

QUANTIFICATION IN MINERALS PROCESSING VIA X-RAY MICRO-TOMOGRAPHY

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Abstract

Minerals processing has faced, over the last century, the challenge of an ever increasing demand for metals and at the same time the steady decline of head grades. To overcome this challenge metallurgists have developed new technologies to process the ore and new ways of quantifying the performance of mineral processing equipment. In this latter category image-based analyses have played an important role in making possible the link between performance and properties of the ore such as grade, mineralogy, grain size, porosity, exposure and mineral associations. Two important image analysis techniques are X-ray Micro-Tomography (XMT) and Automated Mineralogy based on Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy (SEM/EDS). The first has the benefit of being able to delineate the internal structure of the ore in three dimensions in a non-invasive and non-destructive manner. The second, conversely, is destructive and invasive but offers better resolution and direct mineral identification, although only in two dimensions.

It is, thus, one of the objectives of this thesis to formulate a methodology that allows the combined use of these imaging modalities in order to produce a more complete quantification of the ores. The shared information opens the possibility to understand the level of uncertainty in the quantification of the ore's properties such as grain size and stereological effects. Another benefit of this methodology is that XMT scans can now be calibrated so that mineral identification can be performed with an understanding of the level of misclassification. The result is thus a more complete assessment of the ore's properties compared to the traditional individual assessment. The benefits of this new assessment methodology are shown for two important minerals processing systems, heap leaching and liberation by comminution.

Heap leaching performance is the result of a complicated interaction between fluid flow, mass transport and chemical reactions, with the texture of the minerals having a strong influence on the resultant apparent leach kinetics. The prediction and simulation of these processes is thus complex and reliant on the availability of appropriate input data. This thesis presents a method for measuring the kinetics for the leaching of individual mineral grains, with the dependency on mineral type, grain size and distance to the particle's surface being assessed. Importantly, the variability in the kinetics was also measured, with this being an important factor in the time evolution of the apparent leach kinetics. The XMT images of the particles, together with the kinetic variability, were then used as the basis for a parallel particle scale leach simulator. This simulator is able to predict the long term leach rate of different sulphide species based on the initial leach behaviour, a useful tool for rapid leach assessment.

Liberation has been traditionally studied using Automated Mineralogy systems, and has thus been restricted to two-dimensions, with the associated stereology related impacts on the data. In this thesis the benefits of using a three-dimensional assessment are shown. For the first time, mineral grade, surface exposure and particle size have been directly related to each other for a real ore. This allows for substantially improved quantification of mineral liberation and preferential breakage. The quantification of liberation and its association with surface exposure is an important consideration in froth flotation performance. The restricted sample size and stereological biases associated with two-dimensional SEM/EDS analysis has made accurate quantification of this relationship hard. In this thesis a simple model for this relationship is presented. The future direction of this work will thus be to develop improved models for predicting the relationship between ore texture, comminution technique and the flotation performance.

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Plagiarism declaration

I hereby declare that all of the work presented in this thesis – except that which is appropriately acknowledged and referenced as such – is my own, and that it has not been submitted in fulfilment of the requirements of any other degree at Imperial College London or elsewhere.

Francisco Reyes

November 23, 2018

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The most merciful thing in the world, I think, is the inability of the human mind to correlate all its contents. We live on a placid island of ignorance in the midst of black seas of infinity, and it was not meant that we should voyage far. The sciences, each straining in its own direction, have hitherto harmed us little; but some day the piecing together of dissociated knowledge will open up such terrifying vistas of reality, and of our frightful position therein, that we shall either go mad from the revelation or flee from the light into the peace and safety of a new dark age.

The Call of Cthulhu

H.P. LOVECRAFT

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Chapter 1

Introduction

Humankind has been processing minerals for over 6,000 years, and it has become increasingly difficult with more complex ores and lower grades (Craig, 2001). Demand for metals has also soared, pushing today's annual production to around 2.5 billion tonnes (Reichl et al., 2017). The balance achieved between increasing processing difficulty and production requirements has only been possible thanks to the introduction of new technologies, not only in processing, but also in understanding the ores' properties. Such properties are related to the ore's texture, regarded as one of the main drivers affecting the performance of many mineral processing operations such as liberation, extraction and concentration (Kyle and Ketcham, 2015; Wills and Napier-Munn, 2005).

