullion, building and technology has allowed mankind to progress through the ages to modern society. Today more than ever, minerals and metals play a critical role in the support, improvement and maintenance of our daily lives and the development of new technologies (Reardon, 2011; Lusty & Gunn, 2015; Carvalho, 2017). The extraction of minerals from ores is also instrumental to achieving the United Nations' Sustainable Development Goals (UN SDGs), specifically goals seven (affordable and clean energy) and nine (industry, innovation and infrastructure), which directly relate to construction, technology and, societal progress and development (United Nations, 2015).

Although mining is instrumental in meeting the UN SDGs, mining, mineral processing and metallurgy are not waste-free processes (see Figure 1-1) and generate a variety of solid waste types. If not carefully managed, the generation of these wastes may be accompanied by a host of negative environmental side effects, which may violate some of the sustainable development goals. From Figure 1-1, mine waste types may include waste rock, processing wastes from mineral beneficiation (tailings from mills, washeries or concentrators), and metallurgical wastes (poor-grade leach/smelter residues), with the global total annual solid mine waste generation being estimated at 20000-25000 megatons in 2010 (Lottermoser, 2010a). Most of the mine waste material ultimately finds its way into massive heaps or dumps, and as the need for metals increases with increasing population, urbanisation and spread of prosperity, larger volumes of lower grade material are excavated to produce more mining wastes. (Tremblay & Hogan, 2000; Lottermoser, 2010a; Lusty & Gunn, 2015).

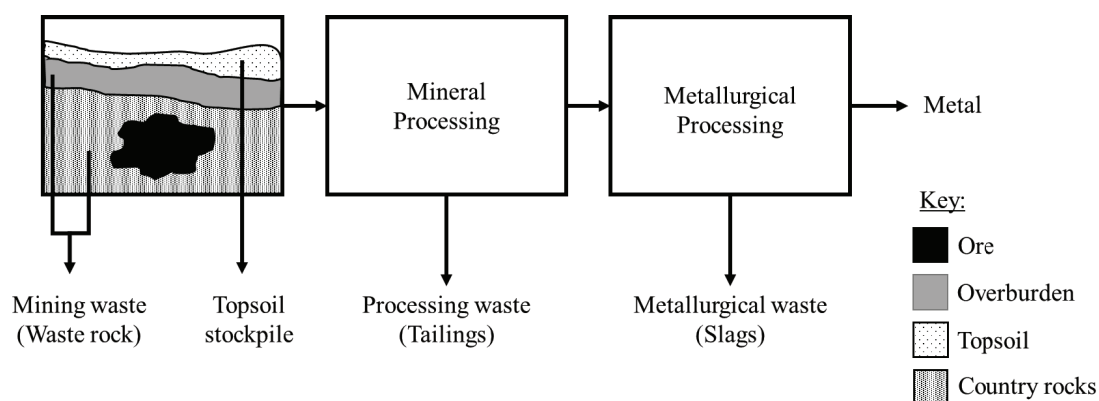


Figure 1-1 Schematic of a mining process with associated solid waste streams. Adapted from Lottermoser (2010b).

Although mining produces a variety of solid wastes, the focus of this study is limited to waste rock material. Waste rock dumps are often a source of a host of environmental problems, one of which is acid rock drainage (ARD). This naturally occurring phenomenon is exacerbated by mining activities, which fragment the parent rock into material that has an exponentially larger surface area exposed to oxidative conditions (Morin & Hutt, 2001; INAP, 2009; Lottermoser, 2010a; McCarthy, 2011;

Jamieson et al., 2015). ARD initially proceeds through the oxidation of sulfide minerals upon their exposure to atmospheric oxygen and moisture. Iron sulfide minerals such as pyrite and pyrrhotite are often found in base and precious metal ores and because of their relative abundance they are typically recognised as the main acid forming minerals in mine wastes; however, all sulfide minerals are susceptible to oxidation (Nordstrom & Alpers, 1999; INAP, 2009). Carbonate (calcite, dolomite and magnesite) and some calcium- and magnesium-bearing silicate minerals have the potential to consume the acid formed through sulfur-bearing mineral oxidation, affecting both the pH and the ionic content of the drainage waters (Plumlee, 1999). In addition to mineralogy, the type of oxidant, pH, temperature, climatic conditions, and the presence of naturally occurring acidophilic bacteria affect the rate of ARD formation (Akcil & Koldas, 2006).

ARD may result in the acidification and salinisation of freshwater systems, accompanied by deleterious metal release. The latter is exacerbated by acidification, as it aids in metal mobilisation. Deleterious metals readily bioaccumulate in living tissue, which may result in toxicity, neurological damage and, potentially severe effects on the health of aquatic life forms and human beings (Department of Water Affairs and Forestry, 1996a; b; Besser & Leib, 2007). Acidification also removes the naturally occurring bicarbonate buffer from the water, which is an essential source of carbon for photosynthetic life forms (Department of Water Affairs and Forestry, 1996a; b; Besser & Leib, 2007). The precipitation of iron oxyhydroxides and metals such as copper, lead and zinc may occur on surrounding soils and sediments of affected water systems (Zheng et al., 2007; Morais et al., 2008) and result in the physical coating and contamination of aquatic life and man-made structures. Evidently, ARD-contaminated water is detrimental to aquatic life and the environment, and is unfit for human utilisation and consumption (Lottermoser, 2010a).

1.1.2 Current ARD assessment strategies

To effectively mitigate the negative impacts of ARD it is essential to have robust protocols for assessing the ARD potential of mine waste material. More commonly these protocols include a suite of standard ARD characterisation and prediction practices, which comprise a series of geochemical static and kinetic tests (Smart et al., 2002; Parbhakar-Fox & Lottermoser, 2015). Geochemical static tests include acid-base accounting (ABA) and net acid generation (NAG) tests, which provide an indication of the extremes of acid formation and neutralisation without indication of the relative rates of these reactions. These tests can be performed on many samples quickly and at a relatively low cost (INAP, 2009). Kinetic tests, such as the humidity cell test (HCT), are performed on potentially acid forming (PAF) or uncertain (UC) samples and aim to assess the lag time for acid formation, the reaction rates, and the change in leachate quality with time (White et al., 1997). The University of Cape Town (UCT) batch biokinetic test (Hesketh et al., 2010) was developed to address the catalysing effects of acidophilic bacteria, which are not addressed by geochemical static or kinetic tests, and provides a method for assessing relative reaction rates of key minerals involved in acid formation and neutralisation in the presence of microbes.

Although the standard tests often adequately assess the ARD potential of mine waste material, in some cases they may fall short. This may lead into the over- or under-engineering for ARD prevention and mitigation, both of which have significant techno-economic, environmental and social consequences (Jennings & Dollhopf, 1995). As an example, the combined costs for ARD treatment of four of the

world's largest mining countries (Canada, Australia, USA and South Africa) were predicted to be around US\$32-72 billion (Cozzolino et al., 2018). With the ARD problem still persistent today, it may be postulated that the practices best at the time would not necessarily remain best practice for years to come. Additionally, the increasing stringency in legislation and the requirement for mines to obtain a social licence to operate (SLO) puts pressure on mines (both new and old) to have adequate strategies for mine waste management and mine site remediation (Owen & Kemp, 2013).

Problems with accurate ARD assessment arise due to the inherent complexity of the mechanisms associated with ARD formation and an incomplete understanding of all the governing factors. Some authors (Morin & Hutt, 1998; Paktunc, 1999; Parbhakar-Fox et al., 2011; Brough et al., 2013; Dyantyi et al., 2013; Becker et al., 2015) have argued that one of these factors is the mineral texture, which is a critical but seldom considered parameter in controlling ARD generation (both in small scale characterisation and prediction methodologies, as well as on the larger field scale).

In mineralogy and geology, texture defines the interrelationship of different mineral grains to one another and their shapes and sizes (Becker et al. 2016). Textural parameters include the exposure of acid forming and acid neutralising minerals to the atmosphere (liberation), their association with other minerals, their grain size distribution and their shape (Parbhakar-Fox et al., 2011).

Historically the lack of focus in this area has been due to:

- the sheer scientific complexity of quantitative mineral textural descriptors (Leigh et al., 1993 - liberation modelling; Parbhakar-Fox et al., 2011 - acid rock drainage index; Little et al., 2015 - quantitative particle shape characterisation; Vos, 2017 - surface mineral grain characterisation);
- the limitations of analytical technology for quantitative textural measurements (from qualitative, manual optical microscopy, which was too slow and labour intensive to process large amounts of data (Jones, 1987) to more advanced, automated, quantitative analytical techniques of today - (Bogner et al., 2007; Becker et al., 2016; Cook et al., 2017);
- the high costs associated with running these measurements to get statistically representative and accurate data (Parbhakar-Fox & Lottermoser, 2015; Brough et al., 2017; Pooler & Dold, 2017), and
- the current accepted protocol for ARD characterisation and prediction (e.g. Global Acid Rock Drainage Guide, American Standard Test Methods) not necessitating quantitative textural measurements, but rather only recommending them (INAP, 2009).

Additionally, the real economic value of automated mineralogy techniques is still not fully recognised even in the context of valuable mineral beneficiation (Gu et al., 2014). In and around the last two decades, however, significant positive developments have occurred in mineral textural quantification coming out of the mineral processing and extractive metallurgy industries. These are of direct relevance to ARD characterisation and include the development of new analytical technology (e.g. automated scanning electron microscope with energy dispersive spectrometry (SEM-EDS) for quantitative mineralogy and X-ray computed micro-tomography (XCT), and new textural descriptors (e.g. Pérez-Barnuevo et al., 2013; Vos, 2017; Jardine et al., 2018). These significant positive advancements in mineral textural quantification provide an ideal opportunity to integrate textural and mineralogical techniques into the ARD assessment “toolbox”.

When considering quantitative textural assessments, however, it is important to consider issues of scale and sample comparability, as waste rock dumps can contain millions of tons of waste material consisting of a range of particle sizes, from massive boulders to fine powder-like material. On the other hand, standard ARD assessment protocols require samples of a few grams (characterisation tests) or kilograms (prediction tests) that can be orders of magnitude smaller than the original parent material. This highlights the key role of representative sampling to enable the reliable interpretation of data and the avoidance of costly miscalculations that may arise during the assessment process (Carrasco et al., 2004; Petersen et al., 2005). Representative sampling may be quantified through a theory of sampling (TOS), with the TOS of Pierre Gy providing a means to do so using mineralogical and textural parameters of the ore (Gy, 1979; Jones, 1987). This emphasises how the value of quantitative mineralogy and texture not only has the means to provide an additional layer of interpretation to commonly practiced ARD assessment strategies, but also to provide a measure of comparison and representativeness across the various scales and data sets.

1.2 Problem statement

The “wicked problem” of freshwater contamination by ARD is today more pertinent than ever. Mining, minerals and metals are vital for the maintenance of the lifestyle of modern mankind, but the pressures of obtaining a social license to operate (SLO) are quickly becoming an essential reality of mine development and planning. It is therefore necessary to find ways of preventing ARD before its formation, in other words, adequately and accurately characterising mine waste material to ensure appropriate mitigation measures are in place. Current ARD characterisation and prediction methods and protocols tend to exclude consideration for mineralogical and textural parameters and their role in ARD formation, partially due to the complexity of these data and the difficulty in obtaining statistically sound textural indicators. This problem is further exacerbated by the costs involved with obtaining mineralogical and textural data and the difficulty in the reconciliation of these data with results of commonly used ARD assessment tools. There is therefore a requirement to formulate a more holistic approach to ARD assessment that includes a more defined role of mineralogy and texture in the ARD assessment “toolbox” and how some of these tools relate to one another.

1.3 Research objectives and project scope

1.3.1 Research objectives

The objectives of the current study are to:

- Synergise the results of textural and mineralogical analyses on the micro-scale (<1mm particle size, characterisation test material) with the results of the commonly practiced geochemical static tests and the UCT batch biokinetic test, with particular consideration for the key minerals involved in acid formation (iron sulfide minerals) and neutralisation (carbonate minerals);
- Synergise the results of textural and mineralogical analyses on the meso-scale (>1mm particle size, prediction tests) with the results of the more routinely practiced humidity cell test, with particular consideration for the key minerals involved in acid formation (iron sulfide minerals) and neutralisation (carbonate minerals);

- Address some of the problems associated with the statistical representativeness of mineralogical and textural data, with more specific consideration for the number of particles, particle size and the sub-sample mass required for analysis through a comprehensive assessment of the sampling errors involved;
- Present a holistic understanding of the role of mineralogy and texture in the ARD assessment “toolbox” alongside more conventional ARD tests (geochemical static tests, the UCT batch biokinetic test and the humidity cell test), as well as the nature of the information these tests provide.

1.3.2 Project scope and limitations

This study focuses on the quantitative assessment of mineralogical and textural parameters (liberation, association, grain size distribution) influencing ARD generation for four gold waste rock samples (samples A, B, C, D) from an African greenstone belt. The data obtained from textural and mineralogical analyses will be integrated with data obtained from geochemical static characterisation tests, humidity cell tests and the UCT batch biokinetic test. Additional attention will be given to resolving some of the difficulties in obtaining a representative sub-sample mass and particle number for textural and mineralogical analyses, as well as to the synthesis of the complete dataset. The data sets obtained during this study are presented and assessed alongside supporting background data (UCT batch biokinetic test, humidity cell test and micro-scale mineralogical data for samples A and B) from the PhD work of A.K.B. Opitz. It should be noted that although data sharing will be present, these data will be used to obtain different information about ARD generation and will be appropriately referenced.

The current study was focused within the following limitations:

- only a gold waste rock (hard rock) was used as a case study, with the findings not being extrapolated to other mine wastes such as coal waste or mine tailings;
- the number of particles that could be assessed to attempt the minimisation of mineralogical and sampling errors was subject to time and cost constraints, particularly for coarser meso-scale fractions. Thus, the pursuit of a minimal statistical error in mineralogical and textural measurement was, within reason, partially replaced with focus on understanding and quantifying the error itself;
- three-dimensional analyses were not considered in this study, introducing the potential for stereological bias associated with two-dimensional measurements;
- only laboratory-scale tests were performed, without correlation to field-scale conditions; and
- no kinetic modelling was conducted during this study.

The broader scope and limitations of this project are best illustrated using a modified version of the “wheel approach” outlined previously by Morin & Hutt (1998). This is provided in Figure 1-2.

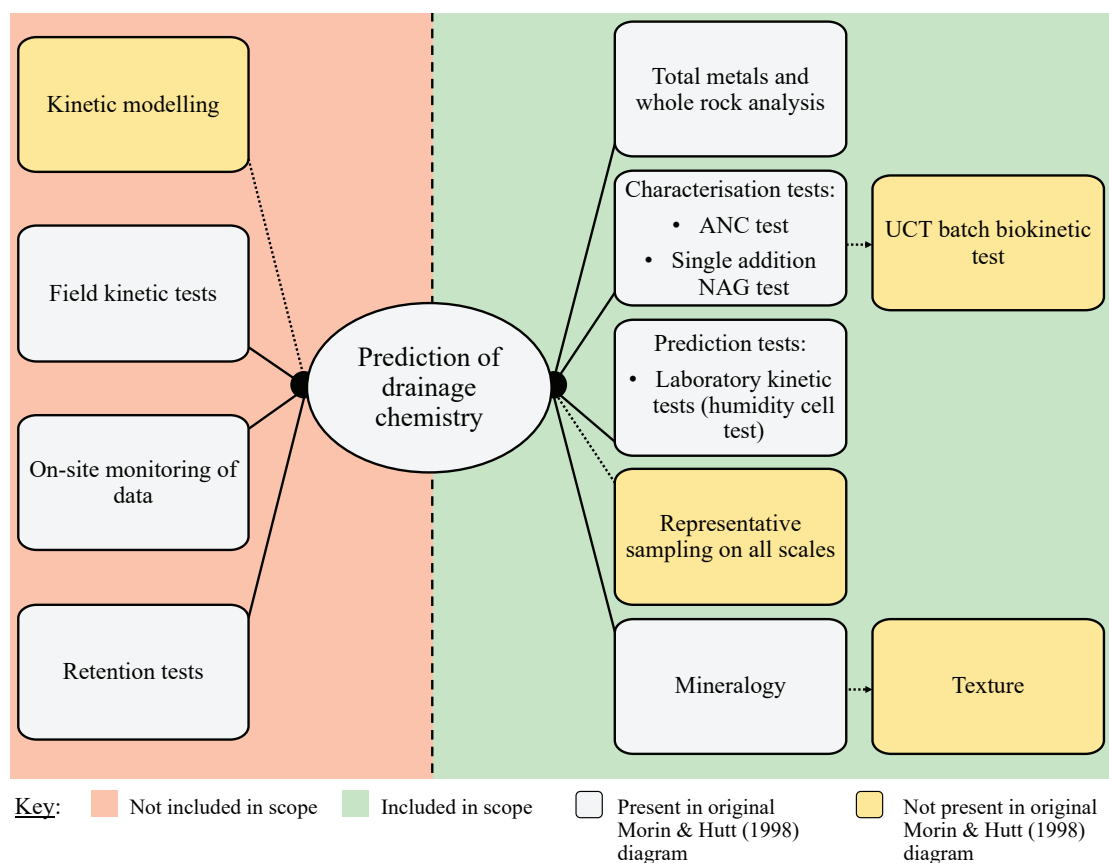


Figure 1-2 Project scope diagram based on the “wheel approach” described by Morin & Hutt (1998) with modifications that highlight specifics of the current project. The red category indicates tests that fall outside the scope of this project, the green category indicates the tests that are included in the scope of this project, grey boxes indicate the tests suggested in the original “wheel approach” diagram and yellow boxes indicate tests that are included in this study but were not addressed by the original “wheel approach” specifically.

1.4 Dissertation structure

This dissertation is structured in seven chapters. This structure is summarised in Figure 1-3. The current chapter (Chapter 1) provided the background to the study, alongside the problem statement, project scope and objectives. Chapter 2 provides a review of the critical literature pertaining to ARD formation, existing tools for ARD assessment, the importance of mineralogical and textural parameters and the means for their assessment, as well as the literature relevant for the sampling and mineralogical error quantification. The project key questions conclude Chapter 2. Chapter 3 describes the methods used for data collection, providing details on the sampling procedure, geochemical static tests, kinetic tests, UCT batch biokinetic tests, as well as mineralogical and textural assessments. The results and associated discussion for the data sets obtained via the methods in Chapter 3 are provided in Chapters 4 through 6, wherein objectives one to three are addressed. Chapter 4 provides the results and associated discussion on the micro-scale and addresses objective and key question one. Chapter 5 provides the results and associated discussion on the meso-scale and addresses objective and key question two. Chapter 6 assesses the errors associated with the data sets gathered in this study, with emphasis on the sampling errors involved and addresses objective and key question three. Chapter 7 provides a concluding discussion for this study, wherein the full set of objectives and the key questions posed in Chapters 1 and 2 are addressed, alongside the recommendations for future work.

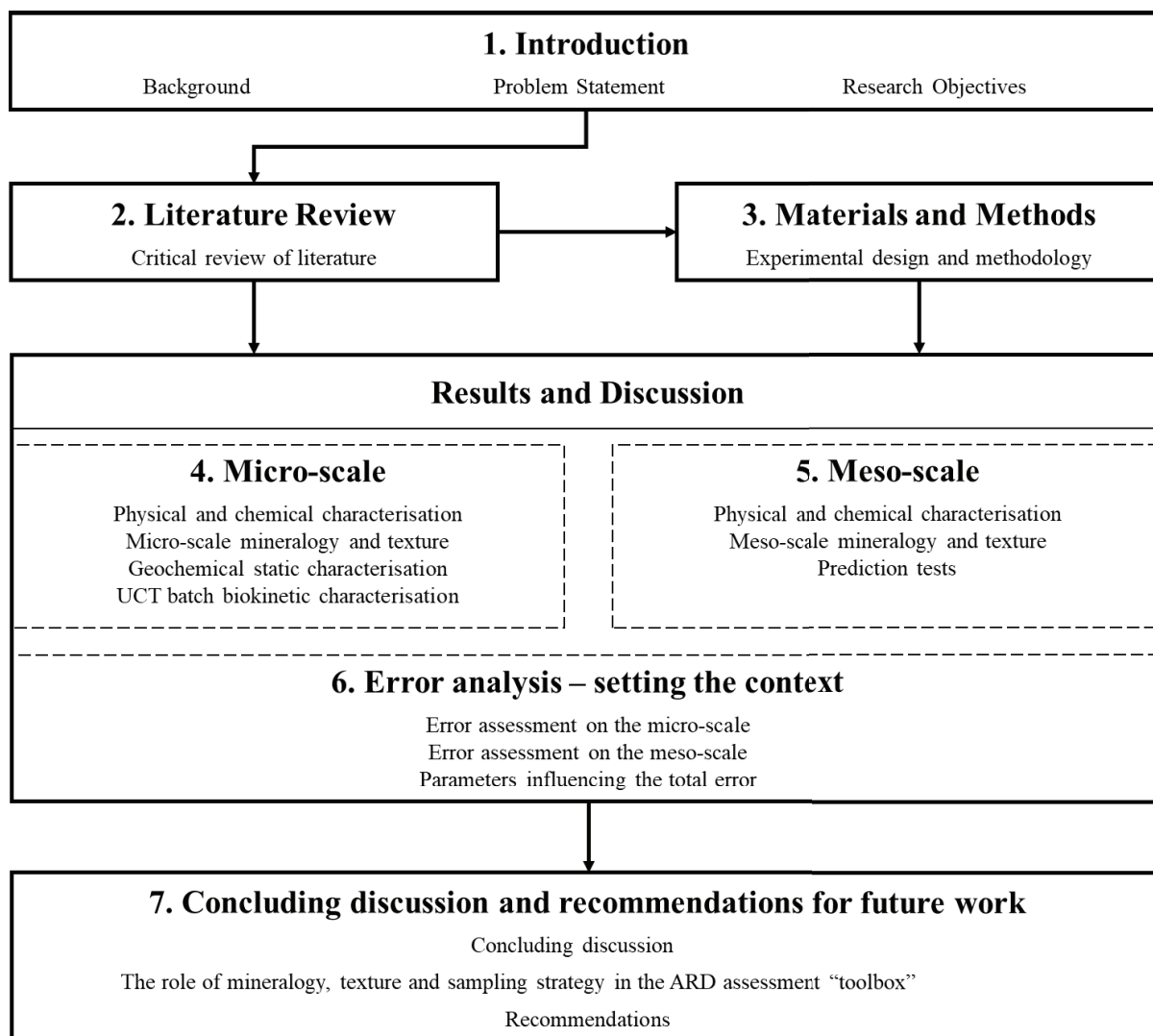


Figure 1-3 Dissertation structure schematic.

Links to data sets, detailed experimental methods and calculations may be found in the Appendix.

2 Literature Review

This chapter provides a non-exhaustive overview of the literature surrounding acid formation and neutralisation, deleterious metal release, the presence of microbes, as well as the commonly used ARD characterisation and prediction practices. More detailed focus is made on mineralogy and texture, the methods of their assessment, as well as the errors commonly encountered during textural analysis and sampling.

2.1 Acid rock drainage in context

ARD forms through a complex series of acid formation and neutralisation reactions at both active and abandoned mining sites. The naturally occurring phenomenon is associated with both waste rock and tailings primarily from the mining of coal, gold, copper, nickel, and lead-zinc ore deposits (Nordstrom & Alpers, 1999; Akcil & Koldas, 2006). Accelerated by the presence of naturally-occurring microorganisms in mine waste material, the oxidation of sulfur-bearing minerals in these wastes leads to acid formation, while acid neutralisation is a result of the dissolution of carbonate minerals and some of the more reactive fast and intermediate weathering silicate minerals (INAP, 2009; Becker et al., 2015). The resulting drainage waters are termed ARD and are characterised by neutral to low pH, high salinity, and elevated levels of metals and salts (INAP, 2009).

Many factors influence the rate of ARD formation and quality. These include the mineralogy of the waste rock, lixiviant pH, type of oxidant (oxygen or ferric iron) and its concentration, mineral texture and morphology (mineral shape and structure), the extent of weathering of the waste material, the presence and respective amounts of trace elements, as well as the naturally occurring microorganism colonies present on the waste material (Evangelou & Zhang, 1995; Akcil & Koldas, 2006; Parbhakar-Fox et al., 2011). The following sections discuss acid formation and neutralisation, trace element release and the effects of acidophilic microorganisms on acid formation, with a more comprehensive overview of these processes provided in Lottermoser (2010c) and the references therein.

2.1.1 Acid formation

The acidic quality of ARD waters results from the oxidation of sulfur-bearing minerals when they are exposed to the atmosphere. Although this is a natural process, it is exacerbated through ore extraction for mining activities, as this fragments the sulfur-bearing parent material (thereby increasing its surface area) and exposes it to the atmosphere (Alpers et al., 1994). Lapakko (2002) summarised the three main pathways for the formation of acid in mine wastes, namely the oxidation of iron sulfides (mainly pyrite and pyrrhotite), dissolution of alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) and jarosite ($\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$), and the dissolution of soluble sulfates.

Acid formation occurs primarily through the oxidation of pyrite, marcasite and pyrrhotite (Plumlee, 1999). Equations (1) to (5) show the simplified mechanism for pyrite oxidation. Equation (1) represents the initial reaction (direct oxidation of pyrite in the presence of oxygen) followed by the oxidation of ferrous to ferric iron in equation (2), which is thought of as the pyrite oxidation rate-limiting step in the absence of microbes (Singer & Stumm, 1970; Evangelou & Zhang, 1995). Reaction

(3) governs the oxidation process at pH <4.5, where ferric iron becomes the primary oxidising agent. A decrease in the lixiviant pH to between 3 and 4.5 yields reactions (4) and (5) (hydrolysis reactions) with the precipitation of Fe(OH)₃ and FeOOH and the substantial release of acidity (Singer & Stumm, 1970; Nordstrom, 1982; Lottermoser, 2010c).

The acid-producing reaction of pyrrhotite is presented in equation (6) (Evangelou & Zhang, 1995; Lapakko, 2002; Parbhakar-Fox & Lottermoser, 2015).

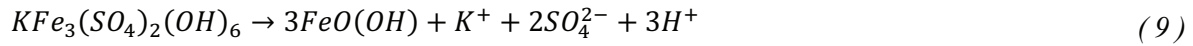
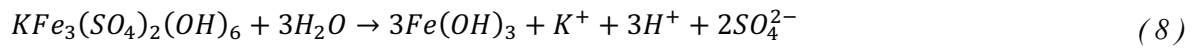
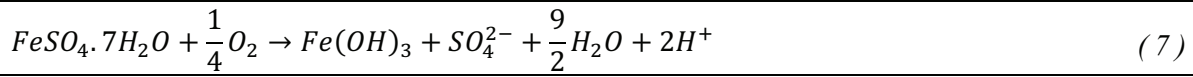
Reactions that are involved in the release of H⁺ ions (and therefore a decrease in pH and subsequent increased concentration of ferric ions in solution) act as a self-catalysing loop that increases the acidity of drainage waters unless one of the reacting components (iron sulfide, ferric iron, oxygen) is removed or the pH raised substantially (Singer & Stumm, 1970). This phenomenon contributes to the reputation of iron sulfides as the chief minerals involved in the formation of ARD. It should be noted that although all sulfide minerals are susceptible to oxidation, their propensity for acid formation and their reaction rates vary (with iron-bearing sulfides having the highest contribution to acidity); however, even in the absence of significant acid release, the release of deleterious elements may be significant (Lottermoser, 2010c).

Table 2-1 Various acid formation reactions (Singer & Stumm, 1970; Evangelou & Zhang, 1995; White et al., 1999; Lapakko, 2002; Parbhakar-Fox & Lottermoser, 2015).

$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$	(1)
$Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O$	(2)
$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$	(3)
$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+$	(4)
$Fe^{3+} + 2H_2O \rightarrow FeOOH_{(s)} + 3H^+$	(5)
$Fe_{(1-x)}S + \left(2 - \frac{1}{2}x\right)O_2 + xH_2O \rightarrow (1-x)Fe^{2+} + SO_4^{2-} + 2xH^+$	(6)

The dissolution of hydrated soluble iron sulfates (melanterite, romerite, copiapite, rozenite and szomolnokite) may also lead to acid formation (Alpers et al., 1994). The latter are generally present as soluble hydrated iron-sulfate minerals occurring as efflorescent salts on weathered pyrite surfaces (also known as “alteration rims”) (Alpers et al., 1994; Blowes et al., 1998). These minerals provide an additional and rapid source of acidity, particularly in very wet environments (for example during rainy season) and play a role in the lag phase of ARD formation (White et al., 1999). Additionally, jarosite formed as a product of the weathering of primary acid forming minerals (pyrite and pyrrhotite) may either react with water or transform to the more stable iron oxide or hydroxide phase, releasing additional acidity (Lapakko, 2002).

Equation (7) shows the equation of the dissolution of the hydrated soluble iron sulfate mineral melanterite. The reactions of jarosite generating acidity are shown in equations (8) and (9) below, with the latter representing the reaction of jarosite to goethite (White et al., 1999).

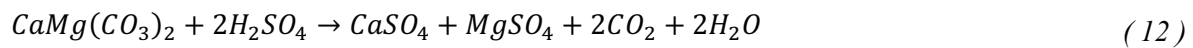


2.1.2 Acid neutralisation

Acid neutralisation may originate from three different sources, namely dissolution of carbonates (primary neutralisation), select silicate minerals, and (oxy)hydroxide minerals, which all provide acid buffering at different pH points during the ARD generation lifetime (Amos et al., 2015). These variations occur due to the stability/solubility of these minerals at different pH conditions and result in a step-wise acid buffering curve (Sherlock et al., 1995).

The primary neutralising minerals are carbonates. These include, in the order of decreasing dissolution rate calcite, dolomite, magnesite and ankerite ($CaCO_3$, $CaMg(CO_3)_2$, $MgCO_3$ and $Ca(Fe,Mg)(CO_3)_2$, respectively) (Lapakko, 2002). Manganese and iron carbonates (rhodochrosite or siderite) however, may not contribute to the net neutralisation potential within the waste material because although they provide initial neutralisation via dissolution, they may re-precipitate following the hydrolysis reactions in equations (2) and (4) to release acid (Skousen et al., 1997). Table 2-2 shows the two pathways for calcite dissolution in equations (10) and (11). The former represents the reaction of calcite with hydrogen ions to form bicarbonate at a pH above 6.5, while the latter represents the reaction of calcite to produce carbonic acid at a pH less than or equal to 6.0 (Blowes & Jambor, 1990). Additionally, the reaction of dolomite with sulfuric acid is shown in equation (12) (Van Tonder et al., 1994).

Table 2-2 Primary neutralising mineral acid neutralisation reactions (adapted from Blowes & Jambor, 1990; Lapakko, 2002 and Van Tonder et al., 1994).



Magnesium- and calcium-bearing end members of fast and intermediate weathering silicate minerals (such as those listed in Table 2-4) and some slow weathering silicates such as chlorite and mica may also offer acid-buffering capacity (Jambor et al., 2007; Becker et al., 2015). Generally speaking, most silicate minerals comprise a limited range of elements, namely Al, Si, O, Ca, Mg, Mn, Fe, Na and K. Thus, the reactions for the weathering of silicates may be grouped into two categories: congruent weathering (equation (13)) and incongruent weathering (equation (14)). The former involves the complete dissolution of the silicate mineral into soluble components, while the latter is more common and proceeds through the formation of another mineral phase (Lottermoser, 2010c). Some examples of

how this happens are shown in the acid neutralising reactions of anorthite (15) and forsterite (16) (Sherlock et al., 1995; Lapakko, 2002).

Table 2-3 Congruent and incongruent dissolution of an arbitrary metal silicate mineral (Lottermoser, 2010c) and the dissolution reactions of plagioclase-feldspar (anorthite) and olivine (forsterite) for acid neutralisation (Lapakko, 2002).

$MeAlSiO_{4(s)} + H_{(aq)}^+ + 3H_2O \rightarrow Me_{(aq)}^{x+} + Al_{(aq)}^{3+} + H_4SiO_{4(aq)} + 3OH_{(aq)}^-$	(13)
$2MeAlSiO_{4(s)} + 2H_{(aq)}^+ + H_2O \rightarrow Me_{(aq)}^{x+} + Al_2Si_2O_5(OH)_4(s)$	(14)
$CaAl_2Si_2O_8 + 2H^+ + H_2O \rightleftharpoons Ca^{2+} + Al_2Si_2O_5(OH)_4$	(15)
$Mg_2SiO_4 + 4H^+ \rightleftharpoons 2Mg^{2+} + H_4SiO_4$	(16)

Although the abovementioned silicate minerals may offer acid neutralisation, the rates of these reactions are many orders of magnitude slower than those of carbonate dissolution, therefore the neutralising capacity from these minerals is long-term or effective for slow acid generation (Sherlock et al., 1995). The relative reactivity and dissolution/weathering potential of various minerals at pH 5 was reported by Kwong, (1993) (after Sverdrup, 1990) and is presented in Table 2-4.

Table 2-4 Neutralising minerals and their reactivity at pH 5 (Sverdrup, 1990; Kwong, 1993; Lawrence & Scheske, 1997) and references therein).

Reactivity at pH 5		Typical minerals
Dissolving	1.00	Carbonates (calcite, aragonite, dolomite, magnesite, brucite)
Fast weathering	0.40	Feldspar (anorthite), olivine (forsterite), pyroxenes (diopside, hedenbergite, jadeite, spodumene, bronzite), wollastonite, garnets, epidotes, nepheline, leucite
Intermediate weathering	0.02	Pyroxenes (enstatite, augite), amphiboles (tremolite, actinolite, hornblende, glaucophane, anthophyllite), serpentine (chrysotile), mica (biotite), chlorite, talc, hypersthene
Slow weathering	0.01	Feldspar (albite, oligoclase, labradorite), clay (kaolinite, vermiculite, montmorillonite)
Very slow weathering	0.01	Feldspar (K-feldspar), mica (muscovite)
Inert	0.004	Rutile, zircon, quartz, sphene

Overall, the relative rates of dissolution of silicate minerals show an inverse relation to the Bowen's reaction series and the order of fractional crystallisation (Bowen, 1922), shown in Figure 2-1.

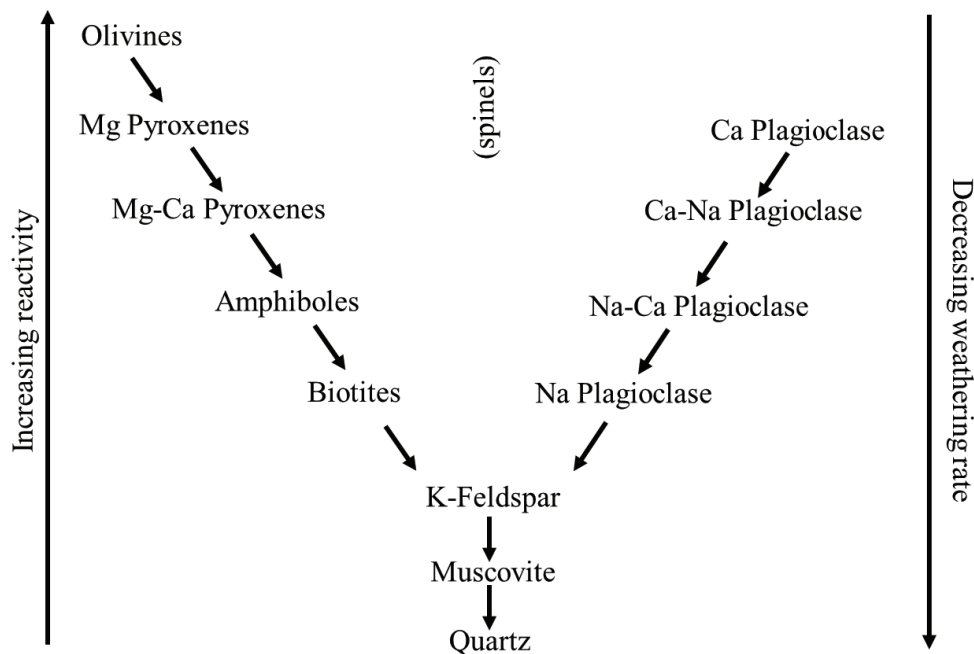


Figure 2-1 Bowen's reaction series for sub-alkaline igneous rocks, adapted from Bowen (1922). Also see Sherlock et al., (1995).

A more comprehensive study of acid neutralisation geochemistry may be found in Sverdrup (1990), Sherlock et al. (1995) and Lottermoser (2010c).

2.1.3 Additional minerals and element release

Problems associated with ARD are not limited to acidification. Acid forming and neutralising reactions release major ionic constituents of rocks such as calcium, sodium, potassium, magnesium, manganese and aluminium. Additionally, although iron-bearing sulfides are the primary contributors to acid formation, other metal sulfides can release transition metals and semi-metals (such as zinc, copper, cobalt, copper, selenium, lead and arsenic) into the environment upon dissolution (Tremblay & Hogan, 2000).

Potentially toxic metals may be present in mine wastes as discrete sulfide minerals or be present as minor constituents in other minerals as a result of solid solution substitution. Discrete metal sulfide minerals may release metals via oxidation (Lapakko, 2002). These metals may remain in the solution or be precipitated as carbonates, oxides or hydroxides. They may also be absorbed onto the surfaces of iron hydroxides (or hydrous ferric oxide) at which point the deleterious metal release and acid formation is delayed (Lapakko, 2002; Parbhakar-Fox et al., 2013).

Sulfide minerals that release deleterious metals upon dissolution include chalcopyrite (CuFeS_2), arsenopyrite (FeAsS), covellite (CuS), galena (PbS) and sphalerite (ZnS). While chalcopyrite and arsenopyrite, in reaction with oxygen, do generate acid in addition to deleterious element release, covellite, galena and sphalerite are non-acid-generating in the presence of oxygen, but do release acid in the presence of ferric iron ions. Reactions (17), (18), (19) and (20) in Table 2-5 represent the oxidation of arsenopyrite, chalcopyrite, galena and sphalerite, respectively, with oxygen as the oxidising

agent. Equation (21) depicts a general equation for acid formation when divalent metals are oxidised by ferric iron (Plumlee, 1999; Lottermoser, 2010c).

Table 2-5 Acid formation and deleterious metal release reactions (Plumlee, 1999). Me = divalent metal.

$FeAsS + \frac{7}{2}O_2 + 6H_2O \rightarrow Fe(OH)_3 + SO_4^{2-} + H_2AsO_4^- + 3H^+$	(17)
$2CuFeS_2 + \frac{17}{2}O_2 + 5H_2O \rightarrow 2Cu^{2+} + 2Fe(OH)_3 + 4SO_4^{2-} + 4H^+$	(18)
$ZnS + 2O_2 \rightarrow Zn^{2+} + SO_4^{2-}$	(19)
$PbS + 2O_2 \rightarrow Pb^{2+} + SO_4^{2-}$	(20)
$2MeS + 4Fe^{3+} + 3O_2 + 2H_2O \rightarrow 2Me^{2+} + 4Fe^{2+} + 2SO_4^{2-} + 4H^+$	(21)

Additional metals and semi-metals that may be released into the environment upon mineral dissolution include nickel and antimony (Ni, Sb), with the concentrations of ions such as arsenic, molybdenum and antimony tending to be elevated when the pH exceeds 7 (Lapakko, 2002; Lottermoser, 2010a). Although the role of non-iron rich sulfides has been discussed to a limited extent herein (as the focus of the current study was on the iron sulfide minerals that were prevalent in the samples used in this study), these minerals are important in ARD formation and metal release and need to be accounted for. The role of these other sulfide minerals has been summarised by Lottermoser (2010c) and the references therein. A comprehensive summary of primary and secondary minerals involved in ARD generation may be found in Nordstrom & Alpers (1999); Plumlee (1999); Morin & Hutt (2001); and Jamieson et al. (2015).

2.1.4 Microbial activity

Whereas sulfur-bearing minerals in mine wastes have the potential to generate acid on their own, the presence of various acidophilic bacteria and archaea can catalyse acid formation through the oxidation of ferrous iron, elemental sulfur and metal sulfides. The extent of pyrite oxidation has been reported to be up to more than 10^6 times greater in the presence of bacteria than without (Hinkle & Koehler, 1947; Singer & Stumm, 1970), although Morin & Hutt (2009) argue that this may be an overestimate. ARD generation is also accelerated through the oxidation of sulfur-bearing ion products of pyrite oxidation (Hesketh et al., 2010). The microbially catalysed oxidation of pyrite is shown schematically in Figure 2-2 below.

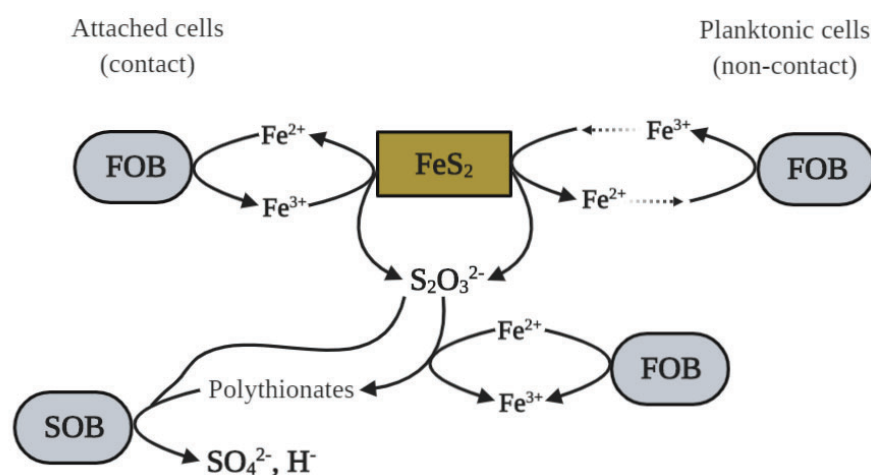


Figure 2-2 The catalysis of the oxidation of pyrite by acidophilic bacteria present in mine sites, with FOB denoting iron-oxidising bacteria and SOB denoting sulfur-oxidising bacteria. Schematic adapted from Bryan (2006).

The microbial leaching of metal sulfides may occur via two different pathways. These are the thiosulfate pathway for acid-insoluble (acid-stable) metal sulfides and the polysulfide pathway for acid-soluble metal sulfides. The thiosulphate pathway activates for acid-insoluble metal sulfides which include minerals like pyrite, molybdenite and tungstenite (WS_2). The release of a thiosulfate molecule, in this case, proceeds after a six-step single electron oxidation process. Only ferrous-oxidising bacteria such as *At. ferrooxidans* and *L. ferrooxidans* can facilitate the leaching of acid-non-soluble metal sulfides, which is very significant at low pH values (around 2) because oxidation of ferrous iron is performed significantly only by these bacteria. In an abiotic medium the release of elemental sulfur may occur (Rohwerder et al., 2003; Rawlings, 2005).

The polysulfide pathway proceeds for sphalerite, galena, arsenopyrite, chalcopyrite and hauerite (MnS_2). This pathway facilitates the removal of electrons via ferric iron and proton attack. The sulfur compounds liberated through this pathway can then be oxidised either abiotically or through the action of *At. ferrooxidans* and *At. thiooxidans*. With the polysulfide pathway, in the absence of acidophilic bacteria it is possible that up to 90% more elemental sulfur may be released (Rohwerder et al., 2003).

The onset of microbial activity has been found to occur at redox potentials above 600mV and pH values below 5 (Bruynesteyn & Hackl, 1982; Hesketh et al., 2010). The latter condition may be correlated with the optimal pH range for microbial activity (Table 2-6).

Table 2-6 illustrates some of the mesophilic microbial species present in waste rock dumps alongside their optimal pH and temperature ranges, as well as the pH and temperature ranges at which these microbial species can survive (Schippers et al., 2014). A more detailed list of microbial species present in mine wastes may be found in Hallberg (2010). The optimal conditions for these bacteria are important to consider, as these conditions, among others, determine the rate of the microbial metabolic activity in waste dumps, and therefore influence the rate of ARD formation. Additionally, from Table 2-6 it may be seen that bacterial activity will begin even at a slightly acidic pH of 5.5 for *At. thiooxidans*, indicating that microbial activity should be considered a contributing parameter even at very slightly acidic conditions.

Table 2-6 Optimal conditions for select mesophilic bacterial species present in waste rock dumps and those used in the UCT biokinetic test developed by Hesketh et al., (2010) (Schippers et al., 2014).

Bacterial species	Optimum pH	pH range	Optimum temperature (°C)	Temperature range (°C)
<i>At. ferrooxidans</i>	2.5	1.3-4.5	30-35	10-37
<i>At. thiooxidans</i>	2.0-3.0	0.5-5.5	28-30	10-37
<i>L. ferrooxidans</i>	1.5-3.0	1.3-4.0	28-30	-
<i>L. ferriphilum</i>	1.3-1.8	-	30-37	Up to 45
<i>At. caldus</i>	2.0-2.5	1.0-3.5	45	32-52
<i>S. benefaciens</i>	1.5	>0.8	38.5	<47

2.2 Tools for ARD characterisation and prediction

Based on the numerous governing factors in ARD formation discussed in section 2.1, it can be seen how the characterisation and prediction of this phenomenon becomes a multidimensional problem. The research into effective ARD characterisation and prediction has been ongoing for decades, with significant strides having been made in the last twenty or so years (provided in Table 2-7 and the Global Acid Rock Drainage Guide (GARD Guide) - The International Network for Acid Prevention (INAP), 2009).

Table 2-7 Resources detailing variation and/or improvements in methodology of geochemical static, kinetic, UCT biokinetic, mineralogical and textural assessments over time.

Test	References
Geochemical static tests	Bucknam (1997); White et al. (1999); Smart et al. (2002)
Kinetic tests	Smart et al. (2002); Lapakko & Antonson (2006); ASTM (2013); Opitz et al. (unpublished)
UCT biokinetic tests	Hesketh et al. (2010); Makaula et al. (2018); Golela et al. (2018)
Mineralogical and textural analyses for ARD assessment	Parbhakar-Fox et al. (2011); Brough et al. (2017); Elghali et al. (2018; 2019)

Although a variety of characterisation and prediction techniques exist, only a select subset are included in the commonly used test suite, with the selected set exhibiting regional variability based on company preference and the local legislature (INAP, 2009; Parbhakar-Fox & Lottermoser, 2015).

The more widespread approach to ARD potential assessment involves the use of geochemical static characterisation tests and kinetic prediction tests. The difference between ARD characterisation and prediction lies within the former providing no indication of the rates of the ARD-forming reactions, yielding a “worst case” scenario of the extremes of acid formation and neutralisation. ARD prediction tests, more commonly tests such as column leach and humidity cell tests, assess the reaction rates associated with ARD generation, providing an estimate of the lag time for the onset of acid formation and the relative weathering rates of the waste material. Neither of these methods, however, address the role of the microbial catalysis effect on acid formation by acidophilic bacteria or for textural and mineralogical complexity. Tests such as the UCT biokinetic test may be used to address the former shortcoming (Hesketh et al., 2010; Becker et al., 2015; Opitz et al., 2016; Makaula et al., 2018).

The following sub-sections discuss only the more commonly used ARD characterisation and prediction tests. A more comprehensive summary of the majority of existing tests may be found in Parbhakar-Fox & Lottermoser (2015) and the references therein.

2.2.1 Geochemical static characterisation tests: acid-base-accounting (ABA) and net acid generation (NAG) tests

Acid-base accounting (ABA) tests are used as part of the screening process for ARD in mine wastes and are performed on finely milled (<75µm top size) material to maximise mineral reactivity. These tests determine the maximum potential of the waste to produce acid, yielding an acid generating potential (AP) and acid neutralising potential (NP). The NP and AP are used interchangeably with acid neutralisation capacity (ANC) and maximum potential acidity (MPA), respectively, with the net acid producing potential (NAPP) being determined as the difference between ANC and MPA, shown by equation (22). The MPA, in turn, requires that the sulfur content of the sample be determined (usually using high temperature combustion methods such as LECO) and is then calculated using equation (23). The frequently quoted shortcoming of this MPA calculation is the assumption that all the sulfur in the sample is pyritic. This assumption ultimately may lead to over- or under-estimation of MPA values due to stoichiometric and dissolution chemistry variation of different sulfur-bearing mineral species. Extensive sulfur speciation may be performed, but this is rarely done because it is a time-consuming and expensive process (Smart et al., 2002). An additional shortcoming of this method is that high pyrite content in some samples may cause an underestimation of the measured NP value using the modified ABA technique due to hydrolysis of ferric iron and the precipitation of ferric hydroxide around pH 4, which may contribute to residual acidity. The ABA tests are also limited with respect to the confidence of the amount of neutralisation potential present in a sample and how these results apply to ARD prediction. These errors in NP measurement arise due to neutralisation by non-carbonate minerals (such as calcium- or magnesium-bearing silicates), as it is uncertain how these minerals would contribute to acid neutralisation in the field (Sobek et al., 1978; Skousen et al., 1997; Paktunc, 1999; Weber et al., 2005).

The ANC test underwent numerous modifications over time (Smith et al., 1974; Sobek et al., 1978; Skousen et al., 1997; Smart et al., 2002). Equations (24) and (25) represent the calculations required to determine the ANC value. The variables in equations (24) and (25) are more commonly determined using the modified Sobek method, which accounts for the re-precipitation of siderite in the sample during the back-titration procedure (Sobek et al., 1978; Skousen et al., 1997).

Table 2-8 Equations used in the determination of static test parameters, where NAPP = net acid producing potential (kg H₂SO₄/t); ANC = acid neutralising capacity (kg H₂SO₄/t equivalent) ; MPA = maximum potential acidity (kg H₂SO₄/t); V_{HCl} = volume of HCl added to the ANC test flask (L); V_{NaOH} = volume of NaOH used to titrate the test flask (L); C = correction constant for molarities of HCl and NaOH used in the test; W_{Sample} = mass of the sample added (g); M_{HCl} = molarity of the HCl solution used for the test. (Smith et al., 1974; Sobek et al., 1978; Skousen et al., 1997; Smart et al., 2002).

$$NAPP = MPA - ANC \quad (22)$$

$$MPA(kgH_2SO_4/t) = (Total \%S) \times 30.6 \quad (23)$$

$$ANC = \frac{[V_{HCl} - (V_{NaOH} \times C)] \times M_{HCl} \times 49}{W_{Sample}} \quad (24)$$

$$C = \frac{V_{HCl \text{ in blank}}}{V_{NaOH \text{ titrated in blank}}} \quad (25)$$

The net acid generation (NAG) test is an additional static characterisation test that is used to give an indication of whether the sample may be classified as potentially acid forming (PAF) based on the NAG pH obtained. Several variations on the NAG test (single-addition NAG, multiple-addition NAG, kinetic NAG) exist and may be performed to obtain a better indication of the NAG potential of a sample, but these are performed rarely, with the single addition NAG test pH more commonly being used for geochemical classification plots such as the one in Figure 2-3. This plot is also commonly used to classify samples as potentially acid-forming (PAF), non-acid forming (NAF) or uncertain (UC) (Paktunc, 1999; Smart et al., 2002).

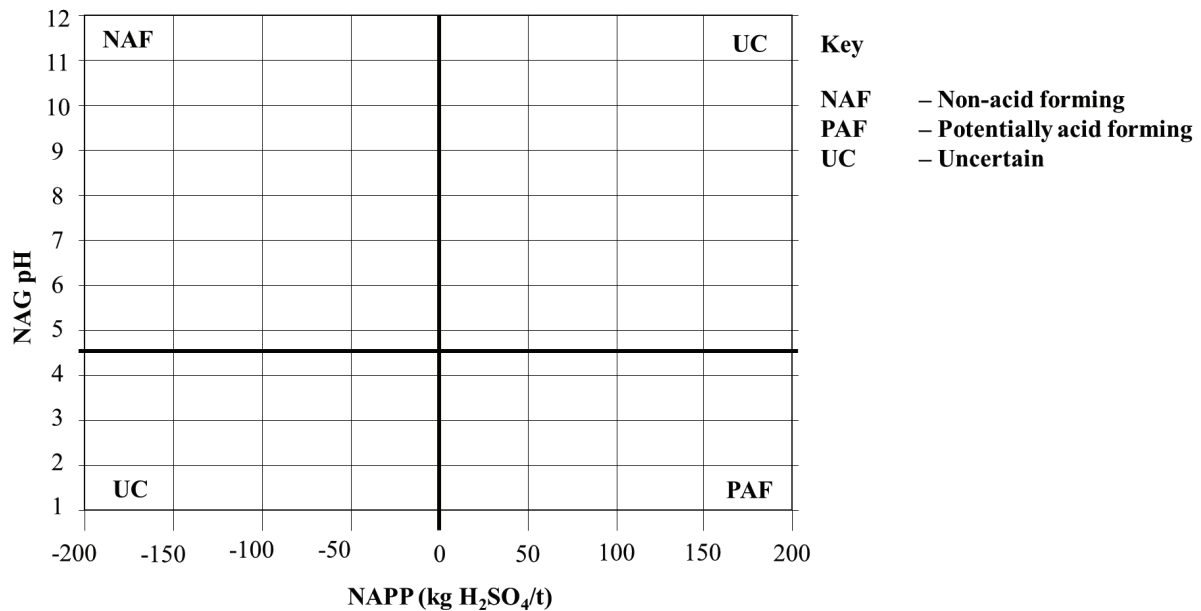


Figure 2-3 Geochemical classification plot, adapted from Smart et al. (2002).

2.2.2 Humidity cell test (HCT)

The humidity cell test (ASTM, 2013) is the more commonly used kinetic test for the prediction of the rates of ARD formation, although column leach tests (outlined by Smart et al. (2002)) are also frequently used. The HCT is performed on samples that have been characterised by geochemical static

tests to be UC or PAF and to obtain data pertaining to the lag time for acid formation (Parbhakar-Fox & Lottermoser, 2015). Data obtained from the HCT has also been applied to the formulation of geochemical models for ARD generation (Maest & Nordstrom, 2017).

The standard HCT procedure subjects a ± 1 kg coarse ($d_{95} = 6.3$ mm) sample to a dry/humid air cycle and a subsequent flush/leach with water (ASTM, 2013). Some main shortcomings of this method are the relatively high associated costs (up to \$5000/20 weeks) and the long and poorly defined timescales (months to years) for the obtaining of meaningful data (ASTM, 2013; Parbhakar-Fox & Lottermoser, 2015; Brough et al., 2017). These time scales can range from a minimum of 20 weeks (Smart et al., 2002), up to 60 weeks (Brough et al., 2013) or even years (INAP, 2009; Lengke et al., 2010; Brough et al., 2017). Additionally, the HCT procedure does not mimic natural climatic conditions present at mine sites, with considerable challenges being faced with upscaling the test results to field scale (Parbhakar-Fox & Lottermoser, 2015).

More recently, HCT work has been combined with textural assessment (see section 2.3) to investigate the controlling parameters in leachate generation and to gain an improved understanding of how HCT results interlink with those of standard static test methods (Brough et al., 2017, 2018); however, textural and mineralogical assessments are not routinely practiced in the context of standard ARD test methodologies due to the assumption that mineralogical/textural changes would be limited over the minimum duration of these tests (Parbhakar-Fox et al., 2013).

2.2.3 UCT biokinetic test

The UCT biokinetic test was developed to address the shortcomings of existing characterisation and prediction tests (lengthy timescales of the HCT and the absence of accounting for microbial effects). Several versions of the UCT biokinetic test have been developed, namely the batch biokinetic test (Hesketh et al., 2010), the draw-and-fill flask biokinetic test (Golela et al., 2018) and the flow-through biokinetic test (Makaula et al., 2018).

The UCT batch biokinetic test, as stated by Hesketh et al., (2010) aims to “provide information on the potential and likelihood of acidification upon microbial colonisation, as well as on the relative kinetics of the acid-consuming and acid-producing reactions”. Its efficacy has also been shown for various waste types, such as hard rock species (Becker et al., 2015; Opitz et al., 2016) and coal (Broadhurst et al., 2013), with the results shown to be meaningful from the perspective of long-term ARD generation and size fractions below 315 μ m. The UCT batch biokinetic test has also been found to enhance the results obtained from conventional geochemical static tests (Broadhurst et al., 2013; Opitz et al., 2016).

The UCT batch biokinetic test method involves the addition of fine particles (sized <150 μ m) to a 250ml Erlenmeyer flask containing an autotrophic basal salt medium at pH 2.0. This mixture is then inoculated with an active mixed culture consisting of *At. ferrooxidans* and *L. ferriphilum*, which are iron-oxidising, as well as *At. caldus* and *Sulfobacillus benefaciens*, which are sulfur-oxidising to a working volume of 150ml. Optimal conditions for these bacteria may be found in Table 2-6, section 2.1.4. The test flask is maintained at a temperature of 37⁰C for 90 days on an orbital shaker set to 150RPM. During this time the pH, redox potential, ferrous and total iron concentration, as well as the microbial population size estimation via viable plate counts may be measured, as required. The frequency of the measurements is

determined based on the variations in the measured parameters with microbial activity (Hesketh et al., 2010).

A limitation of the UCT batch biokinetic test is that it is unable to simulate the field conditions for microbial activity. This is twofold through poor simulation of the natural percolation and contacting channels between lixiviant and waste material, and the batch set-up not being able to account for the washing out of the neutralising minerals, as would happen in the field due to (moisture) precipitation. Work performed by Makaula et al. (2018) aimed to address these shortcomings.

2.3 Mineralogy and texture in the context of ARD

2.3.1 The significance of mineralogy

Mineralogy may be defined as the scientific study of minerals that involves studying their structures, chemical and physical properties, classification, mode of formation and associations. Mineralogy may also refer to the type and abundance of minerals present in a sample/rock (also termed as bulk mineralogy or modal mineralogy). The minerals present in mine wastes may be either primary minerals present originally in the rock, or secondary minerals originating from the dissolution of primary minerals. Section 2.1 demonstrated how the dissolution and precipitation of various minerals is directly responsible for acid formation (2.1.1 and 2.1.3) and neutralisation (2.1.2). Evidently, the type and abundance of the minerals present (mineralogy) in the waste material play a key role in ARD formation and quality.

Research work in heap leaching has shown that mineralogy is important in metal extraction. Some studies have shown the potential of various gangue mineral reactions in an acidic environment to influence leach kinetics, chemistry and ultimately, metal recovery (Chetty, 2018). It may be assumed that the mechanisms dominant in heap leach systems (similar conditions, controls and structure to waste rock heaps) are like those present during ARD formation. Early-stage mineralogical characterisation in heap-leach processes is recommended by Seyedbagheri et al. (2009), with further guidance provided for the use of mineralogy in different stages of ore processing and metal recovery (Chetty, 2018). This thinking could (and should) be applied to ARD characterisation and prediction (Parbhakar-Fox et al., 2011).

The heap leach research findings could be related to waste rock dumps and ARD not only in terms of the drainage chemistry, but also in terms of heap permeability, which may be affected by mineralogy. Silicates such as olivine and chlorite have been found to undergo dissolution to produce reaction products such as silica gel that could decrease percolation efficiency in heaps (Terry, 1983; Tan et al., 2012).

In addition to permeability criteria, it is important to consider the leaching of metal cations from silicate minerals, as this will affect the ARD quality and the potential long-term acid consumption/buffering capacity of the wastes. Biotite mica (with a higher reactivity than muscovite mica) has been shown to consume acid more readily than chlorite at lower pH conditions (Free, 2010), although chlorite was found to be more reactive in acidic systems than silicates such as titanite, epidote, hornblende, muscovite, plagioclase-feldspar and potassium-feldspar (K-feldspar) (Snäll & Liljefors, 2000). Epidote has also been observed to consume acid in long-term (more than 100 days) leaching (Jansen & Taylor,

2003). Clay minerals of the smectite group may also be of significance to ARD formation, as they have the potential to retain acid in their structures (Newman & Brown, 1987; Touret et al., 1990).

Reactions (26) to (30) below represent the dissolution of biotite mica, chlorite, epidote, pyroxene, and amphibole, respectively, in the presence of acid under heap leach conditions (Chetty, 2018). Although these reactions represent the consumption of hydrogen ions, it should be noted that the ferrous iron liberated through the reactions of these minerals could still undergo reaction to ferric iron following equation (2) under the right pH conditions. In this case these reactions, depending on the amount of ferrous iron released, would not necessarily be neutralising.

Table 2-9 Acid-consuming reactions of some common silicate gangue minerals, adapted from Chetty (2018). Minerals down the rows from top to bottom include biotite mica, chlorite, epidote, pyroxene, amphibole.

$(H,K)_2(Mg,Fe)_2Al_2(SiO_4)_3 + 10H^+ \rightleftharpoons 2K^+ + 2Al^{3+} + 3H_4SiO_4 + 2(Fe,Mg)^{2+}$	(26)
$(Fe,Mg)_3[(Si,Al)_2O_5](OH)_4 + 6H^+ \rightleftharpoons 3(Mg,Fe)^{2+} + H_4SiO_4 + Al^{3+} + H_2O$	(27)
$Ca_2Al_2O(Al,Fe)OH[Si_2O_7][SiO_4] + 13H^+ \rightleftharpoons 2Ca^{2+} + 2Al^{3+} + (Al,Fe)^{3+} + 3H_4SiO_4 + H_2O$	(28)
$Ca(Mg,Fe)(SiO_3)_2 + 4H^+ + 2H_2O \rightleftharpoons Ca^{2+} + 2H_4SiO_4 + (Mg,Fe)^{2+}$	(29)
$Ca_2(Mg,Fe)_4Al[Si_7AlO_{22}](OH)_2 + 18H^+ + 4H_2O \rightleftharpoons 2Ca^{2+} + 4(Mg,Fe)^{2+} + 2Al^{3+} + 7H_4SiO_4$	(30)

Based on the variety of acid forming, neutralising and gangue mineral dissolution reactions outlined above and in section 2.1, mineralogy plays a key role in the formation of ARD. It is, however, often overlooked when ARD assessments are performed.

An additional, equally important factor that is often excluded from ARD assessments is mineral texture.

2.3.2 The significance of mineral texture

Mineral texture is a term more often associated with geological studies and has until recently (Parbhakar-Fox et al., 2011; Brough et al., 2017; Elghali et al., 2018) been seldom considered with respect to ARD formation. Texture, although recognised as a critical parameter in the characterisation of ore behaviour, has been primarily a qualitatively (subjectively) assessed parameter, typically utilised in ore deposit exploration rather than processing performance (Pérez-Barnuevo et al., 2013). Based on the various literature describing texture, Jardine et al. (2018) summarised the term as “the geometrical character (grain size and shape) of each constituent in a rock, and the spatial arrangement of these constituents to each other”.

Three general scales of texture classification can be used, namely macro-, meso- and micro-texture. The macro-scale provides information regarding the overall texture without specific information about the location of individual grains and can be considered on the scale of an outcrop. Meso-texture is used to describe the information regarding the grain and phase boundaries, while the micro-texture assesses the individual mineral grains and their orientations (Strotzki, 2010). An alternative way of interpreting meso and micro texture may be that the former can be seen with the naked eye, while the latter would require optical or electron microscopy to discern.

When considering meso and micro texture in the context of ARD forming minerals, the work performed by Parbhakar-Fox et al. (2011) during the development of the acid rock drainage index (ARDI) provides an excellent summary illustration comparison of micro and meso texture to one another. Figure 2-4 is an excerpt from the complete set of illustrations and calculations pertaining to the calculation of the ARDI, while section 2.4.1 and Appendix C.1.1 provide more detail on the calculation of the ARDI and the parameters used.

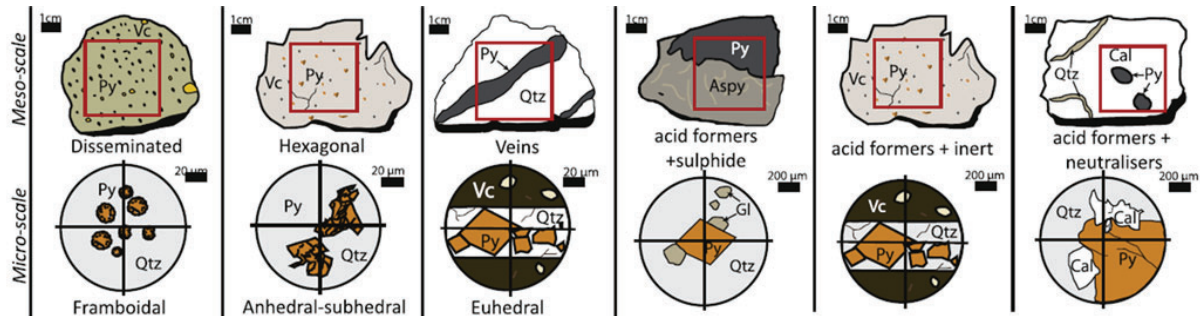


Figure 2-4 Illustration of pyrite (Py) on the meso and micro scales. Qtz = quartz; Aspy = arsenopyrite; Cal = calcite; Vc = volcanic rock. Image sourced from Parbhakar-Fox et al. (2011).

Textural factors that have been previously identified to influence ARD formation include the degree of liberation of minerals of interest (acid forming and neutralising minerals) and their grain size distribution, mineral associations, reactivity and the available reactive surface areas of acid forming and neutralising minerals (Parbhakar-Fox et al., 2011; Brough et al., 2017; Elghali et al., 2018). The necessity for the incorporation of textural and mineralogical analyses into ARD methodologies is shown through several case studies outlined by Brough et al. (2013). These demonstrate that results obtained solely via commonly used ARD assessment techniques may be misinterpreted if inadequate consideration is given for sulfide mineralogy and texture, as well as the neutralisation contributions from various neutralising minerals and their weathering products.

Some of these key parameters are discussed further in section 2.3.3 below.

2.3.3 Textural parameters: particle size, liberation, grain size distribution, sulfide morphology and mineral association

Particle size

A waste rock dump/heap may consist of rocks ranging from very fine, powdered material to enormous boulders, therefore particle size (and the particle size distribution) may be an essential parameter to consider when discussing ARD characterisation, prediction and generation (Erguler & Kalyoncu Erguler, 2015 and the references therein; Elghali et al., 2018).

A particle is a three-dimensional fragment consisting of one or more mineral phases (Figure 2-5). Naturally, the particles within a sample are mostly of irregular size and therefore precise size measurement is unobtainable on a large scale. This has led to the development of an “equivalent diameter” definition to describe the size of irregularly shaped particles in terms of a measurable/obtainable variable. A particle size distribution (PSD) is commonly used to define the continuous size distribution of particles within a certain range and is commonly obtained via sieving or

screening techniques that provide a PSD irrespective of the particle shape. For a more representative PSD the aperture sizes should be chosen in a ratio of $\sqrt{2}$ or $\sqrt[4]{2}$ to one another for a random size or close fractionation, respectively (Mainza & Powell, 2016).

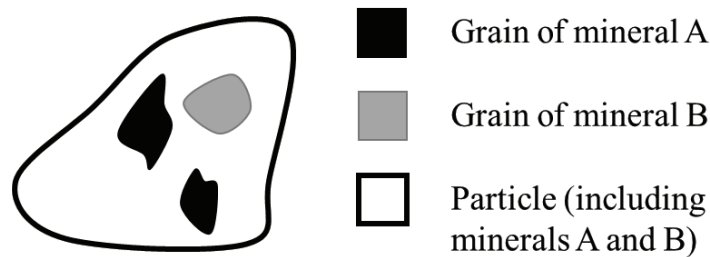


Figure 2-5 Diagram highlighting the difference between particles, minerals and grains.

Heap (bio)leaching process research has at length studied the effects of particle size, as it has been shown to influence metal recovery due to its direct effect on the available/exposed reactive surface area of the leachable minerals (Ghorbani et al. 2011; Fagan-Endres et al., 2017). Based on the similarities of waste rock dumps to leach heaps (highlighted earlier in section 2.3), the effects of particle size in heap leach environments may be related to those in waste rock dumps during ARD formation; however, when considering the translatability of these effects to ARD assessment strategies, this comparison should be taken with a measure of caution, as heap leaching processes generally make use of coarse size fractions (12-25mm top size), as opposed to the size fractions used for common ARD tests (size fractions finer than 75 μ m or finer than 6.3mm) (Ghorbani et al. 2011). The dominating mechanisms, however, may still be investigated.

In leach heaps, rapid initial leaching rates have been observed, with a decreasing rate over time due to the depletion of minerals located closer to the particle surface. Following the leaching of easily accessible surface minerals, mass transfer limitations become an increasingly dominating factor closer to the interior of particles, as the lixiviant must pass deeper into the particle to access leachable minerals. These mass transfer limitation effects are most evident for larger particles, where initial leaching rates are fast due to the preferential oxidation of minerals closer to the surface of the particles, but with leaching rates decreasing over time as surface minerals are depleted. Due to this effect, it is possible that less reactive mineral grains on the surface of the particle will be preferentially leached over the more reactive mineral grains located closer to the particle interior (Ghorbani et al. 2011). Although this reaction process has often been modelled as a shrinking core model, this is not necessarily ideal, with the shrinking core approach likely to be an oversimplification for reactivity of particles larger than 25mm (Robertson, 2017; Chetty, 2018). For finer particle sizes leaching has been found to occur to near completion due to the accessibility/increased liberation of the minerals (surface minerals and fully liberated sulfide grains leached first) (Ghorbani et al. 2011). These effects were also shown for silicate minerals leached in acid medium, where at a fixed particle size of a pure mineral the particle size was shown to have implications for the leaching of metal cations. Finer size fractions showed higher leachability in acid medium than larger size fractions, which was due to the larger collective surface area of fine particles than that of coarser particles to the reactive environment (Snäll & Liljefors, 2000).

These effects may be relevant not only for primary acid forming and neutralising minerals, but also for any non-inert minerals in the waste rock, as their reactivity could have implications for the liberation of previously encapsulated minerals.

Mineral liberation

Liberation is a term which needs to be clearly defined in the context of texture and with respect to ARD assessment. It is the state of a particle consisting of only one phase, with the quality of liberation being fundamentally based on volume (Barbery, 1991). Particles containing multiple minerals can be termed as “unliberated, locked or composite” (Wightman et al., 2016).

Mineral liberation directly affects the available reactive surface area of a mineral to the atmosphere (Evans & Morrison, 2016). This has direct implications for mineral reactivity and has been incorporated in the optimisation of mineral processing circuits (Vizcarra et al., 2010; Johnson, 2016a), specifically to improve recovery in flotation operations (Hunt et al., 2011; Lotter et al., 2011; Tungpalan et al., 2015). In the context of ARD formation, if acid forming and neutralising minerals are treated as the mineral of interest (MoI) or leachable mineral, then their liberation characteristics may yield information about their potential for “recovery”. Minerals present as inclusions in inert materials, such as quartz, will be unavailable for reaction. Alternatively, minerals that are encapsulated in reactive phases may become exposed over time, depending on the dissolution kinetics of the surrounding minerals (Parbhakar-Fox et al., 2011). Additionally, defects in the particle, such as cracks or fractures, have the potential to increase the reactive surface area of the minerals of interest, and consequently, their reactivity (Lapakko, 2002; Ghorbani et al. 2011). Figure 2-6 shows some possible variation in the liberation classification for grains of arbitrary minerals A and B.

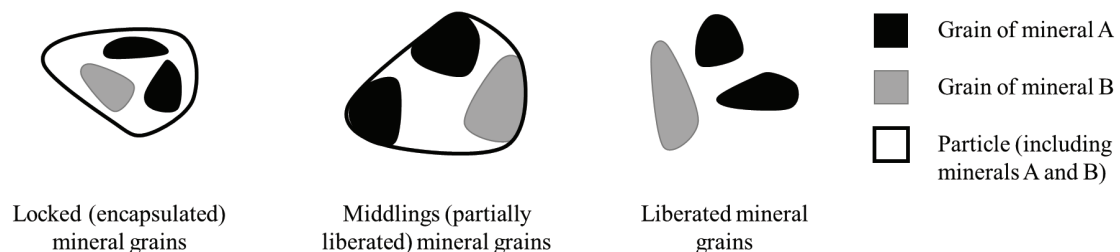


Figure 2-6 Diagrammatic representation of mineral liberation.

When considering the mineral accessibility to oxidative conditions through liberation characteristics it is also important to consider presence of cracks/fractures in the particles as these provide additional access paths to the encapsulated minerals of interest (Lapakko, 2002). The comminution processes applied to the rock (including any blasting that occurs prior to the waste material reaching the dump) will affect the breakage of the material, and therefore the presence and quality of cracks in the particles. This may also be related to the degree of attachment of sulfide minerals (pyrite) to the surrounding rock material, which may ultimately play a role in the propensity of the material for ARD formation (Djordjevic, 2014).

Ghorbani et al. (2011) outlined the importance of the link between mineral grain liberation and the porosity/cracks in the particle. This is highlighted in Figure 2-7 (adapted from Ghorbani et al. (2011)),

where the mineral grain (pyrite, for example) may be variably accessible for particles (a) to (e) during ARD generation. Thus, based on Figure 2-7, it is evident that pyrite locked in another mineral phase in the absence of surface-reaching pores ((d) and (e)) will not be accessible for oxygen or water, and therefore will not likely form ARD, whereas pyrite grains in particles (a) to (c) would be accessible at the surface and via pores, respectively, and therefore be more likely to produce acidic leachate.

Classes	Illustration	Classes	Illustration
(a) Grains exposed to the leach solutions at the surface of particles		(d) Grains from which pores or fissures that do not extend to the particle surface depart	
(b) Grains exposed to the leach solutions via pores or cracks		(e) Grains located inside the particles and not connected to a pore	
(c) Grains which become exposed to the leach solutions only after other grains have reacted			

Figure 2-7 Liberation with consideration for fractures/pores within the particle (adapted from Ghorbani et al., 2011).

When considering liberation as a parameter for ARD it should be noted that the measure of sulfide (or neutralising mineral) liberation becomes more evident as the particle size fraction decreases. At coarser size fractions, other parameters such as mineral association and alteration may play a greater role from the perspective of ARD generation due to the potential of ARD-significant minerals becoming increasingly more locked in other mineral phases. This becomes an important consideration for fine material (static tests and UCT biokinetic test work), where maximum pyrite liberation would increase the efficacy of these tests in determining the “worst case” scenario of ARD formation. Kinetic tests, on the other hand, require a coarser feed, which would predominantly consist of less liberated minerals, with potentially increased liberation in the fines. This was observed by Elghali et al. (2018), where the liberation of Fe-Sulfide and carbonate minerals decreased as the particle size increased.

Grain size distribution

The liberation of a mineral of interest is intricately linked to the grain size distribution (GSD) of that mineral across the sample. The GSD provides the distribution of individual mineral grains within larger particles and throughout the particle size and may be used alongside the PSD to provide an indication of the size fractions in which minerals are likely to become liberated (where the grain size is larger than the particle size) (Johnson, 2016a). The important role of mineral grain size in mineral processing and metal recovery has been shown in several fields of research (Ghorbani et al., 2011; Little et al., 2016; Brough et al., 2017).

The intricate link between the GSD and liberation has been more elegantly illustrated by a liberation spectrum, which provides information on the head grade (overall ore grade) of the MoI and the variation in the grain size distribution across the MoI-bearing particles in the sample (Wightman & Evans, 2014). The liberation spectrum for two hypothetical ores (Ore 1 and Ore 2) is provided in Figure 2-8, where the former has an even GSD across the MoI-bearing particles as indicated by the single distinct gradient corresponding to liberation size L_0 . Ore 2 has two distinct grain distributions (such as individual fine

grains and agglomerated grains/veins) across the MoI-bearing particles, with gradients 1 (corresponding to liberation size 1, $L_{0,1}$) and 2 (corresponding to liberation size 2, $L_{0,2}$). The head grade of the ore may be interpolating from the levelled-off region (region A) to the y-axis.

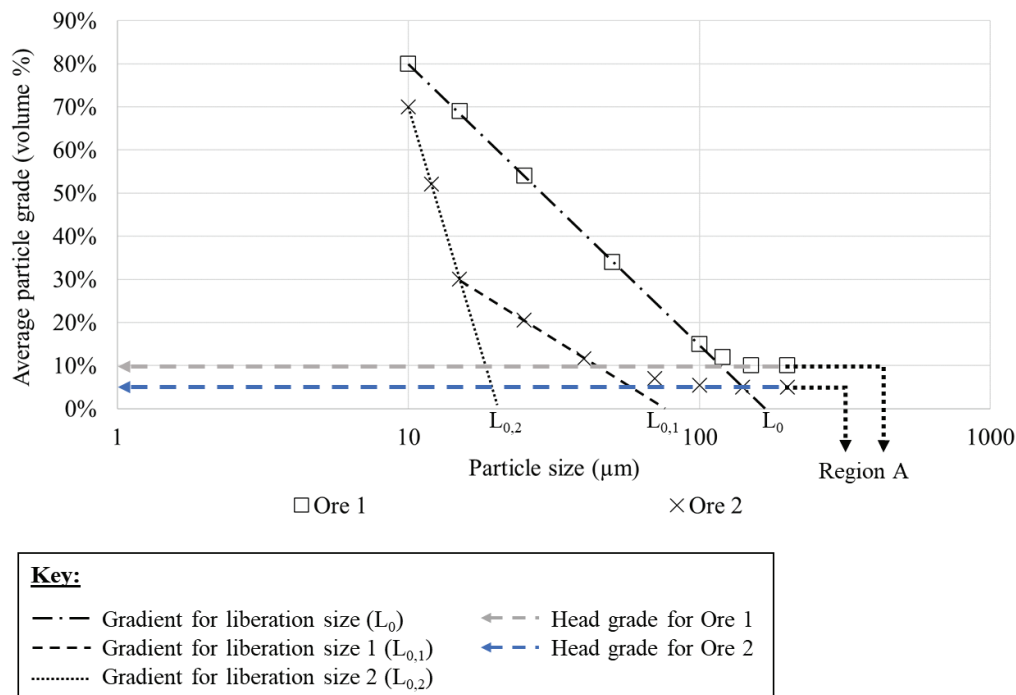


Figure 2-8 Liberation spectrum of a hypothetical mineral of interest, with the diagram created based on Wightman & Evans (2014). L_0 = liberation size of hypothetical Ore 1 that has a gradient corresponding to the x-intercept L_0 ; $L_{0,1}$ = liberation size 1 of hypothetical Ore 2 that has a gradient corresponding to the x-intercept $L_{0,1}$; $L_{0,2}$ = liberation size 2 of hypothetical Ore 2 that has a gradient corresponding to the x-intercept $L_{0,2}$; region A = plateau region of the liberation spectrum, which may be interpolated to the y-axis to obtain the head grade of the ore.

The optimisation of leaching processes requires quantitative knowledge of the mineral grain size distributions. Fine sized particles consisting predominantly of fully liberated grains were shown to have an increased reactivity potential when compared to coarser particles containing encapsulated grains of the mineral of interest (Ghorbani et al., 2011). The relationship between the mineral grain size and liberation was also shown by Brough et al. (2017) in the context of ARD test work where the Fe-Sulfide GSD and liberation characteristics of the waste material were linked to humidity cell test leachate data.

When quantifying grain size it is important to take note of whether the measured value is a “true” indication of the grain size, or whether the measurement used may introduce a stereological bias to the measurement. The latter arises in the case of 2D cross-sectional measurement techniques such as QEMSCAN (Spencer & Sutherland, 2000). In 2D measurements, from which a GSD may be obtained based on the individual grain areas, the grain sizes could be underestimated. This is due to the range of possible grain sizes in the cross section being less than or equal to the true grain size (Sutherland, 2007). For the “true” or unbiased measurement of grain size, a parameter called “phase specific surface area” (or PSSA) may be used, which provides an indication of the mineral grain size irrespective of whether the data obtained was originally one- or two-dimensional. The PSSA is calculated by taking the ratio of the surface area of a mineral to its volume (Sutherland, 2007). The PSSA, however, is a single-value representation of the GSD, which may be used to distinguish ores on the basis of processing

characteristics, but provides little information for pre-process decision-making (Wightman & Evans, 2014).

Sulfide morphology

The particle size, liberation and mineral grain size outlined above all impact mineral dissolution due to the available/exposed reactive surface area. The reactive surface area is also affected by the mineral morphology, as in the case of pyrite, which may have framboidal or euhedral morphology. The former has a surface that resembles that of a raspberry (with framboidal originating from the French word “*framboise*”, meaning raspberry), which leads to framboidal pyrite having larger reactive surface area (and therefore higher reactivity) than the flat-surfaced euhedral pyrite (Weber et al., 2004).

As can be seen in Figure 2-9, euhedral pyrite in image (a) has a visibly flat surface and therefore a comparatively smaller reactive surface area than the framboidal pyrite in image (b), which has a bumpy surface corresponding to the larger surface area. The difference in reactivity of framboidal and euhedral pyrite has been shown in several studies (Boon et al., 1999; Weisener & Weber, 2010).

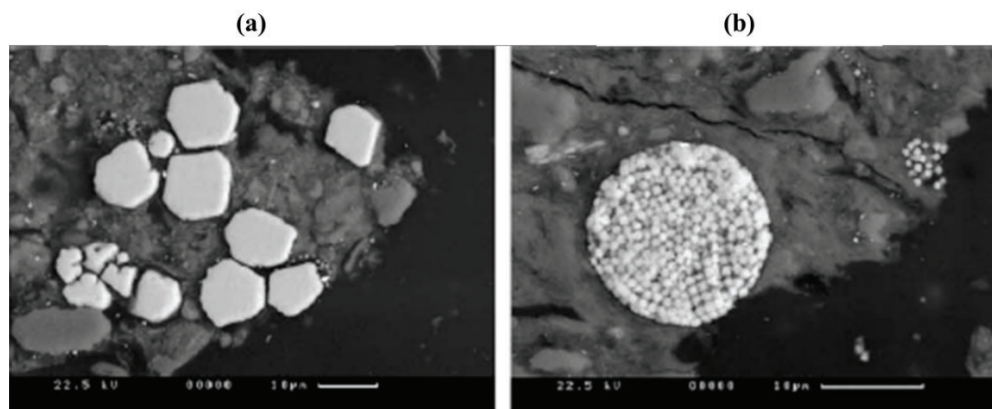


Figure 2-9 SEM images of euhedral (left) and framboidal (right) pyrite (Weber et al., 2004).

Association

In addition to the size of the reactive surface area, the reactivity of minerals may be affected by their proximity to each other, i.e. their association with one another. Mineral association describes the way and extent to which minerals are in contact with one another in a sample. It is important in the context of mineral reactivity, the long-term mineral liberation potential for previously encapsulated minerals and its effects on mineral processing operations (Petruk, 2000; Bonnici, 2012).

The effects of association are particularly evident for sulfide minerals through a phenomenon known as galvanic interaction, which may play a significant role in the rate of sulfide oxidation if sulfide minerals are found associated with one another. Galvanic interaction describes the preferential reactivity of certain sulfide phases over other contacting sulfide phases due to a difference in their standard electrode potentials (INAP, 2009). The electrostatic potentials of pyrite, chalcopyrite, sphalerite, pyrrhotite and galena decrease in this order (Kocabag, 1985) with pyrrhotite, galena and sphalerite exhibiting preferential oxidation over pyrite due to their lower standard electrode potentials. This phenomenon, however, only occurs when these minerals are in contact with one another (INAP, 2009). Through monitoring mineral leaching on a particle-by-particle basis, Ghorbani et al., (2013) showed how this

galvanic effects significantly impacted the leaching of sulfides present in a galvanic cell, with the extent of leaching being dependent on the relationship of the electrostatic potentials between the sulfides. It was found that the association of sphalerite with pyrite decreased over time due to preferential oxidation of sphalerite when it was initially found associated with pyrite.

Mineral association is equally important when considering non-sulfide minerals and their association to sulfide minerals and each other. This has been highlighted by Parbhakar-Fox et al. (2011) in the context of ARD, where sulfide association to sulfide, neutralising and inert minerals was considered as a set of important criteria for estimating the acid formation potential of a sample based on textural characteristics (using the acid rock drainage index, ARDI). Additional resources that have highlighted the importance of mineral association include Petruk (2000); Goodall & Scales (2007); Becker et al. (2008) in the context of mineral recovery from flotation, Arif & Baker (2004) in the context of the mineralogical characterisation of gold ore, and Parbhakar-Fox (2012; Brough et al. (2018); Elghali et al. (2018); Guseva et al. (2018) in the context of ARD test work.

2.4 Methods for mineralogical assessment

It is essential that theoretical knowledge of mineralogy and texture is backed up by reliable quantitative analytical techniques and data processing. Although texture and mineralogy have until recently been sparsely considered in the context of ARD test work, much of the pioneering work in quantitative mineral texture assessment has evolved from mineral processing (comminution and flotation) studies. Additionally, there has been development of custom built analytical technology to quantitatively measure textural parameters such as liberation and grain size distribution from 2D sections (Leigh et al., 1993; Gay, 2004; Wightman & Evans, 2014). Some of the more well-known instruments with this functionality include automated scanning electron microscopy (auto-SEM) systems, such as the QEMSCAN (Quantitative Evaluation of Minerals by Scanning Electron Microscopy), MLA (Mineral Liberation Analyser), TIMA (TESCAN integrated mineral analyser) and Mineralogic instruments (TESCAN, n.d.; ZEISS, n.d.; Thermo Fisher Scientific Electron Microscopy, 2019).

When considering cross-sectional 2D measurements of particles it is essential to consider the implications of stereological bias (the error that arises when computing from 2D to stereological (3D) texture). Stereological bias is smallest for small particles with complex texture and mineralogy and increases with simpler textures and particles containing fewer minerals. Mineral liberation may be under- or over-estimated for materials that are locked, whereas fully liberated minerals will appear liberated in any cross-section. This is highlighted Figure 2-10 (Spencer & Sutherland, 2000), which shows that for particles with complex, fine-grained texture and fully liberated grains the stereological bias is smallest, while for binary particles with limited textural complexity the stereological bias is the largest.

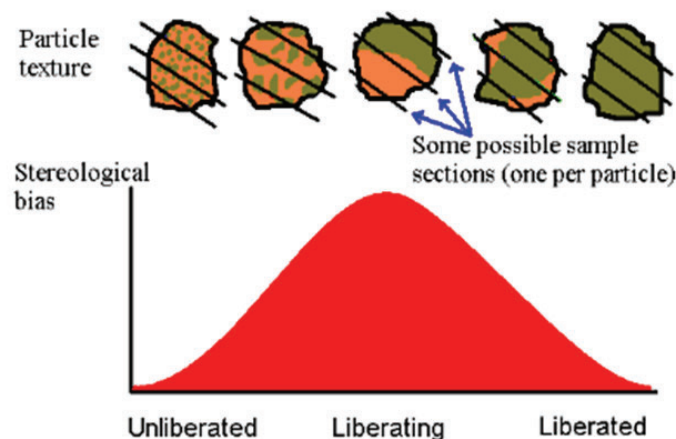


Figure 2-10 Variation of stereological bias with textural complexity of a binary particle. Image sourced from Spencer & Sutherland (2000).

Errors arising due to stereological bias not only affect the measured liberation characteristics but may factor into mineral association calculations. Nonetheless, 2D cross-sections of particles are still very useful for comparative purposes, as it is thought that if one mineral appears more liberated than another in 2D it will also appear more liberated in 3D (Evans & Morrison, 2016); however, it is estimated that particles will appear to be more liberated in 2D than they are in 3D (Spencer & Sutherland, 2000; Lätti & Adair, 2001).

It is possible to adjust mineralogical data computationally to account for the stereological bias, but these adjustment procedures have more extensively been developed for synthetic or simulated binary particles. In practice, the binary model adjustment of the stereological bias is applicable to only very few ores, with others being too texturally and mineralogically complex to allow for binary model approximation. More recently, new steps towards adjusting for the stereological bias in mineralogical measurements have been made (Ueda et al., 2016a; b; c, 2017, 2018a; b) but for the purposes of this study it was considered that more likely, for most ore textures the stereological bias may be considered negligible and bias adjustments could lead to larger errors (Lätti & Adair, 2001). Advances in analytical technology introduce the opportunity to image and quantify mineral texture in three-dimensions using X-ray computed micro tomography (Miller et al., 2009), which may be utilised to eliminate the stereological bias entirely in the future.

In addition to quantitative measurement techniques, some numerical and semi-quantitative techniques have been developed to partially address the absence of the mineralogical component in ARD assessment strategies. These include approaches such as the ARDI and the mineralogical neutralisation potential (Paktunc, 1999; Parbhakar-Fox et al., 2011).

2.4.1 Calculation-based mineralogical assessment (semi-quantitative)

Acid rock drainage index (ARDI)

The ARDI was developed by Parbhakar-Fox (2012) as part of a geochemistry-mineralogy-texture (GMT) approach for screening and characterising the ARD formation potential of mine waste material. This approach was based on the sulfur alteration indices proposed by Blowes & Jambor (1990); Shaw et al. (1998) and Moncur et al. (2009), as well as on texture classification based on the work of Fox et

al. (1997); Lapakko et al. (2006); Smuda et al. (2007); Weber et al. (2004) and Weisener & Weber (2010). The ARDI was designed for the assessment of intact rock texture to predict acid formation.

This method was summarised in Parbhakar-Fox et al. (2011), where the ARDI was proposed as an initial stage classification/screening tool for a large number of samples to select only those that require further testing i.e. sample classified as PAF or uncertain. The ARDI is computed using five textural and mineralogical parameters (parameters A to E) that were selected as having direct control over acid formation. These are sulfide content (A), sulfide alteration (B), sulfide morphology (C), neutraliser content directly surrounding Fe-Sulfide mineral phases (D) and association between acid forming and neutralising minerals (E). Detailed scoring criteria may be viewed in Appendix C.1.1, Appendix Table 16 to Appendix Table 22.

Figure 2-11 provides the visual guide to the interpretation of meso- and micro-scale texture for scoring using the ARDI. For the calculation of the ARDI, meso-scale and micro-scale analyses are recommended to be performed on hand specimen and petrographic thin section samples, respectively. Only Fe-Sulfides are assessed by the ARDI but the presence of other sulfides is recorded for evaluation by parameters D and E. The final ARDI value may be calculated by equations outlined in Figure 2-11. A high ARDI value corresponds to high acid formation potential; low ARDI values indicate low-inert acid formation potential; and a negative value represents acid neutralisation potential. It is important to note that if acid forming sulfides are identified in a sample, for the ARDI to be valid an assessment by all five parameters must be performed. This highlights the importance of considering mineral texture in its entirety, rather than focusing on a single parameter (for example considering only sulfide liberation or only the content of sulfide and neutralising minerals) (Parbhakar-Fox et al., 2011).

A shortcoming of the ARDI lies in its limitation to assess neutralisation potential adequately. This needs to be addressed in further development of this method. The method of ARDI is best suited for mineral deposits with low or negligible contents of carbonates (Parbhakar-Fox et al., 2011).

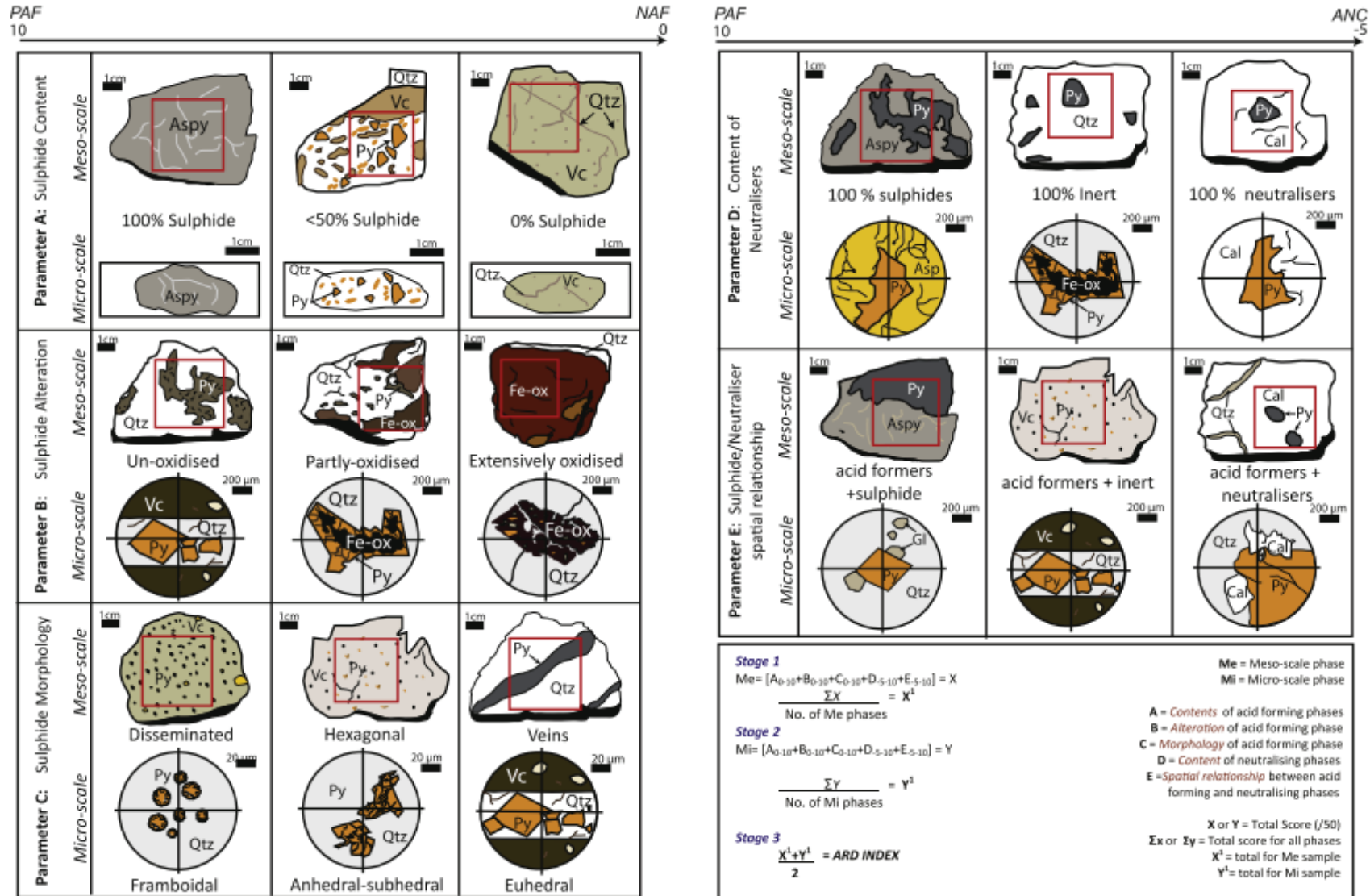


Figure 2-11 ARDI determination. Image sourced from Parbhakar-Fox et al. (2011).

Mineralogical calculation of ANC and MPA

Another computational ARD assessment of solid material is the mineralogical determination of the AF and NP values. A commonly reported methodology is that developed by Paktunc (1999) based on the mineralogical NP calculation initially proposed by Lawrence & Scheske (1997). This approach makes use of the mineralogical composition, abundance and relative reactivity (and stoichiometry with sulfuric acid) of the minerals in the sample. This method was proposed as an alternative or supplementary approach to the ABA tests to address their shortcomings and ascertain the confidence of the characterisation test results (Paktunc, 1999).

Equations (31) and (32) provide the method for calculating the mineralogical NP and AP values. In the NP equation, multiplication factors are used to consider the stoichiometry of the neutralisation of acid produced by pyrite and/or pyrrhotite, as well as to account for the different neutralising mineral reactivities and compositions. The AP is calculated based on sulfide mineralogy and the relative abundance of each sulfide mineral.

Table 2-10 Mineralogical neutralisation (NP, kg H₂SO₄ eq/tonne) and acid generation (AP, kg H₂SO₄ eq/tonne) potentials, where X_i = wt.% of mineral i; c_i = number of non-oxidisable cations in one formula unit of i; n_s = moles of H₂SO₄ from the oxidation of one mole of sulfide mineral s; n_i = moles of mineral I required to consume n_s; ω_i = molecular weight of I in g/mol; k = number of neutralising minerals in the sample; X_s = wt.% of mineral s; n_s = moles of H₂SO₄ from oxidation of one mole of sulfide mineral; w_s = moles of mineral s; m = number of sulfide minerals in the sample (Paktunc, 1999).

$$NP = \sum_{i=1}^k \frac{98 \times 10 \times X_i \times c_i \times n_s}{n_i \times \omega_i} \quad (31)$$

$$AP = \sum_{s=1}^m \frac{98 \times 10 \times X_s \times n_s}{w_s} \quad (32)$$

Other methods referred to for the mineralogical determination of the acid formation and neutralisation potentials are provided in Sobek et al. (1978); Lawrence & Wang (1996) and Plante et al. (2012).

The AP and NP may be corrected for sulfide and carbonate liberation, respectively, by multiplying the AP and NP values by the percentage of respective liberated sulfide or carbonate minerals to adjust for the abundance of unliberated/liberated material (Elghali et al., 2018).

2.4.2 Quantitative mineralogy assessment techniques

A variety of mineralogical and textural analysis techniques exist to quantitatively assess mineral abundance and textural parameters of ores. Analytical techniques such as X-ray diffraction (XRD), X-ray fluorescence (XRF) and automated scanning electron microscopy (auto-SEM), are discussed in greater detail, while those which are important to note but were not used during this study specifically will be mentioned only briefly.

X-ray diffraction (XRD)

XRD is an assessment technique that is used to distinguish different mineral phases from one another based on their differences in crystal structure and mineral chemistry. It is a non-destructive technique

that exposes a finely powdered sample, prepared as a flat and reflective plate, to monochromatic X-rays that are passed through a cathode tube. The interaction of the X-ray with the atoms of the mineral lattice produces constructive interference patterns that yield a diffractogram of the sample. The diffractogram is a plot of X-ray beam angles versus the intensity of the X-ray, and this is interpreted using software to produce information regarding the presence of minerals or mineral phases (de Villiers, 2016). A shortcoming of this technique is the enhancement or suppression of peaks by micas or amphiboles due to their pronounced crystal habit, which affects the accuracy of mineral determination. Furthermore, because this method relies on crystalline mineral diffraction, it is poorly suited for amorphous materials. Additionally, this method has detection limits on certain minerals and trace phases, with difficulty in mineral detection at abundances below 1% (Parbhakar-Fox & Lottermoser, 2015; de Villiers, 2016).

Quantitative information (quantitative XRD or QXRD) may be obtained from regular XRD data using software that allows the fitting of the diffractogram with calculated X-ray patterns of minerals from a database. Methods such as the Rietveld refinement use a non-linear least squares fit to model the diffractogram and reduce the difference between the calculated and measured diffractogram. The Rietveld refinement technique allows for the calculation of the compositions of phases in solid solution and quantification of poorly crystalline iron and aluminium phases (MINTEK, 2011; Bunaciu et al., 2015; Parbhakar-Fox & Lottermoser, 2015; de Villiers, 2016). The goodness of fit of the calculated and measured diffractogram is generally interpreted using error parameters calculated by the software. These include the GOF (goodness of fit) and R_{wp} (R-weighted pattern) values, which provide an indication of peak accountability by the calculated pattern. Although the general aim is to decrease these values as much as possible, it is important to note that their magnitude also depends on the original measurement parameters, therefore focusing on minimising the size of the diffractogram difference curve is a better approach to ensure a good data fit (Toby, 2008; Bunaciu et al., 2015; de Villiers, 2016).

Additional information on the technique and associated errors may be found in Toby (2008) and Bunaciu et al. (2015).

X-ray fluorescence spectrometry (XRF)

XRF is a technique used to measure the abundance of elements in a sample, with an element detection range spanning fluorine to uranium and concentrations between 100% and below 1ppm. The instrument consists of an X-ray source (heated cathode in a vacuum chamber), an energy or wavelength dispersion system (EDS or WDS), a system for the detection and measurement of the emitted signals and a measurement processing system for data output. The method of assessment involves subjecting a sample (prepared as a fusion disc or pressed powder briquette) to a beam of X-rays. Secondary X-rays are produced from the emissions of photons from the sample atoms. In WDS systems the secondary X-rays are directed at an analysing crystal that reflects only specific wavelengths. In EDS systems the secondary X-rays are detected and sorted into electron signals that represent all the energies of the photons released from the sample. The resulting EDS X-ray spectrum is then subjected to software that converts the element peak information into compositions based on the peak intensity (Kable & Becker, 2016).

Automated scanning electron microscopy (SEM)/energy dispersive spectrometry (EDS) systems

Automated SEM/EDS (auto-SEM/EDS) systems developed as an improvement on the manual optical microscopy (see sub-section on additional techniques relevant to ARD characterisation) techniques used for mineralogical and textural analyses. This was necessary to allow improved quantification of the complex mineralogy present in different ore bodies (which was not always possible using traditional optical microscopy), as well as to decrease the time taken for manual mineralogical and textural analyses (Gottlieb et al. 2000; Wightman et al., 2016).

Auto-SEM/EDS systems acquire mineralogical and textural information through a combination of backscatter electron (BSE) brightness and EDS measurements. The method of analysis is similar to EDS XRF, where the concentration of elements in the sample is determined using primary X-rays produced from the contact of a high energy electron beam with the sample; however, backscatter electrons are also detected. The BSE measurement yields a BSE image, which may be used to identify the particles and minerals in the resin-mounted sample and to define mineral boundaries for X-ray acquisition. The data generated includes false-colour images relaying topographical, elemental and structural information about the sample, as well as quantitative data associated with the pixels of these images. These quantitative data may then be formulated to yield modal mineralogy, mineral liberation, association, grain size distribution, and other user-defined parameters (Pownceby & MacRae, 2016; Wightman et al., 2016).

Some auto-SEM/EDS instruments are the mineral liberation analyser (MLA), TESCAN integrated mineral analyser (TIMA), Mineralogic instruments and quantitative evaluation of minerals using scanning electron microscopy (QEMSCAN). Although the other auto-SEM/EDS techniques are also frequently used, this study relies on QEMSCAN measurements as the primary source of textural data.

When considering textural data obtained from systems such as the QEMSCAN, it is important to recognise that data is classified based on a user-defined Species Identification Protocol (SIP), which may be based on a built-in mineral database available in the FEI software package. Additionally, some textural parameters such as mineral liberation may be categorised based on user-defined specification of what constitutes a liberated/unliberated grain. For example, liberated grains may be defined as having 100%, 90-100%, 80-100%, etc. of their area exposed to the surroundings, therefore it should be noted that an (almost) pure grain having even a single perimeter pixel of an alternative mineral in the image section may be classified as unliberated if the user-defined “liberated” category is specified as a 100% of the area exposed to the surroundings. Typically, a slightly lower number (more commonly 80% or 90%) is used to enable more reasonable values for liberation estimates (Gottlieb et al., 2000; Goodall, 2008; Wightman et al., 2016). Similar caution should be exercised when setting up other categorisers in the program.

Additional techniques relevant to ARD characterisation

Optical microscopy is a tool resembling the earlier version of auto-SEM technologies. It involves the observation of prepared sections of specimens using reflected or transmitted light microscopy and makes use of the interaction of plane-polarised light with the sample. The technique allows for the distinction of various mineral species and approximate particle and mineral grain sizes. This tool may

be used to identify the presence of acid forming and neutralising minerals, as well as to provide textural information for qualitative techniques such as the ARDI. Some disadvantages of this method include its subjective nature, the limitation in resolution (in practice around 5µm), as well as the difficulty in statistical validation of the results (Parbhakar-Fox & Lottermoser, 2015; Pirard, 2016).

Additionally, analyses such as electron probe microanalysis (EPMA) for the quantitative assessment of the mineral chemistry of major elements and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for minor and trace element analysis and signatures may be valuable tools in the ARD assessment “toolbox” (Parbhakar-Fox et al., 2011).

X-ray microcomputed tomography (XCT or µCT), although not yet widely practiced, is a technique that may be used to address the issue of stereological bias introduced with 2D textural measurements from SEM techniques. XCT provides a 3D textural analysis of particles alongside a quantitative representation of major mineralogy and mineral distribution, with more recent applications to the structural analysis of ores. The XCT method does however have shortcomings. These include the data-intensive nature of the technique, the information obtained being based on mineral density, which requires manual correlation with the sample mineralogy, the challenges of segmentation of mineral phases, as well as the absence of standardised methods for 3D textural quantification (Guntoro et al., 2019).

2.5 Sampling

Although numerous approaches to ARD assessment have been discussed, it is important to note that waste rock dumps contain millions of tons of material at a range of particle sizes, from large boulders to fine powder. When comparing these magnitudes to those used for laboratory assessment, the issue of sample comparability, in other words representative sampling, arises. It is common for representative sampling to be treated as the responsibility of “someone else” in the analysis chain, introducing the misconception that representative sampling is independent of the final data set. Sampling errors, however, may often be anywhere between 10-1000 times greater than the commonly reported analytical errors associated with the data. This implies that any conclusions drawn from the data sets of incorrectly sampled material will not necessarily represent the parent sample. This, in turn, may result in costly miscalculations in various stages of the mineral processing chain (Carrasco et al., 2004; Petersen et al., 2005).

The above is also true for quantitative textural and mineralogical assessments, where the number of particles (the sample size) required for analysis is an area of concern that is exacerbated as the particle size increases. This is problematic for textural measurements because textural parameters increase in significance with increasing particle size. For texture to be accurately assessed it is necessary, if not to eliminate, then at least to quantify the sampling error, as it provides a direct indication of data representativeness.

Representative sampling follows a theory of sampling (TOS) to quantify the sampling errors. A TOS that has gained considerable popularity in the minerals engineering sector is one developed by Pierre Gy. Pierre Gy’s TOS is based on the assessment of the variability of a population, with focus on quantifying and accounting for the sampling error from all possible sources, rather than assuming that variability in a population will be addressed through randomisation/mixing of the sample (Borgman et

al., 1996). The theory also considers the sample mineralogy, mineral liberation, and the particle size and shape (Jones, 1987).

2.5.1 Sampling error

The error arising from incorrect sampling (or sampling bias) is a non-constant parameter which can only be eliminated qualitatively by following a discrete set of rules. Only once this bias is eliminated can the quantitative approach to sampling theory be applied (Gy, 2004). Samples that do not comply with TOS principles are questionably representative and can be termed only as “specimens”. In principle there is no way to determine sampling errors after the sampling process is complete. To minimise sampling errors, it is necessary to understand how they originate and propagate. In other words, for a sample to not be a specimen, the correct sampling procedure must be followed thoroughly, and all possible sources of error must be documented and quantified. It is, however, physically impossible to eliminate sampling error completely, as this error arises as a function of material heterogeneity (Petersen et al., 2005).

Matter by its very nature is segregational/heterogeneous, whether the individual fragments/particles/molecules belong to solid or fluid material. “Sampling correctness” is achieved when all the groups, fragments or increments of the lot have an equal and non-zero probability of ending up in the sample, while foreign elements have a zero-probability of ending up in the sample (Petersen et al., 2005). Although the TOS requires that material be homogenised/well-mixed, this is not always attainable, especially for severely heterogeneous materials that may be subject to the “nugget” effect. In such cases, incremental/stratified sampling may be used to overcome this segregational property of material (François-Bongarçon, 2004). Techniques such as stratified sampling may be used to increase the sub-sampling accuracy for very coarse material and the stratified sub-samples may then either be separately analysed or recombined in appropriate ratios for a larger bulk sample (Jones, 1987).

“Gy’s formula”

Although the original approach developed by Gy is a formidable mathematical exercise, simplification of the crucial concepts is possible and necessary to enable more practical application (Petersen et al., 2005). Table 2-11 outlines the main constituents to be considered when attempting to calculate the error associated with an analytical result (the Global Estimation Error – GEE). The GEE is the sum of the Total Analytical Error (TAE) (the error most commonly reported by chemists and laboratory technicians) and the Total Sampling Error (TSE). This is shown in equation (33). The TSE, in turn, is made up of all possible contributions to the sampling error, as shown by equation (34). Table 2-11 provides the definitions for these contributors while Figure 2-12 provides a schematic representation of how these errors interlink with one another (Petersen et al., 2005).

Table 2-11 Set of sampling errors outlined by Pierre Gy's theory of sampling (Petersen et al., 2005).

Fundamental Sampling Error (FSE)	Error arising due to the inherent heterogeneity of all materials. This is the minimum practical sampling error in the absence of all others. For a given particle size and density the FSE is a constant value, which can be altered only by fragment size reduction. $FSE = 0$ when the sample is the whole lot, or the lot is strictly homogeneous.
Grouping and Segregation Error (GSE)	Error arising primarily from the sampling procedure. It may be minimised through improvement of sampling techniques but can also be a result of lot heterogeneity. This error depends on the sample mass, whether sample fragments are sampled with an equal probability of selection and whether sampled fragments drag others with them. Composite sampling is a good way to reduce the GSE if segregation is not possible to minimise through mixing.
Incorrect Sampling Error (ISE)	The Increment Delimitation Error (IDE), Increment Preparation Error (IPE) and Increment Extraction Error (IEE) these constitute the Incorrect Sampling Error.
Total Analytical Error (TAE)	This error arises solely from the analysis of results.

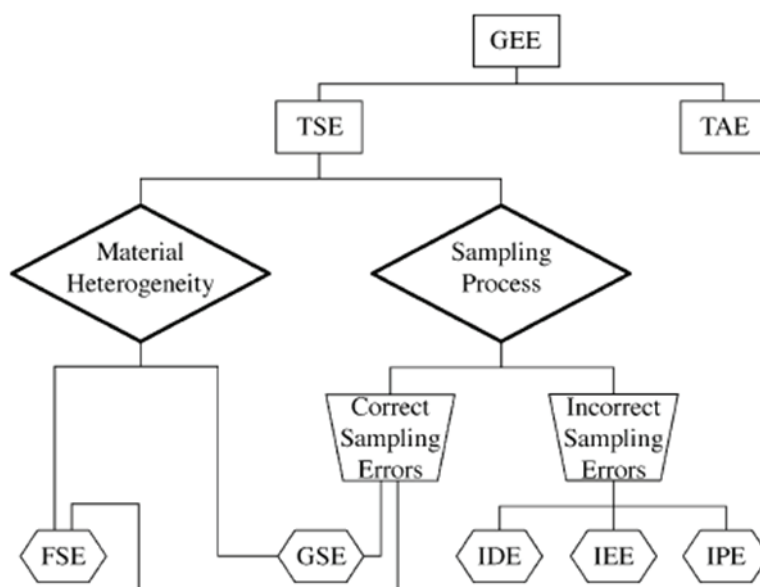


Figure 2-12 The complete scope of errors propagating through an obtained data set, including sampling and analytical errors (Petersen et al., 2005).

Table 2-12 Equations showing the global estimation error and total sampling error (Petersen et al., 2005)

$$GEE = TSE + TAE \quad (33)$$

$$TSE = FSE + GSE + IDE + IPE + IEE \quad (34)$$

The TOS has been simplified to allow for the relative standard deviation of FSE to be calculated, as shown by equation (35) (also termed “Gy’s formula”). This is the so-called “irreducible minimum” of sampling errors that can be obtained for a sub-sample (Minkinen, 2004) when segregation errors and biases are considered negligible/eliminated (François-Bongarçon & Gy, 2002). Thus, when speaking about quantifying sampling error, the error to be calculated is the FSE or variance in FSE. The fundamental error is the relative error in estimating the grade or portion of the desired mineral (Borgman et al., 1996) and is calculated using quantified mineralogical and textural parameters to allow for a tailored sampling approach for differing ores, grades and textures. Several examples of the application the sampling error calculation may be found in Francois-Bongarcon & Gy (2002); Minkinen (2004); Petersen et al. (2005) and Minnitt et al. (2007a; b).