Texture, as a word comes from the Latin *textura* or *texere*, meaning respectively the noun "weaving" and the verb "to weave". Thus, texture refers to the constituent interlinked fabrics of minerals that composes the ore. This web of minerals contains information about how the ore was formed and how certain minerals can be extracted (Craig, 2001); hence the importance of studying and quantifying it in detail. Geologists and metallurgists alike have define the ore's texture as being the spatial arrangement of the chemical and geometrical characteristics of the constituents of the rock (Jardine et al., 2018).

In recent decades image analysis of the internal structure of the ores has provided valuable information on aspects of the ore texture such as grade, mineralogy, grain size, porosity, exposure and mineral association (Beckingham et al., 2013; Cnudde and Boone, 2013; Gottlieb et al., 2000). These imaging techniques have allowed researchers and geometallurgists alike to move from a qualitative assessment to the quantification of such properties and thus a more scientific approach to minerals processing. One of the recent and prominent imaging analysis approaches is X-ray Micro-Tomography (XMT), a tool that has been widely used to delineate in three dimensions the internal structure of opaque objects in fields like medicine (Pratt and Cooper, 2017), material science (Phillion

et al., 2008; Puncreobutr et al., 2012) and engineering (Ghorbani et al., 2011a; Ketcham and Carlson, 2001). Moreover, depending of the subject under study, this technique can be regarded as non-invasive and non-destructive. A second imaging technique widely used in minerals processing is Automated Mineralogy (Gu et al., 2014). This technique is comprised of two measurements, Scanning Electron Microscopy (SEM) and X-ray Energy Dispersive Spectroscopy (EDS). This enables the user to readily distinguish the different minerals in the ore sample at a higher resolution compared to XMT (Gottlieb et al., 2000). However valuable, SEM/EDS-based analyses are destructive and invasive and information provided is limited to only being two-dimensional. There is, thus, a potential in performing a multi-modal imaging assessment that combines these two techniques.

The benefits of such combined assessment are two-fold. Firstly, the sharing of information between modalities, i.e. XMT providing three-dimensional information to SEM/EDS and SEM/EDS providing mineral identification, allows for the mitigation of the corresponding shortcomings of both modalities, and thus the creation of unprecedented levels of information. Secondly, it can enable the calibration of post-processing processes such as mineral identification in XMT. In other words, this combination provides a measurement of how confident can the user be on the quantification of some ore property (e.g. particle size, mineral identification) by adding confidence intervals to the analyses provided.

Most of the literature on the use of X-ray Micro-Tomography and/or Automated Mineralogy in minerals processing has focused on relating performance of different processes to the value of some textural properties (Bérubé and Marchand, 1984; Dhawan et al., 2012b; Dobson et al., 2017; Navarra et al., 2018). But little has been said about the effect of the variability of such properties. Information about the distribution of textural properties can explain the variability experienced in many mineral processes, variability that can ultimately undermine their performance. Lin (2015) for example showed, using XMT, the benefits in understanding the intrinsic variability in the kinetics of leaching when the effects of grain size and exposure are accounted for. In the same work the author showed that understanding this variability can also be used to improve modelling and simulation of heap leaching. Better informed models of mineral processes can later be used for predicting, evaluating and optimising said processes. As examples, this thesis will apply the developed image quantification methodology to heap leaching and mineral liberation after comminution.

Heap leaching suffers from long processing times, which makes the assessment of the impact of operating changes difficult. Predictive modelling is thus a useful tool that can feed-forward outputs to decision and control systems. The problem is then that said models and simulation tools require calibration through time-consuming experiments and suffer from scale-up issues (Bouffard, 2008). Therefore, better informed models and simulation tools that can accurately represent the leaching process at different scales and that

do not require long-term experimental work are of great importance.

Mineral liberation, although extensively studied in the literature, has suffered from biased quantification due to artefacts introduced by the main analysis system, i.e. Automated Mineralogy (Sutherland and Gottlieb, 1991). The main limitation of Automated Mineralogy resides in its two-dimensional nature, where valuable information about the ore's three-dimensional nature is lost. This creates known biases towards the underestimation of size (Little et al., 2016) and the overestimation of certain properties such as grade (King and Schneider, 1998) and surface exposure (Wang et al., 2018). Correcting for these biases can be complicated, involving the analysis of several hundreds of samples (Ueda et al., 2016), and is always dependant of the ore's texture (Maire and Withers, 2014). In this thesis a methodology to quantify and correct for these biases is presented.

In this work it will be demonstrated that X-ray Micro-Tomography and Automated Mineralogy can be used separately—and together—as tools to shed light on the relationship between ore properties and the resultant performance of mineral processes. The processes of heap leaching and mineral liberation will serve as the main examples and focus of this thesis.