Table 2-13 FSE variance equation and its sub-samples, where σ_r = FSE variance; M_s = sub-sample mass (g); M_L = mass of the lot (g); f = shape factor (generally approximated as 0.5); g = granulometric/grain size distribution factor; c = mineralogical composition factor (sometimes also referred to as the “constitution” factor); l = liberation factor; d_i = d_{95} of the sample (cm); a = decimal proportion of the metal of interest; ρ_m = density of the mineral of interest (g/cm³); ρ_g = density of gangue (g/cm³); C = sampling constant; d_l = liberation size of the mineral of interest (top size at which $\geq 85\%$ of the largest mineral grains have been liberated (cm); b = customisable parameter, which may be conservatively estimated as 1.

$$\sigma_r^2 = \sum_{i=1}^N \left(\frac{1}{M_s} - \frac{1}{M_L} \right) f c g l d_i^3 \quad (35)$$

$$c = \frac{1-a}{a} [(1-a)\rho_m + a\rho_g] \quad (36)$$

$$l = \left(\frac{d_l}{d_i} \right)^b \quad (37)$$

$$C = f c g l \quad (38)$$

Gy’s safety line

It is often necessary to obtain a representative sub-sample without having prior mineralogical information. For such instances, Pierre Gy proposed a “safety line”, which may be represented in the form of a log-log graph that plots the sample mass versus the particle d_{95} (see equation (39) and Figure 2-13). Sub-samples landing in the region above or on the safety line may be considered representative samples, while those landing in the region below the safety line may be considered specimens. This is a useful “rule-of-thumb” approach for finding the minimum sub-sample mass required for a representative sample when a more detailed calculation is not feasible (Gy, 1979).

Table 2-14 Equation for Gy's safety line, where M_S = minimum sample mass (g), d = top size or d_{95} of the particles in the sample (cm) (Gy, 1979; Lotter et al., 2018).

$$M_S = 125000d^3 \quad (39)$$

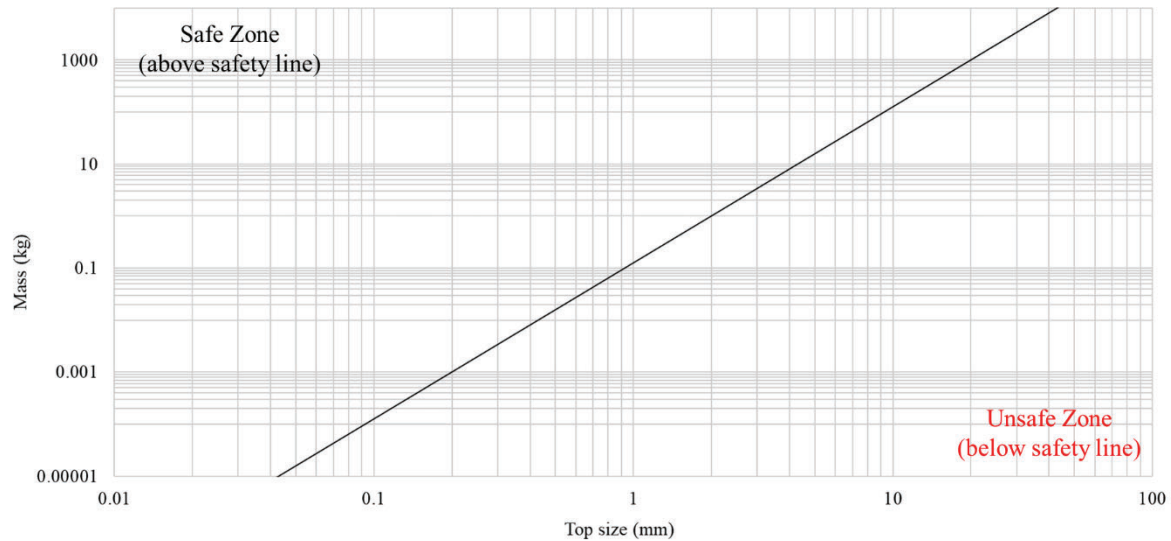


Figure 2-13 Gy's safety line plot showing the minimum sub-sample mass requirements for sub-sample mass (kg) at a particular sub-sample particle top size (mm).

2.5.2 Sampling and acid rock drainage

Sampling is especially important to consider for the purposes of ARD characterisation and prediction, as the particle size scales of lab tests are much smaller than those of the mine waste heaps. Additionally, the sampling of the lot (parent sample) must account for the lot variability. A sample set taken from the site of interest must include examples of all (or as many as possible) types of lithology, geology and alteration present at the site, as well as the respective particle sizes of site material. Ideally, sampling for the purposes of ARD assessment should be performed at the start of mining operations to ensure the development of adequate planning for ARD prevention and mitigation. Although these represent the ideal requirements for sampling, the adequacy of this recommended approach is limited by budget and the difficulty in the selection of samples (Parbhakar-Fox & Lottermoser, 2015; Elghali et al., 2018).

2.6 Statistical analysis in the context of textural measurements

Mineralogical errors

Measurement errors propagate into the reported results quickly due to many factors. Increasing the number of samples or analyses is a widely used method to decrease analytical errors. In the case of textural analyses, however, this may pose a problem due to the number of particles required per measurement, the cost of analyses per representative sample and the sample assessment time. Thus, a trade-off must be made between minimising the error but also the associated time and cost (Evans & Napier-Munn, 2013).

When considering the distribution of minerals within a sample and their abundance, a number of grains may be counted in a microscope field. This process is termed point counting and is described by Van der Plas & Tobi (1965). Point counting methods may account for the errors associated with liberation, grain size distribution or mineralogical data (Evans & Napier-Munn, 2013). For a mineral of interest, Napier-Munn, (2015) indicated that if the grain of the sought mineral is present, this is termed as “success” (a counted point), while its absence is termed as “failure”. The successes and failure proportions can then be defined using a binomial distribution. Equation (40) can be used to obtain the standard deviation of a binomial distribution of the mineral grains of interest (Napier-Munn, 2015).

Table 2-15 Standard deviation of the binomial distribution. σ_{AE} = standard deviation; p = proportion of the mineral of interest; N = the total number of counted points (Evans & Napier-Munn, 2013; Napier-Munn, 2015).

$$\sigma_{AE} = \sqrt{\frac{p(1-p)}{N}} \quad (40)$$

The uncertainty in the number of counted points increases as the magnitude of p decreases, therefore it is often also necessary to ascertain the confidence surrounding the counted points. The confidence around the interval of the proportion of the sought mineral may be calculated using equation (41). From this, the number of measured points N required for a specified error margin can be found using equation (42), where E relative error (Napier-Munn, 2015).

Table 2-16 Confidence intervals for mineralogical data. e = margin of error; p = proportion of the mineral of interest; N = the total number of counted points; E = relative error; z_{α} was defined by Napier-Munn (2015) as “the standard normal deviate for a 2-sided α confidence level” - for a 90% or 95% confidence level z_{α} may be fixed at 1.96 or 1.64, respectively (Napier-Munn, 2015).

$$e = \pm z_{\alpha} \sqrt{\frac{p(1-p)}{N}} \quad (41)$$

$$N = \frac{z_{\alpha}^2(1-p)}{pE^2} \quad (42)$$

The above expressions are only true if np and $n(1-p)$ are more than five, or alternatively, if N is large or the p -value is approximately 0.5. The value of p close to zero or one renders the normal distribution approximation skewed (Napier-Munn, 2015).

For measurements obtained using MLA and QEMSCAN instruments uncertainties arise due to the number of particles assessed being limited to the number of resin blocks prepared, as well as time and cost constraints. In these cases, the confidence intervals on liberation data may be reported to provide an indication of the possible deviation of the data. The equations for the variance of the cumulative liberation yield, Y_C , and the confidence interval associated with this are provided by equations (43) and (44) below (Napier-Munn (2015), with the equation originally being developed in the work of Leigh et al. (1993). For multiple blocks analysed using SEM, a t-test may be used to assess the confidence intervals around mean mineral compositions (Napier-Munn, 2015).

Table 2-17 Confidence intervals and variance for liberation data, where Y_C = the cumulative liberation yield as a proportion, at a composition C; N_0 = number of particles having a composition < C; N_1 = number of particles having a composition of at least C (Leigh et al., 1993; Napier-Munn, 2015).

$Variance(Y_C) \approx 1.25Y_C^2(1 - Y_C)^2 \left[\frac{1}{N_0} + \frac{1}{N_1} \right]$	(43)
$Y_C \pm z_{\alpha}\sqrt{Variance(Y_C)}$	(44)

2.7 Summary of key literature

Acid rock drainage, a natural process caused by the dissolution of sulfur-bearing, carbonate, various silicate, gangue and other minerals, and exacerbated by mining activities, has been identified as a complicated, multi-dimensional problem. The drainage quality is controlled by pH, oxidant type and concentration, temperature, climatic setting, mine waste mineralogy and texture, as well as the complex naturally-occurring microbial consortium present in mine wastes (Evangelou & Zhang, 1995; Nordstrom & Alpers, 1999; Morin & Hutt, 2001; Akcil & Koldas, 2006; INAP, 2009).

The ARD problem does not have a single approach solution. Tests such as geochemical static characterisation tests (Bucknam, 1997; White et al., 1999; Smart et al., 2002) and kinetic tests (Smart et al., 2002; Lapakko & Antonson, 2006; ASTM, 2013) have been more routinely used in ARD characterisation and prediction strategies; however, the practices best at the time have not proven to be absolute long-term best practice. Persisting high ARD-associated remediation costs (Tremblay & Hogan, 2000; Cozzolino et al., 2018) and environmental consequences have shown that ARD characterisation and prediction require certain adjustments, with the incorporation of ARD prediction in the earliest stages of mine development and throughout the lifetime of the mine, as well as after mine closure (Parbhakar-Fox & Lottermoser, 2015). A combinational approach to ARD assessment has been suggested that includes geochemical static, prediction, biokinetic, kinetic, mineralogical and textural analyses by several authors (Morin & Hutt, 2001; Parbhakar-Fox et al., 2011; Brough et al., 2013; Dyantyi et al., 2013; Becker et al., 2015; Parbhakar-Fox & Lottermoser, 2015).

Sections 2.1 and 2.3 demonstrated how the mineralogy of the ARD-generating waste material plays a key role in the resulting drainage quality, with a comprehensive summary of ARD-significant minerals being available in Nordstrom & Alpers, (1999); Plumlee (1999); Morin & Hutt (2001) and Jamieson et al., (2015). Mineral texture has also been identified as a governing factor in ARD formation and quality (Parbhakar-Fox et al., 2011; Brough et al., 2013; Elghali et al., 2018), with textural parameters such as mineral liberation, association, grain size distribution and particle size appearing more commonly as significant factors in the heap leach research space (Ghorbani et al., 2011(a); Ghorbani et al., 2011(b); Ghorbani et al., 2013(a,b); Fagan-Endres et al., 2017) and more recently as an important component of ARD test work (Parbhakar-Fox et al., 2011; Brough et al., 2017; Chetty, 2018; Elghali et al., 2018, 2019).

For mineralogical and textural measurements to be meaningful, quantitative (rather than merely subjective) and be integrative with existing ARD assessment protocols, it is essential that the theoretical knowledge of mineralogy and texture be backed up with reliable quantitative analytical techniques and appropriate data processing. Additionally, the different scales of assessment (micro-scale for characterisation, meso-scale for prediction, field-scale for field conditions) need to be considered when

correlating the various tools in the ARD assessment “toolbox” due to the variation in the information gained on each of those scales. For textural measurements it is essential to take note of stereological bias (Lätti & Adair, 2001; Evans & Morrison, 2016) and the errors arising from an insufficient number of particles/mineral grains of interest being assessed also needs to be taken into account (Evans & Napier-Munn, 2013). Additionally, the challenges of representative sampling need to be addressed, as discrepancies in data sets may occur as a result of poor sampling technique on both a large and small scale (Carrasco et al., 2004; Petersen et al., 2005).

Building a quantitative, statistically sound understanding of textural measurements for ARD-significant minerals and assessing the role of texture in the ARD assessment “toolbox” will ultimately allow for an improved approach to evaluating the ARD potential of mine waste material, and in turn, for the appropriate and adequate development ARD mitigation and prevention strategies.

2.8 Research questions

The key literature reviewed in this chapter highlighted largely an absence of and need for a quantitative, statistically sound approach to the assessment of mineralogy and texture in the context of the existing and widely used ARD characterisation and prediction protocols. Although the influence of mineral texture is recognised, it yet requires a more defined role in the existing ARD assessment strategies. The meaningful and effective integration of quantitative mineralogy and texture into the ARD assessment “toolbox” requires a deeper understanding of the key mineralogical and textural parameters in terms of their influence on ARD formation and the kind of information they yield on different scales of assessment. Additionally, as the representative sampling of material largely depends on the sample mineralogical and textural characteristics, as well as providing a means to compare samples across different scales, the assessment of the sampling error is necessary to consider in the context of textural measurement.

The following key questions arose from the literature reviewed and are aimed at addressing each of the objectives set out in Chapter 1 of this study:

- i. Which textural/mineralogical parameters are to be considered when interpreting the results of ARD characterisation (geochemical static, UCT batch biokinetic) tests (micro-scale) and how do the textural and mineralogical data enhance these results?
- ii. Which textural/mineralogical parameters are to be primarily considered when interpreting the ARD prediction (humidity cell) test results (meso-scale) and how do the textural and mineralogical data enhance these results?
- iii. What is the role of sampling (particularly on the meso-scale) for textural analysis, including consideration for sub-sample mass, number of particles of interest and relevant analytical errors?
- iv. How do texture and mineralogy fit in as “tools” in the ARD assessment “toolbox”?

3 Materials and methods

This chapter addresses the details of the experimental procedures used throughout this study to collect, process and interpret data. All experimental work was carried out in the Department of Chemical Engineering unless otherwise indicated. The descriptions of the procedures outlined in this chapter are represented schematically in Figure 3-1 and include:

- the sampling and sample preparation for characterisation, prediction and mineralogical test work;
- static tests, UCT batch biokinetic test, kinetic test methods;
- other chemical methods of analyses such as LECO Sulfur, XRF and QXRD;
- mineralogical and textural data collection and processing using QEMSCAN, and
- statistical assessment.

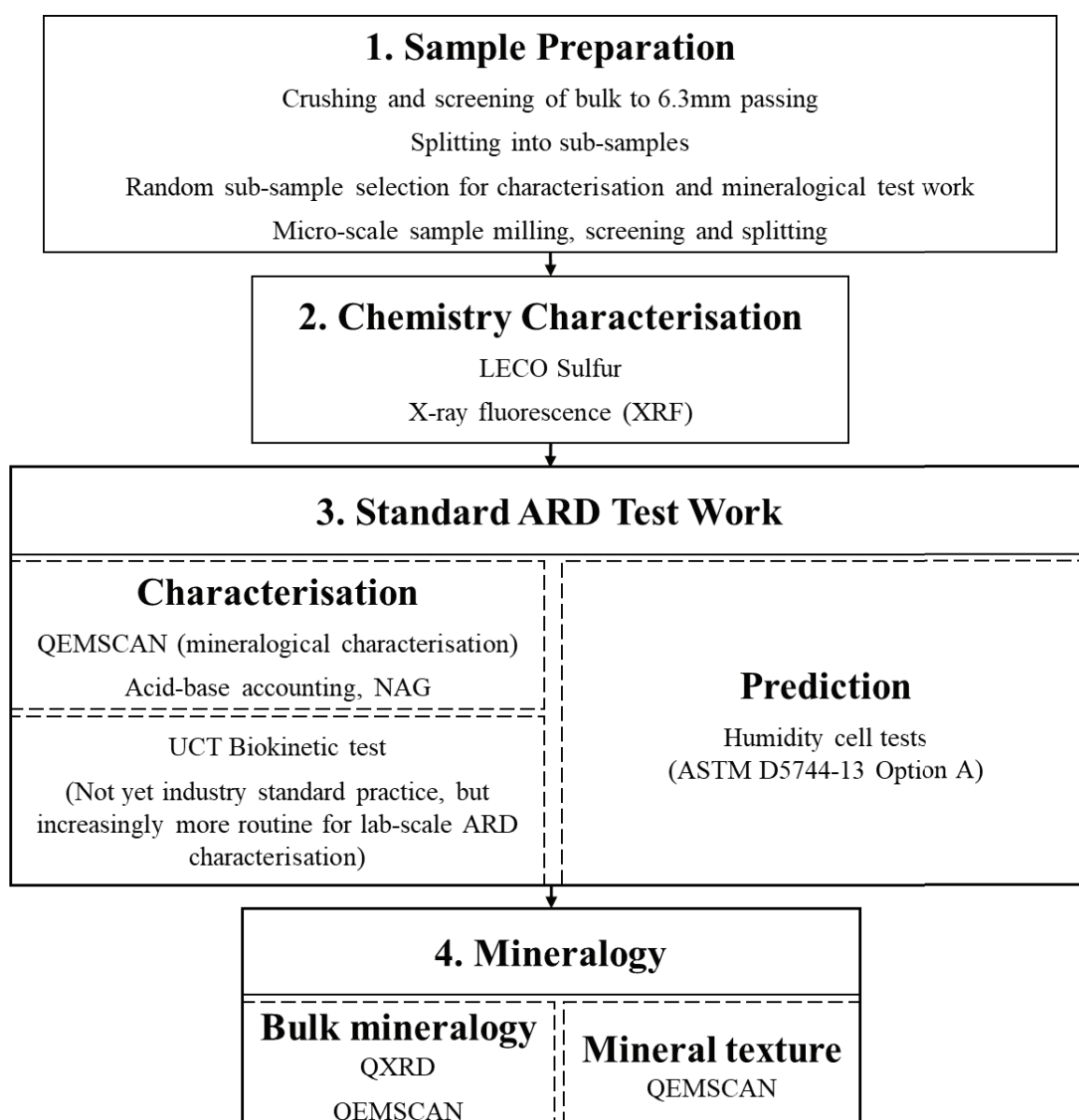


Figure 3-1 Schematic diagram depicting the experimental work carried out during the current study.

3.1 Physical characterisation

3.1.1 Samples

The samples used in this study were taken from an Archaean mesothermal greenstone belt deposit in Africa. Greenstone belts, although located in various parts of the world, have similar characteristics, which are assumed to be linked to similar mineralisation processes. Goldfarb et al. (2001) indicated that Archaean gold deposits are some of the most important sources of gold globally, with the characteristics of most Archaean gold deposits being linked to those of orogenic gold deposits. The minerals present in the gold waste rock from this greenstone belt were outlined by Opitz et al. (2016) and included primarily pyrite, pyrrhotite, calcite, chlorite, iron oxides/hydroxides (such as magnetite), ferro-actinolite (amphibole), plagioclase-feldspar (albite), K-feldspar, biotite (Fe-mica) and quartz.

The samples were labelled A, B, C and D. Samples A and B were sub-sampled from an existing waste rock pile and were received and prepared for humidity cell test work outside of this study (Opitz, unpublished; Opitz et al., 2016). Samples C and D were received as crushed drill core samples from an exploration site and were prepared for analysis during this study. All samples were minimally oxidised. Details of the four samples are presented in Table 3-1 below.

Table 3-1 Summary of sample details for samples A, B, C and D.

Sample	Received as	Top size	Mass received	Sampling method
A	Sub-sampled waste rock	>6.3mm	130kg	Bulk splitting
B	Sub-sampled waste rock	>6.3mm	116kg	Stratified sampling (sub-sampling of size fractions)
C	Crushed drill core	>6.3mm	17kg	Stratified sampling (sub-sampling of size fractions)
D	Crushed drill core	>6.3mm	36kg	Stratified sampling (sub-sampling of size fractions)

3.1.2 Sample preparation

The sample preparation for samples A, B, C and D is summarised in Figure 3-2, which provides an overview of all the steps taken during the sampling process. Some types of data collected during these steps, such as raw data for the particle size distribution (PSD), is also included. Figure 3-2 also indicates stages in the sampling process where samples were selected for chemical, characterisation, prediction and mineralogical analyses and some important points for TOS calculations.

A sample was crushed to obtain the size reduction required for kinetic tests (<6.3mm). The screen closest to this size had an aperture size of 6700µm, therefore this was used as the top size fraction. The sample was then screened to obtain a bulk particle size distribution (PSD) with size fractions of +6700µm (90% passing), +5600/-6700µm, +4000/-5600µm, +2000/-4000µm and +0/-2000µm, with subsequent splitting of the +0/-2000µm fraction into +1000/-2000µm, +850/-1000µm, +600/-850µm, +425/-600µm, +150/-425µm and +0/-150µm. Material larger than 150µm was dry-screened, while material smaller than 150µm was wet-screened to minimise particle agglomeration.

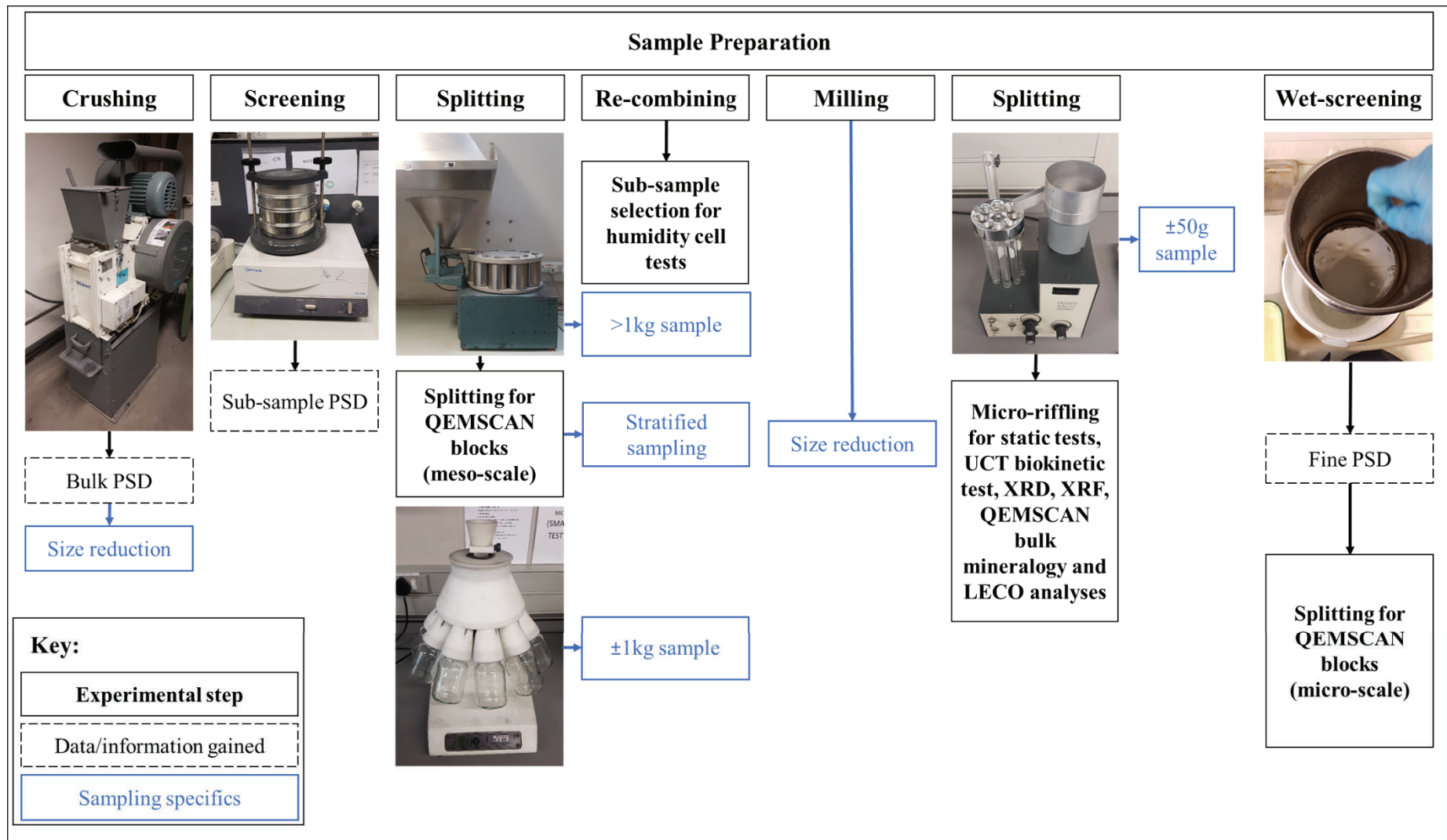


Figure 3-2 Schematic of the sample preparation performed on samples A, B, C and D, indicating sampling steps in the process for different experiments (solid outline boxes) and the types of data collected throughout the process (dotted outline boxes). Blue outlined boxes highlight sampling specifics that are important to consider for theory of sampling (TOS) calculations.

Following the screening process, stratified sampling was utilised for each of the size fractions to obtain ± 1 kg sub-samples for kinetic tests and QEMSCAN coarse block preparation (see section 3.3.2), with the samples used for kinetic tests having the size fractions re-combined and homogenised prior to placement in the column. A sub-sample was then randomly selected for milling to pass through a 150 μ m aperture size and split for XRF, QXRD, geochemical static tests (ABA and single-addition NAG), UCT batch biokinetic tests, and wet-screening for fine PSD (size fractions: +150 μ m, +106/-150 μ m, +75/-106 μ m, +53/-75 μ m, +25/-53 μ m and +0/-25 μ m) and sized QEMSCAN block preparation. Masses were recorded appropriately for the sub-samples obtained at each sub-sampling stage. Samples A, B, C and D had a d_{80} of 75 μ m, and were used for both static and UCT batch biokinetic tests at this particle size distribution without further pulverising for consistency between the two sets of tests.

The sampling process was followed consistently for all samples A, B, C and D; however, samples A and B were received as ± 3 kg sub-samples crushed to pass a 6700 μ m screen. Fine material (<150 μ m) for these two samples was also obtained pre-milled. These sub-samples were subjected to the sub-sampling procedure corresponding to the points in the sampling process relevant to the sizes they were received at. Samples C and D were obtained as crushed drill core at a size larger than 6.3mm and then subjected to the complete sampling procedure beginning at the crushing stage.

In this study, feed material used for geochemical static and UCT batch biokinetic tests was collectively referred to as SCT (standard characterisation test) or micro-scale feed material. Humidity cell test feed material was referred to as HCT or meso-scale feed material.

3.2 Chemical characterisation

3.2.1 Total sulfur analysis

The sulfur content of the samples was analysed using a high temperature combustion method with infrared spectrophotometry on a LECO S632 analyser operated at the UCT by the analytical laboratory team. Triplicate 13.54% S calibration standards were used during analyses, with calibration checks being performed prior to analysis, mid-analysis and post-analysis. The mass per standard was approximately 0.34g.

Total sulfur analyses were performed in triplicate on micro-scale feed material and pulverised sub-samples of meso-scale size fractions corresponding to those used for QEMSCAN analyses. The masses of the test samples used were between 0.15g and 0.21g per LECO S analysis. Replicate sub-samples of size fractions above 1000 μ m were prepared from individually pulverised sub-samples of the relevant size fraction. This was used to provide an indication of the variation between replicate samples of the largest meso-scale size fractions.

3.2.2 X-ray fluorescence (XRF) spectrometry

The sample chemistry was assessed using XRF spectrometry analysis in the Department of Geological Sciences at the UCT. All samples were prepared as pressed pellets due to the sulfur content exceeding 1% in all samples, with higher sulfur contents being damaging to the platinum crucibles used for fusion disc preparation.

Samples were submitted for analyses at a particle size passing 150 μ m. This material was pulverised to a fine powder. 6g of this pulverised sample was mixed with a few drops of Mowiol binder liquid to bind the powder together in a mould. This mixture then had a 10000kg mass applied to it by a hydraulic cold press and die.

The XRF analyses were performed on unsized samples A, B, C and D. Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, Cr and Ni were assessed as oxide %, while Zn, Cu, Ni, Mo, Nb, Zr, Y, Sr, Rb, U, Th, Pb, Co, Mn, Cr, V, F, Cl and Sc were assessed as individual element concentrations. Although sulfur (S) was also reported by XRF data, the LECO S values for sulfur content were used, as the XRF analyses yielded oxide sulfur data, which for samples with high sulfur content is less accurate. A Panalytical Axios WDS XRF spectrometer with a rhodium end-window X-ray tube was used. Natural rock standards were used to calibrate the instrument, with calibration accounting for background correction, absorption correction and line overlap correction.

The XRF data were used to validate the mineralogical results obtained using QEMSCAN and QXRD.

3.2.3 Acid-base accounting

The acid generation potential of the samples was determined using the acid neutralisation capacity (ANC), maximum potential acidity (MPA) and net acid generation (NAG) tests to obtain a geochemical static test characterisation plot. The static tests required a sample mass of ± 2 g for the ANC test and ± 2.5 g for the NAG test. The milled bulk sub-samples were split into 10g portions, which allowed five and four replicates for the ANC and NAG tests, respectively.

Maximum potential acidity (MPA)

The maximum potential acidity was determined from equation (45) below, which assumes that a sample having a sulfur content of 1% will generate 30.6kg H₂SO₄ per ton of the sample material (Smart et al., 2002). The sulfur content (Total wt. % S) was determined using LECO S.

Equations (46) and (47) provide liberation-corrected values of the MPA and NP, based on the approach by Brough et al. (2018) and Elghali et al. (2018), who computed the MPA and NP to take into account only the liberated proportion of sulfide and carbonate material in the sample based on the total sulfur and total inorganic carbon contents, respectively. This resulted in the MPA and NP values decreasing due to the locked proportion of material not being available for reaction. For this study the liberation correction was performed only for the acid-forming minerals, as the total sulfur content was available, while the total inorganic carbon assay was not performed during this study. The L_S represents the wt. % of the liberated Fe-Sulfide minerals. This value for the samples was obtained from QEMSCAN. The middlings minerals were considered as available to the oxidative environment.

For description of locked, middlings and liberated mineral categories please refer to the details in section 3.3.2.

Table 3-2 Maximum potential acidity (MPA) calculation (Smart et al., 2002), liberation-corrected MPA and NP for sulfide and primary neutralising (dissolving) minerals. L_S = wt. % of liberated Fe-Sulfides in the sample; L_N = wt. % of liberated carbonate (dissolving) minerals in the sample. $S\%_{LECO}$ = total sulfur content based on the LECO S method; $TIC\%$ = carbon content from total inorganic carbon assay.

$$MPA(kgH_2SO_4/t) = (Total \%S) \times 30.6 \quad (45)$$

$$MPA_{liberation\ corrected}(kgH_2SO_4/t) = S\%_{LECO} * (L_S) * 30.6 \quad (46)$$

$$NP_{liberation\ corrected}(kgH_2SO_4/t) = TIC\% * (L_N) * 81.6 \quad (47)$$

Acid neutralisation capacity (ANC) test

The ANC test used for this study was the modified Sobek method, which accounts for the re-precipitation of siderite in the sample during the back-titration procedure (Sobek et al., 1978; Skousen et al., 1997; Weber et al., 2004). $\pm 2g$ of finely milled sample was allowed to react in a 250mL Erlenmeyer flask with hydrochloric acid (HCl) of a concentration corresponding to that recommended by the fizz rating test (Table 3-3). The fizz rating was determined by adding 25% HCl solution dropwise to some finely milled sample and assessing “magnitude” of the effervescence. The fizz ratings used during this study may be found in Appendix A.1.1, Appendix Table 13.

Table 3-3 Fizz rating determination for geochemical static tests. Adapted from Smart et al. (2002).

Reaction	Fizz rating	Molarity of HCl (mol/L)	Volume of HCl (mL)	Molarity of NaOH (mol/L)
No reaction	0	0.5	4	0.1
Slight reaction	1	0.5	8	0.1
Moderate reaction	2	0.5	20	0.5
Strong reaction	3	0.5	40	0.5
Very strong reaction	4	1.0	40	0.5
Carbonate (limestone)	5	1.0	60	0.5

The mixture was heated until complete reaction with the HCl, with de-ionised water being added throughout the heating process to prevent the experiment from boiling dry. Following cooling the solutions were filtered and the filtrate pH was measured. The solutions were then back-titrated to pH 4.5 against standardised NaOH with molarity corresponding to the appropriate fizz rating. 30% H_2O_2 was added in 15-minute intervals to the solutions after repeated back-titration to pH 4.5. Following the stabilisation of the pH at 4.5, the back-titration and H_2O_2 addition procedures were repeated up to pH 7. Following pH stabilisation at pH 7, the process was repeated every 24h for the total duration of 72h. The experiments were conducted as five replicates. Blank experiments containing no sample were set up in triplicate and subjected to the same conditions and experimental steps as the test samples.

The ANC was determined based on the amounts and molarity of the HCl and NaOH used in the sample-containing and blank experiments (equations (48) and (49) in Table 3-4). The NAPP was determined as the difference between the ANC and MPA, as shown by equation (50). A liberation-corrected NAPP was determined in addition to the regular MPA by multiplying the MPA value by the percentage of liberated sulfide material in the sample as per equation (46).

Table 3-4 Equations used in the determination of static test parameters, where NAPP = net acid producing potential (kg H₂SO₄/t); ANC = acid neutralising capacity (kg H₂SO₄/t equivalent) ; MPA = maximum potential acidity (kg H₂SO₄/t); V_{HCl} = volume of HCl added to the ANC test flask (L); V_{NaOH} = volume of NaOH used to titrate the test flask (L); C = correction constant for molarities of HCl and NaOH used in the test; W_{Sample} = mass of the sample added (g) (Smith et al., 1974; Sobek et al., 1978; Skousen et al., 1997; Smart et al., 2002).

$$ANC = \frac{[V_{HCl} - (V_{NaOH} \times C)] \times 49}{W_{Sample}} \quad (48)$$

$$C = \frac{V_{HCl \text{ in blank}}}{V_{NaOH \text{ titrated in blank}}} \quad (49)$$

$$NAPP = MPA - ANC \quad (50)$$

Single-addition net acid generation (NAG) test

The single-addition NAG test involved the addition of 15% H₂O₂ to ±2.5g of sample in a 500mL Erlenmeyer flask to rapidly oxidise the sulfide minerals in the sample. The solution was left in a fume cupboard to react overnight, followed by the heating of the sample for 2h the following day to ensure the complete reaction of sulfide minerals and the decomposition of H₂O₂. The sample was then back-titrated to pH 4.5 and pH 7, with the molarity and volume of NaOH used during the titration process being recorded for the calculation of the NAG potential using equation (51). Figure 3-3 shows various steps during the static testing process.

Table 3-5 Net acid generation potential calculation based on the volume and molarity of NaOH used during the back-titration procedure to pH 4.5 and pH 7. Adapted from Miller et al. (1997), where NAG = net acid generation; V_{NaOH} = volume of NaOH used during back titration (L); M_{NaOH} = molarity of NaOH used during the back-titration (mol/L); W_{Sample} = mass of the sample added (g).

$$NAG = \frac{49 \times V_{HCl} \times M_{NaOH}}{W_{Sample}} \quad (51)$$

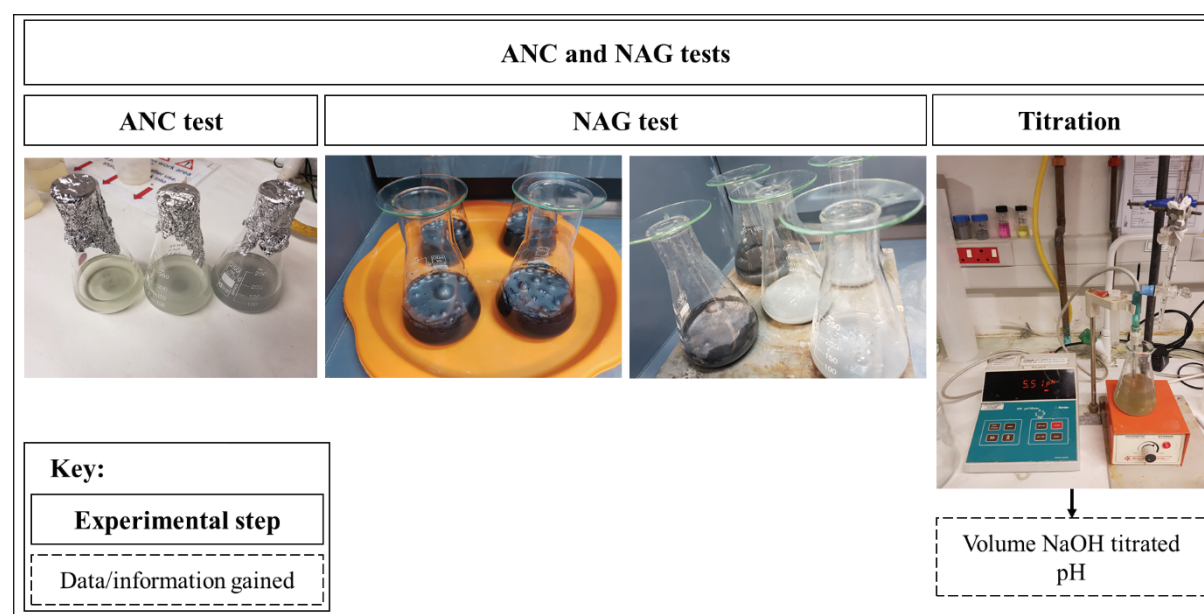


Figure 3-3 Various steps during the static testing process, with images from left to right illustrating the post-heating ANC test, NAG test flasks before 24h reaction time, NAG test flasks during boiling and titration set-up for back-titration for both ANC and NAG tests.

3.2.4 UCT batch biokinetic test

The UCT batch biokinetic test was performed on samples C and D, with test results for samples A and B being referenced from Opitz et al. (2016) and the test procedure for samples C and D being followed as described by Hesketh et al. (2010) and Opitz et al. (2016).

±7.5g of sample was combined with autotrophic basal salts (ABS) medium at pH 2 in a 250mL Erlenmeyer flask. The total working volume was 150mL. The biotic flasks were inoculated with a volume of a mixed mesophilic microbial culture corresponding to 10^9 cells (1.29mL), determined prior to inoculation through cell counts under a microscope. The mixed mesophilic culture contained an approximately 50:50 mixture of iron and sulfur oxidising bacteria and archaea.

The flasks were maintained on an orbital shaker for 90 days at 150 revolutions per minute (RPM) and 37°C, with sampling performed for the first 30 days daily, and the frequency decreasing over the next 60 days, depending on the changes (or lack thereof) in the measured parameters. The sampling routine involved the removal of flasks from the shaker, the measurement of the pH and redox potential, followed by the recording of the mass of the flask and subsequent topping up with de-ionised water to the starting mass. The flasks were then sampled for the measurements of ferrous and total iron concentrations (via spectrophotometric assay) and sulfate concentrations (via turbidimetric assay). Please refer to Appendix A.2 for detailed methodology.

Table 3-6 provides the UCT batch biokinetic test experimental matrix for samples C and D. Triplicate experiments were run for uninoculated pH-controlled samples, uninoculated non-pH-controlled, inoculated pH-controlled and inoculated non-pH-controlled flasks. An additional control experiment was run using sample A (inoculated non-pH-controlled) to allow for comparison between the sample C and D test data with those of samples A and B in Opitz et al. (2016). A biotic control was run to monitor the growth of the culture over the duration of the test. The UCT batch biokinetic test was thus performed on a total of 27 flasks, with an extra flask for the biotic control. Figure 3-4 shows the biokinetic test flasks on the shaker.

Table 3-6 Sample set matrix for the UCT batch biokinetic test. pH was controlled to 2 for pH-controlled flasks.

Sample	Un-inoculated pH-controlled	Un-inoculated not pH- controlled	Inoculated pH- controlled	Inoculated not pH-controlled
A	None	None	None	3
C	3	3	3	3
D	3	3	3	3

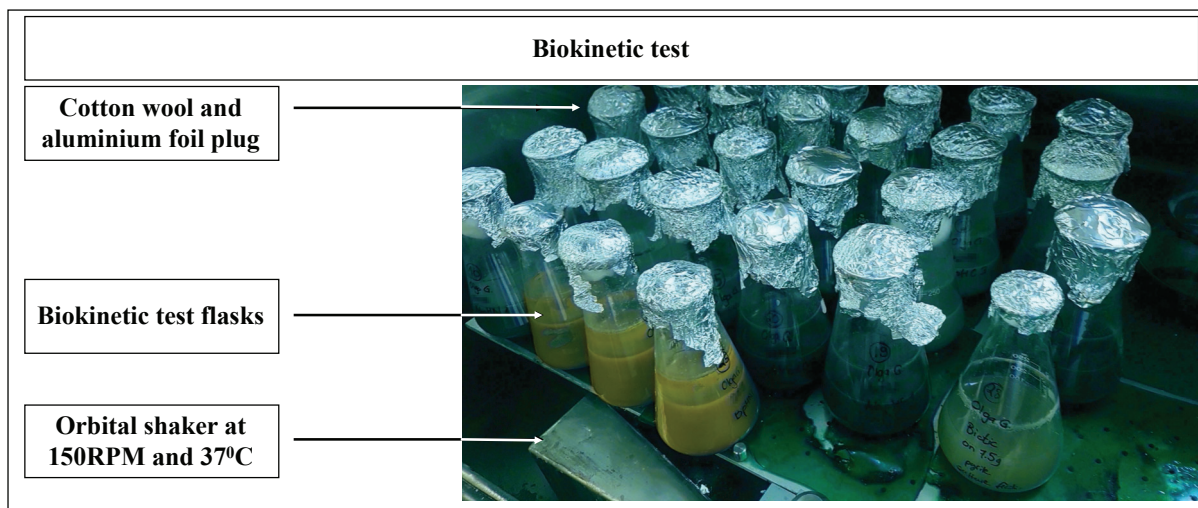


Figure 3-4 UCT batch biokinetic test orbital shaker set-up at 150RPM and 37°C.

3.2.5 Humidity cell test

The humidity cell test experiment was set up and performed according to the procedure outlined in ASTM (2013) Option A for samples C and D. This involved the placement of $\pm 1\text{kg}$ of well-mixed (homogenised) meso-scale feed material into a prepared pre-washed, dried and filter-paper-lined humidity cell test column. The volume of solution used for the flood leach was 500mL. Following the addition of the leach solution, the sample remained in contact with the solution for two hours, after which the columns were drained and the leachate collected. The mass of the flood leach solution was recorded before addition to each column and after collection of the leachate into collection bottles. This solution was then filtered, and samples were taken for pH, redox potential, electrical conductivity, ferrous iron, total iron and sulfate analyses. Following the flood leach, the columns were allowed to rest for 24h. A three-day dry air cycle was then started, followed by a three-day humid air cycle. The air was supplied to the column at a flow rate of $\pm 5\text{L}/\text{min}$. The humidity for the three-day humid air cycle was controlled using a hot plate at a constant temperature of approximately 30°C. A schematic of the humidity cell test experiment is presented in Figure 3-5. Duplicate water-fed humidity cells were run for samples C and D.

In addition to the standard water-fed procedure, acid-fed humidity cell tests were run. These were performed according to similar experiments performed for samples A and B by Opitz et al (unpublished) to deplete any neutralisation potential in the columns and to provide an indication of the acid formation potential in an acidic environment. The pH of the acid feed was made up using deionised water that was acidified to pH 2 using 98% H_2SO_4 (added drop-wise under pH control). Duplicate acid-fed humidity cells were run for sample D and triplicate acid-fed cells were run for sample C.

Samples of both the water and acid column feed solution were analysed for the same parameters as the column leach samples to provide an indication of deviations from the feed that occurred as a result of weathering of the waste material.

Humidity cell tests were not disassembled after the completion of this project and are still in progress.

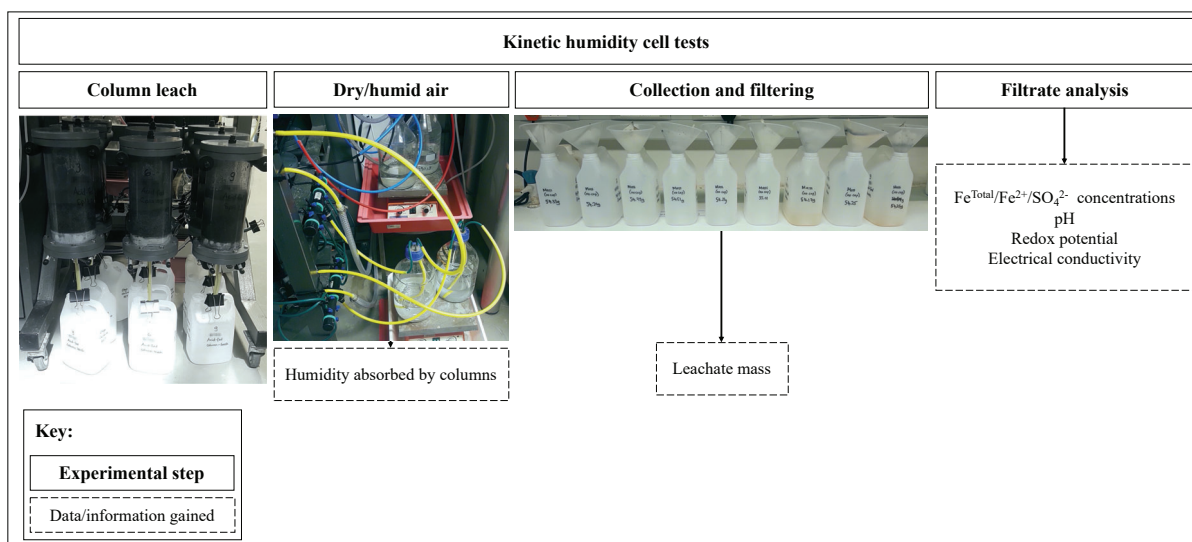


Figure 3-5 Humidity cell test experimental schematic showing the columns, dry and humid air supply, and the filtration step after leachate collection.

3.3 Mineralogical characterisation

3.3.1 QXRD

Sub-samples from the milled material were split into $\pm 4\text{g}$ samples and micronised with ethanol for 10 minutes using a McCrone microniser, to ensure a PSD of below $10\mu\text{m}$. Powder X-ray diffraction (XRD) analysis was performed using a Bruker D8 Advance diffractometer with a LynxEye detector and $\text{CoK}\alpha$ radiation. The scan time was 1.5 hours with a counting time of 1 second per step and a step size of 0.02 degrees. The quantitative phase analysis performed using Rietveld refinement in the Topas 4.1 software (Bruker AXS GmbH, 2008).

3.3.2 QEMSCAN

Size fractions and block types

QEMSCAN analyses were undertaken on polished resin-mounted samples that were prepared as three different types, depending on the particle size and the size range of the size fraction. The three types of sample blocks used in this study were:

- standard 30mm diameter circular blocks, further named as “standard blocks” or abbreviated as SS;
- vertical section 30mm diameter blocks, further named as “vertical section blocks” or abbreviated VS and,
- rough rock holder 70x70mm square blocks, further named as “rough rock blocks” or abbreviated as RR.

SS blocks were prepared for samples in which particle settling effects due to density variation were not expected. VS blocks were prepared to account for these settling effects and were used for broadly delineated size fractions. RR blocks were prepared without consideration for particle settling effects, as

it was assumed that because all particles were relatively large, they would settle evenly within the block. Figure 3-6 provides images of the RR, VS, and SS sample blocks used in this study.

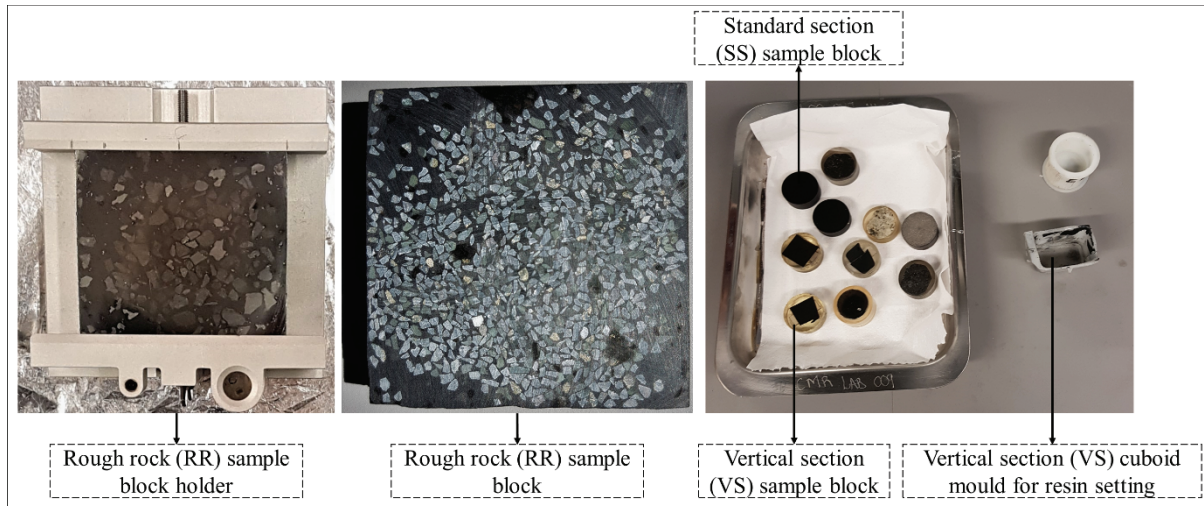


Figure 3-6 Sample blocks for QEMSCAN analysis (not to scale) and the holder used for the RR sample blocks.

The size fractions used for QEMSCAN analyses were $-6700/+2000\mu\text{m}$, $-2000/+1000\mu\text{m}$, $-1000/+425\mu\text{m}$, $-425/+150\mu\text{m}$ and $-150/+0\mu\text{m}$ for all meso-scale feed analyses; $-150/+75\mu\text{m}$, $-75/+53\mu\text{m}$, $-53/+25\mu\text{m}$ and $-25/+0\mu\text{m}$ for micro-scale feed analyses of samples A and B; and an unsized $-150/+0\mu\text{m}$ micro-scale feed sample for each of samples C and D. Table 3-7 and Table 3-8 provide details of the size fractions analysed on the micro- and meso-scale with indication of blocks prepared as SS, VS or RR blocks.

Table 3-7 Number of sample blocks prepared for QEMSCAN analyses from sized and bulk characterisation test feed material. All samples were prepared as standard section (SS) or vertical section (VS) 30mm diameter blocks.

Sample	$-150/+0\mu\text{m}$ (unsized sample)	$-150/+75\mu\text{m}$	$-75/+53\mu\text{m}$	$-53/+25\mu\text{m}$	$-25/+0\mu\text{m}$
A	2 (VS)	2 (SS)	2 (SS)	2 (SS)	2 (VS)
B	2 (VS)	2 (SS)	2 (SS)	2 (SS)	2 (VS)
C	2 (VS)	-	-	-	-
D	2 (VS)	-	-	-	-

Table 3-8 Number of sample blocks prepared for QEMSCAN analyses from sized and bulk HCT feed material. Fractions above $1000\mu\text{m}$ were prepared as rough-rock (RR) blocks of $70\times 70\text{mm}$, while blocks of size fractions smaller than $1000\mu\text{m}$ were prepared as 30mm diameter vertical section (VS) blocks.

Sample	$-6700/+2000$	$-2000/+1000$	$-1000/+425$	$-425/+150$	$-150/+0$
A	3 (RR)	3 (RR)	8 (VS)	6 (VS)	2 (VS)
B	3 (RR)	2 (RR)	8 (VS)	8 (VS)	2 (VS)
C	2 (RR)	1 (RR)	3 (VS)	2 (VS)	2 (VS)
D	2 (RR)	1 (RR)	3 (VS)	2 (VS)	2 (VS)

Sample block preparation

For the sample block preparation, each size fraction was split into sub-samples of appropriate mass. For RR blocks this was between 15g and 30g, for VS blocks this was $\pm 4\text{g}$ and for SS blocks this was $\pm 2\text{g}$. The sample was mixed with graphite powder in a graphite to sample ratio of 1:1 and 2:1 for the VS and

SS blocks, respectively. Following graphite addition, the sample was screened through a mesh corresponding to the d_{100} top size of the fraction (i.e. 75 μ m mesh for -75/+53 μ m size fraction) to ensure that no larger particles were present. The graphite-sample mixture was then placed into a pre-washed, pre-dried and labelled cylindrical QEMSCAN block mould coated with non-stick spray. This was done for the finer size fractions, with the finest fractions requiring pre-rolling with a metal rod to remove potential agglomerates which could otherwise interfere with the quality of the QEMSCAN data.

The graphite-sample mixture was then combined with an Epoxy resin and hardener mixture. The Epoxy resin was warmed and liquefied in an oven beforehand. The ratio of hardener to resin was taken as 1:5. All components were then combined in the block mould and mixed thoroughly to ensure consistency of the mixture. The filled moulds were then placed into a Struers CitoVac vacuum chamber to remove any bubbles from inside the mixture. Following the vacuum chamber, the samples were placed inside an Advanced Laboratory Solutions Technomat Kulzer Heraeus Curer overnight to set the resin-hardener-sample mixture. For VS blocks the resin-sample mixture was prepared in a cuboid mould (see Figure 3-6) and cut into slices after hardening. These slices were then set into the same type of block mould used for SS blocks.

Following curing, the SS and VS blocks were removed from the mould and polished using a Struers TegraPol-11 machine in several stages (from coarsest to finest) using grinding pads and polishing fluid. RR blocks were hand-polished.

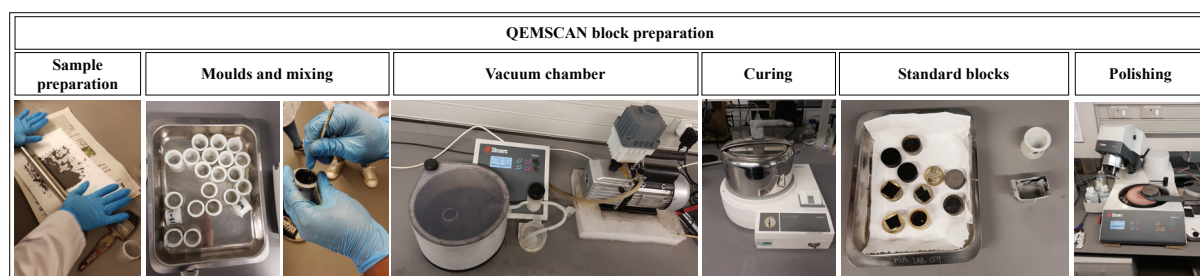


Figure 3-7 QEMSCAN block preparation procedure.

After preparation the sample blocks were placed in a vacuum cupboard until analysis. Prior to analysis the blocks were carbon-coated in a Quorum Q150TE coater to disperse the electron charge.

The procedural steps for the preparation of QEMSCAN sample blocks has been summarised in detail by Donskoi et al. (2018) and references therein, with consideration for some of the potential shortcomings associated with block preparation and the ways in which some of these shortcomings may be rectified.

QEMSCAN measurement settings

Mineral textural data were obtained using a FEG QEMSCAN 650F instrument with two Bruker XFlash 6130 detectors at the UCT. The measurement settings were at 25 kV, with beam current optimisation at 10nA on the Faraday Cup. The chamber vacuum for measurement was taken to be anything below 1×10^{-4} Pa. For backscatter detector calibration, the BSE values were related to each other at a $z=13.0$ mm height. The calibration standards used were gold (BSE 232), copper (BSE 130) and quartz (BSE 42).

The measurement settings used were customised for each sample and size fraction. RR blocks were initially analysed using the field image (FI) setting due to their large size; however, particle mineralogical analysis (PMA) measurements with included field boundaries worked equally well. The PMA with included boundary measurement was used for all sample blocks that had relatively large particles but required all the particles in the block to be measured. A summary of the measurement settings for the meso-scale and micro-scale size fractions is provided in Table 3-9 and Table 3-10, respectively.

Prior to fixing the measurement settings, 100µm fields were run at varying point spacings for the larger size fractions to establish the image quality versus cost per sample trade-off, as the samples were fine-grained, which conventionally would require a smaller point spacing. The running time per block increased as the point spacing decreased. After trial runs of the 100µm fields, however, it was found that reducing the point spacing (improving the resolution) did not drastically improve the elemental composition data for the samples, therefore the measurements were optimised for cost per sample, rather than for image quality.

Table 3-9 Measurement settings used during QEMSCAN operation for meso-scale sample size fractions. FI = field image; PMA = particle mineralogical analysis.

Measurement parameter	-6700/+2000	-2000/+1000	-1000/+425	-425/+150	-150/+0
Point spacing	15µm	15µm	10µm	5µm	3µm
Field size	2500	2500	1500	1500	1500
Measurement type	FI, PMA (include boundary)	FI, PMA (include boundary)	FI, PMA (include boundary)	FI, PMA (exclude boundary)	PMA (exclude boundary)

Table 3-10 Measurement settings used during QEMSCAN operation for micro-scale sample size fractions. PMA = particle mineralogical analysis.

Measurement parameter	Bulk	-150/+75	-75/+53	-53/+25	-25/+0
Point spacing	5µm	5µm	3µm	2µm	2µm
Field size	1500	1500	1000	750	300
Measurement type	PMA (exclude boundary)	PMA (exclude boundary)	PMA (exclude boundary)	PMA (exclude boundary)	PMA (exclude boundary)

QEMSCAN data processing

The processing of the QEMSCAN data was performed using the FEI iDiscover software, which converted the BSE and X-ray information into pixels containing elemental information. These were then classified as minerals through a specially developed, user defined ‘species identification protocol’ (SIP) file. The SIP file parameters (such as enabled elements and peak overlap correction specifications) were adjusted based on “live” viewing of the BSE image in the microscope chamber.

The SIP list entries were grouped into a primary list, wherein the mineral entries were assigned a composition and density to allow for the translation of the 2D cross-section images into volume and mass data. The composition was based either on the general “textbook” mineral composition or on EPMA data for selected minerals (amphibole, chlorite, feldspar, mica) from the work of Opitz

(unpublished). The primary entries were then further grouped into two user defined secondary mineral lists, namely the 'Minerals List' (Table 3-11) and 'Reactivity Groupings List' (Table 3-12), which were used for obtaining sample bulk mineralogy and textural data, respectively. The bulk mineralogy was determined using the 'Minerals List', which grouped the primary list entries into mineral groups without differentiation between the solid solution series end members that had different reactivity potential and/or acid buffering capacity (i.e. hedenbergite and enstatite grouped collectively as a pyroxene entry). This list was also used for data reconciliation with QXRD data, as end-member determination was not possible with the quantitative phase assessment using Rietveld refinement.

The 'Reactivity Groupings List' was based on the 'Minerals List' and Table 2-4 in section 2.1.2 with consideration for solid solution series end-members and the variation in reactivity/weathering/acid buffering potential of different minerals (i.e. hedenbergite and enstatite being grouped in separate Fast Weathering and Intermediate Weathering groups, respectively). The 'Reactivity Groupings List' was used for the assessment of textural parameters, as this allowed the otherwise complex mineralogy of the waste rock samples to be simplified. Also, the use of this list facilitated the thinking around long-term ARD formation potential, as it was based on the reactivity of the minerals associated with Fe-Sulfide or carbonate (dissolving) material.

Note that although the use of the 'Reactivity Groupings List' decreased the apparent textural complexity of the particles, it was assumed that this was not sufficient to significantly increase the stereological bias prevalent in 2D measurements, as the textural relationship of the minerals of interest (Fe-Sulfide and carbonate) to the surrounding mineral matrix remained relatively complex.

Table 3-11 Mineral comprising the ‘Minerals List’, which was used for computing the bulk mineralogy of samples A, B, C and D based on discrete minerals, without consideration for their weathering/reactivity potential. This list was also used for data reconciliation with XRD mineralogy.

Mineral	Grouping
Pyrite	Pyrite
Pyrrhotite	Pyrrhotite
Other Sulfide	Other Sulfide
Calcite	Carbonate
Dolomite	
Forsterite	Olivine
Fayalite	
Epidote	Epidote
Zoisite	
Diopside	Pyroxene
Hedenbergite	
Wollastonite	
Enstatite	
Ferrosilite	
Augite	Amphibole
Hornblende	
Actinolite	
Grunerite	
Biotite	Mica
Annite	
Muscovite	
Chlorite	Chlorite
Talc	Talc
Bytownite	Plagioclase-Feldspar
Albite	
Orthoclase	K-Feldspar
Magnetite	Fe-Oxide
Hematite	
Goethite	
Quartz	Quartz
Titanite	Titanite

Table 3-12 Minerals comprising the 'Reactivity Groupings List', which was for textural analyses to allow simplification of the textural data. This list aimed to consider the reactivity/weathering /acid buffering potential of the samples and was based on Table 2-4 and considered the solid solution series end members of minerals.

Mineral	Density	Average formula	Grouping
Pyrite	5.01	FeS ₂	Fe-Sulfide
Pyrrhotite	4.61	Fe _(1-x) S (0<x<0.17)	
Other Sulfide	-	PbS, ZnS, CuFeS ₂ , FeAsS	Other Sulfide
Calcite	2.71	CaCO ₃	Dissolving
Dolomite	2.84	CaMg(CO ₃) ₂	
Ankerite	3.05	Ca(Fe ²⁺ ,Mg,Mn)(CO ₃) ₂	
Bytownite	2.71	(Ca,Na)(Si,Al) ₄ O ₈	Fast Weathering
Forsterite	3.24	Mg ₂ SiO ₄	
Fayalite	4.39	Fe ²⁺ ₂ SiO ₄	
Diopside	3.40	CaMgSi ₂ O ₆	
Hedenbergite	3.55	CaFe ²⁺ Si ₂ O ₆	
Wollastonite	2.84	CaSiO ₃	
Epidote	3.45	Ca ₂ Al ₂ (Fe ³⁺ ,Al)(SiO ₄)(Si ₂ O ₇)O(OH)	
Zoisite	3.30	Ca ₂ Al ₃ (SiO ₄)(Si ₂ O ₇)O(OH)	
Biotite	3.09	K(Mg,Fe ²⁺) ₃ AlSi ₃ O ₁₀ (OH,F) ₂	
Enstatite	3.20	MgSiO ₃	Intermediate Weathering
Ferrosilite	3.95	(Fe ²⁺ ,Mg)SiO ₃	
Augite	3.40	(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al) ₂ O ₆	
Goethite	3.80	Fe ³⁺ O(OH)	
Hornblende	3.23	Ca ₂ (Mg, Fe, Al) ₅ (Al, Si) ₈ O ₂₂ (OH) ₂	
Actinolite	3.04	Ca ₂ (Mg,Fe ²⁺) ₅ Si ₈ O ₂₂ (OH) ₂	
Talc	2.75	Mg ₃ Si ₄ O ₁₀ (OH) ₂	
Chlorite	3.20	(Mg,Fe) ₃ (Si,Al) ₄ O ₁₀ (OH) ₂ ·(Mg,Fe) ₃ (OH) ₆	
Grunerite	3.45	Fe ²⁺ ₇ Si ₈ O ₂₂ (OH) ₂	
Annite	3.17	KFe ²⁺ ₃ AlSi ₃ O ₁₀ (OH,F) ₂	
Albite	2.62	NaAlSi ₃ O ₈	Slow Weathering
Orthoclase	2.56	KAlSi ₃ O ₈	
Magnetite	5.5	Fe ²⁺ Fe ³⁺ ₂ O ₄	
Hematite	5.30	Fe ₂ O ₃	
Muscovite	2.82	KAl ₂ (Si ₃ Al)O ₁₀ (OH,F) ₂	
Quartz	2.62	SiO ₂	Inert
Titanite	3.48	CaTiSiO ₄	

The QEMSCAN calculated element chemistry data were validated against XRF and LECO S data using the data validation parity charts in iDiscover, while the bulk mineralogy was validated with the QXRD data in Microsoft Excel in a similar set of charts. Separate parity charts were created for the SCT and HCT feed material for samples A, B, C and D. These parity charts may be viewed in Appendix B.5.2.

The liberation and association data were obtained using the built-in categorisers in the iDiscover software for mineral liberation and association. The association data were normalised with respect to the portion of Fe-Sulfide material that was liberated, with the liberation cut-off specified to include material that had 90% or more of its particle area exposed to the surrounding environment (resin in the sample block). The locked category was defined as the MoI having a 0%-29% exposed area, while a MoI exposed area of 30%-90% was classified as middlings.

3.3.3 Acid rock drainage index (ARDI)

Although the ARDI was not explicitly computed during this study (for it to be meaningful it would require the consideration of all parameters simultaneously for each particle in the sample/size fraction), referencing to parameters A, B, C, D and E was made throughout the study. Details of all ARDI parameters and their ranking are provided in Appendix C.1.1.

3.3.4 Mineralogical ANC and NP

The mineralogical MPA (AP) and ANC (NP) were calculated using equations (52) and (53), as well as the modal mineralogy obtained from the QXRD data. The minerals considered were pyrite, pyrrhotite, calcite and dolomite. The assumptions for calculating the NP were that the equation (11) took place (in conditions of pH <6.4) and that the n_s and n_i values were those of the dominant Fe-Sulfide mineral in the sample.

Table 3-13 Mineralogical neutralisation (NP, kg H₂SO₄ eq/tonne) and acid generation (AP, kg H₂SO₄ eq/tonne) potentials, where X_i = wt.% of mineral i ; c_i = number of non-oxidisable cations in one formula unit of i ; n_s = moles of H₂SO₄ from the oxidation of one mole of sulfide mineral s ; n_i = moles of mineral i required to consume n_s ; ω_i = molecular weight of i in g/mol; k = number of neutralising minerals in the sample; X_s = wt.% of mineral s ; n_s = moles of H₂SO₄ from oxidation of one mole of sulfide mineral; w_s = moles of mineral s ; m = number of sulfide minerals in the sample (Paktunc, 1999).

$$NP = \sum_{i=1}^k \frac{98 \times 10 \times X_i \times c_i \times n_s}{n_i \times \omega_i} \quad (52)$$

$$AP = \sum_{s=1}^m \frac{98 \times 10 \times X_s \times n_s}{w_s} \quad (53)$$

3.4 Error quantification

A variety of errors were considered in this study, with the three main sources assessed being the sampling error (error associated with sample mass and calculated using the Gy's theory of sampling), the mineralogical error (the error associated with the number of particles analysed – also termed as the analytical error for mineralogical/textural measurements) and the analytical error/error computed from replicate experiments.

The sampling error outlined in section 2.5 showed how the fundamental sampling error (FSE) may be obtained; however, it required the detailed recording of the mass at every sampling step, as well as the textural parameters for calculating the sampling constant C . Prior to undertaking the FSE calculation the mass and particle top size of a sub-sample were compared to Gy's sampling safety line. If the sub-sample was found to fall in the "safe zone", the sampling error was considered negligible, as the safety line considers all possible sources of sampling error; however, if the sample was found to fall in the "unsafe zone", the calculation of the sampling error was performed in detail. The requirements of the minimum sub-sample mass for the micro- and meso-scale test feed material are provided in Figure 3-8, where it can be seen that micro-scale samples after pulverisation satisfied the minimum sub-sample mass criteria, while those used for meso-scale test work did not, as the minimum sub-sample masses were 0.05-0.42g and 31.3kg for the micro- and meso-scales, respectively. It should be noted, however,

that the micro-scale sub-samples were not necessarily representative of the parent sample, as the size reduction step was performed only after obtaining the 1kg sub-sample of the bulk parent sample. This initial bulk sub-sampling error was incorporated when calculating the micro-scale FSE using “Gy’s equation”.

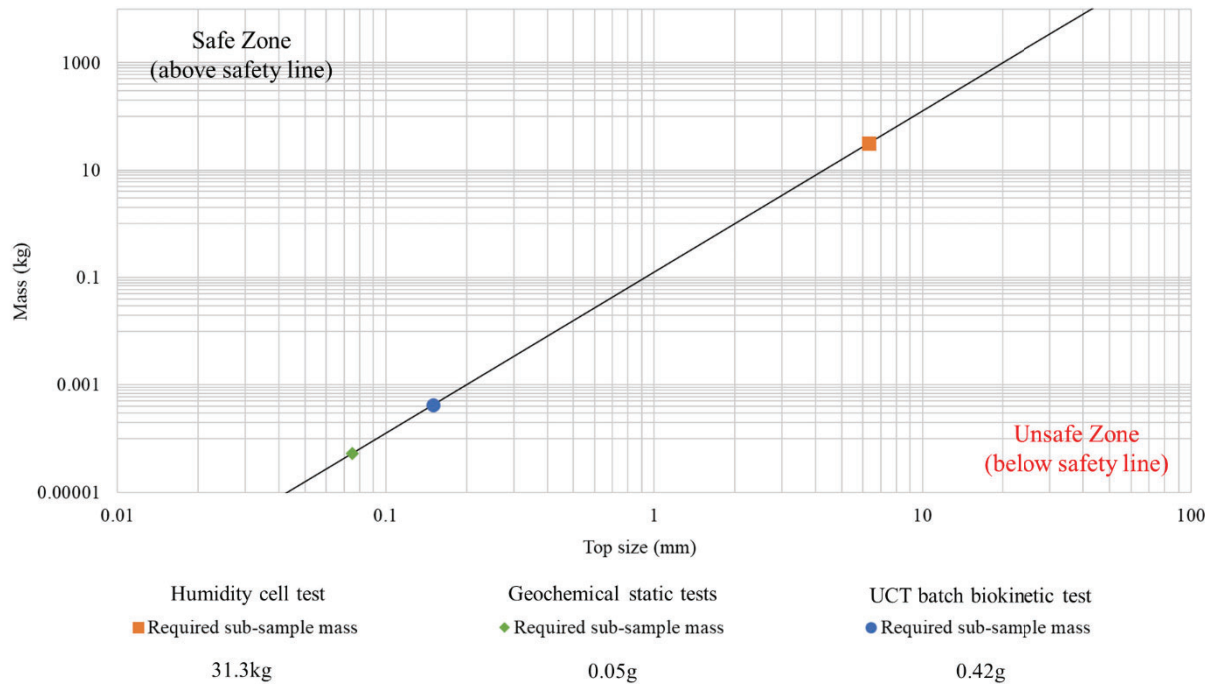


Figure 3-8 Gy’s safety line plot showing the minimum sub-sample mass requirements on the micro- and meso-scales.

For meso-scale material the calculation of the sampling error was an iterative process based on the error obtained when extracting the liberation, grade and shape data from QEMSCAN measurements for each meso-scale size fraction. The parameters used for calculating the sampling constant (C) are presented in Table 3-14.

Table 3-14 Parameters used during the calculation of the FSE and assumptions made.

Parameter	Description	Commonly used values	Values used during calculation
f	Shape factor	1 – cubic particles 0.524 – perfectly spherical particles 0.5 – spheroidal particles 0.1 – flat, disk-like particles	Estimated by categorising the particles in the size fraction/sample according to “roundness”, similar to the method developed by Little et al. (2015)
g	Size distribution factor	1 – all particles of identical size 0.75 – if d_i/d_5 is between 1 and 2 0.5 – if d_i/d_5 is between 2 and 4 0.25 – wide particle size distribution or if d_i/d_5 is greater than 4 (Minnitt et al., 2007a)	Estimated based on the width of the size distribution for the sample/fraction
l	Liberation factor	1 – liberated material or material ground to size below the liberation size 0.03 – minerals of interest very small in comparison to particle size	Calculated as a ratio of the d_{85} liberation size for the MoI (obtained from the GSD) and the sample/size fraction top size)
a	Grade of the lot (% or decimal proportion of the mineral of interest)	-	Obtained from the average grade of the sample/size fraction
ρ_m	Density of the component of interest	-	Estimated from the content and density of the respective Fe-Sulfide minerals in the sample/size fraction
ρ_g	Density of the surrounding mineral matrix	-	Roughly estimated as the total mass over the total volume of the sample or size fraction, as obtained from QEMSCAN.

The parameters used in the calculation were different for each individual sample, depending on the sample mineralogy and texture. A bulk sub-sampling error was calculated for the initial sub-sampling of the parent material. When calculating the sub-sampling error for each size fraction taken for QEMSCAN analysis, the bulk sub-sampling error was incorporated into the sum of the squares of the fundamental sampling variances of the individual size fractions.

The meso-scale sub-sampling error was considered synergistically with the mineralogical error arising due to the number of particles of interest assessed using equation (40), section 2.6, as the mass of a sub-sample was linked to the number of particles in that sub-sample. Thus, with each new sample block assessed, the sampling error was re-calculated based on the new number of particles and the added sample mass used for making the additional block.

4 Results and Discussion: Micro-scale

This chapter addresses objective one and key question one and provides the results and discussion surrounding micro-scale data for the four samples A, B, C and D. The first objective of the study was to *synergise the results of textural and mineralogical analyses on the micro-scale (<1mm particle size, characterisation test material) with the results of the commonly practiced geochemical static tests and the UCT batch biokinetic test, with particular consideration for the key minerals involved in acid formation (iron sulfide minerals) and neutralisation (carbonate minerals)*. The key question addressing this objective was “*which textural/mineralogical parameters are to be considered when interpreting the results of ARD characterisation (geochemical static, UCT batch biokinetic) tests (micro-scale) and how do the textural and mineralogical data enhance these results?*”.

The various data sets included and discussed in this chapter are the physical and chemical characterisation of the SCT feed material, as well as the results of the ARD characterisation (ABA, ANC and NAG) and UCT batch biokinetic tests. This builds towards the formulation of an understanding of the role of the mineralogy and micro-scale texture in the interpretation of ARD characterisation test results, which, in turn, contributes towards addressing objective four (understanding the role of mineralogy and texture in the ARD assessment “toolbox”). The experimental procedures have been presented in Chapter 3, with detailed methods provided in Appendix A. Complete data sets may be found in Appendix B.

4.1 Particle size distribution

The bulk particle size distributions (PSDs) of the pulverised micro-scale material were obtained through the combinational wet and dry screening of $\pm 100\text{g}$ sub-samples of samples A, B, C and D. These data are presented in Figure 4-1. The PSDs were used to ascertain that most of the SCT material was finer than the top size required for characterisation testing and to select the size fractions for mineralogical and textural analyses using QEMSCAN (see section 4.4). The relevant size fractions used for screening and analysis are provided in Table 4-1.

Table 4-1 Size fractions used for the screening of micro-scale material for samples A, B, C and D.

	Micro-scale	Size fractions for textural and mineralogical analyses
Size fraction (μm)	+150/-212	-212/+75
	+108/-150	
	+75/-108	
	+53/-75	-75/+53
	+38/-53	-53/+25
	+25/-38	
	+0/-25	-25/+0

From Figure 4-1, the d_{50} for the SCT feed material was found to be between $20\mu\text{m}$ (sample B) and $22\mu\text{m}$ (samples C and D) and d_{90} to be between $85\mu\text{m}$ (sample D) and $110\mu\text{m}$ (sample A). Although the micro-scale material was coarser than the $75\mu\text{m}$ top size recommended for static tests (Smart et al., 2002), over 75% of the micro-scale material was $75\mu\text{m}$ or finer and was considered to be sufficiently fine for static and UCT batch biokinetic test work. The SCT feed was therefore not pulverised further to avoid

increasing the mass of the fines in the sample. The particle size distributions for all samples were similar below the 75 μ m screen size, whereas at larger screen sizes, PSDs for samples C and D deviated from those of samples A and B. This may be attributed to samples A and B being received as crushed waste rock samples, while samples C and D were received as crushed drill core samples.

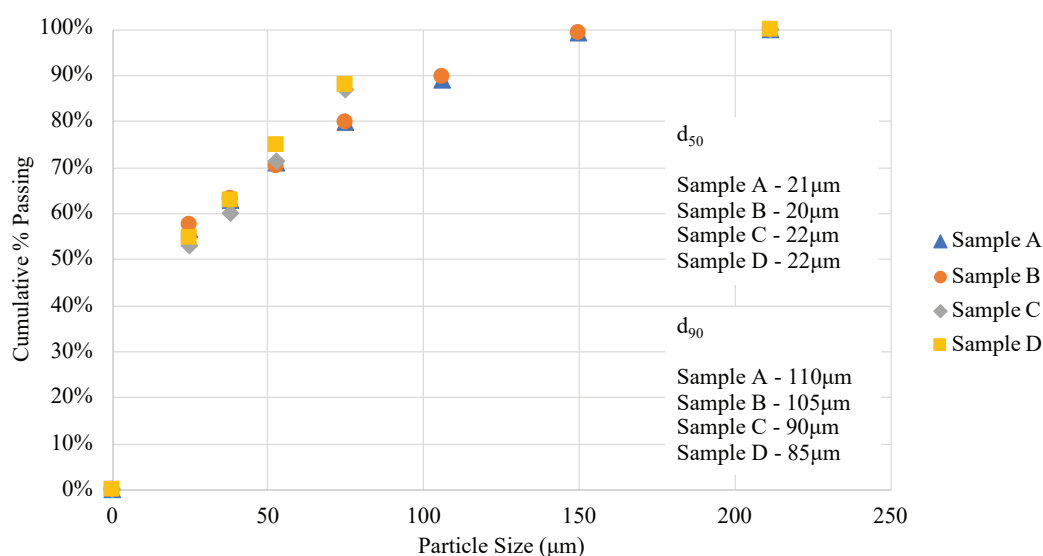


Figure 4-1 Particle size distribution of the unsized pulverised feed material obtained via combinational wet and dry screening for samples A, B, C and D with indication of sample d_{50} and d_{90} .

4.2 Chemical characterisation

The LECO total sulfur (LECO S) and X-ray fluorescence (XRF) characterisation for the bulk samples A and B were performed through the work of Opitz et al. (2016) and are summarised below alongside LECO S analyses of samples C and D performed during the current study.

4.2.1 LECO total sulfur results

Table 4-2 provides the total sulfur content of samples A, B, C and D. The highest sulfur content was found in sample C (9.5%), followed in decreasing order by samples B, A and D (3.2%, 2.3% and 2.0%, respectively). The error shown is that obtained from triplicate samples submitted for analyses.

Table 4-2 Micro-scale LECO S results (as mass % of the sample) for samples A, B, C and D for sized and bulk material.

Sample	A	B	C	D
Sulfur content as wt.% of the sample	2.3% $\pm$ 0.02% (Opitz et al., 2016)	3.2% $\pm$ 0.05% (Opitz et al., 2016)	9.5% $\pm$ 0.1%	2.0% $\pm$ 0.05%

4.2.2 Chemistry from XRF

Oxide and elemental compositions were converted to element wt% for the purpose of comparability across samples and are presented in Table 4-3. Elements that reported in trace amounts for all samples are excluded from Table 4-3 but the complete XRF data set may be found in Appendix B.2, Appendix

Table 13. The delineations for major, minor and trace elements were selected as >1 wt%, 0.1-1.0 wt% and <0.1 wt%, respectively, partially based on Lee (2016).

The major element chemistry was dominated by Si for samples B, C and D at 25.0%, 19.0% and 24.7%, respectively, with sample A having major chemistry dominated by Fe at 22.5% and Si at 22.4%. Fe was the next largest major element contributor for samples B, C and D at contributions of 12.6%, 13.1% and 22.5%, respectively. The remaining major element constituents for sample A were Al, S, Ca, Na and Mg at contributions of 2.4%, 2.3%, 2.1%, 1.9%, and 1.8%, respectively. Sample B remaining major element contributions were from Al, S, Na, K, Ca and Mg at 4.7%, 3.2%, 2.2%, 2.2%, 2.0% and 1.0%, respectively. The next highest major contributor for sample C were S, Ca, Al, Mg, K and Ti at contributions of 9.5%, 7.1%, 3.9%, 2.0%, 1.7% and 1.0%, respectively. The remaining sample D major element contributions were from Ca, Mg, S and Al at 3.2%, 2.2%, 2.0% and 1.4%, respectively.

The minor elements (at compositions between 0.1 and 1.0 wt %) for samples A and D were dominated by K at compositions of 0.4% and 0.3%, respectively. Sample C was dominated by Zn and Mn at 0.2%. The remaining minor element chemistry was dominated by Ti, Mn, F and Cr for sample A; Ba, Cr, F, Mn, P, Sr, and Ti for sample B; P, Na, F and Cr for sample C and Ti, P, Na, Mn and F for sample D, all at values of 0.1%.

Table 4-3 Sample element chemistry for samples A, B, C and D obtained via XRF. Sulfur concentration is that obtained from LECO S analyses. For major elements, the relative analytical uncertainty of the XRF analyses is commonly assumed to be around 0.5-1% (Rousseau, 2001).

Element wt %	Sample A	Sample B	Sample C	Sample D
Al	2.4%	4.7%	3.9%	1.4%
Ba	Trace	0.1%	Trace	Trace
Ca	2.1%	2.0%	7.1%	3.2%
Cr	0.1%	0.1%	0.1%	Trace
F	0.1%	0.1%	0.1%	0.1%
Fe	22.5%	12.6%	13.1%	22.5%
K	0.4%	2.2%	1.7%	0.3%
Mg	1.8%	1.0%	2.0%	2.2%
Mn	0.1%	0.1%	0.2%	0.1%
Na	1.9%	2.2%	0.1%	0.1%
P	0.2%	0.1%	0.1%	0.1%
S	2.3%	3.2%	9.5%	2.0%
Si	22.4%	25.0%	19.0%	24.7%
Sr	Trace	0.1%	Trace	Trace
Ti	0.1%	0.1%	1.0%	0.1%
Zn	Trace	Trace	0.2%	Trace
H₂O⁻	5.7%	4.2%	n.a.	n.a.
LOI	0.9%	3.1%	n.a.	n.a.

4.3 Bulk mineralogy

The bulk mineralogy was assessed using QXRD and QEMSCAN techniques, with the former being used for data reconciliation purposes. These data are presented in Table 4-4 and summarised in Figure 4-2.

Quartz was present in all samples at an abundance of over 30%. For sample A the remaining mineralogy primarily comprised Fe-oxide (magnetite), amphibole (ferro-actinolite), plagioclase-feldspar (albite) and Fe-Sulfide (pyrrhotite). For sample B the remaining mineral contributions were from plagioclase-feldspar (albite), mica (biotite/Fe-mica), Fe-oxide (magnetite), K-feldspar, Fe-Sulfide (pyrite), carbonate (calcite), chlorite and amphibole (ferro-actinolite). For sample C the remaining major mineral abundance was followed by Fe-Sulfide (pyrrhotite), carbonate (calcite), titanite, chlorite and K-feldspar. For sample D the remaining mineralogy was dominated by amphibole (ferro-actinolite and grunerite), Fe-oxide (magnetite), Fe-Sulfide (pyrrhotite), carbonate (calcite), chlorite and mica (biotite/Fe-mica). Table 4-2 excludes minerals that were detected at an abundance below 1% for all samples.

The above results were consistent with the major element chemistry data, which for all samples was dominated by Si (consistent with quartz abundance) and Fe (consistent with the high Fe-oxide, Fe-Sulfide and Fe-bearing amphibole mineral abundance). The remaining major element constituents for sample A were Al, Ca, Na, Mg and S; for sample B were Al, Na, K, Ca, Mg and S; for sample C were Ca, Al, Mg, K, Ti and S; and for sample D were Ca, Mg, Al and S, which corresponded with the silicate and Fe-Sulfide mineral chemistry. Data reconciliation charts may be found in Appendix B.5.2.

Table 4-4 Bulk mineralogy for samples A, B, C and D obtained via XRD and QEMSCAN, corresponding with Figure 4-2.

Mineral	Sample A		Sample B		Sample C		Sample D	
	XRD	QEM-SCAN	XRD	QEM-SCAN	XRD	QEM-SCAN	XRD	QEM-SCAN
Pyrite	1.7%	1.7%	6.8%	7.7%	<1%	2.0%	<1%	<1%
Pyrrhotite	4.7%	5.1%	<1%	<1%	26.8%	29.2%	5.3%	4.2%
Carbonate	1.4%	1.3%	4.9%	2.2%	16.7%	12.5%	5.0%	2.9%
Epidote	1.4%	<1%	2.2%	<1%	2.5%	<1%	<1%	<1%
Pyroxene	1.8%	2.1%	<1%	1.1%	<1%	<1%	<1%	3.4%
Amphibole	16.4%	17.3%	1.8%	3.8%	<1%	<1%	32.7%	36.3%
Mica	<1%	<1%	8.7%	9.5%	<1%	7.6%	3.6%	1.6%
Chlorite	1.1%	3.3%	2.2%	2.1%	6.0%	4.7%	3.6%	4.8%
Talc	<1%	<1%	<1%	<1%	<1%	<1%	<1%	1.9%
Plagioclase-Feldspar	15.6%	11.6%	24.1%	21.3%	<1%	<1%	1.1%	<1%
K-Feldspar	<1%	1.5%	7.3%	8.7%	2.7%	5.3%	<1%	0.1%
Fe-Oxide	20.7%	21.0%	8.1%	10.6%	<1%	<1%	8.0%	8.9%
Quartz	35.3%	32.3%	33.0%	30.8%	37.4%	30.7%	36.5%	34.6%
Titanite	<1%	<1%	<1%	<1%	7.1%	4.8%	<1%	<1%

Figure 4-2 was based on the 'Minerals List' to allow for the comparison of the bulk mineralogy between the QXRD and the QEMSCAN analyses and includes the bulk mineralogy of the HCT feed material alongside the XRD and SCT bulk mineralogy from QEMSCAN analyses.

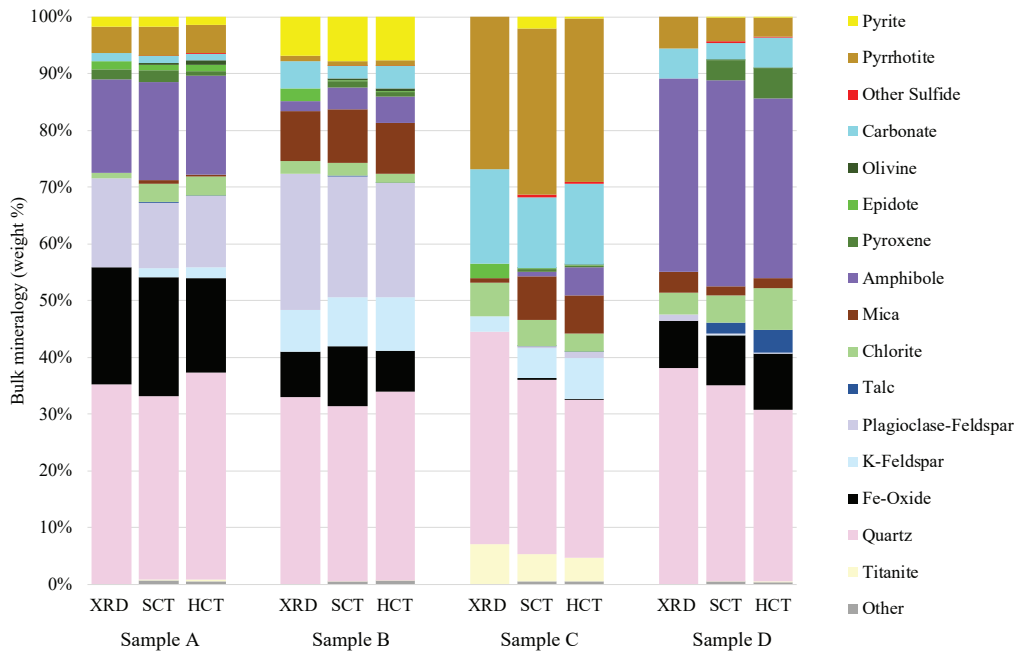


Figure 4-2 Bulk mineralogy for samples A, B, C and D based on the ‘Minerals List’ in Table 3-11. The bulk mineralogy was obtained from XRD and QEMSCAN, with the QEMSCAN bulk mineralogy being represented as that of the SCT feed material and HCT feed material, for comparison. QEMSCAN HCT mineralogy was obtained from reconstituting the sized meso-scale material to represent a sample as a whole. Variations in sample mineralogy, especially for the HCT material may be due to the sampling error which is greater for coarse material (see section 6) and/or the difference in resolution used for micro- and meso-scale measurements.

The ‘Reactivity Grouping List’ was used to obtain the bulk mineralogy by weathering rate presented in Figure 4-3, with the main minerals contributing to the groupings for all samples being provided in Table 4-5. Details of the minerals contributing to the groupings were presented in section 3.3.2.

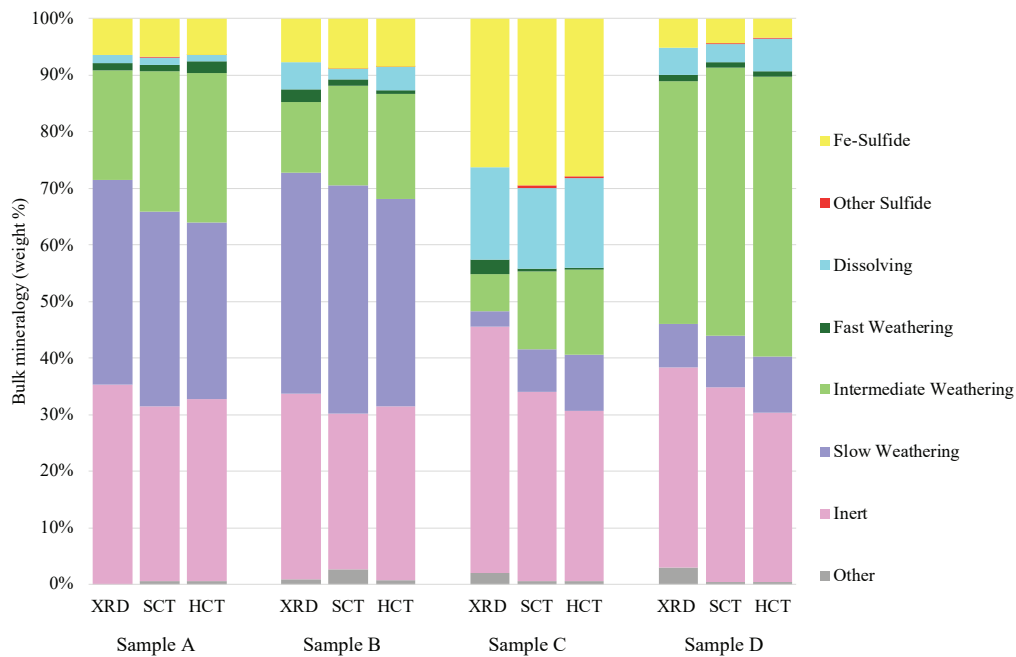


Figure 4-3 Bulk mineralogy for samples A, B, C and D based on the ‘Reactivity Grouping List’ in Table 3-12. The bulk mineralogy was obtained from XRD and QEMSCAN, with the QEMSCAN bulk mineralogy being represented as that of the SCT feed material and HCT feed material, for comparison. HCT mineralogy was obtained from reconstituting the sized meso-scale material to represent a sample as a whole.

Table 4-5 Major mineral contributors to each of the mineralogical sub-groups for samples A, B, C and D, listed in order of their abundance.

Sample	A	B	C	D
Fe-Sulfide	Pyrrhotite	Pyrite	Pyrrhotite	Pyrrhotite
Other Sulfide	Chalcopyrite	Chalcopyrite	-	-
Dissolving	Calcite	Calcite	Calcite	Calcite
Fast Weathering	Epidote	Epidote	Epidote	Ca-plagioclase
Intermediate Weathering	Amphibole (ferro-actinolite, grunerite)	Fe-mica, chlorite	Chlorite, Fe-mica	Amphibole (ferro-actinolite, grunerite), chlorite, Fe-mica
Slow Weathering	Magnetite, plagioclase-albite	Plagioclase-albite, magnetite, K-feldspar	K-feldspar	Magnetite, goethite
Inert	Quartz	Quartz	Quartz, Titanite	Quartz
Other	Apatite	Apatite	Apatite	Apatite

4.4 Micro-scale mineral texture

The following sub-section presents the mineral texture results on the micro-scale for samples A, B, C and D, including the grain size distribution, liberation and association data. These data were obtained for sized SCT feed material for samples A and B and the unsized SCT feed material for samples C and D. For the GSD, the l_{50} and l_{90} represent the sizes at which 50% and 90% of the grains are of or smaller than that size. These were used instead of the d_{50} and d_{90} to differentiate the GSD and PSD notation.

4.4.1 Grain size distribution on the micro-scale

Fe-Sulfide grain size distribution on the micro-scale

The grain size distributions (GSDs) of the micro-scale feed material of samples A, B, C and D are presented in Figure 4-4. Sample D was found to have the finest Fe-Sulfide GSD (l_{50} of 10 μ m and l_{90} of 25 μ m), while sample B was found to have the coarsest Fe-Sulfide GSD (l_{50} of 23 μ m and l_{90} of 55 μ m). The Fe-Sulfide GSD for samples A and C was similar, with sample A (l_{50} of 13 μ m and l_{90} of 44 μ m) containing slightly finer grains of Fe-Sulfide minerals than sample C (l_{50} of 14 μ m and l_{90} of 50 μ m). The fineness of the Fe-Sulfide grain size may be used to infer the likelihood of encapsulation, as finer grains have an increased chance of being found associated with other mineral phases, as opposed to coarse grains that would liberate at larger size fractions from the surrounding matrix (Evans & Morrison, 2016).

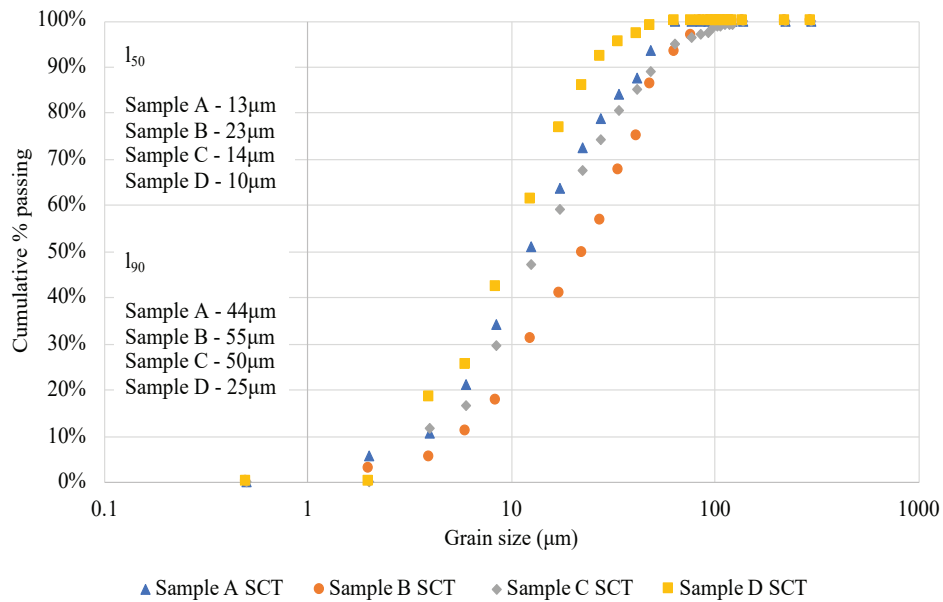


Figure 4-4 Grain size distribution of the Fe-Sulfide minerals in the sample SCT feed material for samples A ($N_S=75829$), B ($N_S=6395$), C ($N_S=56068$) and D ($N_S=11805$), where N_S is the total number of Fe-Sulfide-bearing particles analysed in the sample.

Dissolving mineral grain size distribution on the micro-scale

The dissolving mineral GSDs of the micro-scale feed material of samples A, B, C and D are presented in Figure 4-5. Samples A, B and D were found to have similar GSDs (I_{50} of 9µm, 8µm and 9µm, and I_{90} of 21µm, 24 and 22µm for samples A, B and D, respectively), with sample D containing coarser grains towards the finer end of the distribution. Sample C was found to have the coarsest dissolving mineral GSD (I_{50} of 11µm and I_{90} of 34µm). The GSD of the dissolving minerals may indicate the likelihood of their encapsulation in other mineral phases and therefore the likelihood of them reacting to completion during characterisation testing.

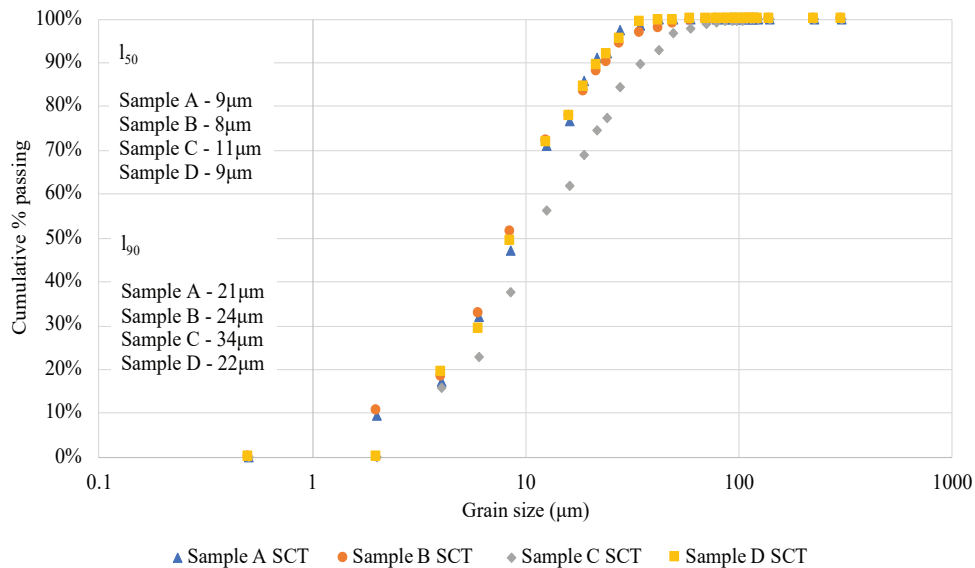


Figure 4-5 Grain size distribution of the Dissolving minerals in the sample SCT feed material for samples A ($N_D=3278$), B ($N_D=166263$), C ($N_D=64100$) and D ($N_D=16446$), where N_D is the total number of dissolving mineral-bearing particles analysed in the sample.

4.4.2 Micro-scale liberation and association

In addition to considering the relative abundances of the reactive and inert mineral phases, it was important to consider the interrelationship of these phases with each other, specifically the liberation and association of the acid forming (Fe-Sulfide) and neutralising (dissolving) minerals. These parameters were assessed as they had potential implications for ARD generation (Parbhakar-Fox, 2012; Brough et al., 2017; Elghali et al., 2018). The Fe-Sulfide liberation and association were considered per size fraction for samples A and B, as well as for the unsized samples A, B, C and D.

Particles were classified as liberated if >90% of the MoI area was exposed to background, while particles with <90% of the MoI area exposed to background were classed as unliberated. As <90% of the area still presented a considerably large potential reactive surface area, the unliberated category was further split into “locked” and “middlings” sub-groups. The “locked” category was defined as the MoI having a 0%-29% exposed area, while a MoI exposed area of 30%-90% was classified as “middlings”. The stacked bar charts used to illustrate the liberation and association data represent a 100% of the MoI material in the specified size fraction, with a 100% of the MoI material being either liberated (yellow for Fe-Sulfide or cyan for dissolving minerals) or associated with another reactivity group (red, dark green, light green, purple, pink or grey, which were used to represent Other Sulfide, Fast Weathering, Intermediate Weathering, Slow Weathering, Inert and Other categories, respectively). The liberation and association assessment was applied to the Fe-Sulfide and Dissolving mineral categories only.

Fe-Sulfide liberation and association on the micro-scale

When considering the Fe-Sulfide liberation and association data in Figure 4-6, the Fe-Sulfide material in sample B had the highest degree of liberation (94%), followed by samples A, C and D (73%, 71% and 48%, respectively). These liberation results are consistent with the results of the Fe-Sulfide GSD provided in Figure 4-4 for samples B and D, with the finest GSD (sample D) yielding the lowest proportion of liberated Fe-Sulfide minerals, while the coarsest GSD (sample B) yielded the largest proportion of liberated Fe-Sulfide minerals. For the sized material of samples A and B, the Fe-Sulfide liberation increased as the size fraction decreased up to the -25/+0 μ m size fraction, where the Fe-Sulfide material appeared less liberated than in all other fractions. This deviation from the trend may be due to limitations in resolution, as fine particles may not necessarily be accurately measured using QEMSCAN (Little et al., 2015). This was especially evident for Fe-Sulfide grains that were a single pixel in size, as association even from a single side could result in a greater reported degree of encapsulation than the “true” value. Therefore, for finer fractions, the degree of liberation was expected to be underestimated by QEMSCAN. Additionally, for liberated grains the stereological bias may become more prevalent, as the complexity of particles containing increasingly more liberated minerals decreases (Spencer & Sutherland, 2000); however, it was not expected that the stereological bias would have shifted liberated grains significantly into the unliberated category.

The line plots in Figure 4-6 serve to show the mass distribution of the Fe-Sulfide material across the size fractions, primarily to provide an indication of which fractions would control the liberation behaviour, but also to assess how much Fe-Sulfide material reported to the +75 μ m size fraction, as the samples contained some oversize material larger than the 75 μ m aperture size. The line plots showed that over 90% of the Fe-Sulfide material was found in the size fractions finer than 75 μ m.

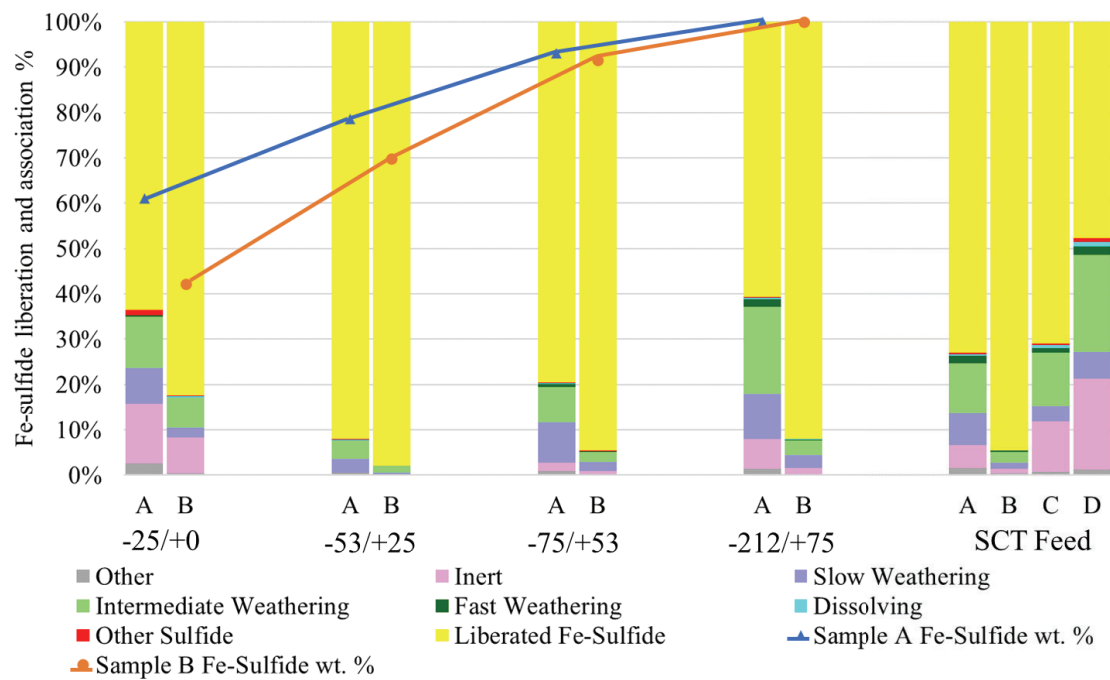
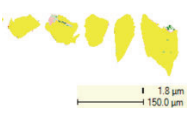
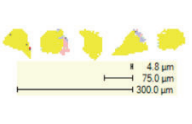
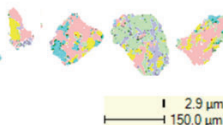
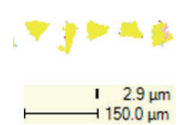
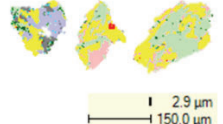
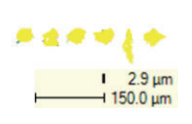


Figure 4-6 Fe-Sulfide liberation and association for samples A, B, C and D (QEMSCAN). The association describes the interrelationship of unliberated Fe-Sulfide mineral grains with other minerals present in the waste rock sample. These data correspond to those presented in Table 4-6. The sample A and B Fe-Sulfide wt. % plots represent the mass distribution of Fe-Sulfide across the size fractions in the samples.

Table 4-6 corresponds with the Fe-Sulfide liberation and association plots in Figure 4-6 and presents the number of particles assessed and false-colour images of Fe-Sulfide-bearing particles in the liberated and unliberated categories.

Table 4-6 The mass % distribution of the total Fe-Sulfide in the sample between liberated (>90% area exposed) and unliberated (<90% area exposed) categories. N_S = number of measured Fe-Sulfide-bearing particles.

Sample	N _S	Unliberated		Liberated	
		Mass % Fe-Sulfide	Particles	Mass % Fe-Sulfide	Particles
A	75829	27%		73%	
B	6395	6%		94%	
C	56068	29%		71%	
D	11805	52%		48%	

The results of this sub-classification are provided in Table 4-7. Overall, sample D showed the largest proportion of the Fe-Sulfide mass (17%) that was locked (corresponding to it having the most fine-grained Fe-Sulfide GSD in Figure 4-4), followed by samples C, A and B containing 10%, 8% and 1% in the locked category, respectively.

Table 4-7 The mass % distribution of the total Fe-Sulfide in the sample between liberated (>90% exposed area), middlings (30%<exposed area<90%) and locked (<90% exposed area) categories.

Sample	Unliberated mass % Fe-Sulfide		Liberated mass % Fe-Sulfide
	Locked	Middlings	
A	8%	19%	73%
B	1%	5%	94%
C	10%	19%	71%
D	17%	35%	48%

Figure 4-6 showed that for all samples, the unliberated Fe-Sulfide minerals were primarily found associated with inert, intermediate weathering and slow weathering material. This is linked to the relative abundance of these reactivity groups in the samples, based on the bulk mineralogy provided in Figure 4-3. The implications of these associations are more important for the less liberated Fe-Sulfides, especially those found in the locked category of samples D, A and C, as this material may not necessarily be available to the oxidative conditions of characterisation tests as readily as Fe-Sulfide material in the middlings or liberated categories.

Dissolving mineral liberation and association on the micro-scale

When considering the mineral liberation and association data for the dissolving category, only samples B, C and D were assessed, as these contained dissolving minerals at an abundance of or above 5%, which was thought to lower the sampling errors involved (see section 6.1.3). In Figure 4-7 the dissolving material in sample B had the highest degree of liberation (84%), followed by samples C (69%) and D (50%). When considering the GSD for samples B, C and D in Figure 4-5, it was expected that sample C would yield the largest degree of dissolving mineral liberation; however, sample B contained the largest proportion of liberated dissolving minerals. The dissolving minerals were nonetheless more liberated for sample C than for sample D, which was consistent with their respective coarser and finer GSDs. Table 4-8 corresponds with the dissolving mineral liberation in Figure 4-7 and is presented alongside the number of particles assessed and false-colour images of dissolving-mineral-bearing particles in the liberated and unliberated categories.

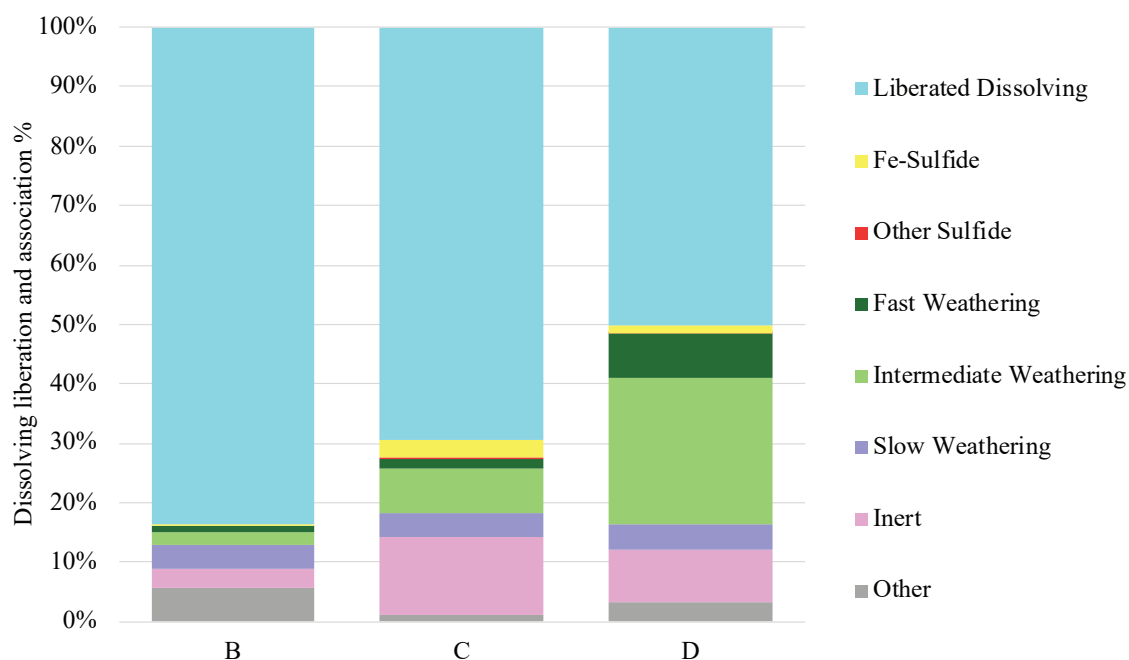
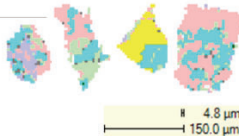
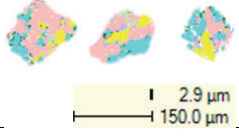
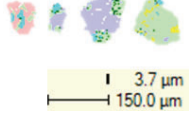


Figure 4-7 Dissolving mineral liberation and association for samples B, C and D (QEMSCAN) on the micro-scale. The association describes the interrelationship of unliberated dissolving mineral grains with other minerals present in the waste rock sample. These data correspond to those presented in Table 4-8.

Table 4-8 The mass % distribution of the total dissolving minerals in the sample between liberated (>90% area exposed) and unliberated (<90% area exposed) categories. N_D = the number of dissolving mineral-bearing particles assessed.

Sample	N_D	Unliberated		Liberated	
		Mass % Dissolving	Particles	Mass % Dissolving	Particles
B	166263	16%		84%	
C	64100	31%		69%	
D	16446	50%		50%	

The results of the “locked” and “middlings” sub-classification are provided in Table 4-9. Overall, sample D showed the largest proportion of locked dissolving minerals (26%), followed by samples C and B, which had 13% and 6% dissolving minerals in the locked category, respectively.

Table 4-9 The mass % distribution of the dissolving minerals in samples B, C and D between the liberated (>90% exposed area), middlings (30%<exposed area<90%) and locked (<90% exposed area) categories.

Sample	Unliberated mass % dissolving		Liberated mass % dissolving
	Locked	Middlings	
B	6%	10%	84%
C	13%	18%	69%
D	26%	24%	50%

Figure 4-7 showed for all samples that the unliberated dissolving minerals were primarily associated with inert and intermediate weathering minerals, with lesser associations to fast weathering, slow weathering and Fe-Sulfide minerals for samples C and D. Unliberated dissolving minerals in sample B were also largely associated with the “Other” category, which predominantly contained apatite. The implications of these associations are more important for the locked dissolving material, as it may not be as readily available to the oxidative conditions of characterisation tests as that in the middlings and liberated categories.

The Fe-Sulfide and dissolving mineral liberation and association data suggest that some Fe-Sulfide material found in the locked categories may not react completely during characterisation tests, depending on the reactivity of the associated minerals. Fe-Sulfide or dissolving minerals locked in slow weathering or inert material would require that they be physically liberated/broken off, whereas those locked in other sulfide, dissolving, fast weathering or intermediate weathering categories would be subsequently liberated upon the reaction of those mineral phases in the aggressive chemical conditions of the geochemical static characterisation and/or UCT batch biokinetic tests. These tests have the underlying expectation that the grinding size required for the tests (-75µm and -150µm, for the static and UCT batch biokinetic tests, respectively) is sufficient to liberate the acid forming and neutralising minerals in the sample. For samples with a fine GSD, however, the recommended grinding size may not necessarily be sufficient. This concept has been recognised in flotation applications, where the grinding size required for sufficient liberation of the mineral of interest (MoI) is determined for each individual ore type based on the mineralogy and the liberation size of the MoI (Hunt et al., 2011; Tungpalan et al., 2015). It is therefore possible that a “one size fits all” approach would not necessarily be applicable to the MoIs in ARD characterisation test work.