1.1 Objectives

In response to the above stated needs for a more complete assessment of the ore properties and a better understanding of how these properties are related to the variability expressed in minerals processing, the following objectives are proposed:

- Obtain a more detailed quantification of textural related properties from images by calibrating X-ray Micro-Tomography with Automated Mineralogy assessments.
- Assess the level of uncertainty when quantifying mineral ores using X-ray Micro-Tomography.
- Quantify and correct for biases occurring in Automated Mineralogy assessments by the use of X-ray Micro-Tomographic images.
- Use quantification information to develop better simulation models of mineral processes for prediction and evaluation.

1.2 Thesis structure

The thesis starts with a description of the general techniques used and developed for this work, continuing with specific applications in two mineral processing systems. Each chapter contains an introduction to the topic with the necessary literature to show the

motivation and need for the work done. Each chapter also contain a section explaining the experimental setup and methods used to answer the objectives set. Finally a discussion and conclusion section is included in each chapter, addressing the achievement of the chapter's aims.

Chapter 2 contains up-to-date background theory and tools present in the literature that are relevant to this work. A description of the main imaging techniques used in minerals processing, with their fundamentals, applications and limitations is included. A brief introduction to image processing is also provided, with specific application to 3D image sets, describing the main stages taken when quantifying information in the form of images. This chapter therefore provides the basics onto which the work of this thesis is built. More importantly, this chapter signals the need for the work done in this thesis regarding the evaluation of uncertainty in some quantification analyses and the potential for modelling when using information on the variability of the process being studied.

Chapter 3 presents the possible gains from combining different imaging techniques to study textural properties such as size, porosity and mineralogy. A novel methodology for combining two imaging analyses is introduced as a way to quantify the levels of uncertainty and error when using them. This chapter is intended as an appraisal of the two most used quantification techniques.

Chapters 4 and 5 describe applications of the methodologies developed to different aspects of mineral processes, namely extraction and liberation. Chapter 4 addresses the need for better prediction tools for the leaching process that take into consideration the intrinsic variability of the leaching kinetics. Chapter 5 presents a novel way of using the 3D nature of X-ray Micro-Tomography in the assessment of liberation due to comminution via the quantification of grade and surface exposure. These chapters are presented as examples, but should not limit the applicability of the methodology to different ores and/or mineral processing systems.

Finally, Chapter 6 contains the aggregated conclusions and achievements of this work with an in-depth discussion about the contributions and directions of possible future work.

Chapter 2

Background

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2.1 Introduction

Recent estimates put the cumulative total world production of refined metals at 60 billion metric tons, but more astonishing is the fact that of those, 2.5 billion tonnes were extracted in 2015 alone (Craig, 2001; Reichl et al., 2017). The steep growth in production worldwide since 1980 is shown in Figure 2.1 as an illustration of the demand for metals. This growth is, however, co-occurring with a decrease in the average head grades of the minerals from which the metals are being extracted. Figure 2.1 also shows an example of this using copper head grade data from the United States as a proxy for the global trend.

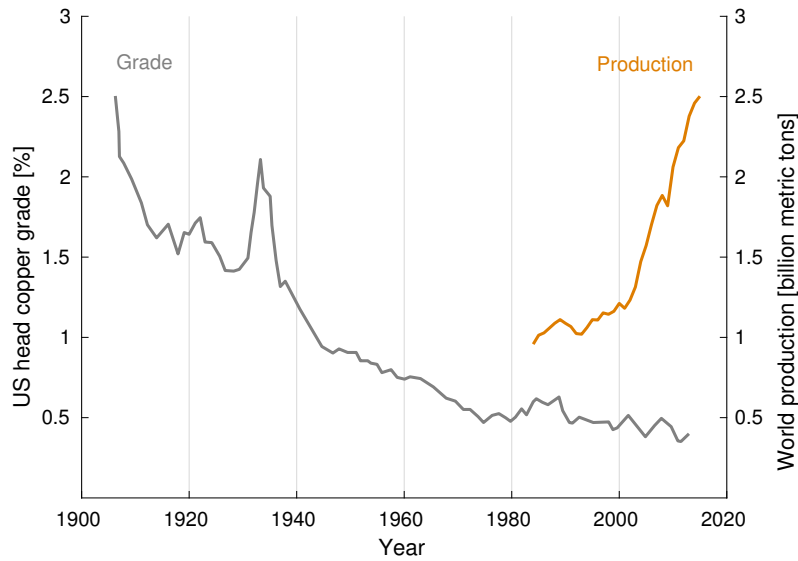


Figure 2.1: Annual world production of metals, in contrast with the decrement of the ore's head grade. Data from Reichl et al. (2017) and US Geological Society (2015).