4.5 Static test characterisation

4.5.1 Geochemical static test results

The geochemical static test results of the ANC, single addition NAG, and MPA tests for samples A, B, C and D are presented in Table 4-10. Samples A and B were classified as potentially acid forming (PAF), sample C uncertain (UC) and sample D non-acid forming (NAF), which was due to the difference between the MPA and ANC values. Samples C ($290 \pm 3.1 \text{ kg H}_2\text{SO}_4/\text{t}$) and B ($97.9 \pm 1.4 \text{ kg H}_2\text{SO}_4/\text{t}$) reported the largest MPA due to their higher sulfur and respective Fe-Sulfide mineral contents, while the MPA values for samples A and D were similar ($70.4 \pm 0.7 \text{ kg H}_2\text{SO}_4/\text{t}$ and $61.5 \pm 1.4 \text{ kg H}_2\text{SO}_4/\text{t}$, respectively), based on similarity in sulfur and Fe-Sulfide mineral contents. The ANC was the highest for sample C at $187 \pm 0.1 \text{ kg H}_2\text{SO}_4/\text{t}$, followed by samples B, D and A ($91.9 \pm 0.0 \text{ kg H}_2\text{SO}_4/\text{t}$, $78.0 \pm 0.0 \text{ kg H}_2\text{SO}_4/\text{t}$ and $62.7 \pm 0.0 \text{ kg H}_2\text{SO}_4/\text{t}$, respectively) due to the difference in dissolving mineral (calcite)

content of the samples, but also due to the dissolution of intermediate weathering (Fe-mica, chlorite, ferro-actinolite) and slow weathering (magnetite) minerals, which are not usually considered in ANC testing (Opitz et al., 2018).

Table 4-10 Results of static characterisation tests for samples A, B, C and D. The error shown is that obtained from one times the standard deviation obtained from three replicates of the ANC test for samples A and B, and five replicates of the ANC test for samples C and D. LECO S errors are one times the standard deviation obtained from triplicate analyses. The NAPP errors were propagated from the MPA and ANC error values while the NAG pH errors are those obtained from one times the standard deviation obtained from four single addition NAG test replicates.

Sample	LECO (UCT) Total S %	MPA [kg H ₂ SO ₄ /t]	ANC [kg H ₂ SO ₄ /t]	NAPP [kg H ₂ SO ₄ /t]	NAG pH	ARD Classification
A	2.3±0.0	70.4±0.7	62.7±0.0	7.7±0.7	2.5±0.0	PAF
B	3.2±0.0	97.9±1.4	91.9±0.0	6.0±1.4	2.4±0.0	PAF
C	9.5±0.1	290±3.1	187±0.1	102±3.14	6.45±0.1	Uncertain
D	2.0±0.1	61.5±1.4	78.0±0.0	-16.5±1.4	5.73±0.0	NAF

4.5.2 Liberation-corrected MPA

The liberation and association data in section 4.4.2 showed that not all Fe-Sulfide and dissolving minerals were fully liberated, with some being found in the locked category. Liberation-corrected values of the MPA for samples A, B, C and D were therefore calculated based on equation (46) in section 3.2.3.

After the liberation correction the MPA value for sample B changed only slightly (from 97.9±1.4kg H₂SO₄/t to 92.0±1.4kg H₂SO₄/t), as it had the highest degree of Fe-Sulfide liberation (94%). Samples C showed a decrease in MPA from 290±3.1kg H₂SO₄/t to 206±3.1kg H₂SO₄/t, followed by samples D (which decreased from 61.5±1.4kg H₂SO₄/t to 29.5±1.4kg H₂SO₄/t) and A (from 70.4±0.7kg H₂SO₄/t to 51.4±0.7kg H₂SO₄/t). Although this decrease was not proportional to the amount of liberated Fe-Sulfide material for the samples, sample C had a much higher sulfur content than samples A, B and D, which magnified the MPA value.

The NAPP values were calculated based on the liberation-corrected MPA values and the chemical ANC values and changed from 7.7±0.7kg H₂SO₄/t to -11.4±0.7kg H₂SO₄/t for sample A, from 6.0±1.4kg H₂SO₄/t to 0.13±1.4kg H₂SO₄/t for sample B, from 102±3.14kg H₂SO₄/t to 18.4±3.1kg H₂SO₄/t for sample C and from -16.5±1.4kg H₂SO₄/t to -48.5±1.4kg H₂SO₄/t for sample D. This changed the classification of samples A and B to Uncertain and PAF/Uncertain, respectively.

These results are summarised in Table 4-11.

Table 4-11 Results of the liberation correction for the MPA. Correction was carried out as described in section 3.2.3, equation (46). NAPP values were calculated as the difference between the liberation-corrected MPA and chemical ANC. L_S = amount of liberated Fe-Sulfide minerals in the sample.

Sample	LECO (UCT) Total S %	MPA [kg H ₂ SO ₄ /t]	NAPP [kg H ₂ SO ₄ /t]	L_S	ARD Classification
A	2.3±0.0	51.4±0.7	-11.4±0.7	73%	PAF
B	3.2±0.0	92.0±1.4	0.13±1.4	94%	PAF/Uncertain
C	9.5±0.1	206±3.1	18.4±3.1	71%	Uncertain
D	2.0±0.05	29.5±1.4	-48.5±1.4	48%	NAF

4.5.3 Mineralogical MPA and NP

As the sample mineralogy showed considerable pyrrhotite (most of the Fe-Sulfide in samples A, C and D) rather than pyrite, except for sample B (primarily pyrite), and the presence of some dolomite in the dissolving mineral category of sample B, the mineralogical MPA and NP were calculated using the method outlined by Paktunc (1999). This was done to assess potential under- or overestimation of the MPA and ANC values during the conventional geochemical classification due to the variation in sample mineralogy. These calculations were performed with consideration for pyrite, pyrrhotite, calcite and dolomite. A mineralogical NAPP was also calculated from these values, all of which are presented in Table 4-12.

Table 4-12 Mineralogical MPA and NP determined by the method outlined in Paktunc (1999) using the bulk mineralogy from QXRD.

Sample	MPA [kg H ₂ SO ₄ /t]	NP [kg H ₂ SO ₄ /t]	NAPP [kg H ₂ SO ₄ /t]	ARD Classification
A	81.6	14.0	67.6	PAF
B	123	49.4	73.1	PAF
C	309	164	145	Uncertain
D	60.8	49.3	11.5	Uncertain

The smallest changes in MPA values (between chemical and mineralogical) were observed for samples D and A, where the MPA values changed from 61.5±1.4kg H₂SO₄/t to 60.8kg H₂SO₄/t for sample D and from 70.4±0.7kg H₂SO₄/t to 81.6kg H₂SO₄/t for sample A. The MPA values changed from 97.9±1.4kg H₂SO₄/t to 123kg H₂SO₄/t for sample B and from 290±3.1kg H₂SO₄/t to 309kg H₂SO₄/t for sample C. The NP values changed from 62.7±0.0kg H₂SO₄/t to 14.0kg H₂SO₄/t for sample A, from 91.9±0.0kg H₂SO₄/t to 49.4kg H₂SO₄/t for sample B, from 187±0.1kg H₂SO₄/t to 164kg H₂SO₄/t for sample C and from 78.0±0.0kg H₂SO₄/t to 49.3kg H₂SO₄/t for sample D. These variations did not have an effect on the overall PAF/NAF/UC classification for samples A, B and C; however, sample D was re-classified as uncertain due to the mineralogical neutralisation potential being lower than that predicted by the geochemical static tests. The mineralogical NP was, however, lower for all samples than the chemically determined ANC. This was thought to occur due to the potential contribution of the Fe-oxyhydroxide and neutralising silicate minerals to the chemical ANC, based on the analysis of the mineralogy of the ANC and NAG test residues of samples A and B (Opitz et al., 2018).

4.5.4 Geochemical characterisation plot

The geochemical classification plot in Figure 4-8 serves to summarise the results of the chemical, liberation-corrected and mineralogical characterisation test data and to plot the samples in the respective PAF/NAF/UC regions for the purposes of comparison.

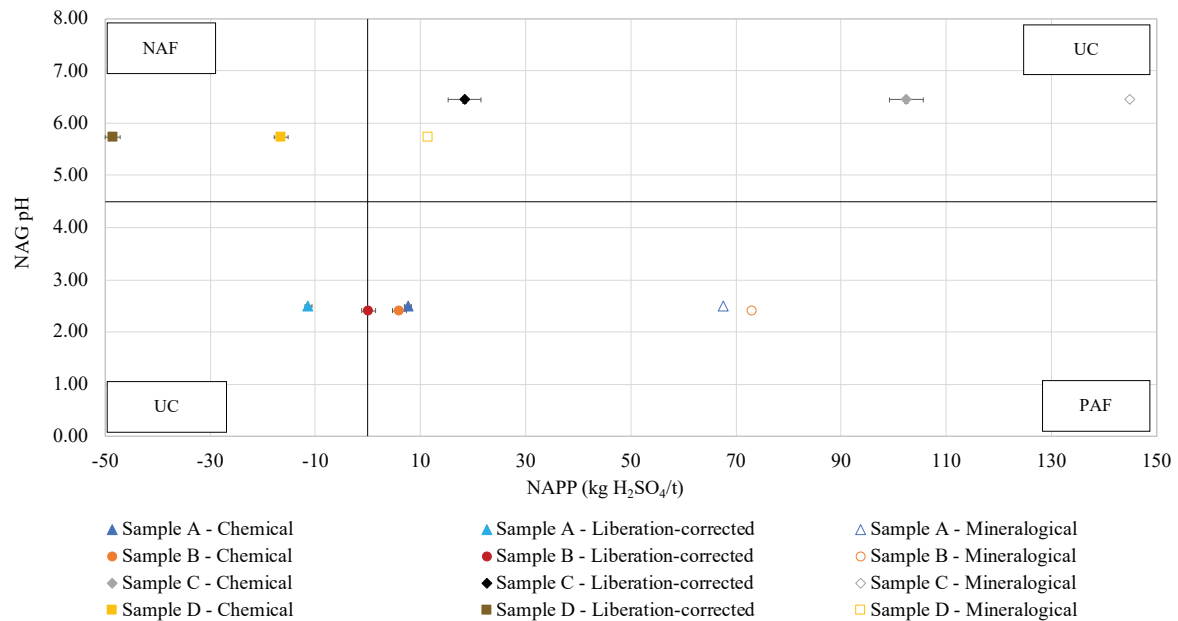


Figure 4-8 Experimental and mineralogical geochemical characterisation plot for samples A, B, C and D. PAF = potentially acid forming; UC = uncertain; NAF = non-acid forming.

Based on the various calculation of the PAF/NAF/UC potential of the samples, the adjustment for liberated Fe-Sulfide and dissolving minerals affected some of the samples in terms of their placement on the geochemical characterisation plot. Samples A and B moved from the PAF region into the UC region, while samples C and D remained in the UC and NAF regions, respectively. Additionally, using the mineralogical MPA and NP calculation shifted sample D from the NAF to the UC category. Overall, the mineralogical MPA and NP method appeared to shift the samples into the positive NAPP direction on the chart, which would indicate a higher likelihood of acid formation, while the Fe-Sulfide liberation correction shifted samples into the negative NAPP direction, indicating a lower sample reactivity due to Fe-sulfide mineral encapsulation.

4.6 UCT batch biokinetic test

This sub-section presents the results for the UCT batch biokinetic tests for samples C and D. This test was performed on samples A and B in previous work performed outside this study (Opitz et al., 2016) and the results of those findings will only be referenced as required, rather than presented again. During the current study a sample A “cross-experimental” control was performed to allow for some comparison with the previously published results of samples A and B, as these were performed at a different time and with a microbial consortium that was not identical to the one used during this study. The cross-experimental control results as compared with sample A data from Opitz et al. (2016) may be found in Appendix B.4.1.

Figure 4-9 to Figure 4-13 present the profiles of the pH, redox potential, total iron and sulfate concentrations over the 90-day period of the tests. The pH profiles, in conjunction with the redox potential profiles, were used to infer microbial activity/inactivity, with redox potential profiles providing an indication of the relative concentrations of ferrous and ferric ions in solution. The pH profiles provided an indication of the abundance of H^+ ions in solution, from which the dissolution of acid-forming minerals was inferred. The inoculated experiments aimed to provide an indication of acid formation potential of the sample under biotic conditions, while the uninoculated experiments aimed to provide an indication of the presence of naturally occurring microorganisms in the sample and their behaviour under aqueous conditions.

4.6.1 pH and redox potential profiles

The pH and redox potential profiles for inoculated, uninoculated, pH-controlled and non-pH-controlled experiments for sample C are provided in Figure 4-9, and for sample D in Figure 4-10.

Non-pH-controlled experiments

The non-pH-controlled experiments were used to assess whether the sample could be characterised as potentially acid forming (PAF) or non-acid forming (NAF) without the removal of the neutralising capacity. The pH profile for these experiments increased to above 8 in the first few days. This rapid initial increase in pH was attributed to the dissolution of calcite in the sample, which was similar to the spike seen in other UCT batch biokinetic test work (Broadhurst et al., 2013; Dyantyi et al., 2013) and the UCT batch biokinetic test results for sample B (Opitz et al., 2016). For sample C, after the initial spike the pH decreased to between 7 and 8 over days 2-9. For sample D the non-pH-controlled profiles this pH drop proceeded more slowly over the course of days 2-29. This difference in pH decrease was attributed to the difference in Fe-Sulfide mineral contents between samples C and D, where sample C had considerably more Fe-Sulfide than sample D (31% vs. 4%, respectively). The pH then settled at around 7.7 for both samples C and D – a pH range unfavourable for the microbial species used in the test (Table 2-6, section 2.1.4 and section 2.2.2, (Schippers et al., 2014). The slightly alkaline pH, particularly for sample D, was attributed to the dissolution of intermediate weathering minerals. This behaviour was similar to that observed by Dyantyi et al. (2013) for chlorite and mica contributing to the neutralisation potential; however, for sample D the primary intermediate weathering minerals were iron end member amphiboles (ferro-actinolite and grunerite), which suggests that these minerals potentially contributed to the solution chemistry in addition to the chlorite and mica in the sample. The potential contribution of Fe-oxide minerals (magnetite) to the neutralisation potential in samples was also highlighted by Opitz et al. (2018).

The pH profiles discussed above were supported by the redox potential profiles, which remained well below the 650mV line. Although the non-pH-controlled redox potential profiles for samples C and D did rise slowly, there was an absence of microbial activity, as the redox potential remained below 450mV over the 90 days of the experiment. Similarities in the inoculated non-pH-controlled profiles between samples C and D may be explained by high pH conditions, which provided an unfavourable environment for acidophilic microbial activity. The raised pH hindered microbial activity, as supported by the redox potential profiles for sample B where, irrespective of inoculation, the redox potential profile settled at a value of ± 300 mV.

pH-controlled profiles

The pH-controlled profiles were used to inform the microbial activity upon the depletion of any neutralisation capacity present in the sample. The pH-controlled profiles for both samples C and D showed similar behaviour after day 21, settling at a pH of approximately 1.9. This behaviour, alongside the slight differences in the pH-controlled profiles between days 10 and 25 was attributed to the difference in neutralising and acid-forming minerals in the sample. After the depletion of the carbonate minerals by pH-control, the pH profile for sample C dropped spontaneously to 1.4 by day 17, which may be attributed, alongside the low redox potential (less than 450mV) until day 23, to rapid dissolution of abundantly present pyrrhotite. The slight rise in pH for sample C (days 17-23) and sample D (days 17-23) was attributed to the dissolution of intermediate weathering minerals, as indicated in a previous study (Becker et al., 2015). Additionally, the pH-control for sample C was terminated after day 9, while the pH control for sample D was required until day 21. This suggests the dissolution of intermediate weathering amphibole minerals, and/or the dissolution of the locked dissolving minerals, which were present to a greater extent in sample D (13% versus 26% locked dissolving minerals for samples C and D, respectively).

The pH-controlled redox potential profiles for samples C and D provided indication of microbial activity in the flasks, as the redox potential increased with time, settling to between 680mV and 720mV by day 21, with limited fluctuation thereafter. The redox potential for sample C reached peak microbial activity (above 650mV) later than sample D for both the inoculated and uninoculated flasks, even though the pH profile dropped to 2 at similar days (9 for sample C and 8 for sample D).

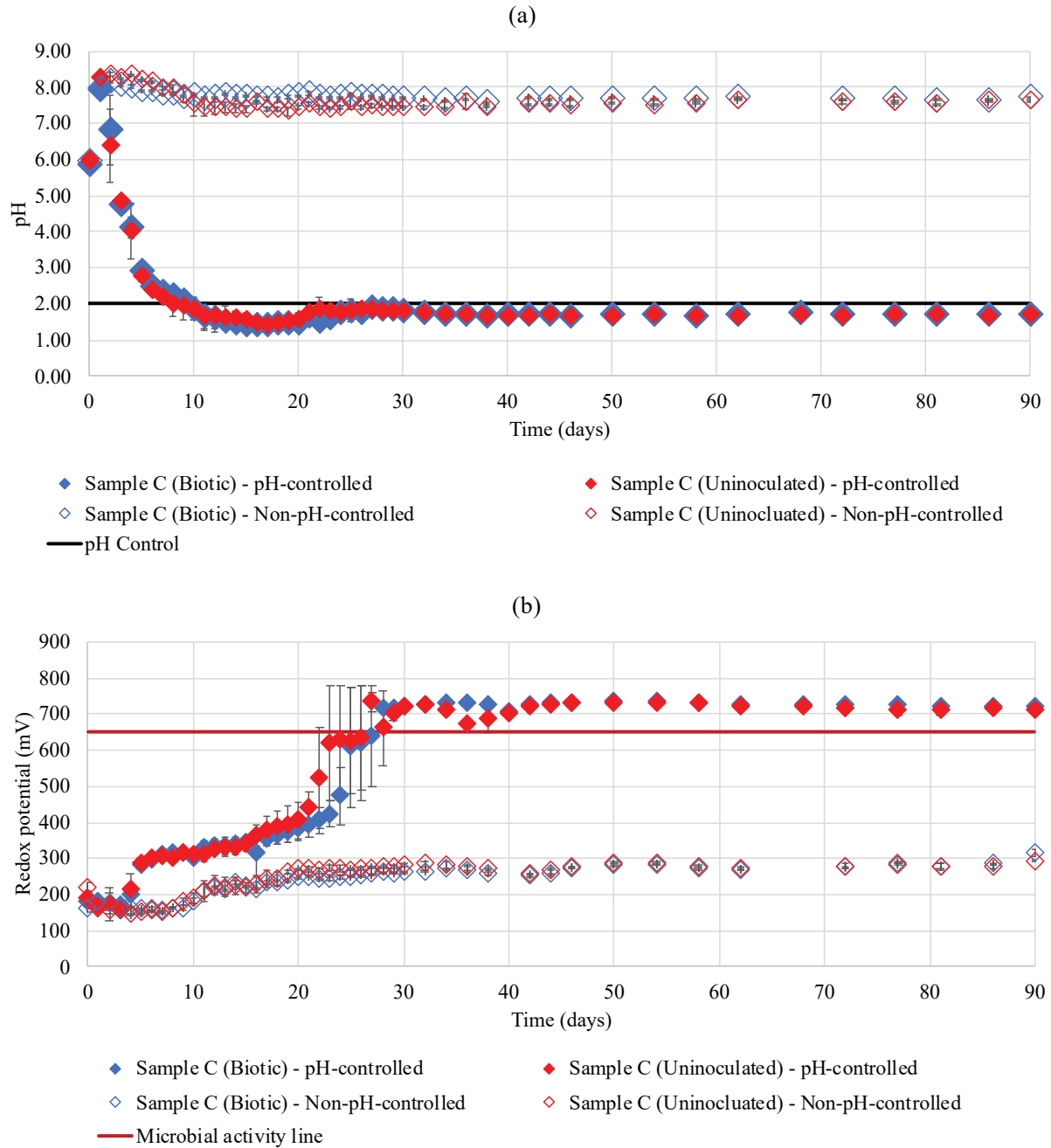


Figure 4-9 pH (a) and redox potential (b) profiles for sample C for inoculated and uninoculated flasks under pH-controlled and non-pH-controlled conditions. The error reported is that obtained from one times the standard deviation, which indicates the variation between the triplicate samples used in the test. The large error bars on some data points (specifically for the pH-controlled flasks) are due to variation in microbe adaptation to the environment in each replicate flask.

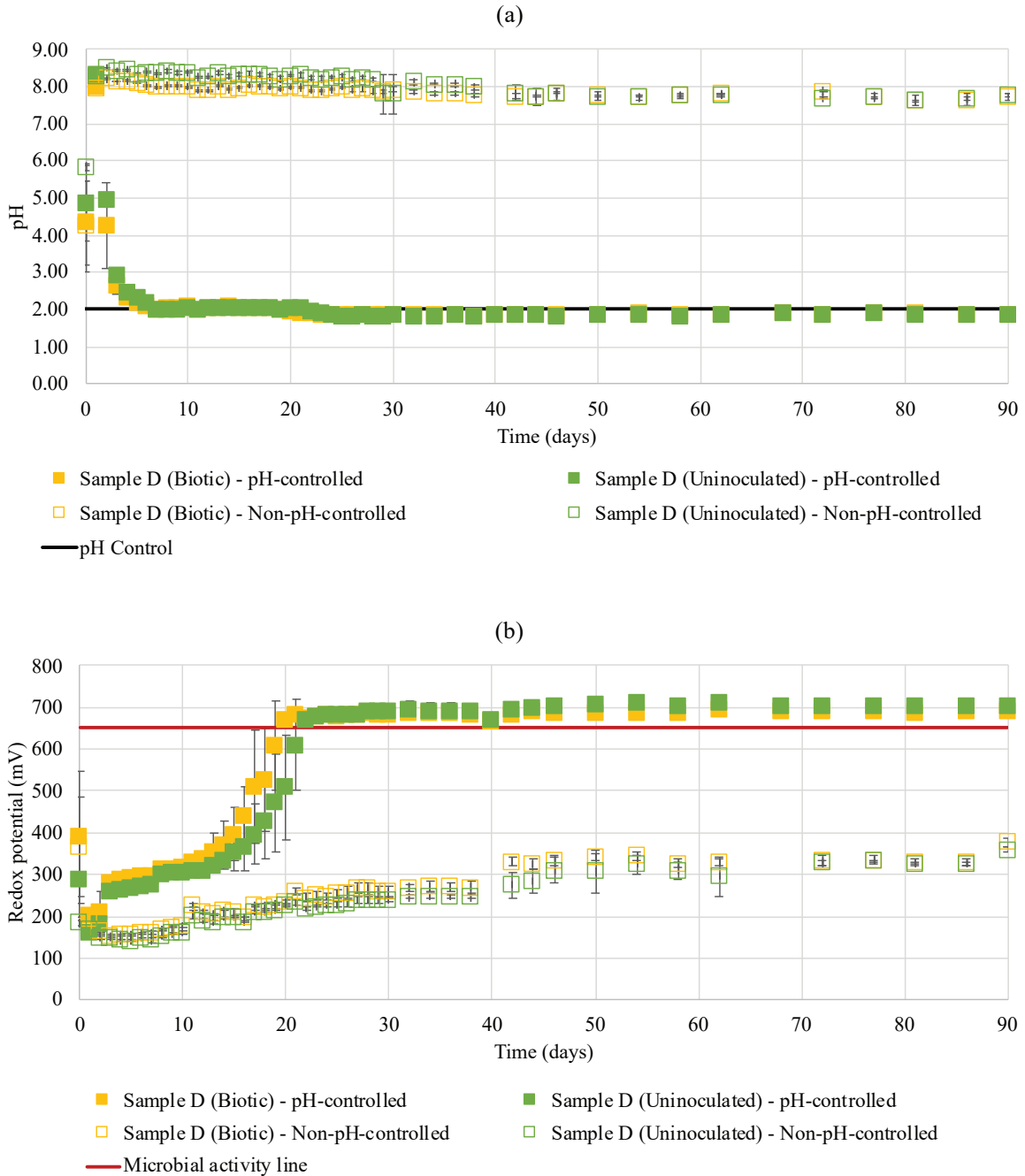


Figure 4-10 pH (a) and redox potential (b) profiles for sample D for inoculated and uninoculated flasks under pH-controlled and non-pH-controlled conditions. The error reported is that obtained from one times the standard deviation, which indicates the variation between the triplicate samples used in the test. The large error bars on some data points (specifically for the pH-controlled flasks) are due to variation in microbe adaptation to the environment in each replicate flask.

The above pH and redox potential profile results were consistent with the results of the geochemical static characterisation in section 4.5 for sample D, which was classified as NAF. The UCT batch biokinetic test results for sample A (Opitz et al., 2016) were also consistent with the PAF classification, as the pH profile for both inoculated and uninoculated tests did, after an initial spike due to calcite dissolution, settle at around pH 2. This, alongside the redox potential profile, which rose to 700mV, provided indication of microbial activity for sample A. Samples B and C were classified as PAF and

uncertain, respectively via ABA testing, whereas the UCT batch biokinetic test classified these as NAF using the non-pH-controlled test. These results indicate that although a sample's neutralisation potential may be lower than the acid formation potential (based on the respective dissolving and Fe-Sulfide mineral contents), the presence of even a limited neutralisation capacity may inhibit microbial activity in a batch shake flask test scenario, which is a limitation of the test (Opitz et al., 2016). What is important, however, is that when the pH does become acidic (pH-controlled samples C and D), the microbes adjust quickly and maintain the low pH environment, which indicates that samples may still be potentially acid forming once the neutralisation potential has been depleted. This depletion of neutralisation capacity may occur in the field, where rainfall and/or run-off may wash out the neutralisation potential, and has been tested in other studies in the context of the UCT biokinetic test (Makaula et al., 2018).

4.6.2 Total iron and sulfate ion concentrations

The ferrous (Figure 4-11(a) and Figure 4-12(a), for samples C and D, respectively) and total iron (Figure 4-11(b) and Figure 4-12(b), for samples C and D, respectively) concentration profiles were used to gain an understanding of the sulfide and iron-bearing mineral dissolution. In addition to the plotted test data, Figure 4-11 and Figure 4-12 show the maximum total iron concentration possible from the dissolution of Fe-Sulfide minerals in samples C and D. These were calculated from the amount of Fe-Sulfide in the sample, the amount of iron in the Fe-Sulfide minerals, the working volume of the test and the amount of iron coming in with the ABS media and inoculum. Figure 4-13(a) and Figure 4-13(b) also include the maximum possible sulfate ion concentration in the tests. This was calculated from the total sulfur results obtained from LECO, as Fe-sulfides were found to be the main source of sulfur based on the mineralogy. The maximum sulfate concentration also considered the sulfate introduced during pH control. The maximum sulfate line therefore indicates the total sulfate that was introduced to the solution with the sample, ABS media, inoculum and the pH control solution for the duration of the entire test.

The iron concentration plots showed a distinct difference between the pH-controlled and non-pH-controlled profiles, where the former showed a considerable increase in the iron concentration, while the latter showed a negligible increase in iron concentration. Additionally, there was an approximate difference of 4g/L of total iron between samples C and D, which may be attributed to the difference in Fe-Sulfide content of the two samples. Although the total iron concentration of sample C remained below the total possible iron concentration from sulfide dissolution (potentially due to the formation of some iron-bearing precipitates in the flasks, as can be seen from the red colour in sample C flasks in Figure 4-14), the total iron profile of sample D settled above the maximum iron concentration attainable from Fe-Sulfide dissolution alone. This was thought to occur due to the dissolution of intermediate weathering Fe-bearing amphibole minerals (ferro-actinolite and grunerite at an abundance of 36.3% (QEMSCAN)) (Dyantyi et al., 2013), and or Fe-oxide (magnetite at an abundance of 8.9% (QEMSCAN)) (Opitz et al., 2018). For sample D, the iron concentration being above the maximum possible Fe-Sulfide iron concentration provides a further indication of the potential dissolution of these minerals during the test.

The slow drop in the total iron concentration in the test flasks over time was thought to occur due to the formation of iron precipitates such as jarosite and/or ferrihydrite (Hesketh et al., 2010; Opitz et al.,

2018), which was supported by the colour change observed in the flasks as the redox potential increased (Figure 4-14). The colour became more prominent as the pH decreased, but primarily, as the redox potential (and therefore the microbial activity) increased.

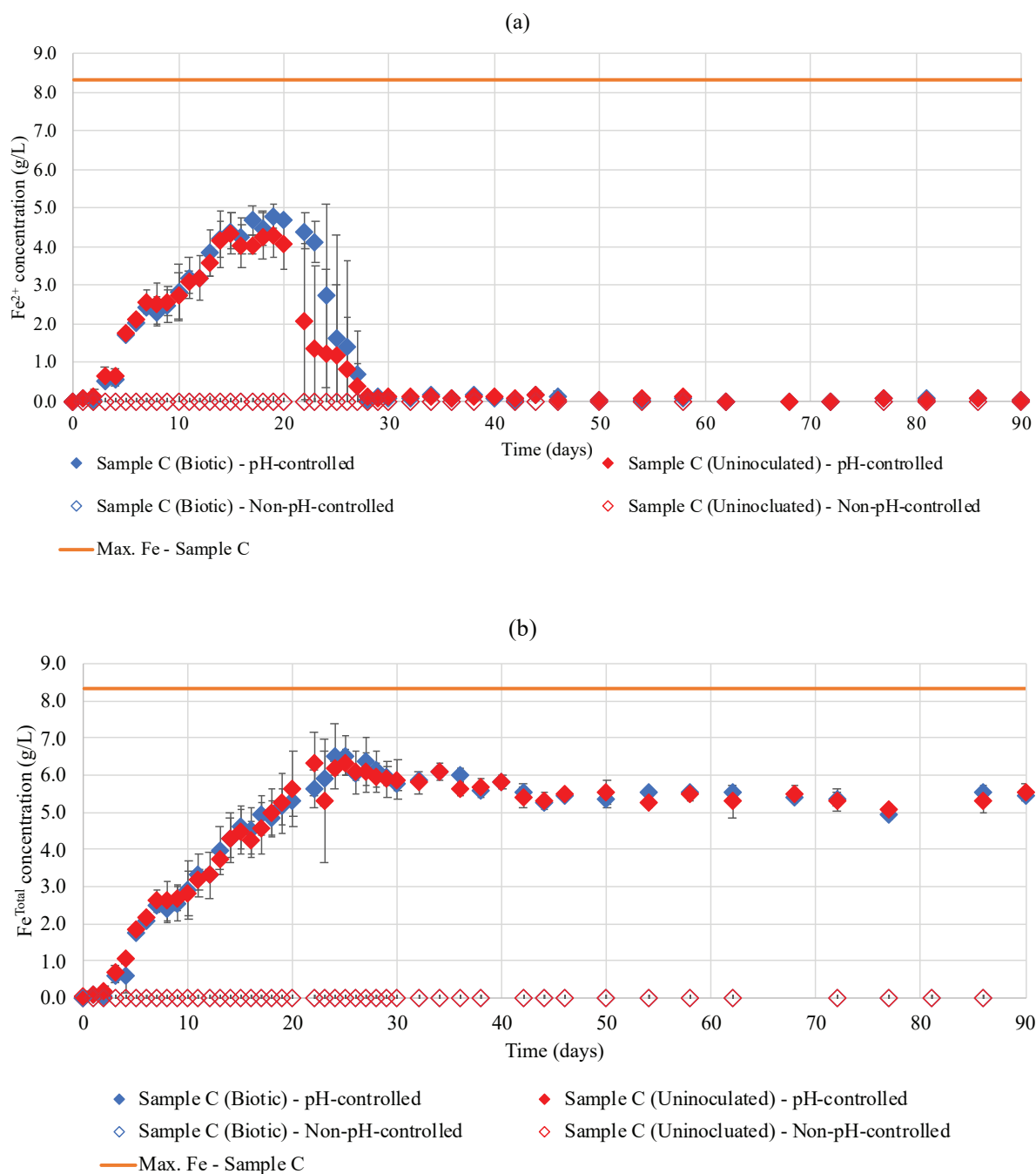


Figure 4-11 Ferrous (a) and total (b) iron concentrations for pH-controlled, non-pH-controlled, inoculated and uninoculated tests for sample C, with indication of the maximum possible iron concentrations achievable from Fe-Sulfide dissolution iron coming in with the ABS media and inoculum. The error reported is that obtained from one times the standard deviation, which indicates the variation between the triplicate samples used in the test. The large error bars on some data points (specifically for the pH-controlled flasks) are due to variation in microbe adaptation to the environment in each replicate flask.

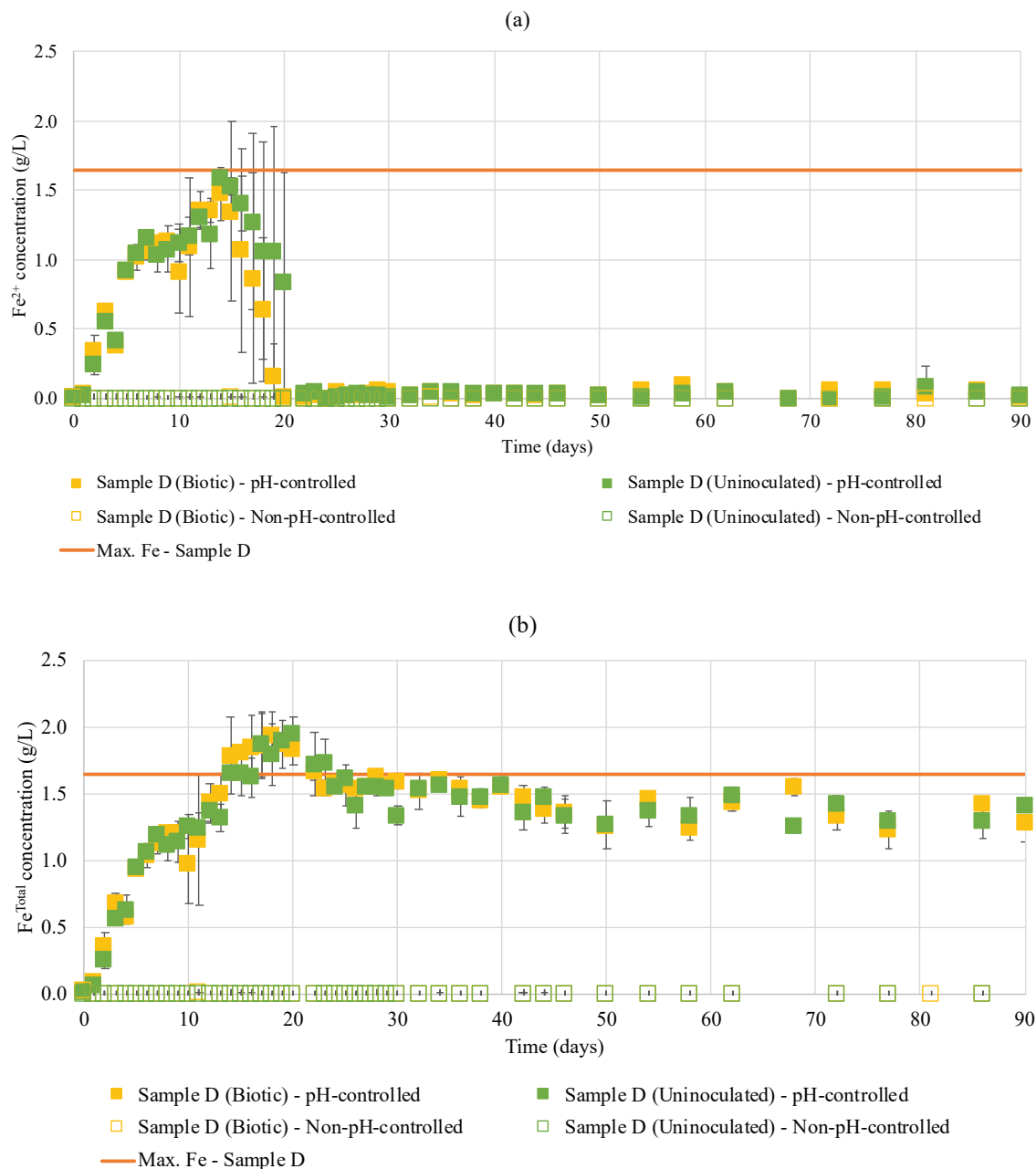


Figure 4-12 Ferrous (a) and total (b) iron concentrations for pH-controlled, non-pH-controlled, inoculated and uninoculated sample D with indication of the maximum possible iron concentrations achievable from Fe-Sulfide dissolution and iron coming in with ABS media and inoculum. The error reported is that obtained from one times the standard deviation, which indicates the variation between the triplicate samples used in the test. The large error bars on some data points (specifically for the pH-controlled flasks) are due to variation in microbe adaptation to the environment in each replicate flask.

The sulfate ion concentration profiles for the inoculated, uninoculated, pH-controlled and non-pH-controlled samples C and D are provided in Figure 4-13 (a) and (b), respectively. The purpose of the sulfate ion profiles was to track the sulfide mineral dissolution, as the iron concentrations were not guaranteed to fluctuate solely as a result of Fe-Sulfide mineral reaction. The sulfate concentrations for all experimental flasks of samples C and D remained below the maximum possible sulfate concentration from Fe-Sulfide dissolution, which was similar to the total iron concentration profile of sample C. The lower than maximum sulfate concentration may suggest incomplete Fe-Sulfide dissolution due to

textural limitation (Fe-Sulfide material in samples C and D not being thoroughly liberated, see section 4.4.2).

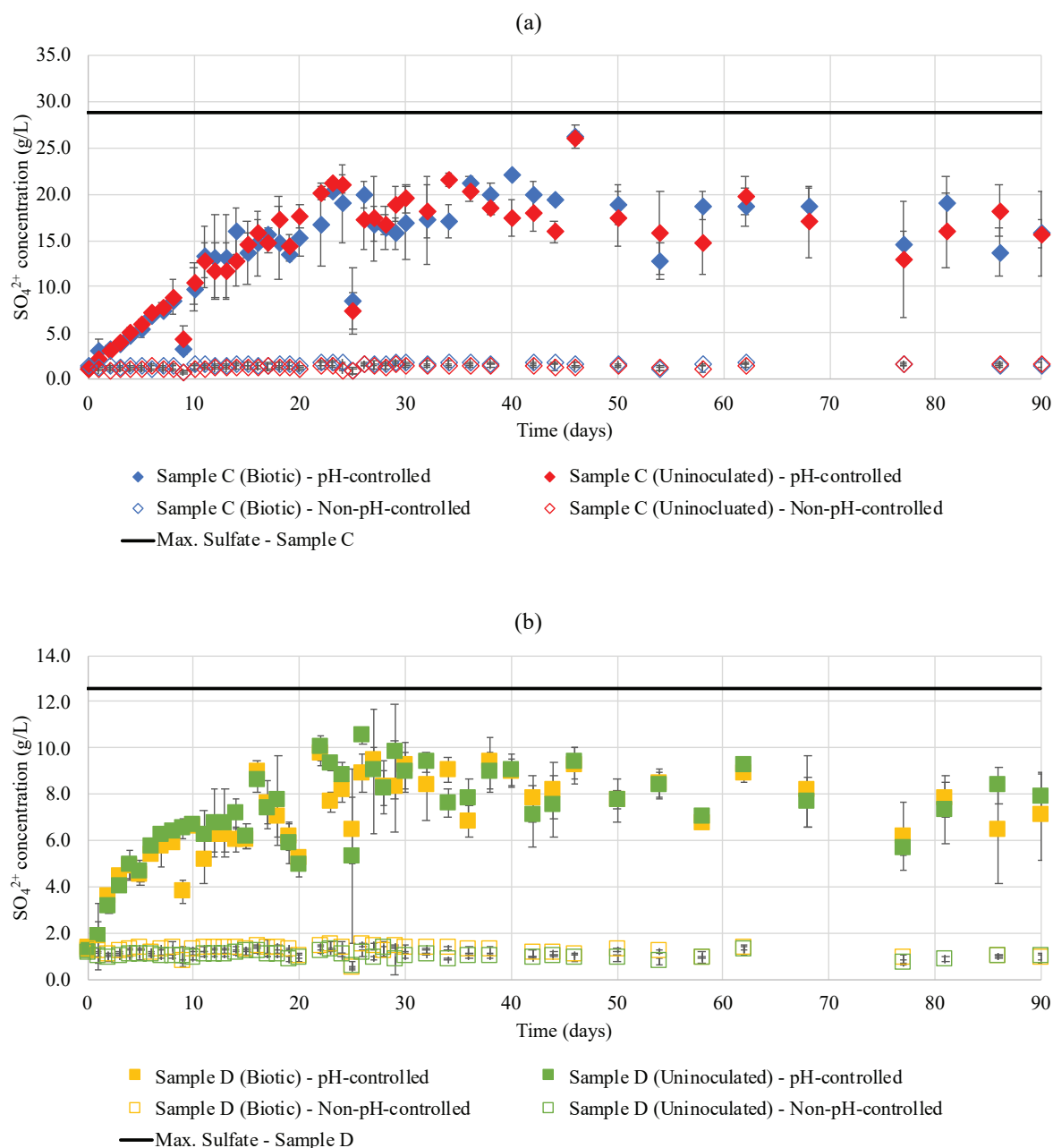


Figure 4-13 Sulfate concentration over for inoculated, uninoculated, pH-controlled and non-pH-controlled samples C (a) and D (b). The maximum possible sulfate concentrations attainable from the dissolution of sulfide minerals, pH control and the sulfate introduced with ABS media and inoculum is shown on the plot. The error bars shown indicate one times the standard deviation between triplicate test flasks. Large error bars may be due to the inherent variability within the turbidimetric sulfate assay, in addition to a difference in microbial adaptation in replicate flasks.

Figure 4-14 shows the colour progression within the pH-controlled batch biokinetic test experiments for samples C and D over the duration of the test. This served as a supportive measure for the profiles presented in Figure 4-9 to Figure 4-13 and provided a more visual representation of the evolution of ferrous (green colour) and ferric (yellow/red/brown colour) iron in the flasks. Although only pH-

controlled tests are shown, the non-pH-controlled tests retained the Day 1 colour characteristics for both samples C and D for the duration of the tests. The days indicated for the flasks are to be interpreted with consideration for the error bars shown in the profiles presented in Figure 4-9 to Figure 4-13, as they were not consistent across replicates prior to day 30 (after which the error between replicates was lower).

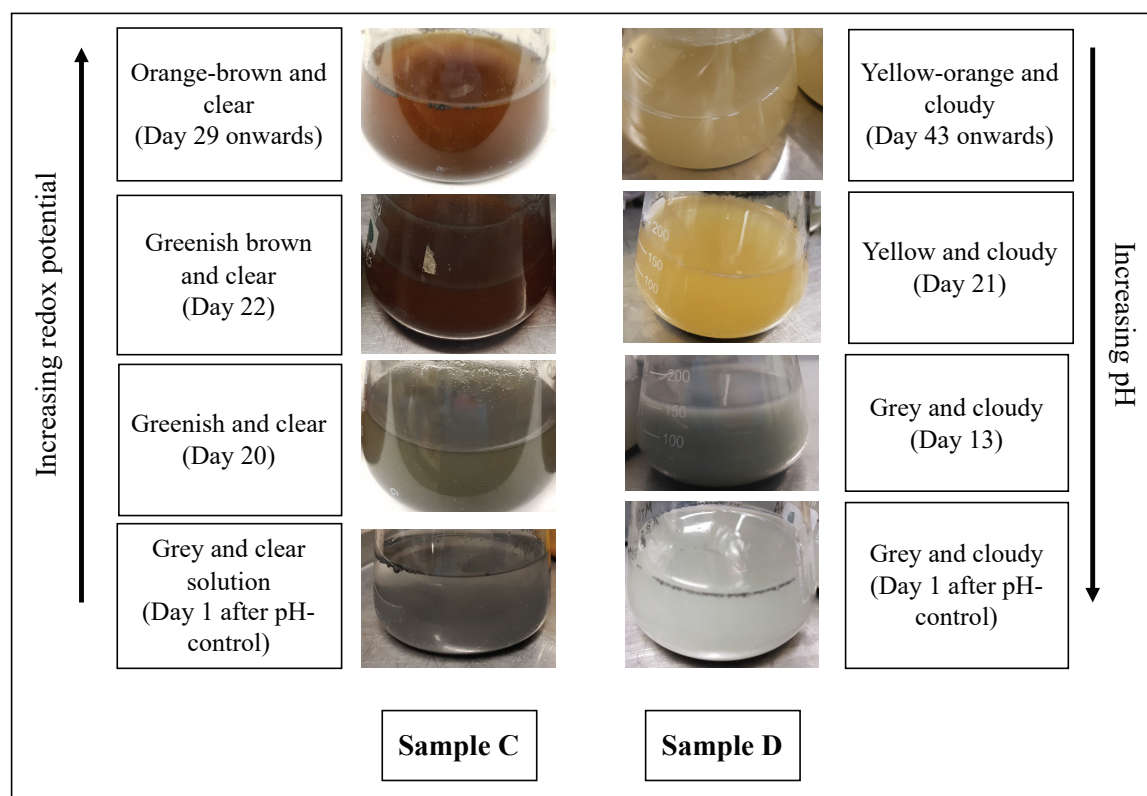


Figure 4-14 Colour change in the pH-controlled UCT batch biokinetic test experiments over the course of the 90 days for samples C and D. Non-pH-controlled tests retained the colour of the Day 1 flasks for the duration of the test.

4.7 Summary

The results and associated discussion in Chapter 4 achieved objective one and provided insight into how the interpretation of geochemical static and UCT batch biokinetic tests is not necessarily complete without understanding the sample mineralogy and texture. Knowledge of the mineralogy played a key role in positioning samples on the PAF/NAF/UC characterisation spectrum, as this was chiefly based on primary acid forming and neutralising mineral abundance. Additionally, the interpretation of the UCT batch biokinetic test profiles depended strongly on the knowledge of the intermediate weathering minerals (and their solid solution series end members) and slow weathering Fe-bearing minerals in the samples (Broadhurst et al., 2013; Dyantyi et al., 2013; Becker et al., 2015; Opitz et al., 2018). Finally, the texture results suggested that having a “one size fits all” approach to the top size of ARD test material may not necessarily provide the extremes of acid formation and neutralisation in all cases, as some of the fine-grained Fe-Sulfide or dissolving minerals may remain encapsulated. This concept of an ore-customised grind size has been applied in flotation processes (Evans, 2010; Hunt et al., 2011; Wightman & Evans, 2014; Tungpalan et al., 2015) and may need to be considered for ARD characterisation test work in future.

5 Results and Discussion: Meso-scale

The current chapter addresses objective two and research question two of this study. These were to *synergise the results of textural and mineralogical analyses on the meso-scale (>1mm particle size, prediction tests) with the results of the more routinely practiced humidity cell test, with particular consideration for the key minerals involved in acid formation (iron sulfide minerals) and neutralisation (carbonate minerals) and answer “which textural/mineralogical parameters are to be primarily considered when interpreting the ARD prediction (humidity cell) test results (meso-scale) and how do the textural and mineralogical data enhance these results?”*.

The various data sets included and discussed in this chapter include humidity cell test data, as well as the textural and mineralogical analyses of the HCT feed material. These build towards understanding how meso-scale texture and mineralogy may contribute to the ARD assessment “toolbox”, which in turn contributes to addressing objective four (understanding the role of mineralogy and texture in the ARD assessment “toolbox”). The experimental procedures have been presented in Chapter 3, with detailed methods provided in Appendix A. Complete data sets may be found in Appendix B.

5.1 Particle size distribution

The PSD for the meso-scale material was obtained through the dry-screening of the parent sample. The size fractions used to obtain the PSDs, as well as the size fractions used for the meso-scale textural analyses are provided in Table 5-1. The smallest aperture size used for the parent material screening stack was 2000 μm , with this fraction being further screened into the -2000/+1000 μm , -1000/+425 μm , -425/+150 μm and -150/+0 μm fractions after stratified sub-sampling of the parent material.

Table 5-1 Size fractions used for screening of meso-scale material for samples A, B, C and D, as well as the size fractions selected for textural analyses.

	Meso-scale screening	Size fractions for textural and mineralogical analyses
Size fraction (μm)	-6700/+5600	-6700/+2000
	-5600/+4000	
	-4000/+2000	
	-2000/+0	-2000/+1000
		-1000/+425
		-425/+150
		-150/+0

The meso-scale PSDs for samples A, B, C and D are presented in Figure 5-1. These were used to compare sub-sample PSDs to verify similarity and therefore adequate representation of all size fractions in each sub-sample. The d_{50} of samples A, B, C and D were found to be between 2250 μm (sample D) and 2900 μm (samples A and B), while the d_{90} between 5800 μm (samples A and D) and 6300 μm (sample C). During the crushing stage, once a d_{90} of 6300 μm was obtained (the particle top size required for humidity cell tests, based on ASTM (2013)), the feed material was not crushed further to avoid the generation of excessive fines and the subsequent skewing the PSD in favour of finer material. Most of the material ($\pm 50\%$) for all samples was found in the -6700/+2000 μm size fraction.

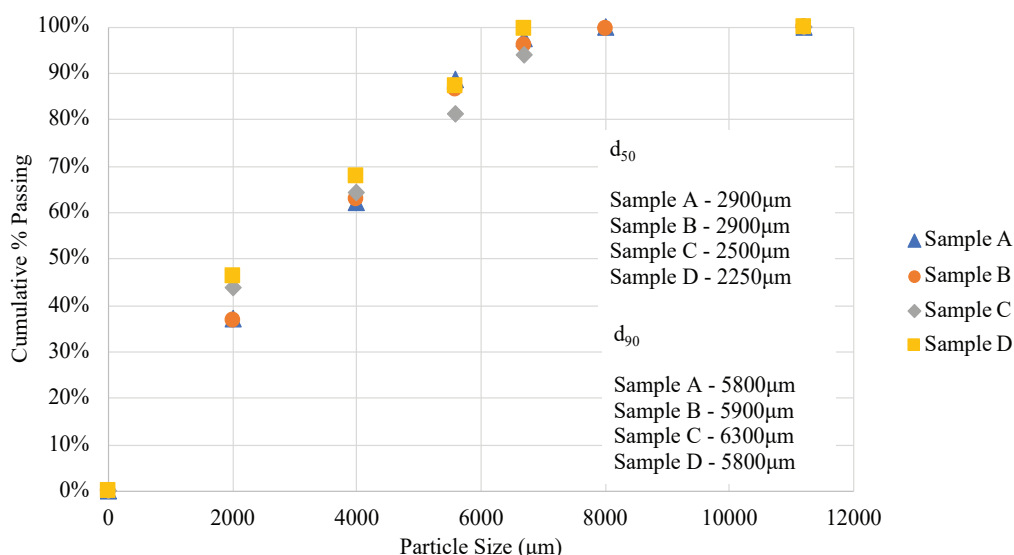


Figure 5-1 The PSD of the meso-scale samples A, B, C and D after crushing. The parent sample PSDs were representative of those of the sub-samples used for the HCT.

5.2 Chemical characterisation

5.2.1 LECO total sulfur results

The size fractions for textural and mineralogical analyses were assessed individually for total sulfur content. These data are presented in Table 5-2 for samples A, B, C and D alongside the sample total sulfur content for comparison. The sample total sulfur content was reconstituted from the sample total sulfur values using the PSD and the sulfur content of the individual size fractions, with consideration for the propagation of the individual uncertainties associated with the results. Size fractions larger than 1000μm were prepared from individually pulverised sub-samples of the relevant size fraction to provide an indication of the variation between replicate samples. The individual sub-samples were split to have the same mass as those prepared into blocks for textural and mineralogical analyses.

Overall the sulfur content increased as the size fraction decreased for all samples. The -6700/+2000μm size fraction for samples A and B, however, showed a slightly higher sulfur content. This was thought to occur due to the preferential breakage and deportment of softer sulfide minerals into finer size fractions (Evans, 2010), which would result in higher total sulfur contents in those fractions.

Table 5-2 LECO S results for samples A, B, C and D for the sized meso-scale material, with size fractions corresponding to those used for QEMSCAN analyses. These are presented alongside the sample total sulfur content for comparison. The error reported is that from one times the standard deviation obtained from triplicate analyses and for the reconstituted sample total sulfur the error is that obtained from the propagation of the uncertainties associated with the sulfur contents of the individual size fractions.

Size fraction (μm)	Sulfur content as wt.% of the sample			
	A	B	C	D
Sample (reconstituted)	3.44% $\pm$ 1.44%	4.70% $\pm$ 1.92%	9.52% $\pm$ 0.66%	1.45% $\pm$ 0.18%
-6700/+2000	3.59 $\pm$ 0.70	4.93 $\pm$ 1.00	8.29 $\pm$ 0.25	1.35 $\pm$ 0.05
-2000/+1000	2.76 $\pm$ 0.55	3.25 $\pm$ 0.67	8.97 $\pm$ 0.54	1.43 $\pm$ 0.14
-1000/+425	2.90 $\pm$ 0.63	3.75 $\pm$ 0.66	10.2 $\pm$ 0.16	1.51 $\pm$ 0.04
-425/-+150	3.46 $\pm$ 0.77	4.82 $\pm$ 1.09	12.7 $\pm$ 0.06	1.61 $\pm$ 0.10
-150/+0	4.14 $\pm$ 0.07	6.47 $\pm$ 0.12	13.4 $\pm$ 0.00	1.89 $\pm$ 0.02

5.3 Meso-scale mineral texture

The following sub-section presents the findings of the mineralogical and textural analyses performed using the QEMSCAN for the sized meso-scale HCT feed material, as well as for the overall HCT feed. Data sets include the grain size distribution, as well as the liberation and association data for the Fe-Sulfide and dissolving minerals. When considering the mineral liberation and association data for the dissolving category, only samples B, C and D were assessed, as these had a calcite content at an abundance of or above 5% (from either XRD or QEMSCAN), which was thought to lower the sampling errors involved (see Chapter 6). The texture definitions used were defined as those outlined in section 4.

5.3.1 Grain size distribution on the meso-scale

Fe-Sulfide grain size distribution on the meso-scale

The sample GSD was used to provide an indication of the potential liberation characteristics of the HCT feed material. The Fe-Sulfide GSDs for samples A, B, C and D are presented in Figure 5-2. The grain size l_{50} for samples A, B, C and D were 65 μm , 118 μm , 105 μm and 40 μm , respectively. The sample l_{90} for samples A, B, C and D were 200 μm , 210 μm , 550 μm and 118 μm , respectively. Sample D had the finest Fe-Sulfide grain size distribution overall, while samples B and C had the coarsest GSDs, with sample C containing the coarsest Fe-Sulfide grains of all samples.

The Fe-Sulfide grains in all samples were smaller than 2000 μm and the l_{50} for all samples was finer than the top size of the finest size fraction (150 μm). This suggested a large degree of encapsulation of the Fe-Sulfide grains, even in the finer size fractions where a higher degree of liberation would be expected. For samples with the coarsest GSDs (samples B and C), however, a higher degree of liberation was expected overall than for the samples with the finer GSDs (samples A and D). Sample C had a GSD spanning the broadest range of grain sizes. This could be attributed either to the limitations of the QEMSCAN when distinguishing clustered Fe-Sulfide grains, or the potential bimodality of the Fe-Sulfide grain distribution based on the shape of the GSD for sample C (Wightman & Evans, 2014). Liberation was also expected to begin in larger size fractions for sample C than for any other sample due to the presence of the largest Fe-Sulfide grains. At finer sizes (less than 50 μm), however, sample C

had grains that were finer than those of sample B, suggesting that Fe-Sulfide grain liberation would not necessarily be the largest for sample C in the finer size fractions.

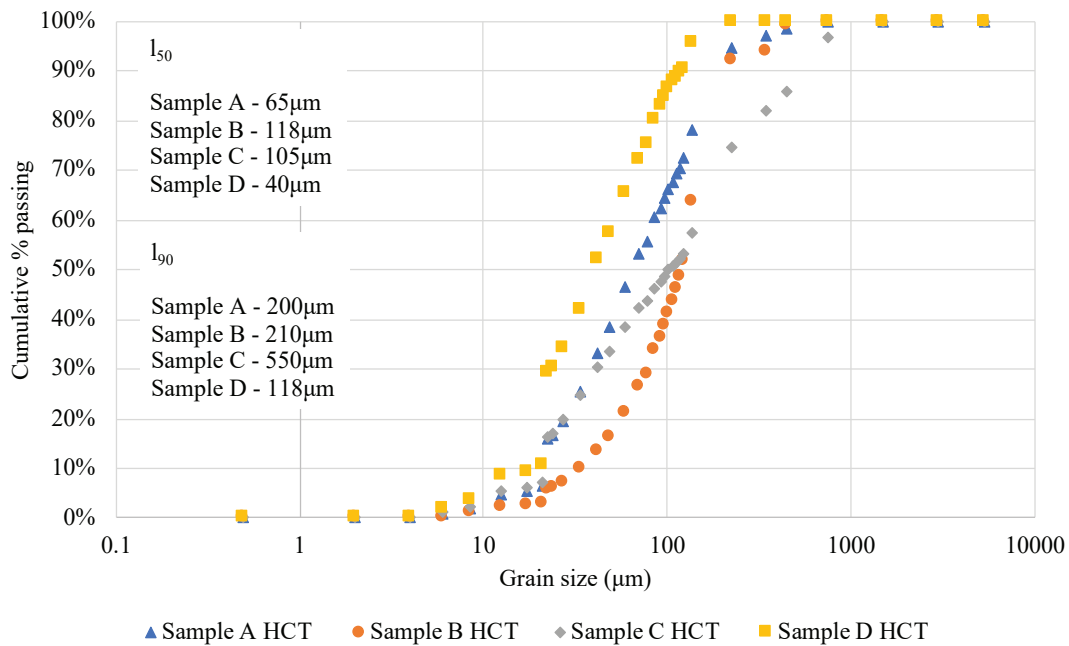


Figure 5-2 Unsized sample grain size distribution for meso-scale samples A ($N_S=24201$), B ($N_S=52273$), C ($N_S=60897$) and D ($N_S=17859$), where N_S is the total number of Fe-Sulfide-bearing particles analysed.

Dissolving mineral grain size distribution on the meso-scale

The dissolving mineral GSDs for samples B, C and D are presented in Figure 5-3. The l_{50} for samples B, C and D were determined as 55μm, 65μm and 46μm, respectively. The sample l_{90} for samples B, C and D were determined as 185μm, 165μm and 115μm, respectively. Samples B and C had the coarser dissolving mineral GSD at coarser grain sizes, while at finer grain sizes sample B had the finer GSD. Overall, sample D showed the finer dissolving mineral GSD. The GSD of all samples, however, was relatively fine, indicating that liberation of the dissolving minerals could occur predominantly in the finer fractions.

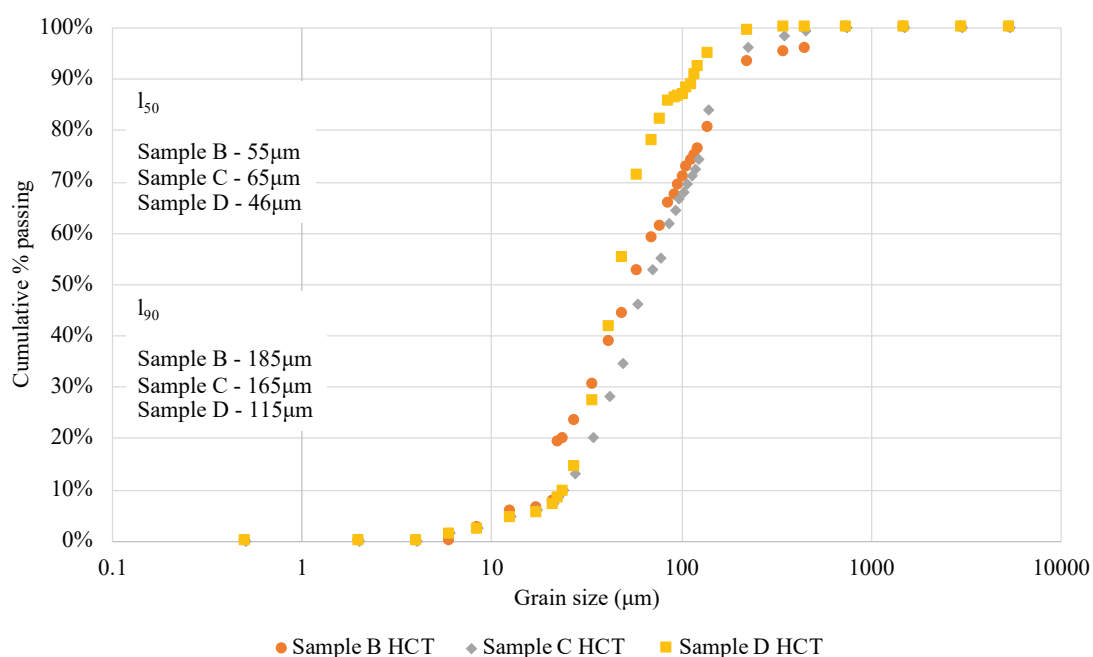


Figure 5-3 Unsized dissolving mineral grain size distribution for meso-scale samples B ($N_D=81804$), C ($N_D=146442$) and D ($N_D=29060$), where N_D is the total number of dissolving mineral-bearing particles analysed.

The GSDs of the Fe-Sulfide and dissolving minerals were compared in Table 5-3 for samples B, C and D. In samples B and C, the Fe-Sulfide grains were coarser than the dissolving mineral grains based on the comparison of the l_{50} and l_{90} values, while sample D had l_{50} and l_{90} values of the Fe-Sulfide and dissolving mineral grains that were similar to one another.

Table 5-3 Comparison of l_{50} and l_{90} for the Fe-Sulfide and dissolving mineral grains from the sample GSDs in Figure 5-2 and Figure 5-3.

	Fe-Sulfide l_{50}	Dissolving l_{50}	Fe-Sulfide l_{90}	Dissolving l_{90}
Sample B	118 μm	55 μm	210 μm	185 μm
Sample C	105 μm	65 μm	550 μm	165 μm
Sample D	40 μm	46 μm	118 μm	115 μm

5.3.2 Meso-scale liberation and association

Fe-Sulfide liberation and association on the meso-scale

The reactivity of minerals associated with Fe-Sulfides has been highlighted as one of the important parameters for assessing ARD potential on the meso-scale (Parbhakar-Fox, 2012, parameter E). The association of Fe-Sulfides to other sulfide material was ranked as the highest ARD-forming association due to galvanic interaction, while Fe-Sulfide association to primary neutralising minerals was ranked as having the lowest ARD-forming potential. Fe-Sulfide association to fast weathering non-neutralising minerals was ranked more acid-forming than association to slow weathering non-neutralising minerals and primary neutralising minerals, and less acid-forming than association to sulfide and inert minerals such as quartz. This underlines how Fe-Sulfides encapsulated in more reactive material can be subsequently liberated upon the onset of acidic conditions, as the surrounding mineral matrix could dissolve if these surrounding gangue minerals are sufficiently reactive.

The meso-scale Fe-Sulfide liberation and association data for samples A, B, C and D are provided in Figure 5-4 for the sized and reconstituted HCT feed material. The liberation and association classifications were defined as in section 4.4.2. All samples showed the largest degree of association to the intermediate weathering, inert and slow weathering mineral categories, as well as some association to dissolving minerals, particularly for samples B, C and D. These associations were linked primarily to the abundance of each of these groups in the samples. The inert category was dominated by quartz for all samples, with some titanite in this grouping for sample C. In samples A and D, the intermediate weathering and slow weathering categories were dominated by Fe-rich amphiboles (ferro-actinolite, grunerite) and magnetite, respectively, with sample A containing some plagioclase-albite in the slow weathering category and sample D containing some chlorite and Fe-mica in the intermediate weathering category. The intermediate weathering category in sample B comprised primarily Fe-mica and chlorite, with the slow weathering category being dominated by plagioclase-albite, K-feldspar and magnetite. Sample C contained chlorite in the intermediate weathering category and K-feldspar in the slow weathering category. The associations to intermediate weathering, slow weathering and inert minerals suggest that in the absence of acidic lixiviant, the Fe-Sulfides encapsulated in these relatively unreactive minerals may not necessarily become liberated over time.

Overall the lowest associations were to the other sulfide, fast weathering and the “other” categories, which contained arsenopyrite and chalcopyrite, epidote and Ca-plagioclase, and apatite, respectively. Although the association of Fe-Sulfide with fast weathering minerals was low, this group could potentially consume acid in the long-term through the dissolution of minerals such as epidote (Jansen & Taylor, 2003).

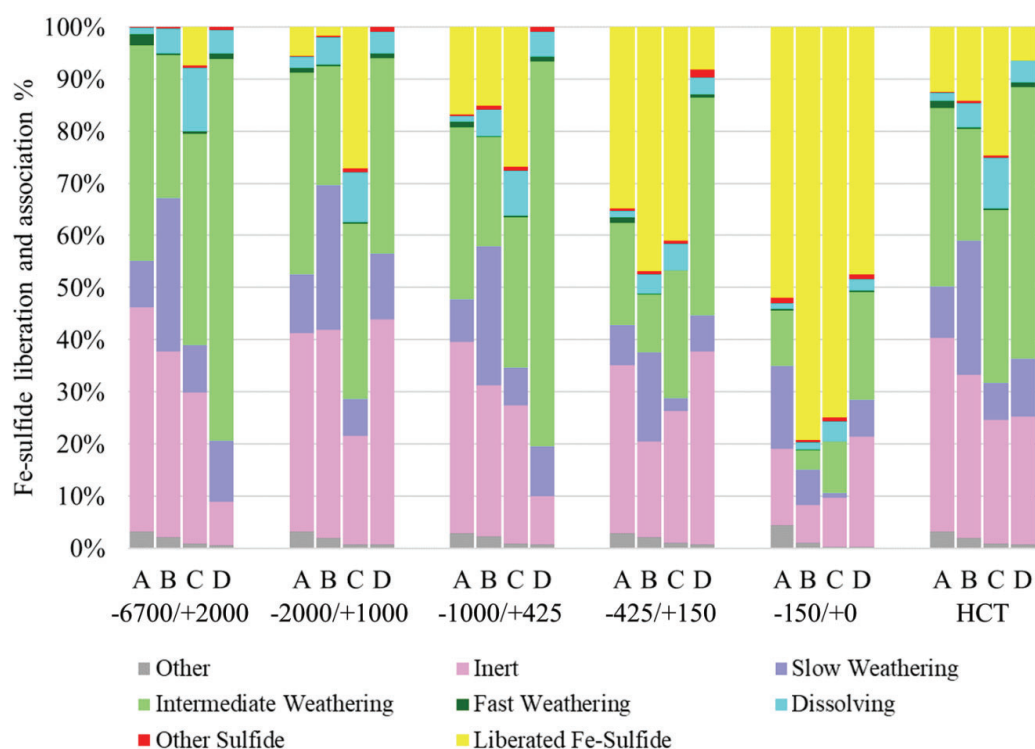


Figure 5-4 Fe-Sulfide liberation and association for samples A, B, C and D by size. The association describes the interrelationship of unliberated Fe-Sulfide mineral grains with other minerals present in the waste rock sample. The liberation and association data were calculated based on the Fe-Sulfide mass % distribution throughout the sample, rather than the Fe-Sulfide distribution in the fraction.

From Figure 5-4, the Fe-Sulfide liberation increased with decreasing particle size/size fraction for all samples. Samples A, B and D contained Fe-Sulfides in the -6700/+2000 μ m size fraction that were entirely associated with other minerals. This was similar to recent studies wherein the liberation of Fe-Sulfide minerals was found to be negligible at particle sizes above 2.4mm, with the liberation becoming more prominent with decreasing size fraction (Elghali et al., 2018, 2019). Sample C, as was suggested by it containing the coarsest Fe-Sulfide grains (Figure 5-2), had liberated Fe-Sulfide material in the coarser size fractions, starting with the -6700/+2000 μ m size fraction (with liberated material consisting of large grain clusters). The largest liberation for the HCT sample overall was observed for sample C, followed by samples B, A and D, respectively. This was consistent with the GSDs for the samples provided in Figure 5-2. Although Fe-Sulfide liberation for sample B began only in the -2000/+1000 μ m size fraction, at the -425/+150 μ m size fraction and finer the Fe-Sulfide liberation for sample B was the largest of all samples. This behaviour was supported by the GSD in Figure 5-2, where at finer values of the grain size (below 50 μ m) sample B had the coarsest Fe-Sulfide GSD of all samples.

For the reconstituted HCT sample the Fe-Sulfide liberation was limited. This arose from the large contribution from the size fractions where the Fe-Sulfides were primarily unliberated, namely the -6700/+2000 μ m and -2000/+1000 μ m size fractions. From Figure 5-1, over 50% of the sample mass was present in these fractions, which, based on Figure 5-4, had little to no liberation of the Fe-Sulfide minerals. These findings highlight the importance of considering the sample PSD when assessing the ARD potential, which has been suggested by recent ARD kinetic test work (Erguler & Kalyoncu Erguler, 2015; Elghali et al., 2018, 2019).

Figure 5-5 presents false colour images of some of the Fe-Sulfide-bearing particles in samples A, B, C and D. These provide some indication of the Fe-Sulfide grain shape and diversity across the samples. Sample A showed distinct variations in the Fe-Sulfide grains, which were present as veins, coarse grains and disseminated fine-grained Fe-Sulfides that were all associated to other mineral categories to varying degrees. The Fe-Sulfide-bearing particles in sample B consisted of discrete euhedral (pyrite) grains of varying sizes, which ranged from disseminated to clustered texture. The Fe-Sulfide-bearing particles in sample C consisted of massive sulfides that either made up entire particles or were intergrown with other minerals, leading to the fine-grained appearance in some of the particles. Sample D contained particles which had larger irregular (anhedral) Fe-Sulfide grains, as well as Fe-Sulfides that were largely intergrown with other minerals, primarily the intermediate weathering amphiboles.

The variation in Fe-Sulfide texture has implications for the ARD potential of waste material, as described by Parbhakar-Fox (2012), parameter C. Disseminated Fe-Sulfides were considered to be more acid-forming than larger grains or veins, as they presented a larger surface area for reactivity; however, the grain shape of the Fe-Sulfides (morphology) also needed to be taken into account, as it affected reactivity in the following order framboidal>anhedral>subhedral>euhedral, where framboidal morphology was the most reactive and euhedral morphology the least (Parbhakar-Fox, 2012). Considering this alongside Figure 5-5, differences in the ARD potential between the samples A, B, C and D could be influenced by the variation in Fe-Sulfide texture in addition to the mineralogy and liberation and association characteristics. A comprehensive assessment of the ARDI to include the Fe-Sulfide texture, as well as all other parameters, could be performed on the meso-scale material to assess the role of texture on the meso-scale. This would involve the assessment of the complete ARDI of each particle in the -6700/+2000 μ m size fraction (as it contains the most texturally intact examples of the

material) of the sample. Following this, an averaged value of the ARDI for this size fraction could be obtained. Although this would not necessarily represent the full sample, this approach could provide an indication of the textural relationship in the sample and act as an additional estimate of the sample ARD potential. Because the assessment of the ARDI requires the assessments of all parameters on a single example/particle, however, this computation was not possible within the limitations of the iDiscover computing software (as it would require the construction of nested categorisers to perform simultaneous computations of all parameters for all particles).

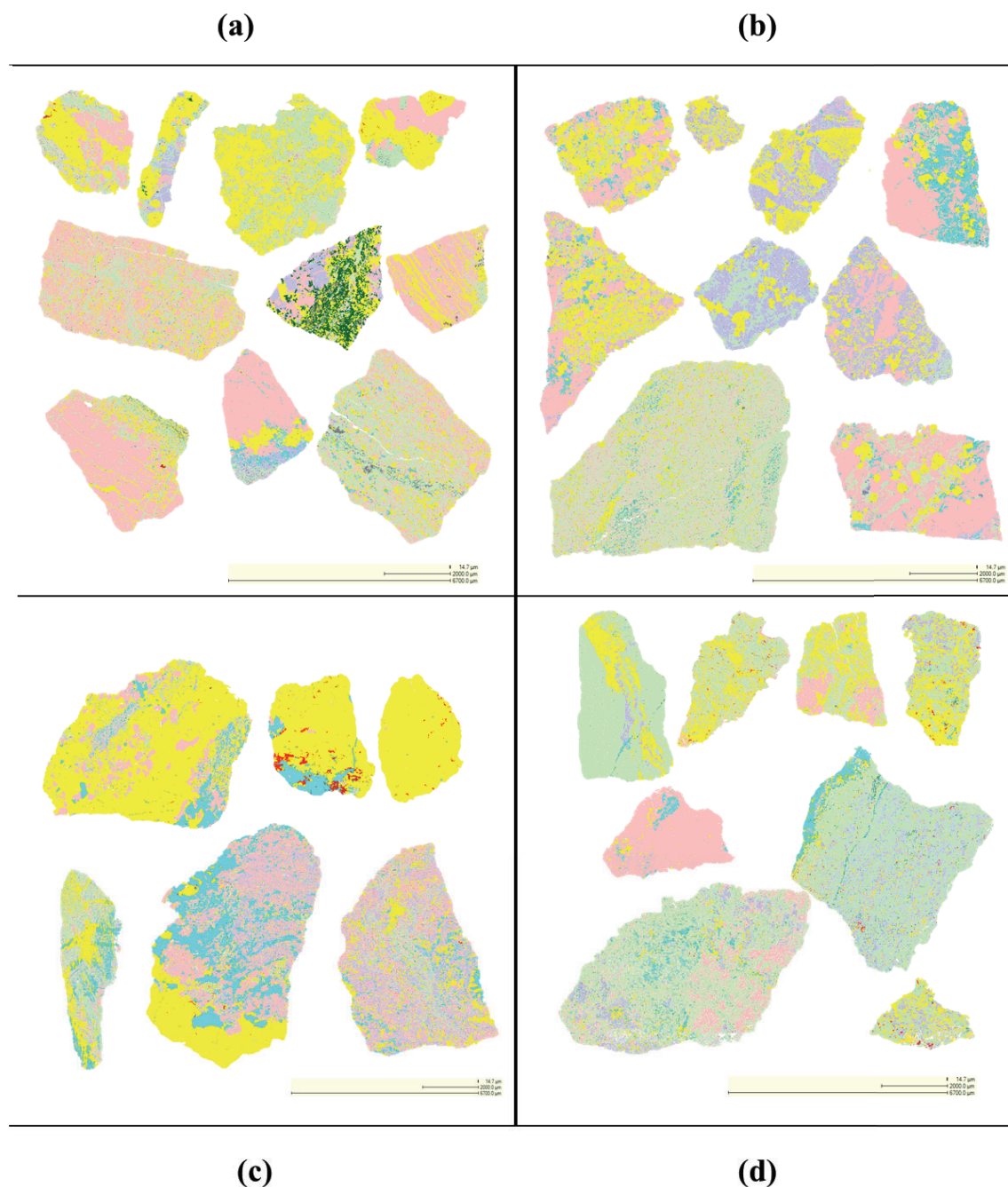


Figure 5-5 False-colour images of Fe-Sulfide-bearing particles for samples A (a), B (b), C (c) and D (d) in the -6700/+2000µm size fraction representing the variation in Fe-Sulfide texture and mineral association. See Figure 5-4 for colour legend.

To gain a better understanding of the onset of liberation in the samples and the variation in the Fe-Sulfide grain populations apparent in Figure 5-5, the Fe-Sulfide liberation was represented by the liberation spectrum approach described by Wightman & Evans (2014).

The gradient corresponding to the liberation size, L_0 , for samples A, B, C and D varied for the four samples. Samples A and B had intermediate liberation sizes of 455 μm , while sample D had the finest liberation size of 350 μm . The liberation spectrum for sample C suggested variation in the Fe-Sulfide grain populations. The finer grain population had a liberation size $L_{0,1}$ of 500 μm , while the second population of Fe-Sulfide grains had a liberation size, L_0 , of 8000 μm .

The irregularities in the liberation spectrum, particularly for sample C, but also to a lesser extent for sample D, were attributed to the variation in the Fe-Sulfide grain populations, which were evident from Figure 5-5(c) and Figure 5-5(d). This behaviour was similar to samples assessed by Wightman & Evans (2014), which had a variation in the grain populations. The feed grade of samples A, B and D was similar to that reported by QEMSCAN (at 6.8 wt.%, 7.7 wt.% and 4.2 wt.% for A, B and D, respectively) while sample C showed a large deviation in the feed grade from that reported through QEMSCAN (31.2 wt.%). This difference was attributed to the variation in grain population in the sample, which was represented by the irregularity of the liberation spectrum curve.

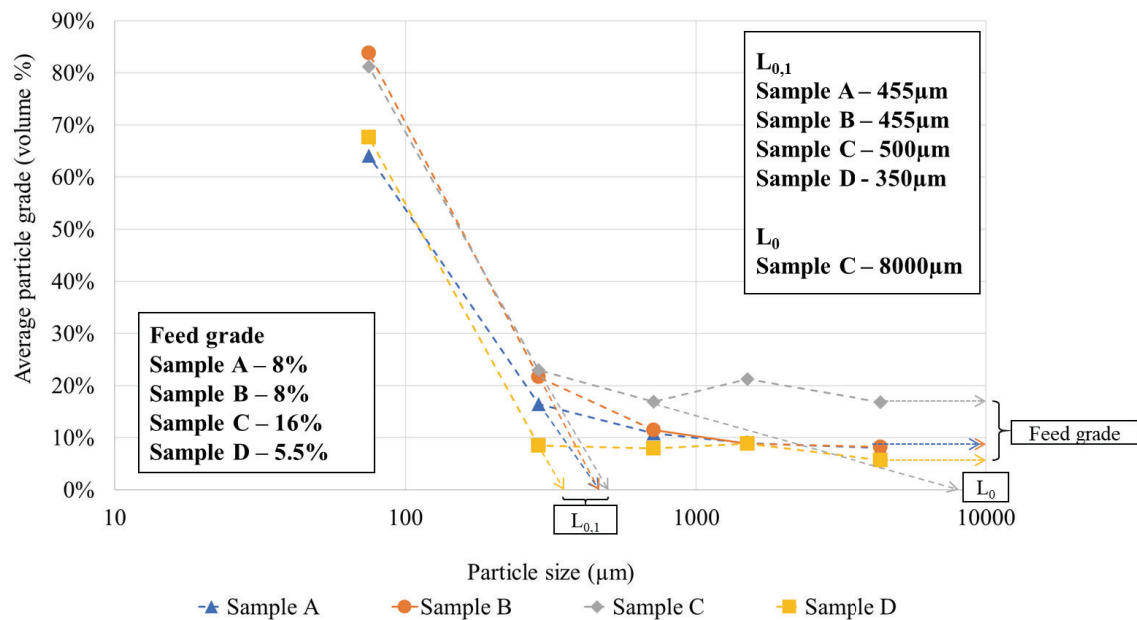


Figure 5-6 Fe-Sulfide liberation spectrum for samples A, B, C and D based on Wightman & Evans (2014).

The degree of liberation has been documented to have an influence during ARD test work (Brough et al., 2017; Elghali et al., 2018), where samples with higher Fe-Sulfide liberation were found to be more likely to produce acidic leachate during humidity cell testing. Elghali et al. (2018) also found that the degree of Fe-Sulfide liberation was negligible at size fractions above 2.4mm for the Archaean gold porphyry system used during their study. This was similar to the trend observed in Figure 5-4 where liberation was negligible for particles larger than 2mm for all samples except sample C, which had the coarsest GSD and an early liberation size of 8000 μm from Figure 5-6.

The unliberated category was assessed in terms of locked and middlings sub-categories, as was done in section 4.4.2 to assess how much of the unliberated material was unavailable for reaction due to near-complete encapsulation. The results of this are provided in Table 5-4. Overall the amount of locked Fe-Sulfide material increased as the size fraction increased, with the highest degree of locking being present for samples A and D (55% and 63% locked Fe-Sulfides, respectively), followed closely by sample B (54%). Sample C contained the lowest amount of encapsulated Fe-Sulfide material (36%) for the sample overall.

Due to the variation in the Fe-Sulfide encapsulation/liberation over the size fraction range it was necessary to re-visit the PSD in Figure 5-1 to assess the size fractions which would control the HCT material behaviour. Based on Figure 5-1, the d_{50} of all samples A, B, C and D was larger than 1000 μ m, meaning that more than 50% of the material and consequently, most of the Fe-Sulfides could be found in the -6700/+2000 μ m and -2000/+1000 μ m size fractions. Sample A had liberated Fe-Sulfides in the -6700/+2000 μ m size fraction, with 73% of the unliberated Fe-Sulfides located in the locked category. This was similar for sample B, which contained predominantly locked Fe-Sulfides (68%) in the -6700/+2000 μ m size fraction. Sample C contained liberated Fe-Sulfide material (7%) in the -6700/+2000 μ m size fraction and the lowest amount of locked Fe-Sulfides (46%). Sample D exhibited the highest degree of Fe-Sulfide encapsulation in the largest size fraction (89%), with no liberation of this material even in the -2000/+1000 μ m and -1000/+425 μ m size fractions.

Table 5-4 The mass % distribution of the Fe-Sulfides in sized and reconstituted meso-scale material of samples A, B, C and D between liberated (>90% exposed area), middlings (30%<exposed area<90%) and locked (<90% exposed area) categories. N_s represents the number of Fe-Sulfide-bearing particles analysed.

Sample	Size fraction	N _s	Unliberated mass % Fe-Sulfide		Liberated mass % Fe-Sulfide
			Locked	Middlings	
A	-6700/+2000	280	73%	27%	0%
	-2000/+1000	875	56%	39%	5%
	-1000/+425	386	40%	43%	17%
	-425/+150	2861	27%	38%	35%
	-150/+0	19799	10%	38%	52%
	HCT	24201	55%	33%	12%
B	-6700/+2000	470	68%	32%	0%
	-2000/+1000	1297	57%	41%	2%
	-1000/+425	1120	46%	39%	15%
	-425/+150	3060	19%	34%	47%
	-150/+0	46326	3%	17%	80%
	HCT	52273	54%	32%	14%
C	-6700/+2000	465	46%	47%	7%
	-2000/+1000	1302	32%	41%	27%
	-1000/+425	1316	39%	34%	27%
	-425/+150	2215	26%	33%	41%
	-150/+0	55599	7%	18%	75%
	HCT	60897	36%	39%	25%
D	-6700/+2000	406	89%	11%	0%
	-2000/+1000	871	44%	56%	0%
	-1000/+425	653	65%	35%	0%
	-425/+150	1421	51%	41%	8%
	-150/+0	14508	15%	37%	48%
	HCT	17859	63%	31%	6%

Dissolving mineral liberation and association on the meso-scale

The dissolving mineral liberation and association data for samples C and D are provided in Figure 5-7. The liberation and association were defined for the dissolving minerals in the same way as for the Fe-Sulfide minerals.

Similarly to the Fe-Sulfide minerals the dissolving minerals were chiefly associated with intermediate weathering, slow weathering and inert minerals with lesser associations to fast weathering and other sulfide minerals. The association of dissolving minerals to fast weathering and other minerals was larger than that of the Fe-Sulfide minerals, especially for sample C, which had relatively large Fe-Sulfide and dissolving mineral contents (31% and 13%, respectively, from QEMSCAN, Table 4-4). The association of dissolving minerals was governed chiefly by the mineralogy. The fast weathering minerals in sample D comprised primarily Ca-bearing plagioclase feldspar, which could explain its relatively large association to the dissolving minerals.

Although the implications of the mineral associations are usually highlighted for the acid forming minerals, it is important to note that the availability of dissolving minerals to neutralise any formed acidity also depends on their liberation and their proximity to the Fe-Sulfide minerals. The latter point was highlighted in the ARDI classification, where greater association of Fe-Sulfide minerals with dissolving minerals was ranked as less potentially acid forming than association to fast weathering, slow weathering or inert non-neutralising minerals (Parbhakar-Fox, 2012, parameter E).

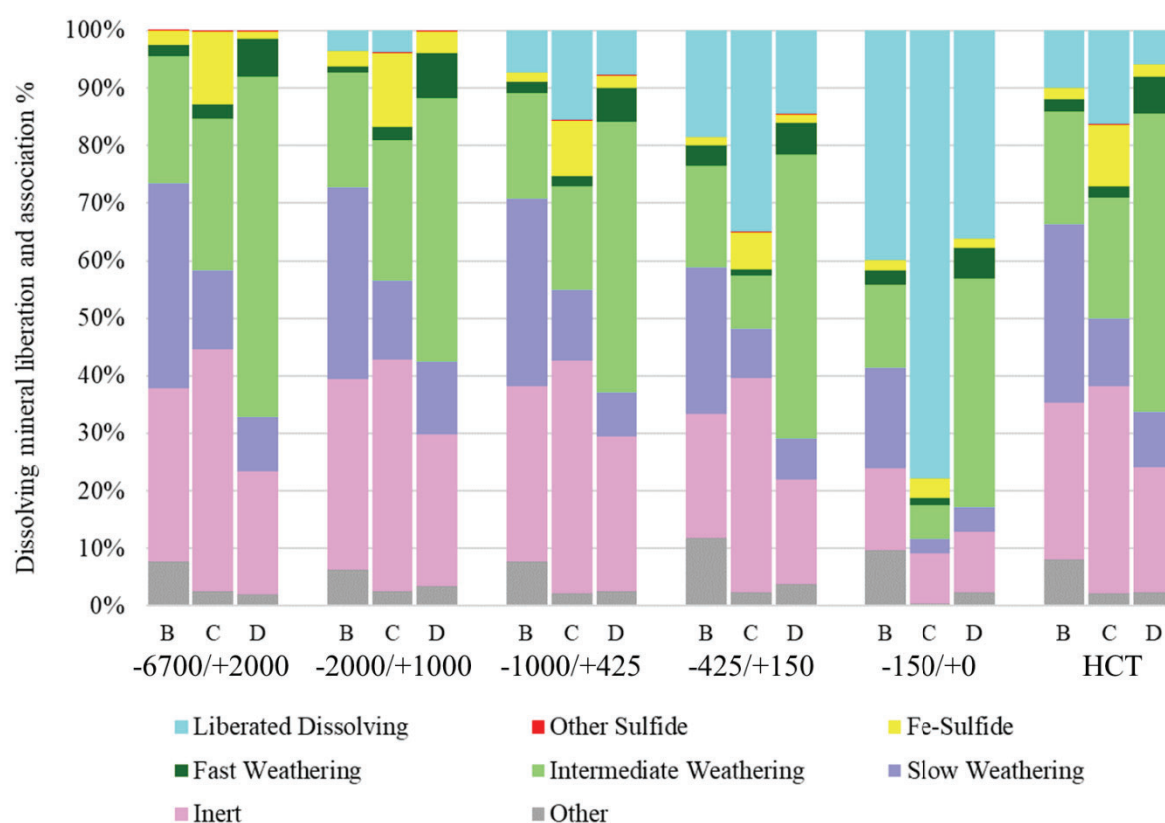


Figure 5-7 Dissolving mineral liberation and association for samples A, B, C and D by size. The association describes the interrelationship of unliberated dissolving mineral grains with other minerals present in the waste rock sample. The liberation and association data were calculated based on the dissolving mineral mass % distribution throughout the sample, rather than the dissolving mineral distribution in the fraction.

The sample liberation of the dissolving minerals in samples B, C and D was limited. This was expected based on the dissolving mineral GSDs in Figure 5-3, which reported relatively fine grains with a l_{50} of 55 μm , 65 μm and 46 μm for samples B, C and D, respectively and a l_{90} of 185 μm , 165 μm and 115 μm for samples B, C and D, respectively. The liberation did, however, increase with decreasing particle size, which was similar to the trend reported by Elghali et al. (2018) for carbonate minerals in the assessed samples. The -6700/+2000 μm size fraction contained dissolving minerals that were entirely associated with other minerals for all samples. For samples B and C, the liberation of dissolving minerals began in the -2000/+1000 μm size fraction, while sample D showed liberation only from the -1000/+425 μm size fraction and finer.

Figure 5-8(a), Figure 5-8(b) and Figure 5-8(c) provide examples of some of the dissolving mineral-bearing particles in samples B, C and D, respectively. The dissolving minerals in all samples appeared predominantly as large veins and smaller grains disseminated among the various mineral groups.

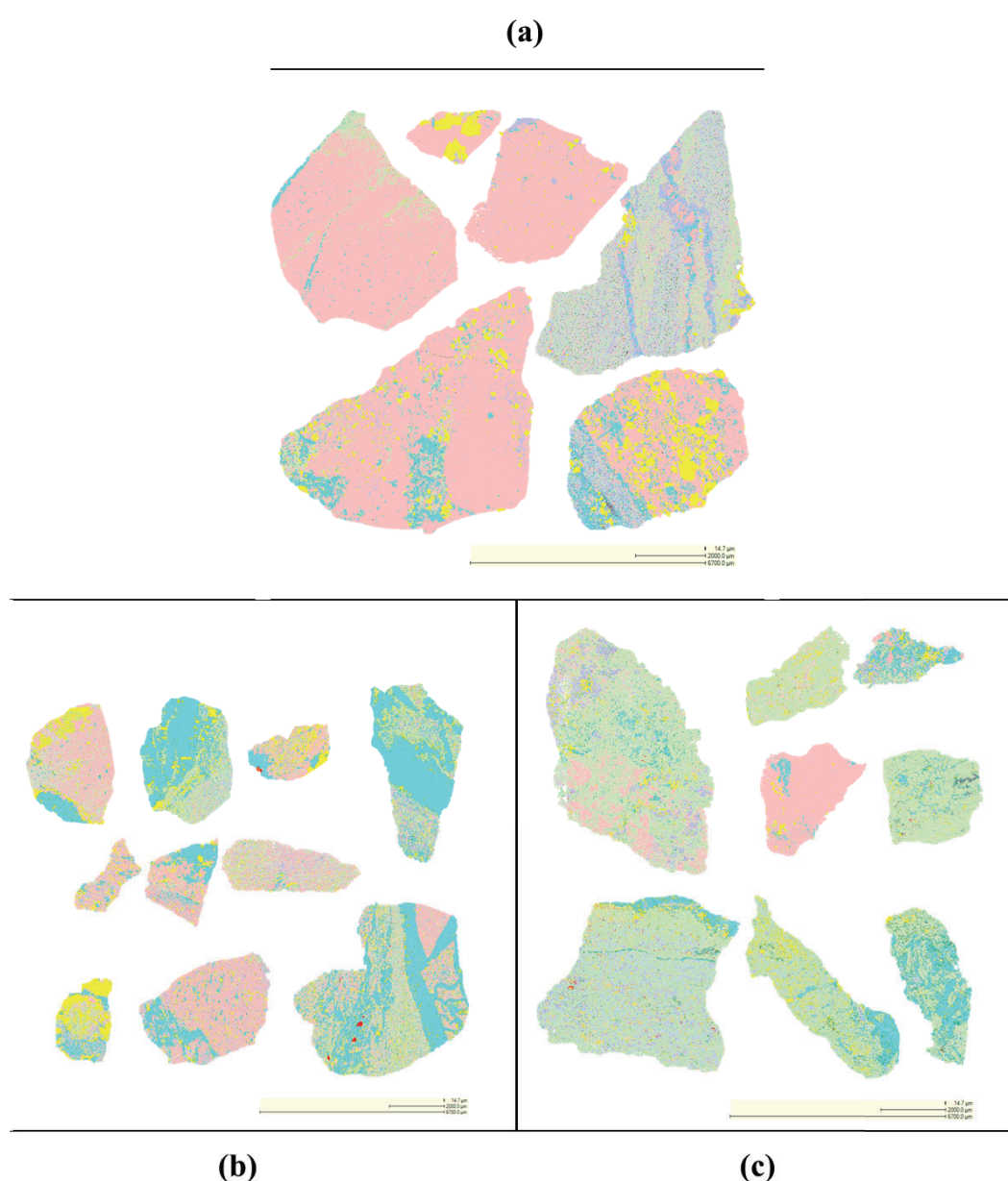


Figure 5-8 False-colour images of dissolving mineral-bearing particles for samples B (a), C (b) and D (c) representing the variation in the dissolving mineral texture and mineral association. See Figure 5-7 for colour legend.

As for the Fe-Sulfide minerals, the dissolving mineral grains were plotted on a liberation spectrum to better understand the distribution of grain populations. The liberation spectra for the dissolving minerals in the HCT feed are provided in Figure 5-9. The liberation size for the dissolving mineral grains in sample C was found to be larger than those of samples B and D (550 μm vs. 340 μm and 350 μm , respectively). This difference in liberation size was supported for samples C and D by the dissolving mineral GSD, which showed that sample C contained the coarsest dissolving mineral grains. This held true for sample B only at finer grain sizes. Although the particle images showed that there was some variation in the grain populations of the dissolving minerals, the liberation spectrum for the dissolving minerals was considerably less crooked than was observed for a bimodal grain distribution (sample C in Figure 5-6), which suggests that the population of the dissolving grains was less variable than that of the Fe-Sulfide grains.

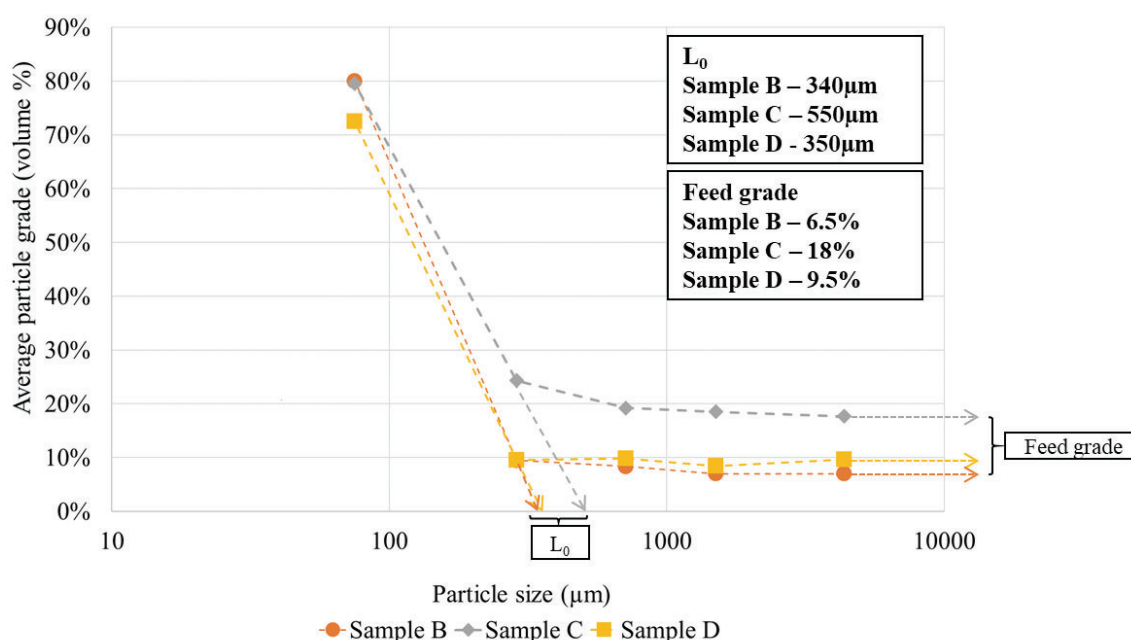


Figure 5-9 Dissolving mineral liberation spectrum for samples B, C and D based on Wightman & Evans (2014).

The unliberated category was assessed for the abundance of locked and middlings dissolving minerals. These data are presented in Table 5-5. Overall, the highest degree of dissolving mineral encapsulation was observed for sample B (67%), followed closely by sample D (64%) as was shown by their finer liberation sizes in Figure 5-9 (340 μm and 350 μm for samples B and D, respectively). Sample C had the lowest percentage of locked dissolving minerals (36%) and a corresponding larger liberation size of 550 μm .

Table 5-5 The mass % distribution of the dissolving minerals in the meso-scale material of samples A, B, C and D between liberated (>90% exposed area), middlings (30%<exposed area<90%) and locked (<90% exposed area) categories. N_D represents the number of dissolving mineral-bearing particles analysed.

Sample	Size fraction	N _D	Unliberated mass % Dissolving		Liberated mass % Dissolving
			Locked	Middlings	
B	-6700/+2000	519	82%	18%	0%
	-2000/+1000	1784	70%	26%	4%
	-1000/+425	2402	62%	30%	8%
	-425/+150	8037	44%	33%	23%
	-150/+0	69062	10%	24%	66%
	HCT	81804	67%	22%	11%
C	-6700/+2000	465	46%	54%	0%
	-2000/+1000	1298	40%	56%	4%
	-1000/+425	1275	32%	52%	16%
	-425/+150	1991	23%	42%	35%
	-150/+0	141413	6%	16%	78%
	HCT	146442	36%	48%	16%
D	-6700/+2000	457	71%	29%	0%
	-2000/+1000	1058	66%	34%	0%
	-1000/+425	1131	59%	33%	8%
	-425/+150	2741	56%	27%	17%
	-150/+0	23673	16%	28%	56%
	HCT	29060	64%	30%	6%

5.4 Humidity cell test

Humidity cell tests are usually performed on samples that are classified as PAF or uncertain via geochemical characterisation testing (Parbhakar-Fox & Lottermoser, 2015). From the geochemical characterisation tests (Figure 4-8, section 4.5.1), samples A and B were classified as PAF (which would provide the largest expectation of ARD generation), sample C was classified as uncertain due to its high Fe-Sulfide and dissolving mineral contents, and sample D was classified as NAF. Humidity cell tests were performed during this study on samples C and D and during the work of Opitz (unpublished) on samples A and B.

The 40-week duration of the study was relatively close to that recommended by Davis et al. (2019), who suggested that 50 weeks would be a sufficient time frame for potentially acid-forming samples to generate acid, if such behaviour was likely. The HCT data include the profiles for pH, redox potential, cumulative sulfate concentration, sulfur extraction as a percentage of the total sulfur in the sample (based on LECO), cumulative iron concentration, and iron extraction as a percentage of the total iron in the sample (based on XRF). The ion extraction profiles were represented as cumulative concentration plots to provide an indication of the leaching behaviour of the waste material over time, while the pH and redox potential profiles were presented as the mean weekly values. During this study these data sets were reported for samples C and D. Corresponding data sets for samples A and B may be found in Opitz et al. (unpublished) and will be referred to, rather than presented directly.

5.4.1 pH and redox potential profile

The humidity cell test pH and redox potential profiles for samples C and D are presented in Figure 5-10(a) and Figure 5-10(b).

Water-fed HCT profiles

The water-fed pH profiles of both samples C and D remained circumneutral over the 40 weeks of the test. Samples A and B similarly produced no acidic leachate after 40 weeks of the test (Opitz, unpublished), or over 100 weeks of the test for sample A (Opitz et al., unpublished). This occurred even though Fe-Sulfide minerals were present in all samples (7%, 8%, 31% and 4% from Table 4-4, QEMSCAN for samples A, B, C and D, respectively), which would lead to an expectation of acidic leachate formation. The samples did however contain neutralisation capacity (1%, 2%, 13% and 3% from Table 4-4, QEMSCAN for samples A, B, C and D, respectively), the presence of which was thought to cause the rising of the pH above the feed pH level over the duration of the test (Opitz et al., unpublished), particularly for samples B, C and D.

In addition to the mineralogy, the meso-scale liberation and association showed that most of the Fe-Sulfides were unliberated (locked) and associated with intermediate weathering, slow weathering and inert minerals, which would limit their potential for reactivity under neutral pH conditions. A higher degree of liberation was shown to be a contributing factor in acidic leachate generation in HCT test work through quantitative Fe-Sulfide liberation analysis (Brough et al., 2017). This is important to consider for sample C, as it had the largest Fe-Sulfide content, as well as the highest degree of Fe-Sulfide liberation, which would lead to an expectation of acidic leachate formation. Sample C, however, produced no acidic leachate after 40 weeks, which was attributed to the high dissolving mineral content and the relatively large association of dissolving minerals with the Fe-Sulfide material. For sample D, a large degree of locking was observed for both the Fe-Sulfide and dissolving minerals, which was thought to inhibit Fe-Sulfide leaching. Additionally, from section 5.3.2, it is important to highlight that the size fraction which was not thought to pose as much of an ARD risk due to it containing predominantly locked material (-6700/+2000 μ m size fraction) (Elghali et al., 2018) accounted for approximately 50% of the material in the columns.

The redox potential profiles were plotted to provide an indication of the relative abundance of the ferric and ferrous ions in solution, from which the dissolution of Fe-bearing minerals and the presence/absence of microbial activity could be inferred. Given the circumneutral pH of the leachates, and the iron solubility at these levels, no (detectable) microbial activity was expected in the columns over the period of the test (as was similarly demonstrated by the UCT batch biokinetic test results in section 4.6). This was confirmed by the water-fed column leachate redox potential remaining below 350mV for most weeks, with the remaining fluctuations largely being consistent with those of the de-ionised water feed.

Acid-fed HCT profiles

The acid-fed column experiments for samples C and D were set up following the work developed by Opitz (unpublished). The acid-fed HCT experiments for samples C and D were meant to accelerate the long time frames for acid formation in humidity cell tests and to demonstrate the progression of acid

formation and mineral leaching once the neutralisation capacity of the sample had been depleted (Opitz et al., unpublished).

The addition of an acidic lixiviant depleted the neutralisation capacity steadily over the first 12 weeks for sample C and over just 6 weeks for sample D, which may be attributed to the difference in dissolving mineral contents. The fluctuation of the pH during the neutralisation capacity depletion process (especially for sample D on weeks 3 and 5 and sample C between week 7 and 10) may be due to the dissolution of fast and intermediate weathering minerals such as chlorite and ferro-actinolite that were determined to be present in the sample through the bulk mineralogy (section 4.3). Thereafter the pH fluctuation was limited to between 2 and 3.5. The slight raising of the pH in acidic conditions due to the dissolution of intermediate weathering minerals was shown during UCT batch biokinetic test work (Becker et al., 2015) and was therefore not discounted as a possibility in an acid-fed HCT environment. Additionally, minerals such as Fe-mica (biotite) and chlorite (both of which were present in sample C and D) were shown to consume acid in heap leach systems (Free, 2010; Chetty, 2018). Similarly, Lapakko et al., (2006) suggested that Ca- and Mg-bearing silicates contribute to the neutralisation potential within humidity cells. In the current study, however, although acid buffering definitely occurred, the fast weathering and intermediate weathering minerals were predominantly Fe-bearing end-members (chamosite, ferro-actinolite, Fe-mica). This implies that although some neutralisation would be offered, with decreasing pH, the iron released from silicate mineral dissolution could undergo hydrolysis and subsequent reprecipitation with the re-release of acidity (see section 2.1.1).

The redox potential profile for the acid-fed columns showed a slight increase over the duration of the test, with the highest redox potential values of 500mV and 520mV (for samples C and D, respectively) being reached at 14 weeks. After this point, however, the profile decreased, settling at around 420mV for both samples. This slightly raised redox potential was attributed to the feed solution acidity rather than to microbial activity, as the pH of the acid-fed column leachate was only slightly elevated over that of the acid feed. Overall there was little to no evidence of microbial activity in the columns based on the leachate analysed.

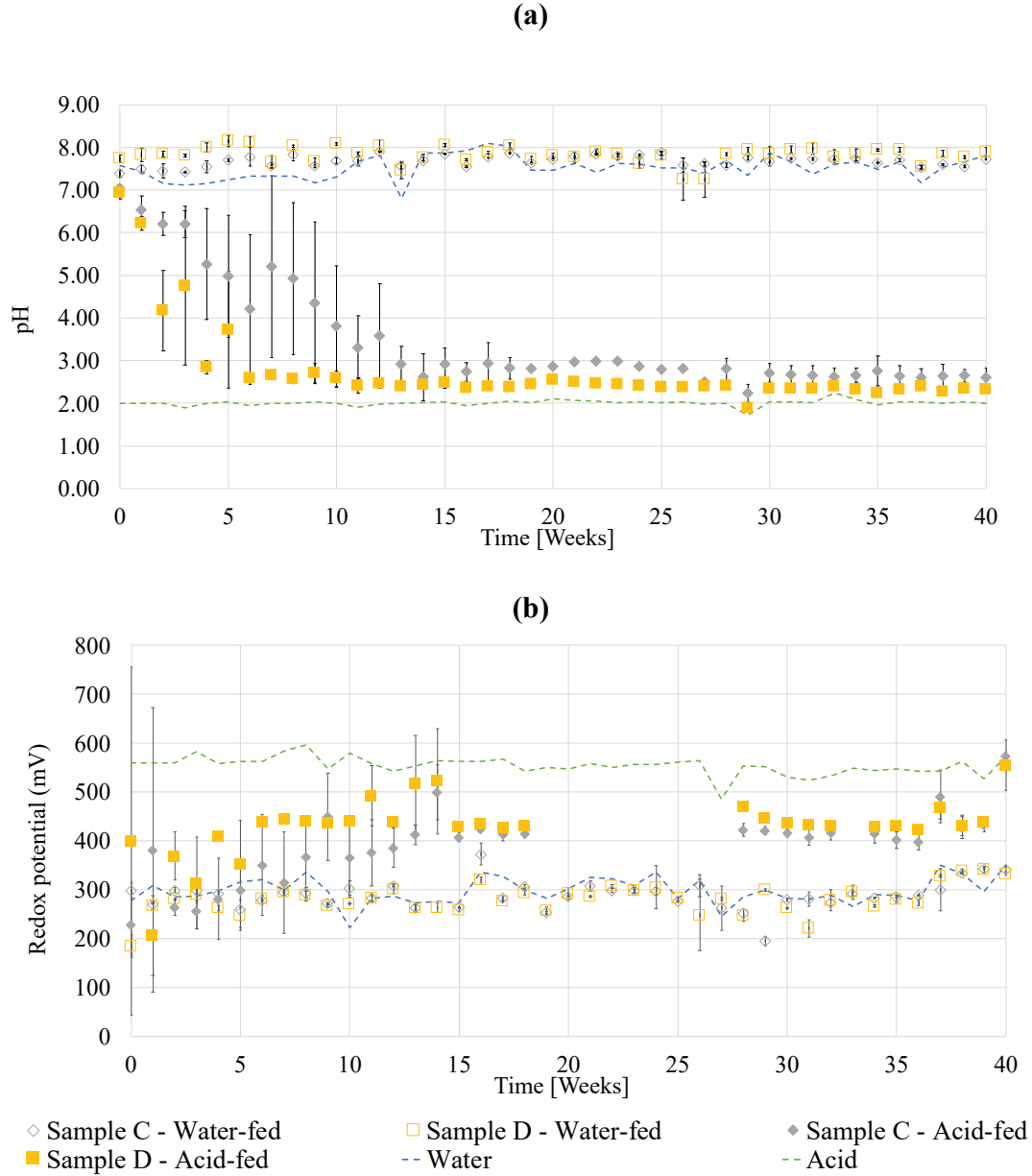


Figure 5-10 pH (a) and redox potential (b) profiles for acid- and water-fed columns of samples C and D, alongside the leach solution pH and redox profiles. The error bars indicate one times the standard deviation obtained from duplicate analyses for the water-fed samples and acid-fed sample D, and from triplicate analyses of acid-fed sample C. Average pH and redox potential fluctuations were attributed to the absence of a pH or redox control on the quality of the de-ionised water (which was de-ionised municipally-supplied water).

The larger error bars on some data points may be attributed to a variety of factors. These include the possible deviation of the samples from one another due to sub-sampling errors (see section 6), as well as due to the potential variation in the percolation channels or voids formed in the column, which could occur due to the depletion of surface minerals (Fagan-Endres et al. 2017; Ghorbani et al. 2011) or due to the formation of silica gel from the dissolution of intermediate weathering silicate minerals such as chlorite (Tan et al., 2012; Chetty, 2018). The latter points, however, cannot be inferred from this study directly and would need to be investigated further to be definitive.

It is important to note that although there was considerable deviation between individual acid-fed columns within a sample, over time (after week 6 for sample D and week 12 for sample C, i.e. after neutralisation capacity depletion) this difference became minimal, introducing the possibility that all reactive minerals on the surface have been leached, with any further fluctuation in pH requiring access to minerals located deeper within the particle, as shown in the work of Ghorbani et al. (2011).

5.4.2 Sulfate and total iron concentration profiles

The cumulative sulfate and total iron concentrations were used to provide an indication of the mineral leaching in the HCT over the 40 weeks of the test. Figure 5-11(a) provides the cumulative total iron concentration over the 40 weeks of the test, while Figure 5-11(b) shows the total iron extraction as a percentage of the total iron in the sample. Figure 5-12(a) provides the cumulative sulfate concentration over the 40 weeks of the test, while Figure 5-12(b) shows the sulfur extraction as a percentage of the total sulfur in the sample. While iron profiles provided a general indication of the leaching of all Fe-bearing minerals in the sample, sulfate and sulfur profiles were used to infer Fe-Sulfide dissolution specifically, as these were the primary source of sulfur in the samples. For the acid-fed experiments the sulfate and sulfur concentrations were corrected for the additional sulfate coming in with the acidic feed (these values being subtracted from the recorded sulfate concentrations in the leachate).

Water-fed HCT profiles

For the water-fed experiments, the total iron concentration and extraction plots in Figure 5-11 showed negligible increase in the iron concentration and extraction over the 40 weeks, reaching values of 0.007g/L and 0.0008g/L for total iron, and 0.003% and 0.002% for iron extraction for samples C and D, respectively. This was not surprising and provided limited indication of mineral dissolution in the columns, considering the limited iron solubility and likely formation of iron oxide/hydroxide precipitates in the column at the circumneutral pH of the leachate (Lottermoser, 2010c). Sulfate concentrations for samples C and D, however, did indicate some dissolution of Fe-Sulfides in the columns. Both the sulfate concentration and the sulfur extraction for sample C (6.5g/L and 1.2%) were larger than for sample D (0.48g/L and 0.39%) after 40 weeks of the test.

When considering the liberation characteristics (section 5.3) alongside Figure 5-11 and Figure 5-12, sample C had the highest degree of Fe-Sulfide liberation, even in the top two size fractions where most of the Fe-Sulfide mass was concentrated. Sample D, on the other hand, showed limited liberation across the sample, with Fe-Sulfide liberation beginning minimally only in the -1000/+425 μ m size fraction, with a large remaining proportion of unliberated Fe-Sulfides (52%) even in the -150/+0 μ m fraction. Additionally, some Fe-Sulfides were found associated with dissolving minerals. These textural characteristics, alongside the sulfate concentration and circumneutral pH suggest that Fe-Sulfide dissolution was occurring with local neutralisation by calcite and was controlled largely by Fe-Sulfide liberation, particularly in the larger size fractions that contained over 50% of the sample mass. Similar behaviour was observed for water-fed experiments for samples A and B (Opitz et al., unpublished).

Acid-fed HCT profiles

The acid-fed total iron concentration and extraction plots in Figure 5-11 showed a substantially larger increase over 40 weeks than the water-fed experiments. Sample C reached an iron concentration and

extraction of 0.57g/L and 0.22%, respectively, while sample D reached 0.76g/L and 0.17% for iron concentration and extraction, respectively, over 40 weeks. Sample C, while having a higher Fe-Sulfide content than sample D, reported lower total iron values (0.57g/L) after 40 weeks than sample D (0.76g/L). The initial lower iron concentrations for sample C were due to the neutralisation by dissolving minerals raising the pH in the first 10 weeks of the test, which would limit the soluble iron concentrations. After 26 weeks, however, the iron extraction for sample C increased faster than for sample D, resulting in a larger iron extraction overall. This suggested an increased rate of Fe-Sulfide dissolution, most likely due to the presence of ferric iron in solution.

Most of the iron in sample D was hosted in the intermediate weathering amphiboles, whereas sample C contained Fe-Sulfides as the dominant Fe-bearing minerals. Additionally, the difference in iron composition (13.1% and 22.5% for samples C and D, respectively, Table 4-3) and difference in reactivity between amphibole and Fe-Sulfide minerals suggests that while the Fe-bearing intermediate weathering minerals are the dominant source of iron for sample D, Fe-Sulfide dissolution is more prominent for sample C. Similar observations were made for the UCT batch biokinetic test, where the total iron profile for sample D (Figure 4-12(b)) was above that of the maximum possible iron from Fe-Sulfide dissolution, whereas for sample C (Figure 4-11(b)) it was below.

It should be noted that for sample C, the sulfate concentration and sulfur extraction for the water-fed and acid-fed experiments were similar. This further supports that in sample C the main minerals likely to be partaking in the HCT behaviour are the Fe-Sulfide and dissolving minerals. The test behaviour was therefore thought to be controlled by the largest size fractions (-6700/+2000 μ m and -2000/+1000 μ m) where over 50% of the sample mass was concentrated and where Fe-Sulfide minerals were already liberated for sample C. The Fe-Sulfide oxidation in sample D was thought to occur chiefly in the finer size fractions, where greater liberation was present, but with iron being contributed chiefly by slow weathering and intermediate weathering minerals, as the Fe-Sulfides were predominantly locked and associated with intermediate weathering minerals.

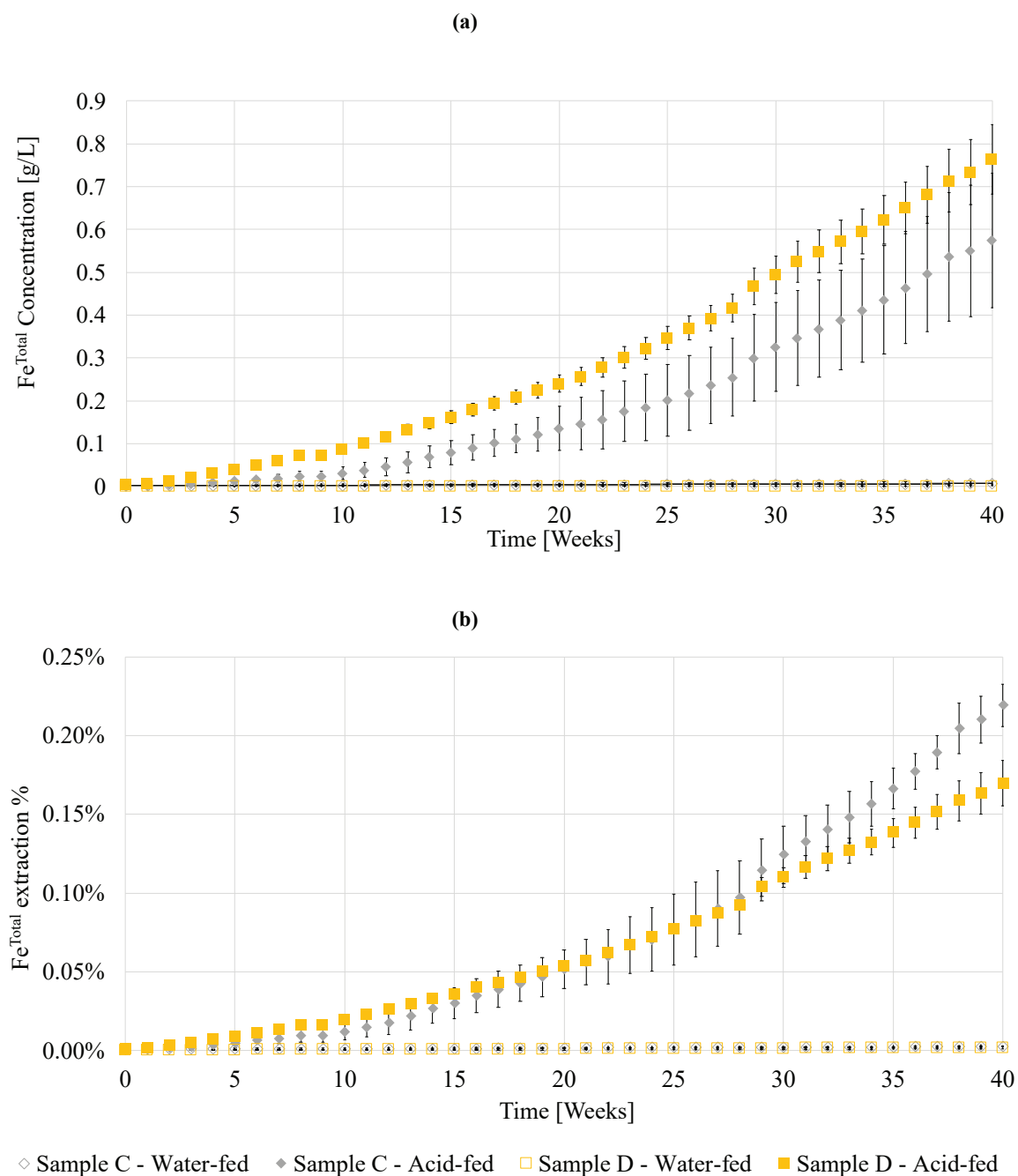


Figure 5-11 Cumulative total iron concentration [g/L] (a) and cumulative total iron extraction (b) over the 40-week test period for acid- and water-fed samples C and D. Total iron concentrations were derived using the 1,10-phenanthroline method, while iron extraction was calculated using the cumulative total iron concentration and the total iron in the sample that was obtained from XRF analyses. Error bars indicate one times the standard deviation between the replicate tests. Error bars increase due to the cumulative nature of the data.

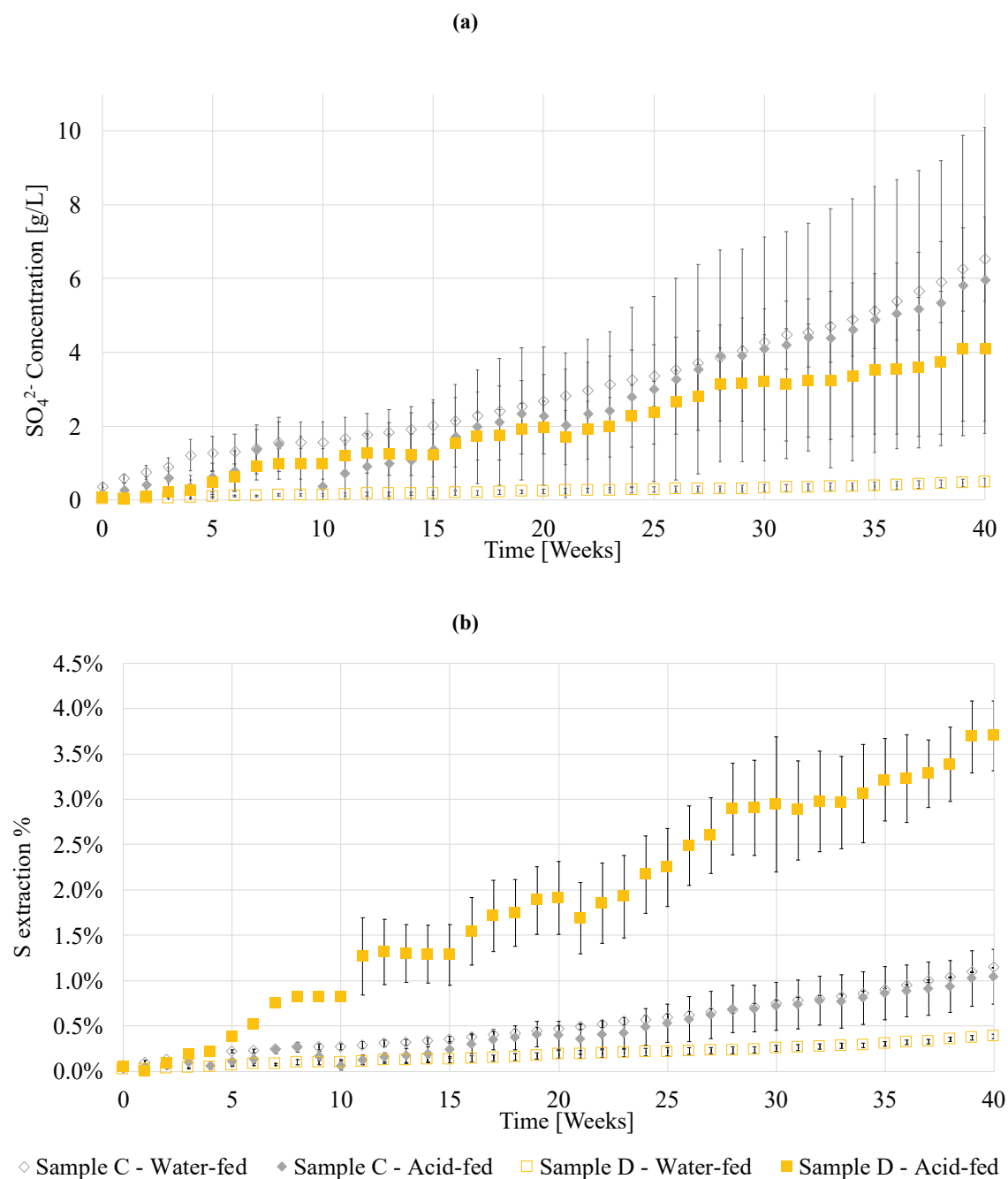


Figure 5-12 Cumulative sulfate concentration [g/L] (a) and cumulative sulfur extraction (%) (b) over the 40-week test period for acid- and water-fed samples C and D. Sulfate concentrations were derived using the turbidimetric method, while the sulfur extraction was calculated using the cumulative sulfate concentration and the total sulfate expected from sulfate dissolution. The latter was back-calculated from the sulfur content of the samples obtained from LECO S analyses. Error bars indicate one times the standard deviation between the replicate tests. Error bars increase due to the cumulative nature of the data.

5.5 Summary

The results and associated discussion in Chapter 5 achieved the second objective and aimed to show that the interpretation of humidity cell test (HCT) behaviour is not possible (or is limited) without the knowledge of the sample mineralogy and the texture of the acid-forming and neutralising minerals. The liberation, association and grain size distribution have been highlighted in previous studies as factors that influence humidity cell test behaviour (Erguler & Kalyoncu Erguler, 2015; Brough et al., 2017; Elghali et al., 2018; Davis et al., 2019). These textural parameters were similarly thought to affect the leaching behaviour during the current study, as even those samples that were classified as potentially acid-forming and uncertain in section 4.5 and 4.6 failed to generate acidic leachate over 40 weeks of the HCT. This behaviour was attributed to the predominantly locked nature of most of the Fe-Sulfides for sample D, and the presence of associated dissolving minerals for sample C. Here the importance of considering the sample particle size distribution was evident when observing that approximately 50% of the sample mass was concentrated in the -6700/+2000 μ m size fraction where the liberation of Fe-Sulfide and dissolving minerals was negligible. These findings were similar to those of Elghali et al. (2018, 2019) where liberation was found to be negligible at particle sizes larger than 2.4mm. It should be noted that although no acidic leachate generation was observed for the water-fed columns over 40 weeks (and therefore the interpretation of the effects of the mineralogy on the leachate quality was limited), given enough time, upon the onset of acidification it would be expected that the effects of the mineralogy on the leachate quality would be similar to those observed for the acid-fed experiments, especially for sample C, which showed similar Fe-Sulfide dissolution during both water-fed and acid-fed experiments based on the sulfur release profiles.

6 Error analysis – setting the context

The current chapter addresses objective three and research question three of this study. The third objective was to *address some of the problems associated with the statistical representativeness of mineralogical and textural data, with more specific consideration for the number of particles, particle size and the sub-sample mass required for analysis through a comprehensive assessment of the sampling errors involved*. The key question addressing this objective was “*what is the role of sampling (particularly on the meso-scale) for textural analysis, including consideration for sub-sample mass, number of particles of interest and relevant analytical errors?*”. These findings build towards understanding how meso-scale texture and mineralogy may contribute to the ARD assessment “toolbox”, which in turn contributes to addressing objective four (understanding the role of mineralogy and texture in the ARD assessment “toolbox”).

Based on Chapters 1 to 3, it is evident that the focus of this study was on mineral texture. When undertaking mineralogical and textural analyses, however, a common area of concern was the statistical soundness of the measurements, especially for larger particle sizes. Statistical soundness generally decreases with a decrease in the number of particles analysed, while the number of particles analysed, in turn, tends to decrease as the particle size increases due to the plausible number of particles per sample block and the associated costs of measurement. Additionally, laboratory analyses assess sub-samples that are many orders of magnitude smaller than the parent material. This introduces the question of how representative these small sub-samples actually are of the parent material (Petersen et al., 2004). Two sources of error were therefore assessed in this study, namely the sampling error (measure of how different individual samples are from one other, which applies to data sets from any and all analyses in this study) and the mineralogical error (analytical error associated with the number of assessed particles by the QEMSCAN).

All individual data sets were initially assessed for potential sources of error. Table 6-1 provides a summary of the various errors associated with the chemical, mineralogical and textural data sets used in this study. Table 6-1 shows that a source of error which propagated across all data sets was the sampling error. Sampling errors often far exceed those arising from analyses (Carrasco et al., 2004; Petersen et al., 2005). Consequently, experiments performed on the sub-sampled material may yield data which are difficult to correlate across various tests and/or relate to the behaviour of the parent sample. The sampling errors associated with the data thus set the context for the interpretation of the data across the various analyses and provided a means to bridge discrepancies between data sets.

An additional source of error in 2D measurements was the stereological bias. It should be noted that although the stereological bias was acknowledged in this study, it was not quantitatively accounted for. It was assumed that the complexity of the texture, as well as the fine-grained nature of the majority of the MoIs decreased the magnitude of the stereological bias (Spencer & Sutherland, 2000). Additionally, although the correction for stereological bias is recommended, some researchers have argued that potentially for a majority of ore textures the application of correction factors to 2D mineralogical and textural data could actually decrease the accuracy of the data rather than enhance it (Lätti & Adair, 2001). For the purposes of this study the stereological bias was not explicitly corrected for, even though this is a recommended mathematical exercise that has been investigated in much detail in recent years (Ueda et al., 2016a; c, 2017, 2018a; b).

Table 6-1 Various sources of error arising for samples A, B, C and D. SE = sampling error arising due to the splitting of samples from a bulk sample; AE = analytical error arising due to the detection/determination limits of the analytical techniques used or; the generally reported standard deviation arising due to the spread of data points associated with a sample of a population or; the mineralogical error arising from the number of particles analysed for mineralogy and texture (approximated with binomial distribution and considered to decrease with size fraction due to the larger number of particles analysed) and; SB – stereological bias associated with 2D measurements.

Scale	Experiment	Sources of error
Micro	Geochemical static tests	Bulk sub-sampling; sub-sampling after pulverisation (SE) Test solution concentration, for example the NaOH used for titration and HCl used for dissolution; measurement of relevant parameters (AE)
	UCT batch biokinetic test	Bulk sub-sampling; sub-sampling after pulverisation (SE) Composition determination of ABS media and inoculum; measurement of relevant parameters (AE)
	QXRD	Bulk sub-sampling; sub-sampling after pulverisation (SE) Goodness of fit (AE)
	XRF	Bulk sub-sampling; sub-sampling after pulverisation (SE) Measurement technique (AE)
	LECO Total sulfur	Bulk sub-sampling; sub-sampling after pulverisation (SE) Measurement technique (AE)
	LECO Total sulfur sized	Bulk sub-sampling; sub-sampling after pulverisation (SE) Measurement technique (AE)
	QEMSCAN Bulk mineralogy	Bulk sub-sampling; sub-sampling after pulverisation (SE) Number of particles analysed (AE)
	QEMSCAN Sized mineralogy and texture	Bulk sub-sampling; sub-sampling after pulverisation (SE) Number of particles analysed (AE) Stereological bias associated with 2D measurements (SB)
Meso	Humidity cell test	Bulk sub-sampling (SE) Measurement of leachate chemistry (AE)
	LECO total sulfur sized	Bulk sub-sampling (SE) Measurement technique (AE)
	Sized mineralogy and texture	Bulk sub-sampling; sub-sampling of fractions (SE) Number of particles analysed per fraction (AE) Stereological bias associated with 2D measurements (SB)

6.1 Errors associated with textural analysis

This sub-section provides the calculation of the total error on the micro- and meso-scales, with focus more specifically on the sampling error contribution to the total error. The micro- and meso-scale sub-sections provide an evaluation of the errors arising from sampling (SE) and the number of particles assessed (AE). Additionally, the meso-scale section provides an investigation into some of the parameters influencing the sampling error equation and includes an alternative evaluation of the AE for the meso-scale in the form of confidence intervals over cumulative liberation data. Although the Fe-Sulfide minerals are used as a case-study for the error calculations, these calculations can be performed on any MoI, provided the mineralogical and textural data for that mineral are available.

6.1.1 Micro-scale

This section provides the results for the SE and AE calculation on the micro-scale. The sampling errors were calculated based on equations (35) to (38) in Table 2-13, with the FSE equation parameters obtained as described in Table 3-14. The analytical error in the context of QEMSCAN data was taken to be the error arising as a result of the number of particles analysed (Table 2-15) and was incorporated into the final error as described in section 3.4. These two sources of error were used to provide an indication of the errors associated with the textural and mineralogical data.

Although sampling error was considered on the micro-scale, at the fine particle top size of micro-scale material the sub-samples were expected to fall in the “safe” zone of Gy’s safety line after the initial bulk sub-sampling and size reduction via pulverisation. This error was therefore not expected to affect the micro-scale data sets. The bulk sub-sampling error prior to sample size reduction, however, was expected to propagate to the final data sets, introducing potential deviation between micro-scale and meso-scale results. Additionally, the calculation of the AE via the binomial distribution point counting equation was considered sufficient, as the number of particles assessed was large (Napier-Munn, 2015).

The SE and AE were two separately calculated values (σ_{SE} and σ_{AE} , respectively). The total errors or standard deviation associated with the mineralogical and textural measurements (σ_t) that consider both the AE and SE (including the bulk sampling error) are presented in Table 6-2 alongside the sampling and mineralogical standard deviations.

Table 6-2 The calculated sampling error (SE), the analytical error due to the number of particles analysed (AE) and the total standard deviation by size for samples A, B, C and D. σ_{SE} = standard deviation associated with sampling; σ_{AE} = standard deviation associated with the QEMSCAN measurement; σ_t = standard deviation associated with the textural measurements obtained from the square root of the sum of σ_{SE}^2 and σ_{AE}^2 .

Sample	Error pertains to	σ_{SE}	σ_{AE}	σ_t
A	Bulk parent sample	0.36%	-	0.36%
	Micro-scale total	0.39%	0.09%	0.40%
B	Bulk parent sample	0.34%	-	0.34%
	Micro-scale total	0.37%	0.05%	0.37%
C	Bulk parent sample	0.43%	-	0.43%
	Micro-scale total	0.44%	0.09%	0.44%
D	Bulk parent sample	0.70%	-	0.70%
	Micro-scale total	0.72%	0.05%	0.72%

The micro-scale total errors were minimal (0.40%, 0.43%, 0.44% and 0.72% for samples A, B, C and D, respectively), even following sub-sampling of the bulk parent material (6700 μ m top size). These errors were found to be almost equivalent to the error arising from the sampling of the parent material for all samples (0.36%, 0.34%, 0.43% and 0.70% for samples A, B, C and D, respectively). This suggested that using Gy’s “safety line” for micro-scale material was a valid form of sampling error estimation after pulverisation. Additionally, the bulk parent material sub-sampling yielded minimal sampling standard deviations, which contradicted the results of Gy’s “safety line” for the parent material sampling (requirement of a minimum of 31.3kg of material for a representative sub-sample, section 3.4). This is not surprising considering that the “safety line” assumes a 10% relative sampling error (Minnitt et al., 2007b). These results do, however, highlight the importance of calculating ore-specific

sampling errors based on the mineralogical and textural data. The sampling error portion of the total error was also expected to propagate across the full set of measurements in this study.

6.1.2 Meso-scale

Evaluating the total error

The sampling error on the meso-scale was evaluated similarly as for the micro-scale; however, as this study assessed individual size fractions for mineralogy and texture on the meso-scale, the sampling error portion of the total error was calculated for each of the size fractions individually, treating the mass of that size fraction in the parent sample as the new “parent” sample for the size fraction. The bulk parent sample SEs from Table 6-2 were incorporated into the sampling error of each size fraction on the meso-scale.

For size fractions above 1000 μm , rather than considering multiple blocks of the same size fraction as replicates, blocks of the sample size fraction were taken to represent a single sub-sample to increase the total sub-sample mass and number of particles assessed. The total errors (σ_t) that consider the AE and SE are presented in Table 6-3. A method for the calculation of the total error is provided in Appendix C.2.

From Table 6-3, the calculated total sampling errors decreased with decreasing size fraction/particle size. The largest total error was calculated for the -6700/+2000 μm size fraction, with samples A and D having the largest total error and sample C having the lowest total error. Although the top size of the material was the same for the -6700/+2000 μm size fraction as for the bulk parent sample, other parameters influenced the value of the sampling error, such as the liberation size of the MoI in the size fraction, the range of the size fraction and the MoI grade of the size fraction. Some of the parameters influencing the FSE equation were investigated further (see section 6.1.3).

Additionally, it should be noted that the σ_{AE} was calculated based on the binomial distribution assumption, which is only applicable for a large number of particles and a value of p (ratio of MoI-bearing particles to the total number of assessed particles) close to 0.5 (Napier-Munn, 2015). The largest size fractions in the meso-scale material, however, contained relatively few particles and had a value of p which was sometimes close to or equal to 1 (as was the case for the -6700/+2000 μm size fraction in sample C, which yielded 0% for the value of σ_{AE}). This was caused by the presence of single MoI pixels in the particles, which rendered the binomial distribution approximation skewed (Napier-Munn, 2015). An additional approach was therefore taken to establish the uncertainty surrounding some of the textural data with the help of confidence intervals on the cumulative liberation data.

Table 6-3 Total errors by size for meso-scale HCT feed material of samples A, B, C and D as calculated with consideration for SE and AE and based on Fe-Sulfides as the MoI. σ_{SE} = standard deviation associated with sampling; σ_{AE} = standard deviation associated with the measurement; σ_t = standard deviation associated with the textural measurements obtained from the square root of the sum of σ_{SE}^2 and σ_{AE}^2 .

Sample	Size fraction	σ_{SE}	σ_{AE}	σ_t
A	-6700/+2000	6.52%	1.59%	6.71%
	-2000/+1000	2.66%	1.24%	2.93%
	-1000/+425	1.93%	1.81%	2.64%
	-425/+150	0.69%	0.72%	1.00%
	-150/+0	0.37%	0.09%	0.38%
B	-6700/+2000	3.99%	1.28%	4.19%
	-2000/+1000	1.36%	1.06%	1.72%
	-1000/+425	1.60%	0.94%	1.86%
	-425/+150	0.61%	0.44%	0.75%
	-150/+0	0.37%	0.05%	0.36%
C	-6700/+2000	2.69%	0.00%	2.69%
	-2000/+1000	1.35%	0.11%	1.35%
	-1000/+425	0.93%	0.40%	1.02%
	-425/+150	0.48%	0.59%	0.77%
	-150/+0	0.43%	0.09%	0.44%
D	-6700/+2000	4.82%	1.50%	5.05%
	-2000/+1000	1.58%	1.22%	1.99%
	-1000/+425	1.47%	1.32%	1.98%
	-425/+150	0.89%	0.75%	1.16%
	-150/+0	0.71%	0.05%	0.71%

Confidence intervals on the cumulative liberation data

Although the binomial distribution approximation was found to be effective on the micro-scale, on the meso-scale this approximation was not considered adequate due to the limited number of assessed particles. An alternative method to assess the uncertainty surrounding the textural data was used, specifically the application of confidence intervals to liberation data based on the method developed by Leigh et al. (1993). Confidence limits on the cumulative liberation data were calculated for the Fe-Sulfide minerals in samples A, B, C and D for sized meso-scale material and are provided in Figure 6-1.

The confidence intervals provided a visual representation of the errors associated with the Fe-Sulfide liberation data. What is evident from Figure 6-1 is that the upper and lower bounds of the confidence intervals far exceed the AE values calculated from the binomial distribution approximation in Table 6-3. Overall, the magnitude of the upper and lower bounds of the confidence intervals were strongly dependent on the number of particles assessed (see also Table 5-4 for correlation between Figure 6-1 and the number of assessed particles). In sample A (Figure 6-1(a)), for example, a smaller number of particles was assessed for the -1000/+425 μ m size fraction than for the next highest and lowest size fractions in the sample, which on the confidence interval plot reflected as a larger difference between the upper and lower confidence intervals and the cumulative liberation line. Similarly, in Figure 6-1 the finer size fractions had confidence intervals that were closer to the cumulative liberation curve, with the

finest size fraction ($-150/+0\mu\text{m}$) having upper and lower confidence limit curves that were nearly equivalent to the liberation curve. This was evident for all four samples.

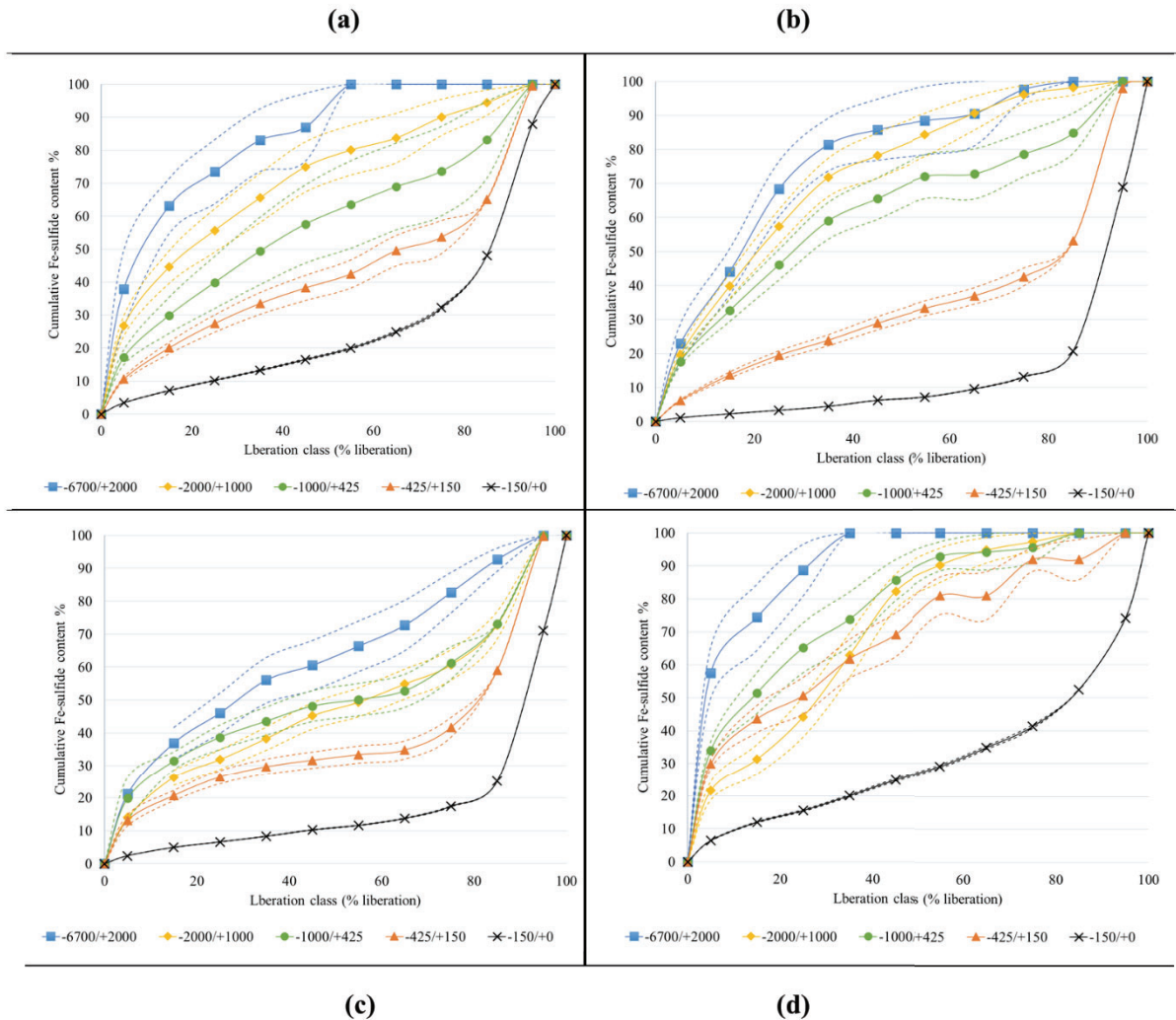


Figure 6-1 Cumulative Fe-Sulfide liberation and associated confidence limits over the data for samples A(a), B(b), C(c) and D(d), calculated based on Leigh et al. (1993). Solid lines indicate the measured values, while dashed lines indicate the confidence limits for corresponding colours.

6.1.3 Parameters influencing the total error

Considering the differences observed on the meso-scale between the bulk sampling error (see Table 6-2) and the sampling error of the individual size fractions (see Table 6-3), the FSE equation was investigated further to better understand which parameters affected the sampling error the most. A scenario analysis was performed to assess the variation in the parameters of “Gy’s equation”. These included

- the variation of the total error (σ_t) with the MoI liberation size (d_l) (Figure 6-2);
- the variation of σ_t with sample grade (a) (Figure 6-3), and
- the effect of the number of blocks analysed on the total error at several different values of the grade (Figure 6-4).

To enable a suitable comparison, some variables were fixed based on sample A and are shown in Table 6-4. Additionally, because the -6700/+2000 μm size fraction was expected to yield the largest sampling errors, the comparative relationships were investigated using only this size fraction.

Table 6-4 Parameters used during the scenario analysis of sampling error. ρ_m and ρ_g in g/cm^3 ; d_i in cm; M_L and M_S in g.

Base case	Size fraction (μm)	f	g	ρ_m	ρ_g	d_i	M_L
Sample A	-6700/+2000	0.307	0.5	4.61	3.19	0.67	850

The parameters in Table 6-4 did not vary and included

- the shape factor, $f=0.307$, based on the particle shapes in sample A;
- size distribution factor, $g = 0.5$, based on sample A;
- the particle top size, $d_i = 0.67\text{cm}$, which was the largest size fraction and therefore the contender for the largest sampling error;
- the mass of the lot, $M_L = 850\text{g}$, based on sample A;
- the density of the critical mineral, $\rho_m = 4.61\text{g}/\text{cm}^3$, based on sample A, and
- the density of the gangue, $\rho_g = 3.19\text{g}/\text{cm}^3$, based on sample A.

When unvaried, the values of M_S , p and d_i were fixed for a 30.1g (approximate mass of sub-sample required for one coarse material sample block). p was 0.93 (based on sample A) and d_i was 0.025cm (based on sample A), respectively. The value of σ_{AE} was calculated for each individual case.

Figure 6-2 shows the effect of a change in liberation size (d_i) on the total error (σ_t). d_i was varied between 100-600 μm , which encompassed the range of the Fe-Sulfide I_{85} values in all samples (see Figure 5-2). The other parameters were fixed. The lot grade, when unvaried, was taken nominally as 5.58%, as per sample A.

Figure 6-2 indicated that the value of σ_t decreased as d_i decreased. This was thought reasonable, as fine-grained minerals are more likely to be disseminated throughout the entire sample, rather than to occur as “nuggets” in only a few particles. This, in turn, would affect the likelihood of an even distribution of the critical mineral grains throughout the lot, which in turn would decrease the sampling error.

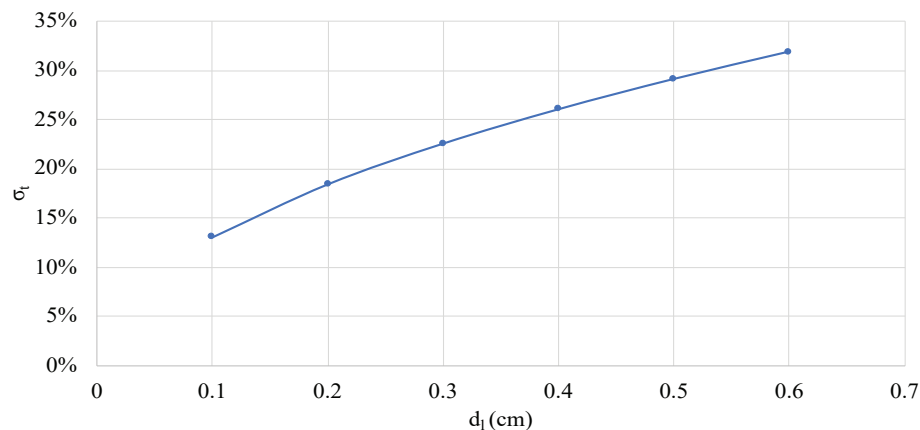


Figure 6-2 The effect of MoI (Fe-Sulfide mineral in this case) mineral liberation size (d_i) on the total error (σ_t) at fixed values of other variables.

The effect of sample grade, a , of the sample on σ_t was also investigated and is presented in Figure 6-3 below. The lot grade (a) was varied between 1-15%. Figure 6-3 shows that higher values of a lead to smaller sampling errors. This effect was more prominent for grades below 5%, where the total error appeared to grow rapidly with decreasing grade. At MoI grades above 5%, however, the effect of a change in grade on the total error became less prominent. This was again linked to the distribution of MoI-bearing particles throughout the entire sample and the likelihood of the distribution of these particles to be representative of the parent sample.

Similar trends of the effect of the grade on the relative mineralogical error have been observed when considering the number of particles analysed, with the effect of the number of particles appearing to influence the error more for lower grade samples (Pooler & Dold, 2017).

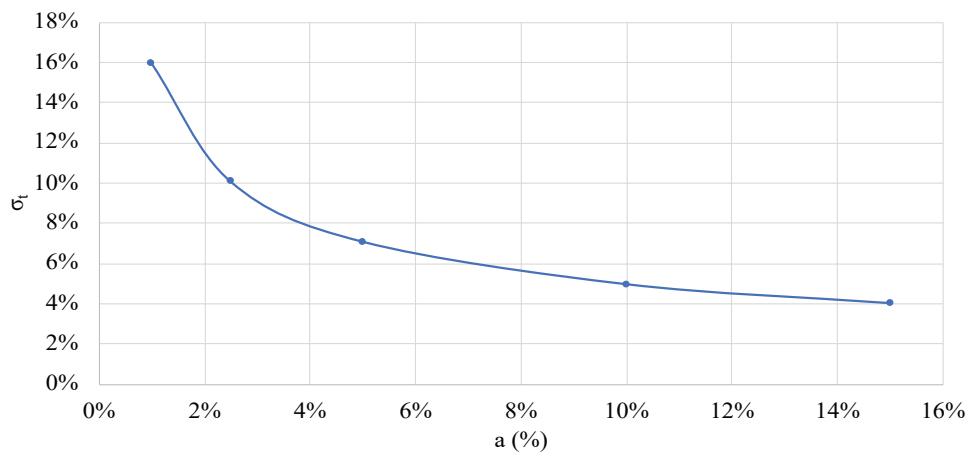


Figure 6-3 The effect of change in sample grade (a) (in this case the grade of Fe-Sulfide material in a sample) on the total error (σ_t) at fixed values of other variables.

Finally, the effects of the number of sample blocks (varied between 1-5) on the total error were also investigated at different values of the lot grade (1%, 2.5%, 5%, 10% and 15%) to provide an indication of the variation of the total error with variation in the sub-sample mass and number of particles analysed. To calculate this, the number of particles containing the MoI (Fe-Sulfide) was taken as the average mass per sample block observed for sample A in the -6700/+2000 μ m size fraction (roughly 30.1g). This investigation showed that, theoretically, an increase in the number of blocks analysed led to a decrease in the total error, with the effect becoming increasingly more prominent for lot grades below 5%, meaning that the lower the grade of the material, the more sample blocks would be recommended for analysis to ensure smaller total errors associated with the data.

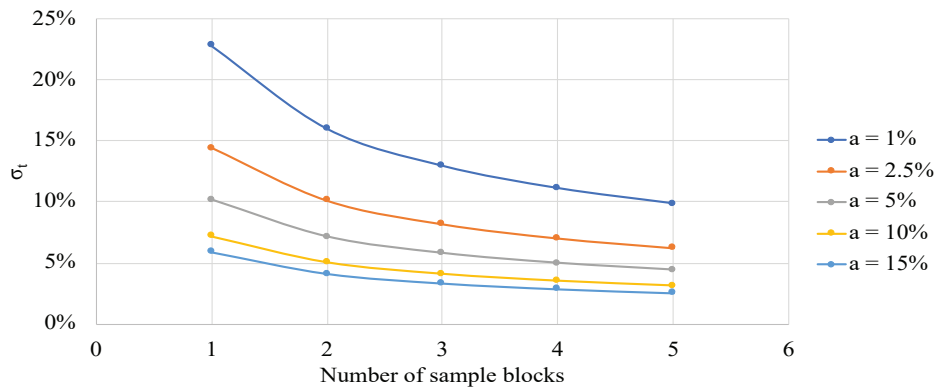


Figure 6-4 Effect of the number of blocks analysed on the total error (σ_t) at different values of the sample grade (a) and fixed values of other variables in the FSE equation.

Following the above theoretical investigation the relevance of the findings was cross-verified with the meso-scale material of samples A, B, C and D. Figure 6-5 provides the results of this consideration. The error decreased as the number of blocks increased, as was expected, with less prominent decrease in error observed after the third sample block. Additionally, the lowest sampling errors were obtained for sample C, which had the highest Fe-Sulfide grade; however, this trend was not consistent for all samples. Sample D, although having the lowest Fe-Sulfide grade, reported lower errors than sample A, which had the higher grade. Based on Figure 6-2 and the liberation size of sample D, this deviation was explained by sample D having the smallest liberation size, which compensated for the low Fe-Sulfide grade. The latter point highlights the importance of a sample-specific sampling error calculation, as the FSE is strongly dependent on various ore characteristics.

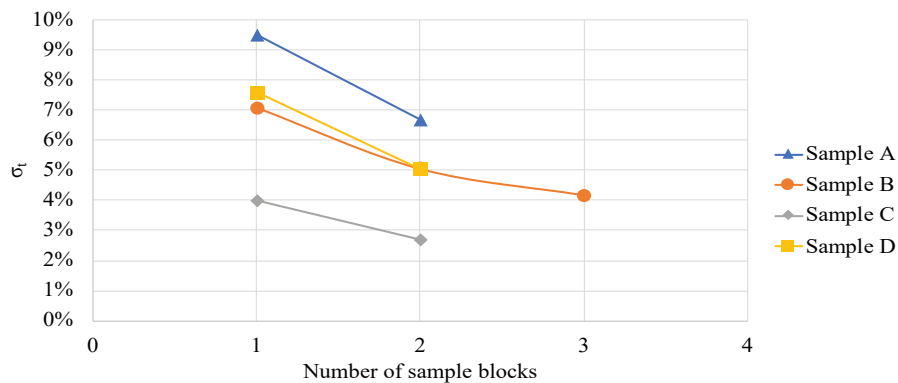


Figure 6-5 Effect of the number of blocks prepared on the total error for the -6700/+2000 μ m size fraction of samples A, B, C and D.

6.2 Summary

The results and associated discussion in Chapter 6 addressed objective and key question three and assessed the issue of representative sampling, sub-sample mass and number of assessed particles, particularly for mineralogical and textural analyses. The error analysis showed that the sampling error was a large contributor to the total uncertainty associated with the textural measurements and other data sets in the study. Additionally, it was found that the uncertainties on the micro-scale were relatively small and that sub-sample masses after pulverisation could be reliably estimated using Gy's "safety

line”. Although the AE was suitably approximated on the micro-scale via the point counting/binomial distribution method due to the large number of particles that could be assessed (Napier-Munn, 2015), this did not necessarily hold true on the meso-scale. In the latter case, the AE should be estimated using alternative methods. In this study this difference in methods was highlighted through the use of confidence intervals on cumulative liberation data; however, other methods may also be employed (such as running numerous sample blocks to increase the number of assessed particles). The FSE equation was also investigated for the effects of some of the mineralogical and textural parameters of the ore.

The calculation of the total error (including SE and AE) should consider the data that will reflect the true mineralogical and textural characteristics of the ore for each new sample, as a “one size fits all” approach such as Gy’s “safety line” may in some cases yield sample masses that are unreasonably large (such as the 31.3kg sample requirement for the humidity cell test). The quantitative assessment of mineral texture enables the calculation of a sample-specific sampling error, which provides a means to assess how sub-samples are inherently different from one another. This may provide a link between data sets of various scales (micro- to meso- to field-scale) and allow for the planning of appropriate sampling strategies/sub-sample masses. In the context of ARD, this could have potential positive implications for some of the issues experienced with the scalability/relatability of laboratory data to field conditions.

It should, however, be noted that a true measure of sample representativeness can only be obtained through diligently following correct sampling techniques and applying the “tailored approach” to each new sampling problem. In the current study, nothing was known about the sub-sampling process or the magnitude of the parent waste-rock sample on site and this was only assumed to have been representative. The results of this study therefore may not with certainty be translatable to the original parent material.

7 Concluding discussion and recommendations for future work

7.1 Concluding discussion

This study addressed the incorporation of detailed textural and mineralogical analyses into existing acid rock drainage (ARD) test strategies through the comprehensive assessment of four waste rock samples from an African greenstone belt gold deposit. The fourth and final objective of the study was to *present a more holistic understanding of the role of mineralogy and texture in the ARD assessment “toolbox” alongside conventional geochemical static tests, the UCT batch biokinetic test and the humidity cell test, as well as the nature of the information they provide*. The research question posed to address this objective was *“how do texture and mineralogy fit in as “tools” in the ARD assessment “toolbox”?”*. Objectives one, two and three and the associated key questions built towards resolving objective four and showed how the individual nuggets of information obtained through ARD characterisation, prediction, mineralogy and texture were not solitary, but rather formed a more comprehensive overview of the ARD potential when drawn together into one holistic assessment.

7.1.1 Re-visiting objectives and research questions one, two and three

Chapters 4, 5 and 6 addressed objectives one (role of texture in the interpretation of micro-scale ARD characterisation tests), two (role of texture in the interpretation of meso-scale ARD prediction tests) and three (the role of sampling in micro- and meso-scale texture quantification), respectively. The comprehensive test suite included assessment of the sample PSD, XRF chemistry and the total sulfur content of the samples via LECO S analyses, geochemical static (ABA, single addition NAG) tests and the UCT batch biokinetic test, as well as the water-fed and acid-fed humidity cell tests. These data were supplemented with bulk mineralogy data from QXRD and QEMSCAN analyses, as well as by the liberation, association and GSD data for the Fe-Sulfide and dissolving minerals obtained via QEMSCAN.

On the micro-scale, the following main points were derived:

- The PAF/NAF/uncertain behaviour of the samples during both standard characterisation tests and the UCT batch biokinetic test was found to be strongly dependent on the acid-forming and neutralising mineralogy. For geochemical static tests this was deduced from the geochemical classification plot, where samples A and B were PAF, with sample B being located closer to the uncertain classification due to the presence of calcite. The acid formation potential of sample C was uncertain due to the higher calcite content alongside the high Fe-Sulfide (pyrrhotite) content. Sample D was classified as NAF due to a higher ratio of calcite to Fe-Sulfide than for other samples.
- UCT batch biokinetic test results showed samples B, C and D to be non-acid forming under non-pH-controlled batch conditions due to rapid calcite dissolution at the start of the test. Even relatively low amounts of calcite elevated the pH to conditions unfavourable for microbial activity. After the depletion of the neutralisation potential under pH-controlled conditions, the

samples remained acidic spontaneously, with slight increase in pH observed due to the dissolution of intermediate weathering silicate minerals, as similarly demonstrated by Becker et al. (2015) and supported by the total iron and sulfate concentration profiles in this study. In the absence of sufficient neutralisation capacity from calcite (sample A) the sample would quickly become acid forming with microbial activity observed almost immediately under inoculated conditions (Opitz et al., 2016).

- Assessment of the Fe-Sulfide and dissolving mineral liberation and GSD indicated that although commonly used ARD characterisation protocols assume that a 75µm top size effectively liberates all key acid-forming and neutralising minerals (Smart et al., 2002), this may not necessarily be the case for all waste types. Coarser-grained samples B and C showed a larger degree of liberation than the finer-grained samples A and D, which had some locked Fe-Sulfide and dissolving minerals that would not necessarily react completely during tests.

On the meso-scale the following points were highlighted:

- From characterisation testing, samples A (PAF), B (PAF) and C (uncertain) provided the highest expectation of acid formation during the water-fed HCTs. The water-fed humidity cell tests for all samples, however, remained circumneutral over 40 weeks of the test. Non-negligible sulfate concentrations in the leachate of samples C and D, however, indicated the oxidation of Fe-Sulfides with neutralisation by dissolving minerals. Samples A and B showed no acidic leachate formation even after over 50 weeks (Opitz et al., unpublished), which was thought to be a sufficient time frame for acid formation if samples were likely to do so (Davis et al., 2019). The circumneutral pH behaviour was explained by a high degree of Fe-Sulfide mineral encapsulation in intermediate weathering, slow weathering and inert minerals for all four samples, which limited the availability of this material to the test environment. Additionally, this behaviour was linked to the abundance of dissolving minerals in sample C, which were found associated to a relatively large extent with Fe-Sulfide minerals.
- The acid-fed HCTs showed a decrease in pH over several weeks with the release of sulfate and iron into the leachate. The lag time was a result of the reaction of calcite, as well as due to the reaction of intermediate weathering silicate minerals (ferro-actinolite, Fe-mica and chlorite).
- The sample PSD was used to assess the distribution of liberated material across the size fractions in the samples. This showed that the mass contribution of the most liberated fractions to the sample was considerably smaller (less than 30% of the material of all samples was found below 1000µm) than of the larger size fractions that had negligible liberation in particles larger than 2000µm for all but sample C. This, aided by the behaviour of the water-fed sample C test profiles suggested that the test behaviour was governed by the largest size fractions that contained most of the Fe-Sulfides in the sample.
- The liberation spectra for the Fe-Sulfide and dissolving minerals showed a liberation size that was smaller than 1000µm for all assessed samples. Sample C showed evidence of a bimodal Fe-Sulfide GSD with an early liberation size of above 2000µm, which was supported by it having the largest amount of liberated Fe-Sulfides of all samples, both in the largest size fraction (-6700/+2000µm) and for the sample overall.

The role of sampling is often overlooked in the analysis of data; however, sampling errors may often be many times greater than the analytical errors encountered during sample analysis (Carrasco et al.,

2004; Petersen et al., 2005). From the error assessment during this study, the following points were derived:

- On the micro-scale the sampling of the parent material dominated the total error.
- On the micro-scale the binomial distribution approximation for estimating the QEMSCAN analytical errors was a reasonable assumption due to the large number of particles assessed. On the meso-scale, however, the latter assumption was not considered applicable, with the assessment of the confidence intervals on the sized Fe-Sulfide liberation data indicating considerably larger errors than estimated by the binomial distribution approximation.
- When investigating the parameters influencing the FSE equation it was observed that in addition to the particle size (as dictated by Gy's "safety line"), the MoI grade had a large effect on the sampling error, with grades below 5% (calculated based on the Fe-Sulfide data) having increasingly more substantial effects on the total error.
- Although a comparative study of the effects of the sampling error across data sets was not performed during this study, it was proposed that sampling has a role to play in linking data sets across the various scales in ARD test work (micro-, meso- and field-scale), as it provides a measure of how representative each sub-sample is of the parent lot.

7.1.2 The role of mineralogy, texture and sampling strategy in the ARD assessment "toolbox"

The analysis of mineralogy and texture has found many applications in the mineral processing industry (Vizcarra et al., 2010; Hunt et al., 2011; Lotter et al., 2011; Pérez-Barnuevo et al., 2013; Tungpalan et al., 2015; Johnson, 2016b; Chetty, 2018). This study aimed to add to the growing pool of research (Lapakko & Antonson, 2006; Lapakko et al., 2006; Parbhakar-Fox, 2012; Kalyoncu Erguler et al., 2014; Brough et al., 2017, 2018; Pooler & Dold, 2017; Elghali et al., 2018, 2019) that suggests the applications of these analyses not only for the purposes of valuable mineral recovery, but also for the assessment of the ARD potential of mine wastes. Textural parameters such as liberation, association and grain size distribution, as well as the sample particle size distribution were therefore highlighted as key parameters for HCT behaviour during this study.

This study showed how the use of chemical, mineralogical and textural data may be used to enhance the interpretation of ARD characterisation and prediction tests. While more commonly used sample chemistry and mineralogy assessment tools (XRF, LECO and QXRD) allow for the identification of the types of minerals present in the sample and the sample chemistry, as well as for data reconciliation with quantitative mineralogy tools (QEMSCAN), the latter introduces a range of possibilities for ARD assessment which include, but are not limited to:

- Bulk mineralogy, with the opportunity to identify minerals present at low compositions and to distinguish between mineral end members, particularly for silicate minerals. The latter point is not adequately attainable with QXRD but is of particular importance for ARD assessment, as it provides valuable insight into the non-carbonate neutralisation potential in waste samples.
- Textural data, which in this study included the assessment of the liberation, association and grain size distribution of acid-forming and neutralising minerals. On the micro-scale these data yield insight into the effectiveness of characterisation tests through an indirect measure of the

acid-forming and acid neutralising mineral reactivities (liberated and locked minerals with their varying association to other minerals, which in turn allows for liberation correction of results). The micro-scale textural assessments may also be used to inform the sample-specific grinding size required for near-complete MoI liberation. On the meso-scale the textural data yields valuable information about the liberation and association of the Fe-Sulfide and dissolving minerals across the sample, which in turn, provides insight into prediction test behaviour. The GSD data on the meso-scale are useful to assess the onset of liberation of the MoI and construct a liberation spectrum, which serves to assess variation in grain populations of the MoI across the sample.

- Sampling constant parameters, such as the MoI grade and the MoI liberation size (sourced from the textural data), as well as the measure of particle roundness, obtained from customised categorisers in the QEMSCAN iDiscover software. These data are especially important for the sampling error calculations on the meso-scale, where the top size of the material may require unreasonably large sub-sample masses from Gy's safety line.

In addition to the above, physical characterisation tools such as PSD data provide insight about the top size of the test material and an indication of the distribution of mass across the size ranges in the sample. This information yields valuable information both for calculating the sampling error and to inform the required extent of pulverisation. Additionally, on the meso-scale the distribution of mass across the size fractions in the sample is of particular importance when considered in conjunction with mineral texture, as size fractions where textural effects are most pronounced (coarse sizes) may often comprise most of the sample mass, and therefore control sample behaviour. The latter point becomes important when interpreting humidity cell test behaviour, as even samples that are expected to generate acidic leachate based on their mineralogy may fail to do so due to the mass contribution of the “texturally significant” coarse size fractions.

The above description is summarised in the schematic in Figure 7-1, which shows the information provided by the various data sets and how these data sets may inform one another. This approach is not sample-specific. Fe-Sulfide and dissolving minerals were used as the key minerals for textural analyses in this study; however, other sulfide, sulfate, and/or non-carbonate neutralising minerals can be chosen as the MoIs. Textural analyses of these minerals could then similarly be applied to the interpretation of either the ARD test suite used in this study or to other customised test sets, albeit with different outcomes from the interpretation. As an example, if non-Fe-bearing sulfides and intermediate weathering minerals are the MoIs, then textural properties of these minerals would need to be obtained (either via QEMSCAN or other SEM tools), and in addition to iron and sulfate assays, chemical assays pertaining specifically to the elements in the MoIs would need to be performed on the test leachates. The sampling error assessment would, similarly, be dependent on the chosen MoI, and, based on the texture and specific properties of this MoI, be subject to different sub-sampling recommendations.

Therefore, although the current study used a set of gold waste rock samples, containing Fe-Sulfides and calcite as the main sources of acidity and neutralisation to demonstrate the usefulness of texture in the ARD assessment “toolbox”, the “tools” in this “toolbox” can ultimately be customised to suit the user's specific requirements. Some examples of how textural and mineralogical assessments have been used for ARD test interpretation include (Dyanty et al., 2013; Kotelo, 2013; Becker et al., 2015; Brough et al., 2017, 2018; Elghali et al., 2018, 2019).

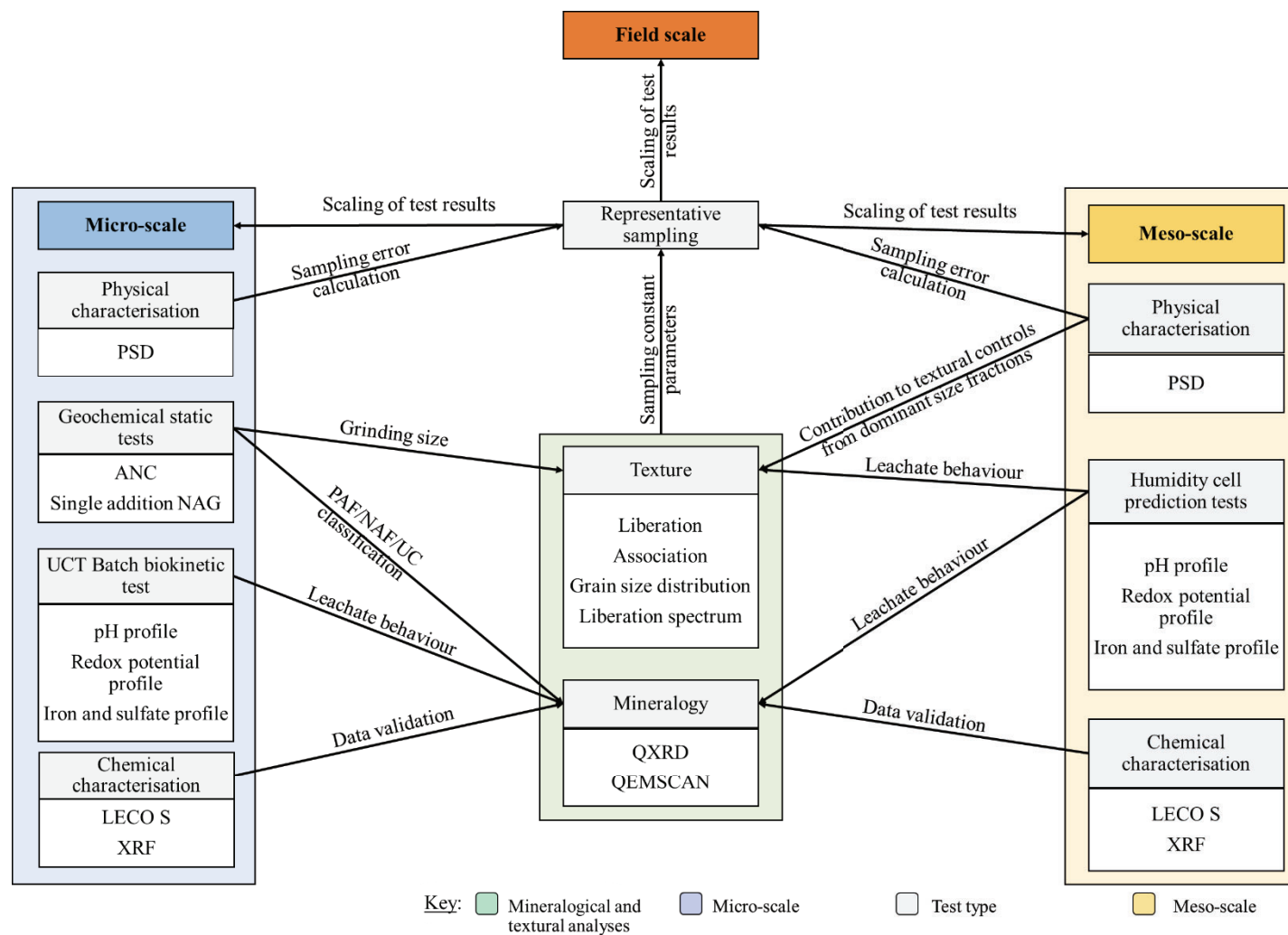


Figure 7-1 Schematic of the integration of the textural and mineralogical data with existing characterisation and prediction tests used during the current study.

7.2 Recommendations for future work

A few opportunities for further investigation have been identified during this study, namely:

- This was limited to performing a comprehensive ARD assessment on gold waste rock samples. The propensity of other waste types (e.g. coal waste material, tailings and waste material comprising sulfides other than pyrite and pyrrhotite) to generate acidic and/or metalliferous drainage is acknowledged and it is recommended that the effects of texture be assessed similarly for these ore types for a more comprehensive outlook of the holistic effects of texture on waste material;
- The ARDI was frequently referenced during this study when referring to Fe-Sulfide texture. Although the quantitative evaluation of each of the ARDI parameters was not feasible during this study (as it would require the evaluation of each particle individually, which is not achievable with the current software), it is suggested that a detailed quantitative computation of the meso-scale ARDI through quantitative textural assessment software could be performed. Such an approach would have to consider the ARDI for each individual particle in a sample and formulate an ARDI estimate based on the entire particle population, which could yield valuable insight into the ARD potential of meso-scale samples based on the Fe-Sulfide texture.
- The assessment of detailed leachate chemistry from characterisation and kinetic testing, as well as sequential chemical extraction to ascertain the leaching of the various minerals in different stages of the tests;
- Assessment of the samples for trace element chemistry and deportment throughout the duration of UCT batch biokinetic testing and humidity cell testing;
- The assessment of the mineralogy and texture of the characterisation and prediction test residues to confirm the reactivity of the various minerals. It could also be beneficial to perform residue analyses of UCT batch biokinetic test and humidity cell test material at various points in the test where the pH/redox potential profiles fluctuate to establish which minerals contribute to these fluctuations and how the material behaves over time. This could involve the setting up of replicate tests which would be “sacrificed” for analysis at various points in time during the tests;
- A more in-depth analysis of the effect of the optimal number of sample blocks required for mineralogical and textural analyses to decrease the sampling and mineralogical errors;
- Assessment of the samples using X-ray microcomputed tomography to assess the effects of and decrease the stereological bias associated with 2D measurements.

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Appendix

A. Materials and methods

A.1. Geochemical static characterisation tests

A.1.1. Acid neutralisation capacity (ANC)

The ANC test used for this study was the modified Sobek method, which accounts for the re-precipitation of siderite in the sample during the back-titration procedure (Sobek et al., 1978; Skousen et al., 1997; Weber et al., 2004).

Reagents

- Standardised 0.5M NaOH solution
- Standardised 0.1M NaOH solution
- Standardised 0.5M HCl solution
- Standardised 0.1M HCl solution
- Certified grade 0.1M NaOH solution
- Certified grade 0.1M HCl solution
- 25% HCl solution
- 30% H₂O₂ solution at pH 4.5 (alkalised by adding dilute NaOH dropwise to the solution)
- 15% H₂O₂ solution at pH 4.5 (alkalised by adding dilute NaOH dropwise to the solution)
- De-ionised water

The reagents were prepared in volumetric flasks of the appropriate volume then transferred to Schott bottles and labelled with molarity and date, after the standardisation procedure. NaOH and H₂O₂ solutions were monitored for precipitation and decomposition, respectively, with the H₂O₂ solutions stored in the fridge to decrease the rate of decomposition to O₂ and H₂O. Special care was taken when preparing NaOH solutions from pellets, as NaOH dissolution in H₂O is an exothermic reaction.

When standardising solutions, a pipette was used to obtain required volumes of 0.1M HCl and NaOH standards. This was done improve the accuracy of the ANC calculation, which depends on the molarity of standardised solutions. Standardisation procedures were performed in triplicate.

When calculating the molarity of the solutions, equation (54) was used, with standardisation performed to pH 7.

Appendix Table 1

Equation for the determination of the standardised solution molarity. M_1 = molarity of solution 1; M_2 = molarity of solution 2; V_1 = volume of solution 1; V_2 = volume of solution 2.

$$M_1 V_1 = M_2 V_2$$

(54)

Fizz rating

1. Place ± 0.5 g of sample on a watch glass.
2. Add a few drops of 25% HCl solution.
3. Depending on the carbonate content, the interaction of the 25% HCl with the sample may cause effervescence to occur. Assign a fizz rating based on the “strength” of the observed effervescence using Appendix Table 1.

Appendix Table 1 Fizz rating recommendations for the ANC test.

Reaction	Fizz Rating	HCl (M)	HCl Volume (mL)	NaOH (M)
None	0	0.5	4	0.1
Slight	1	0.5	8	0.1
Moderate	2	0.5	20	0.5
Strong	3	0.5	40	0.5
Very strong	4	1.0	40	0.5
Carbonate	5	1.0	60	0.5

Digestion

1. Place ± 2.00 g of dry pulverised sample into a 250 ml Erlenmeyer flask.
2. Carefully add HCl to each beaker. The volume and concentration of HCl is based on the fizz rating found in Appendix Table 1.
2. Add 20 ml of de-ionised water to flush the sample to the bottom
3. Prepare triplicate blank solutions with the same volume and concentration as the sample flasks but without solid sample.
4. Heat the combined solid samples and HCl solution at 90°C for 1-2 hours (including the blanks), swirling the flasks frequently and adding de-ionised water as the solution evaporates. The reaction is complete when no gas evolution is visible and particles settle evenly over the bottom of the flask. DO NOT LET THE SOLUTION BOIL DRY.
5. Cool the samples at room temperature for 1 hour.
6. Make up the solution to 125 ml with de-ionised water.
7. Record the mass of water added and the final total mass of the flask and its contents.
8. Measure the pH of the mixture to see that the pH is in the range 0.8 – 1.5.
9. Filter ANC digest solution before back titration using pre-prepared flasks, filter papers and funnels.

Due to the subjective nature of the fizz rating, the appropriate rating for the ANC test was established based on the suspected fizz rating, one rating above and one rating below. Once this was estimated, three test flasks were prepared to ascertain the correct fizz rating. The Sobek digestion procedure for the selected fizz ratings was followed until step 8. Once the pH of the mixture was measured, the fizz rating was selected that fell within range of the required pH.

Appendix Table 2

Fizz rating for samples C and D.

Sample	Fizz Rating	HCl (M)	HCl Volume (mL)	NaOH (M)
C	0	0.5	4	0.1
D	1	0.5	8	0.1

Back Titration

1. Back titrate the solution using the appropriate concentration of NaOH (using burette) from the Fizz Rating table to pH 4.5.
2. Add 10 drops of 30% H₂O₂, leave for 15 minutes.
3. Check pH and back titrate with NaOH to pH 4.5.
4. Repeat steps 2 and 3 until no significant pH change is observed.
5. Back titrate with NaOH to pH 7.0.
6. Add 10 drops of 30 % H₂O₂, leave for 15 minutes.
7. Check pH and back titrate with NaOH to pH 7.0.
8. Repeat steps 6 and 8 until no significant pH change is observed after step 7 (no change in pH decimal places in 15 minutes).
9. Cover with foil and leave the solution for 24 hours.
10. Check pH and adjust with further back titration to pH 7.0 if required.
11. Add 10 drops of 30% H₂O₂, and leave for approximately 24 hours.
12. Repeat steps 10 to 12 over 72 hours.
13. The ANC is calculated per Appendix Table 3.

Appendix Table 3

Equations used in the determination of static test parameters, where NAPP = net acid producing potential (kg H₂SO₄/t); ANC = acid neutralising capacity (kg H₂SO₄/t equivalent); MPA = maximum potential acidity (kg H₂SO₄/t); V_{HCl} = volume of HCl added to the ANC test flask (L); V_{NaOH} = volume of NaOH used to titrate the test flask (L); C = correction constant for molarities of HCl and NaOH used in the test; W_{Sample} = mass of the sample added (g); 49 = A conversion factor of 49 results in the ANC units of kg H₂SO₄/ton; M_{HCl} = molarity of the HCl solution used for the test. (Smith et al., 1974; Sobek et al., 1978; Skousen et al., 1997; Smart et al., 2002).

$NAPP = MPA - ANC$	(55)
$MPA(kgH_2SO_4/t) = (Total \%S) \times 30.6$	(56)
$ANC = \frac{[V_{HCl} - (V_{NaOH} \times C)] \times 49 \times M_{HCl}}{W_{Sample}}$	(57)
$C = \frac{V_{HCl \text{ in blank}}}{V_{NaOH \text{ titrated in blank}}}$	(58)

A.1.2. Single addition NAG test procedure

The single-addition NAG test was carried out as outlined in Smart et al. (2002), following the steps below.

1. Prepare the number of 500mL Erlenmeyer flasks required for the test.
2. Record the mass of the empty flasks.
3. Add approximately 2.5g of pulverised sample to the flasks.
4. Add 250mL of 15% H₂O₂ to the flask and record the total mass of the flask.
5. Place the test flasks on a tray (vigorous reaction may cause the solution to bubble out of the flask as the reaction proceeds) in the fume hood and allow to react over the course of 24 hours.
6. After 24 hours, measure the pH (this is the pre-boil NAG_{pH}).
7. Place the sample flasks on the hot plate and gently heat until the reaction (effervescence) stops.
NB: Do not let the flasks boil dry. Add de-ionised water as necessary.
8. Allow the samples to come to room temperature.
9. Top up the sample to 250mL with de-ionised water.
10. Measure the pH (this is the after-boil NAG_{pH}).
11. Prepare clean flasks and funnels lined with pre-weighed filter paper.
12. Filter the solution.
13. Back-titrate the obtained filtrate to pH 4 and then to pH 7 using the guidelines in Appendix Table 4.

Appendix Table 4 NAG test back-titration guidelines based on the after-boil NAG_{pH}.

NAG _{pH}	Molarity of NaOH solution
> 2	0.1M
≤ 2	0.5M

14. Calculate the sample NAG using equation (59).

Appendix Table 5 Net acid generation potential calculation based on the volume and molarity of NaOH used during the back-titration procedure to pH 4.5 and pH 7. Adapted from Miller et al. (1997), where NAG = net acid generation; V_{NaOH} = volume of NaOH used during back titration (L); M_{NaOH} = molarity of NaOH used during the back-titration (mol/L); W_{Sample} = mass of the sample added (g).

$$NAG = \frac{49 \times V_{HCl} \times M_{NaOH}}{W_{Sample}} \quad (59)$$

A.2. UCT batch biokinetic test

A.2.1. Reagent and inoculum preparation

Autotrophic basal salt (ABS) medium preparation

1. Place a 1000 mL volumetric flask with a stirrer bar inside on a stirrer plate and adjust a regular stirring speed.
2. Add approximately 800mL of water.
3. Adjust pH to 1.94 using 98% H₂SO₄.
4. Add one salt at a time from Appendix Table 6, allowing time for complete dissolution.

5. After complete dissolution, make the volume up to 1000mL and transfer to a clean Schott bottle of appropriate size.
6. Prepare dilute ABS media and autoclave the remainder of the concentrated ABS media.
7. To make 1x ABS media, dilute concentrated ABS media.
8. For ABS media used for culture growth, add trace element solution (TES) at a concentration of 1mL TES per 1L of concentrated ABS media. NB: No TES is added to test media.
9. Concentrated and diluted ABS media should be assessed for Fe^{2+} , Fe^{Total} , SO_4^{2-} , pH and redox potential.
10. Autoclave all concentrated and dilute ABS media, culture growth flasks propped with cotton wool and aluminium foil (for growing and keeping culture), 250mL Erlenmeyer flasks for the biokinetic tests and a 200mL measuring cylinder for transferring media to test flasks.

Appendix Table 6 ABS media composition used for UCT batch biokinetic test experiments.

Salt	Mass (g) in 200mL
$(\text{NH}_4)_2\text{SO}_4$	7.5
Na_2SO_4	7.5
KCl	2.5
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	25.0
KH_2PO_4	2.5
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	0.7

Inoculum preparation

After autoclaving, any work should be done in the laminar flow hood.

1. Collect a small amount of stock culture samples of iron- and sulfur-oxidising bacteria.
2. Conduct cell counts on the sulfur- and iron-oxidising species to establish cell number and corresponding inoculum size for growing the UCT batch biokinetic test cultures, with cell counting being performed using a microscope and counting chamber.
3. Place appropriate amount of ABS medium into culture growth flask, followed by 5% pyrite (based on total working volume e.g. 5g in 100mL, or 12.5g in 250mL).
4. Using sterile pipette tips, add equal cell numbers (based on the cell count and corresponding calculated inoculum volume) of the sulfur- and iron-oxidising stock cultures to obtain a 50:50 ratio of the respective microbial species in the growth flask.
5. Place culture growth flask on orbital shaker in 37°C room at 150RPM.
6. Grow microbial population to appropriate size to allow for the inoculation of 16 flasks ($10^9 \times 16$).
7. Calculate inoculum volume (IV) required once cells are grown.

A.2.2. UCT batch biokinetic test method

1. Clean and dry the 250mL Erlenmeyer flasks which will be used for the test (28 in this case) and plug firmly with cotton and foil. Autoclave prepared flasks.

- Split test samples into $\pm 7.5\text{g}$ portions and place into the prepared test flasks. Appendix Table 7 provides the sample matrix used during this study (also see section 3.2.4).

Appendix Table 7

Sample set matrix for the UCT batch biokinetic test. pH was controlled to 2 for pH-controlled flasks.

Sample	Uninoculated pH-controlled	Uninoculated non-pH-controlled	Inoculated pH-controlled	Inoculated non-pH-controlled
A	None	None	None	3
C	3	3	3	3
D	3	3	3	3
Biotic control	None	None	None	1

- Perform a cell count on the culture from the culture growth flask and calculate the inoculum volume that will need to be added to the test flasks to give a cell concentration of 10^9 cells (this was found to be 1.29mL).
- Add sterile diluted ABS media to the flasks using a sterilised measuring cylinder, to enable a final working volume of 150mL.
- Under laminar flow hood inoculate the appropriate flasks (i.e. uninoculated-labelled test flasks remain uninoculated).
- Record the mass of the test flasks and perform the first sampling for pH, redox potential, Fe^{2+} concentration, Fe^{Total} concentration and SO_4^{2-} concentration (see section A.2.3).
- Place flasks on an orbital shaker set at 37°C and 150RPM.

A.2.3. Chemical assays

Sulfate assay

- Prepare the conditioning reagent as per Appendix Table 8 (procedure below yields 555mL).

Appendix Table 8

Composition of conditioning reagent used for sulfate assay.

Reagent	Quantity
NaCl	75g
HCl (32%)	30mL
Glycerol	50mL
Ethanol	100mL
DI Water	300mL

- Crush BaCl crystals to pass through 20/30 size mesh or finer.
- To a prepared and clean test tube, add 5mL of de-ionised water (for the blank) or sufficiently dilute sample.
- Add 0.25mL conditioning reagent, followed by one micro-scoop of ground BaCl.
- Vortex sample for 30 seconds to a minute for the reaction to proceed and the sample to become turbid.
- Zero the spectrophotometer using the blank at an absorbance of 420nm.

7. Read sample absorbance at 420 nm

Fe-assay using the 1-10 phenanthroline method

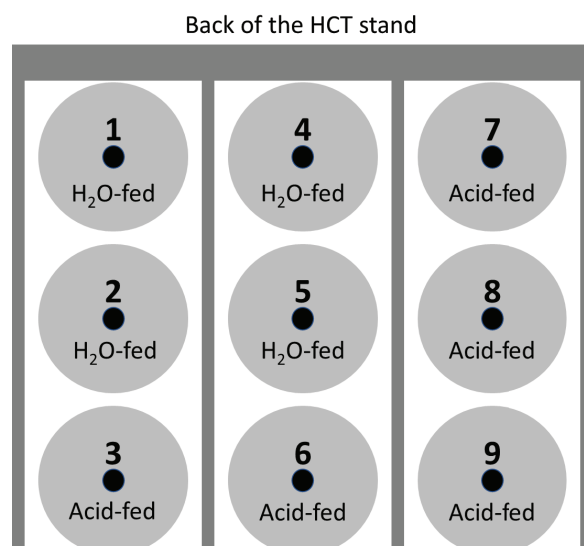
1. To a clean test tube add 1mL of de-ionised water (for blank) or sufficiently diluted sample.
2. Add 2mL of acetate buffer and 2 mL of 1-10 phenanthroline solution to the test tube.
3. Vortex the sample and wait 5 minutes for the reaction to proceed and colour to develop (if Fe^{2+} is present).
4. Zero the spectrophotometer using the blank at an absorbance of 510nm.
5. Read sample absorbance at 510 nm.
6. NB: Return the contents of the cuvette after recording the absorbance for the Fe^{2+} .
7. Add a small spatula tip of hydroxylamine to all the sample test tubes, including the blank.
8. Vortex the sample and wait 5 minutes for the reaction to proceed and colour to develop.
9. Insert the blank sample into the spectrophotometer and observe the reading. If it is below 0.04, zero the instrument using the blank at an absorbance of 510nm. If the reading is above 0.04, re-make the blank, as contamination may have occurred.
10. Read sample absorbance at 510 nm. Do not use the same cuvettes that were used to measure the Fe^{2+} concentration.

Calculate the respective iron and sulfate concentrations using calibration curves (provided in section A.4).

A.3. Humidity cell test

A.3.1. Column set-up details

The humidity cell tests were constructed and set up based on the ASTM (2013) method and that outlined by Opitz et al. (unpublished). The column configuration used for the humidity cell test experiments is provided in Appendix Figure 1.



Appendix Figure 1 Humidity cell test column configuration (top view). Columns 1, 2, 3 and 6 contained sample D, while columns 4, 5, 7, 8 and 9 contained sample C.

The columns were operated using the specifications provided in Appendix Table 9.

Appendix Table 9 Humidity cell test conditions summary.

Air flow rate	5L/min
Leach volume	500mL
Water feed pH	6-8
Acid feed pH	2 (de-ionised water acidified using 98% H ₂ SO ₄)
Temperature of humid air feed bottle	±29 ⁰ C
Dry air cycle	Three days
Humid air cycle	Three days

A.3.2. Sampling

Flood leach

1. Switch rotameters and hot plate off.
2. Clamp all column pipe inlets and outlets (air supply and drainage pipes) to ensure no leach solution travels out of the columns through the pipes during the flood leach.
3. Measure approximately 500mL of de-ionised water using a measuring cylinder and using a Schott bottle cap (so as not to disturb the top layer of the column packing), gently pour the water into the column. Repeat this step using de-ionised water for columns 1, 2, 4 and 5. Reserve a sample of water for analyses.
4. Place a large plastic beaker with a stirrer bar onto a stirrer plate and regulate the stirring speed.
5. Add 98% H₂SO₄ dropwise to the beaker until the pH reaches 2. Take a sample of acid for analyses.
6. Repeat steps 3 and 4 for columns 3, 6, 7, 8 and 9 with the pH 2 acid feed.
7. Leave all columns filled with the leach solution for two hours.

Column sampling

1. Drain the columns into prepared bottles, re-clamp the drainage pipes and unclamp the air inlet pipes.
2. Prepare sample bottles and funnels with pre-weighed filter papers for filtering the column leachate.
3. Filter the column leachate from each column into the corresponding filtrate bottles.
4. Once the filtering is complete, record the mass of the filtrate for each sample.
5. Collect a sample of each sample filtrate into pre-prepared sample bottles and discard the remaining filtrate.
6. Pipette 2mL of each sample into a pre-prepared Eppendorf centrifuge tube and place in fridge for storage.
7. Assay the samples for Fe^{2+} , Fe^{Total} and SO_4^{2-} concentration (as described in section A.2.3) assays for the samples.

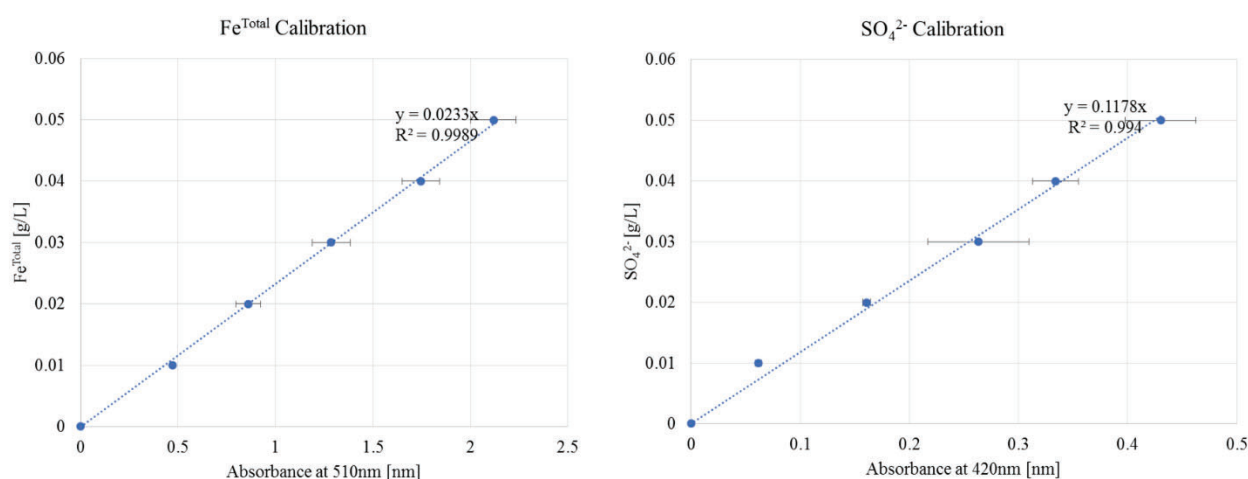
Air cycle

1. On the day following the flood leach, begin the dry air cycle.
2. Ensure air supply pipes are unclipped and the column drainage pipes are clamped.
3. Set the rotameters to a flow rate corresponding to a 5L/min supply to each column.
4. Allow the dry air cycle to run for three days.
5. Following the dry air cycle, begin the humid air cycle.
6. Fill the Schott bottles equipped with port hole caps with de-ionised water and place on a hot plate set to 29°C (to ensure a constant humidity of the humid air supplied to the columns).
7. Switch off the dry air and connect the air supply pipes to the water-filled Schott bottles on the hot plate.
8. Set the rotameters to a flow rate corresponding to a 5L/min supply to each column.
9. Allow the humid air cycle to run for three days. NB: Monitor the water level in the Schott bottles over the three days of the humid air cycle and re-fill as necessary.

A.4. Calibration curves

Calibration curves were obtained from the dilutions of standard solutions of iron and sulfate at 100ppm. The iron standard was prepared from a 1000ppm standard, while the sulfate standard was prepared as indicated in Appendix Table 10.

Reagent	Quantity in 1000mL
Na_2SO_4	0.1479g



Appendix Figure 2

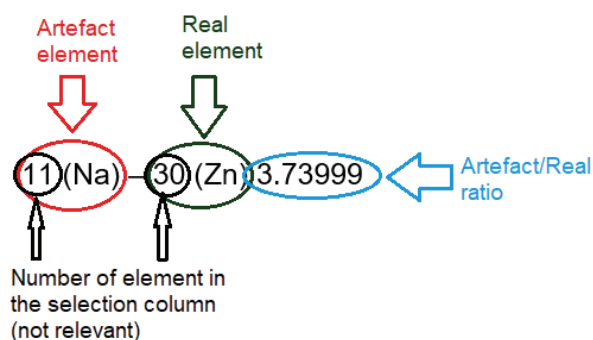
Iron and sulfate concentration calibration curves used for the UCT batch biokinetic and humidity cell tests.

A.5. Mineralogy and texture

A.5.1. QEMSCAN

SIP list creation

The creation of the SIP list required accounting for potential peak overlaps that exist in the spectra of certain elements (such as for sulfur and molybdenum). The built-in option in iDiscover enables all peak overlaps at default element ratios, meaning that during the mathematical fitting of the synthetic spectra all elements that have overlapping peaks may emerge in the pixel information, even if only a subset of those elements is “real”, while the remainder are “artefacts”. To identify the “real” and “artefact” elements, the XRF and XRD data, as well as the documented literature on the ore type used in this study were investigated for the possible minerals and elements. Based on this, the allowable peak overlaps and the ratios for these were set as provided by Appendix Figure 3 and the accompanying description.



Appendix Figure 3 Defining real and artefact elements in iDiscover.

- If $\text{Na}_{\text{concentration}}/\text{Zn}_{\text{concentration}} > 3.73999$ then only Zn will be displayed in the concentration.
- If $\text{Na}_{\text{concentration}}/\text{Zn}_{\text{concentration}} < 3.73999$ then both Na and Zn will show up in Element Concentrations, which may be unwanted for things like sphalerite (ZnS).

Questions:

- Is the artefact element (Ae) present in the composition?
- If yes, is the real element (Re) present in the composition?
- Then, if $\text{Zn}/\text{Na} > \text{ratio}$, then remove Ae

Prior to measurement, the SIP list was tested by identifying discrete minerals in the BSE images to see if the artefact elements were sufficiently eliminated. An example would be locating a grain of pyrite or pyrrhotite and identifying whether it contained Fe and S (which was the desired response) or Fe, S and Mo (which was undesired).

Special cases of overlaps that were possible (such as the Ba and Ti peak overlap in benitoite, but not necessarily in titanite) were evaluated on a case-by-case basis in the BSE image. Some examples of the eliminated overlaps are provided in Appendix Table 11.

Appendix Table 11

Peak overlaps in iDiscover that were deemed unreasonable for measurements performed in the current study.

Element	Artefacts
K	Cd, In, Sn, Sb, U
Na	Ga
Ca	Sc, Cd, In, Sn, Sb, Cs, Ba
Al	Se, Br, Yb, Lu
Fe	Ru, Dy, Eu, Tm, Pb
Ti	Pr, V, I, Cs, Ba, La, Ce
Si	Br, Sr, Lu, Ta, W, Re
S	Mo, Nb, Tl, Bi

It should be noted that although the presence of deleterious elements is a factor in ARD quality and some of the elements in Appendix Table 11 could contribute to this, the evaluation of the drainage chemistry in terms of deleterious elements was not the focus of this study. This means that QEMSCAN evaluation, and therefore the SIP editing, was tailored to focus on the bulk mineralogy and major rock-forming minerals in the sample.

The SIP lists were created based on the classification of individual pixels in the measurement debugging application. Pixels were classified based on the synthetic spectra provided in the iDiscover spectral library, as well as by element-based classification such as that shown in Appendix Table 12. The silicate minerals were differentiated based on the ratios of the elements to one another, the BSE value, their appearance in the BSE image (qualitative textural assessment) and their association to one another.

Appendix Table 12

SIP list development mineral classification criteria.

Mineral	Chemistry
Pyrite, pyrrhotite	Fe, S
Arsenopyrite	As, Fe, S
Chalcopyrite	Cu, Fe, S
Galena	Pb, S
Sphalerite	Zn, S
Quartz	Si, O
Calcite	Ca, O
Magnetite, Hematite	Fe, O
Dolomite	Ca, Mg, O
Silicate minerals	K, Ca, Mg, Na, Mn, Fe, Al, Si, O

B. Test results

B.1. Test data

Data sets and some associated calculations for characterisation, prediction, sampling error assessment and mineralogy and texture, may be found on ZivaHub (<https://zivahub.uct.ac.za/>) or figshare (<https://figshare.com/>) through the following link or through searching for the project directly:

Project:

Guseva, Olga (2020): Quantifying texture for acid rock drainage characterization and prediction.

Link:

<https://doi.org/10.25375/uct.12129888>

B.2. XRF

Appendix Table 13 Oxide and element chemistry obtained via XRF.

Oxide/Element	Unit	A	B	C	D
SiO ₂	wt. %	48	54	41	53
TiO ₂	wt. %	0.1	0.2	1.7	0.1
Al ₂ O ₃	wt. %	4.5	8.9	7.4	2.6
Fe ₂ O ₃	wt. %	32	18	19	32
MnO	wt. %	0.1	0.1	0.3	0.12
MgO	wt. %	1.8	1.6	3.3	3.7
CaO	wt. %	3.0	2.7	9.9	4.5
Na ₂ O	wt. %	1.9	3.0	0.1	0.1
K ₂ O	wt. %	0.4	2.6	2.0	0.4
P ₂ O ₅	wt. %	0.2	0.1	0.2	0.2
SO ₃	wt. %	0.8	1.2	15	3.2
Cr ₂ O ₃	wt. %	0.1	0.1	0.2	0.0
NiO	wt. %	0.0	0.1	0.0	0.0
H ₂ O-	wt. %	5.7	4.2	n.a.	n.a.
LOI	wt. %	0.9	3.1	n.a.	n.a.
Y	(ppm)	94	1979		
Zn	(ppm)	72	94	1979	36
Cu	(ppm)	83	54	312	13
Ni	(ppm)	194	248	317	8
Mo	(ppm)	34	52	6	3
Nb	(ppm)	2	6	20	<3
Zr	(ppm)	61	103	148	18
Y	(ppm)	15	15	24	13
Sr	(ppm)	354	596	138	34
Rb	(ppm)	22	84	58	19
U	(ppm)	b.d.	b.d.	<5	<5
Th	(ppm)	3	2	<5	<5
Pb	(ppm)	10	23	50	15
Co	(ppm)	20	17	118	28
Mn	(ppm)	596	627	2470	1239
Cr	(ppm)	543	687	1118	161
V	(ppm)	68	66	252	31
F	(ppm)	1454	1194	1458	1292
S	(ppm)	7594	7667	19120	3892
Cl	(ppm)	179	266	126	416
Sc	(ppm)	6	6	39	8
Ba	(ppm)	433	648	478	<10

B.3. ICP-MS data

Appendix Table 14 Element chemistry obtained from ICP-MS.

Element	Unit	Sample C	Relative standard deviation %	Sample D	Relative standard deviation %
Li	ppm	82.91	0.022	8.858	0.133
Sc	ppm	23.39	0.648	2.680	0.528
V	ppm	204.2	0.743	25.81	0.413
Cr	ppm	813.5	0.838	123.2	0.465
Co	ppm	119.6	0.828	6.493	0.500
Ni	ppm	401.6	0.787	13.96	0.744
Cu	ppm	389.2	1.144	10.04	0.723
Zn	ppm	2300	0.378	33.28	0.396
Rb	ppm	51.95	0.554	15.76	0.393
Sr	ppm	129.4	0.561	32.72	0.459
Y	ppm	15.20	0.811	5.747	0.556
Zr	ppm	129.9	0.814	14.77	0.623
Nb	ppm	18.92	0.723	0.696	0.280
Ba	ppm	349.0	0.664	33.77	0.370
La	ppm	18.82	0.813	3.392	0.165
Ce	ppm	44.54	0.415	6.809	0.209
Pr	ppm	5.971	1.512	0.856	0.747
Nd	ppm	25.39	0.267	3.623	0.463
Sm	ppm	5.580	1.260	0.825	0.662
Eu	ppm	1.816	0.017	0.477	0.402
Tb	ppm	0.763	0.260	0.130	1.062
Gd	ppm	4.779	0.531	0.873	0.956
Dy	ppm	3.710	1.313	0.849	0.996
Ho	ppm	0.745	0.419	0.177	0.990
Er	ppm	1.723	0.783	0.554	1.085
Tm	ppm	0.337	0.060	0.078	1.634
Yb	ppm	1.442	0.616	0.541	1.659
Lu	ppm	0.317	0.928	0.090	1.474
Hf	ppm	3.555	0.961	0.393	1.444
Ta	ppm	1.316	1.278	0.072	3.497
Pb	ppm	56.22	0.468	13.03	0.722
Th	ppm	2.284	0.541	0.687	0.747
U	ppm	0.769	1.124	0.216	0.910

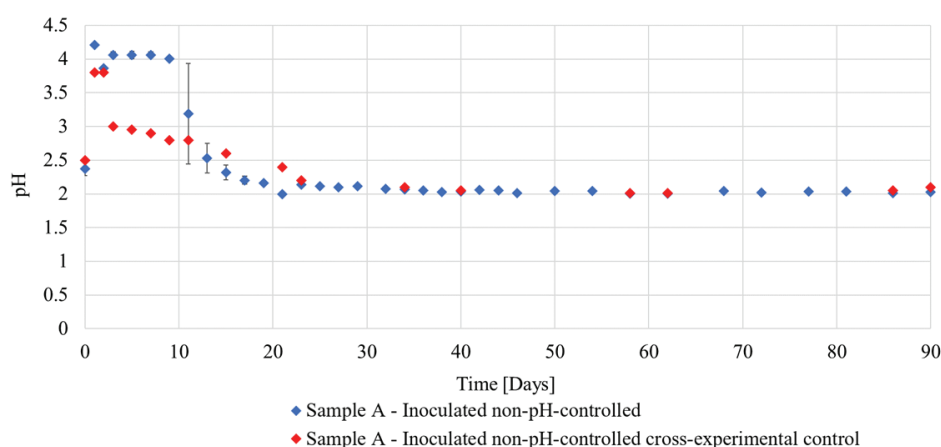
B.4. Characterisation tests

Please refer to section B.1 for characterisation test data.

B.4.1. UCT batch biokinetic test

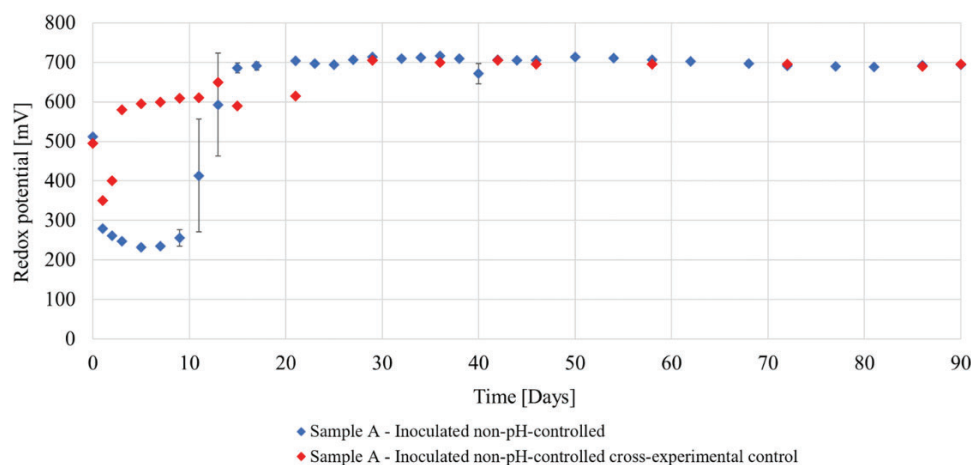
Sample A “cross-experimental” control results

Appendix Figure 4 and Appendix Figure 5 provide the pH and redox potential profiles for the cross-experimental control for the non-pH-controlled UCT batch biokinetic test performed during this study and in the work of Opitz et al. (2016). Although the cross-experimental control showed some variation between the two tests (due to expected differences in the inoculum composition or volume, or differences in the pH and redox probe calibration), it does provide an indication of how the experimental sets may have differed from one another and how they may be compared.



Appendix Figure 4

pH profile for cross-experimental control for UCT batch biokinetic test for non-pH-controlled inoculated sample A plotted against pH results for sample A obtained by Opitz et al. (2016).



Appendix Figure 5

Redox potential cross-experimental control for UCT batch biokinetic test for non-pH-controlled inoculated sample A plotted against redox potential results for sample A obtained by Opitz et al. (2016).

B.5. Mineralogy

Please refer to section B.1 for mineralogy data.

B.5.1. QXRD

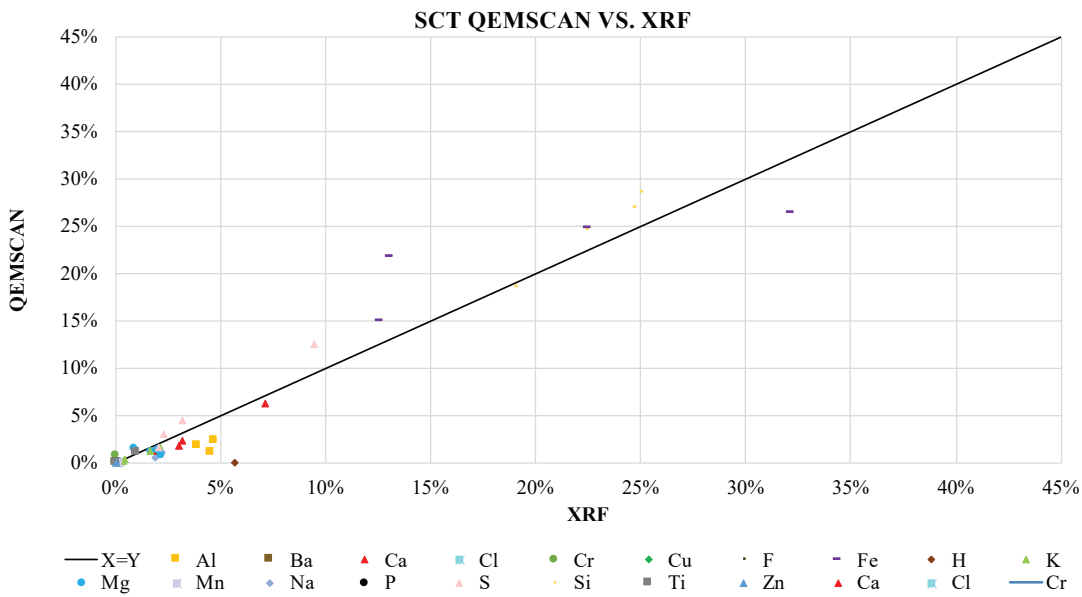
Appendix Table 15

Sample mineralogy for samples A, B, C and D obtained via XRD and QEMSCAN, corresponding with Figure 4-2.

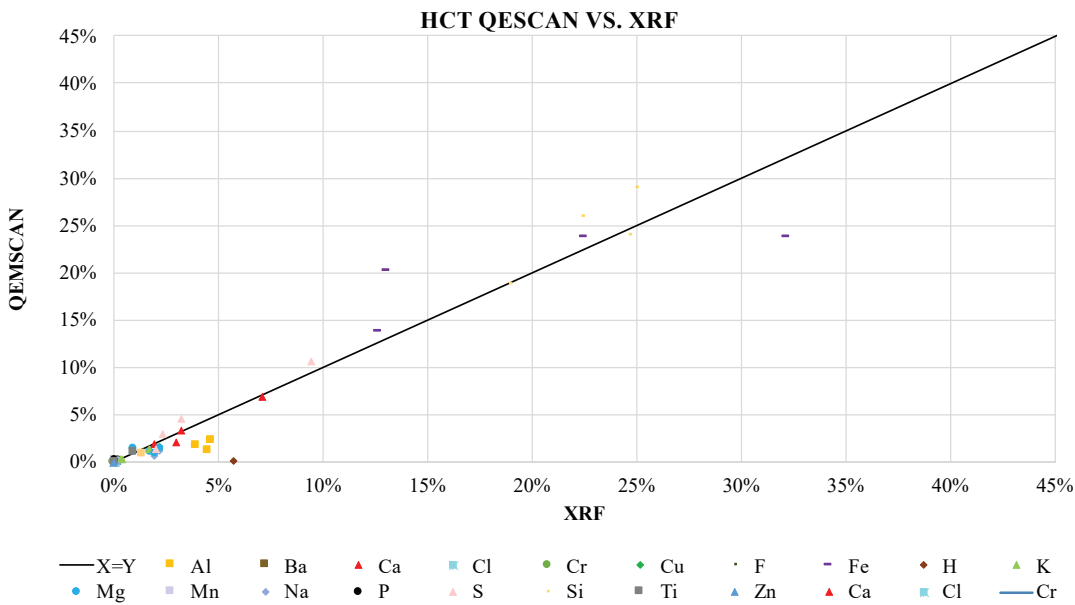
Mineral	Sample A		Sample B		Sample C		Sample D	
	XRD	QEM-SCAN	XRD	QEM-SCAN	XRD	QEM-SCAN	XRD	QEM-SCAN
Pyrite	1.7%	1.73%	6.8%	7.8%	<1%	2.0%	<1%	<1%
Pyrrhotite	4.7%	5.1%	<1%	<1%	26.8%	29.7%	5.3%	5.0%
Other Sulfide	<1%	<1%	<1%	<1%	<1%	<1%	<1%	<1%
Carbonate	1.4%	1.3%	4.9%	2.2%	16.7%	12.5%	5.0%	2.5%
Olivine	<1%	<1%	<1%	<1%	<1%	<1%	<1%	<1%
Epidote	1.4%	<1%	2.2%	<1%	2.5%	<1%	<1%	<1%
Pyroxene	1.8%	2.1%	<1%	<1%	<1%	<1%	<1%	3.0%
Amphibole	16.4%	17.4%	1.8%	3.8%	<1%	<1%	32.7%	34.4%
Mica	<1%	<1%	8.7%	9.6%	<1%	7.6%	3.6%	1.7%
Chlorite	1.1%	3.3%	2.2%	2.2%	6.0%	4.7%	3.6%	5.6%
Talc	<1%	<1%	<1%	<1%	<1%	<1%	<1%	2.0%
Plagioclase-Feldspar	15.6%	11.6%	24.1%	21.5%	<1%	<1%	1.1%	<1%
K-Feldspar	<1%	1.5%	7.3%	8.8%	2.7%	5.3%	<1%	<1%
Fe-Oxide	20.7%	21.0%	8.1%	10.64%	<1%	<1%	8.0%	9.0%
Quartz	35.3%	32.3%	33.0%	31.1%	37.4%	30.7%	36.5%	35.0%
Titanite	<1%	<1%	<1%	<1%	7.1%	4.8%	<1%	<1%
Apatite	<1%	<1%	<1%	<1%	<1%	<1%	<1%	<1%
R_{wp}	5.99	-	8.21	-	6.62	-	6.58	-
GOF	4.42	-	4.56	-	2.10	-	2.46	-

B.5.2. Data reconciliation

XRF

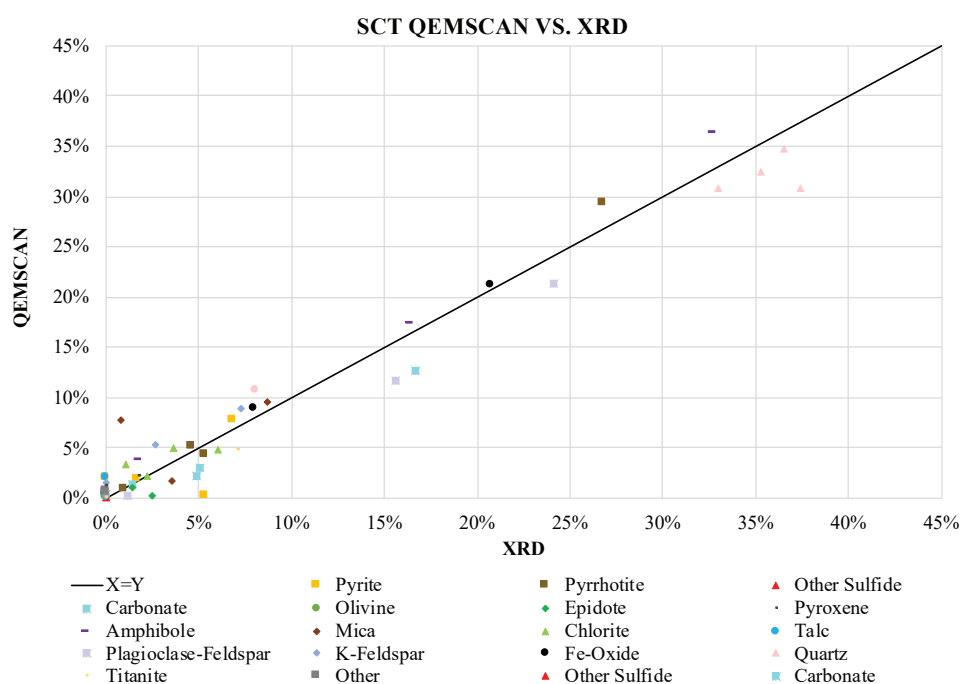


Appendix Figure 6 SCT feed material parity chart between XRF and QEMSCAN for samples A, B, C and D.



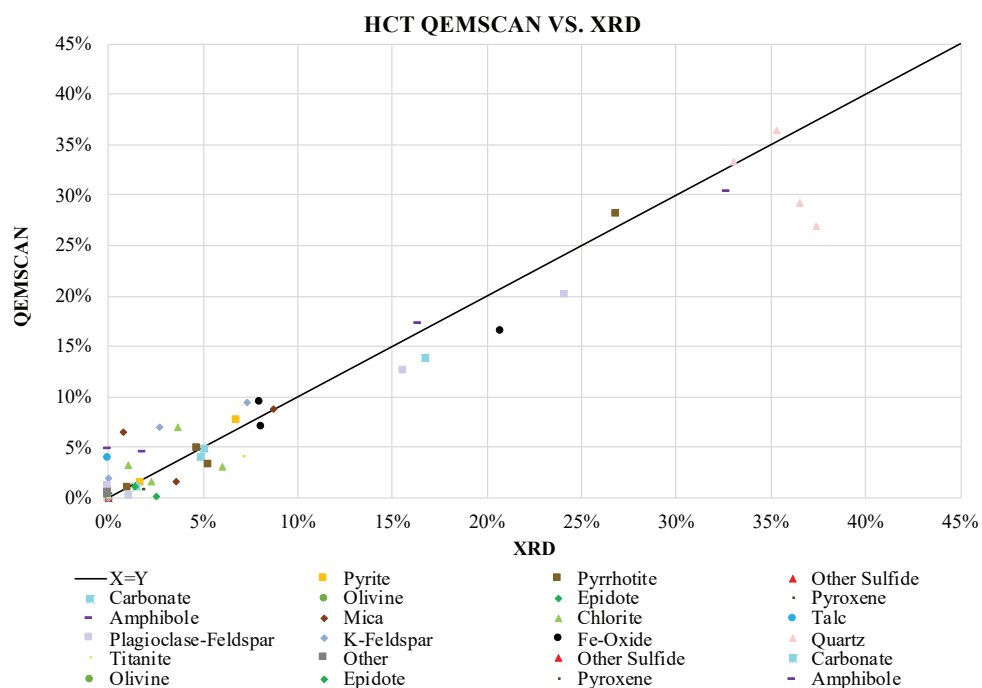
Appendix Figure 7 HCT feed material parity chart between XRF and QEMSCAN for samples A, B, C and D.

QXRD



Appendix Figure 8

SCT feed material parity chart between QXRD and QEMSCAN for samples A, B, C and D.



Appendix Figure 9

HCT feed material parity chart between QXRD and QEMSCAN for samples A, B, C and D.

C. Calculations

C.1. Mineralogy

C.1.1. ARDI

This section provides the parameters for the computation of the ARDI, with the contents of Appendix Table 16 to Appendix Table 22 being adapted/sourced from the work of Parbhakar-Fox (2012). Although the ARDI was not explicitly computed during this study, parameters A to E were important when considering how different textural and mineralogical parameters may affect the ARD formation potential of waste material. A recommendation is made on the quantitative computation of the ARDI for each parameter. It is recommended that all parameters would be calculated based on the largest size fraction (-6700/+2000 μ m) where the mineral texture would be most intact.

Appendix Table 16 ARDI classification.

ARDI	Classification
50 to 41	Extremely Acid Forming (EAF)
40 to 31	Acid Forming (AF)
30 to 21	Potentially Acid Forming (PAF)
20 to 11	Non-Acid Forming (NAF)
10 to 0	Non-Acid Forming <i>or</i> Potential Neutralising Capacity (PNC)
-1 to -10	Acid Neutralising Capacity (ANC)

Parameter A (Appendix Table 17) could be evaluated based on the average Fe-Sulfide area % grade of the particles and would be the same for the meso- and micro-scales, as the size fraction/area assessed would be smaller than that recommended by the ARDI methodology (even for the largest size fraction).

Appendix Table 17 Parameter A for ARDI calculation to be used on the meso- and micro-scale.

Fe-Sulfide Content (%)	ARDI Value
100	10
90	9
80	8
70	7
60	6
50	5
40	4
30	3
20	2
10	1
0	0

Parameter B (Appendix Table 18) could be evaluated based on the presence/absence of alteration rims around the pyrite, as observed from the QEMSCAN data and/or BSE images. In the context of this study these would be taken as 0 – 10%, as no apparent weathering was observed for any samples.

Appendix Table 18 Parameter B for ARDI calculation to be used on the meso- and micro-scale.

Degree of alteration	ARDI Value
0 to 10% fractured and/or altered	10
11 to 20% fractured and/or altered	9
21 to 30% fractured and/or altered	8
31 to 40% fractured and/or altered	7
41 to 50% fractured and/or altered	6
51 to 60% fractured and/or altered	5
61 to 70% fractured and/or altered	4
71 to 80% fractured and/or altered	3
81 to 90% fractured and/or altered	2
91 to 100% fractured and/or altered	1

Parameter C (

Appendix Table 19) could be evaluated qualitatively for the particle of interest on the meso-scale or quantitatively using software. On the micro-scale (

Appendix Table 20) Parameter C could be evaluated qualitatively by observing the BSE images for the samples.

Appendix Table 19 Parameter C for ARDI calculation to be used on the meso-scale.

Morphology	ARDI Value
Disseminated Fe-Sulfides covering c. 50 to 100% of the assessed area	10
Disseminated Fe-Sulfides covering up to 50% of the assessed area	9
Disseminated Fe-Sulfides covering up to 25% of the assessed area	8
Larger individual Fe-Sulfide crystals (e.g. hexagonal, pyritohedron) covering c. 50-100% of the assessed area	7
Larger individual Fe-Sulfide crystals (e.g. hexagonal, pyritohedron) covering up to 50% of the assessed area	6
Larger individual Fe-Sulfide crystals (e.g. hexagonal, pyritohedron) covering up to 25% of the assessed area	5
Fe-Sulfide veins (<20mm) covering c. 50-100% of the assessed area	4
Fe-Sulfide veins (<20mm) covering up to 50% of the assessed area	3
Fe-Sulfide veins (<20mm) covering up to 25% of the assessed area	2
Massive Fe-Sulfide veins	1

Appendix Table 20

Parameter C for ARDI calculation to be used on the micro-scale.

Morphology	ARDI Value
Framboidal: <20µm	10
Framboidal: >20µm	9
Anhedral and highly fractured	8
Anhedral	7
Subhedral-anhedral	6
Subhedral and highly fractured	5
Subhedral	4
Euhedral-subhedral	3
Euhedral and fractured	2
Euhedral	1

Parameter D (Appendix Table 21) could be evaluated by quantitatively by evaluating the particle of interest using a categoriser that accounted for each of the assigned categories in terms of mineral grades.

Appendix Table 21

Parameter D for ARDI calculation to be used on the meso- and micro-scale.

Modal mineralogy around acid-forming phase	ARDI Value
100% sulfide	10
90% sulfide	9
80% sulfide	8
70% sulfide	7
60% sulfide	6
50% sulfide	5
40% sulfide	4
30% sulfide	3
20% sulfide	2
10% sulfide	1
0% sulfide; 0% primary neutraliser	0
0 to 20% primary neutraliser	-1
21 to 40% primary neutraliser	-2
41 to 60% primary neutraliser	-3
61 to 80% primary neutraliser	-4
81 to 100% primary neutraliser	-5

Parameter E (Appendix Table 22) could be evaluated based on the association data between the Fe-Sulfide and other reactivity groupings for the particle being analysed.

Contents	ARDI Value
Sulfide-sulfide boundary 100%; 0% inert	10
Sulfide-sulfide boundary 80%; 20% inert	9
Sulfide-sulfide boundary 60%; 40% inert	8
Sulfide-sulfide boundary 40%; 60% inert	7
Sulfide-sulfide boundary 20%; 80% inert	6
Sulfide-sulfide boundary 0%; 100% inert	5
80% inert (fast weathering); 20% inert (slow weathering)	4
60% inert (fast weathering); 40% inert (slow weathering)	3
40% inert (fast weathering); 60% inert (slow weathering)	2
20% inert (fast weathering); 80% inert (slow weathering)	1
0% inert (fast weathering); 100% inert (slow weathering)	0
80% inert; 20% primary neutraliser	-1
60% inert; 40% primary neutraliser	-2
40% inert; 60% primary neutraliser	-3
20% inert; 80% primary neutraliser	-4
0% inert; 100% primary neutraliser	-5

The above computations were not performed during this study, as the ARDI would need to be considered individually for each particle and then (potentially) be averaged across the sample, considering the contribution of each set of particles and their respective ARDIs to the sample. This was not possible using the QEMSCAN iDiscover during this study, as it would require categorisers to be “nested” within one another to consider parameters A-E together per particle.

C.2. Total iron concentration for UCT batch biokinetic test

$$\frac{(Fe - Sulfide \text{ wt. \% in sample}) \times (\text{sample mass (g)}) \times \% Fe \text{ in } Fe - \text{ sulfides}}{\text{Test volume (L)}} + Fe \text{ in flask from inoculum and/or ABS media}$$

C.3. Sampling error

Appendix Table 23

Guidelines for the calculation of the parameters for the FSE equation used to calculate the sampling error.

Variable	Unit	Definition	Method of calculation
d_i	cm	Sample top size	Top screen size
f	-	Shape factor (how cubic/round/acicular the particles are on average)	Calculated using a categoriser in iDiscover based on and adapted from Little et al. (2015) (QEMSCAN) and/or estimated (Minkinen, 2004)
g	-	Size distribution factor (uniformity of particle size throughout sample)	Calculated based on Minnitt et al. (2007a)
d_l	cm	d_{85} of the mineral of interest grain size distribution	Obtained from the Fe-Sulfide GSD of the sample (QEMSCAN)
ρ_m	g/cm^3	Density of the mineral of interest	Estimated from the content and density of the respective Fe-sulfide minerals in the sample/size fraction. For pyrite-rich sample B this was taken as $5.01 g/cm^3$. For pyrrhotite-rich samples A, C and D this was taken as $4.61 g/cm^3$ (QEMSCAN)
ρ_g	g/cm^3	Density of the matrix around the mineral of interest	Roughly estimated as the total mass over the total volume of the sample or size fraction (QEMSCAN)
a	%	Grade of mineral of interest in the sample/size fraction	Obtained from the average grade of the sample or size fraction (QEMSCAN)
l (or β)	-	Liberation factor used for when critical particles are present as inclusions	Calculated based on Table 2-13, equation (37), where b was taken as 1 (François-Bongarçon & Gy, 2002)

c	g/cm ³	Constitution factor	Calculated based on Table 2-13, equation (36)
C	g/cm ³	Sampling constant	Calculated based on equation (38)
M_L	g	Mass of the lot/parent sample	Taken as the mass from which the sub-sample was obtained. For HCT, this was the mass of the received parent sample.
M_S	g	Mass of sub-sample	Taken as the final mass of the sub-sample obtained from the corresponding M _L .
σ_r² or σ_{SE}²	%	Fundamental sampling variance	Calculated based on Table 2-13, equation (35)

Appendix Table 24 Guidelines for the calculation of the parameters for the mineralogical error calculation.

Variable	Unit	Definition	Method of calculation
N	-	Total number of particles	QEMSCAN particle count
N_s	-	Number of particles of interest	QEMSCAN Fe-Sulfide count
p	-	-	N _s /N
q	-	-	1-p
σ_{ME}	-	Standard deviation associated with the binomial distribution at a 90% confidence interval	$\sqrt{\frac{pq}{N}}$

$$\sigma_t = \sqrt{\sigma_{AE}^2 + \sigma_{SE}^2}$$