The impoverishment of the ore's metal content ultimately affects the energy consumption and the impact on the environment that mining inevitably has. These aspects pose a techno-economic challenge for the minerals industry, that some authors have stated can only be tackled with an integrated modelling framework underpinned by mineralogy (Baum, 2014; Ntlhabane et al., 2018). This integration, known as geometallurgy, is an effort to predict minerals processing performance using geological data such as mineral grain size, mineralogy, degree of liberation, etc. (Delbem et al., 2015). According to Parian et al. (2018) the study of how the ore's texture changes after breakage due to comminution is the missing link between geology and minerals processing.

Quantification of these geological properties has long been done by imaging techniques. From simple unassisted vision analysis to cutting-edge microscopy, image analysis has given valuable insights into the internal structure and textural characteristics of mineral samples. As shown in Figure 2.2, each imaging technique has a region of operation depending on the sample size and the scale of the feature to be analysed.

Many of these assessments have become indispensable for relating performance of

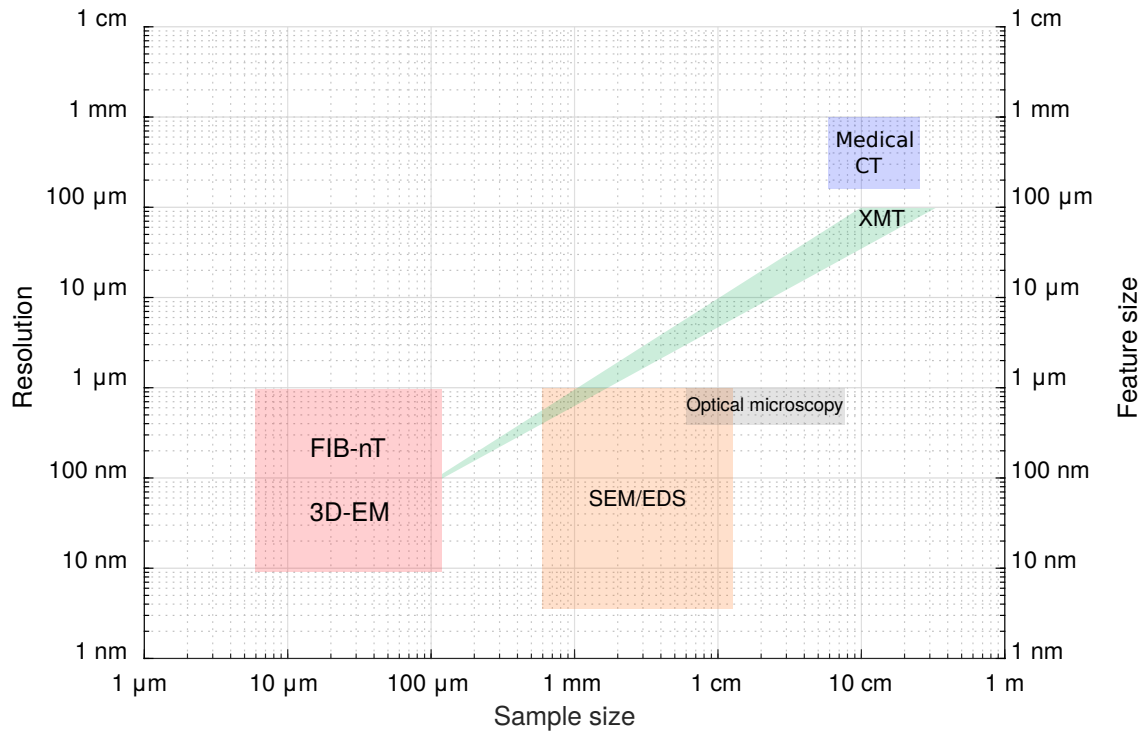


Figure 2.2: Different imaging techniques with their usual sample size, resolution and feature size that can be analysed. Adapted from Bultreys et al. (2016).

mineral processing equipment with mineralogy (Kyle and Ketcham, 2015). Applications can be found in most of these mineral processing equipment, including, but not limited to, milling (Leißner et al., 2016a), flotation (Jordens et al., 2016; Tungpalan et al., 2015) and heap leaching (Naderi et al., 2011). A common factor in these studies is the use of two analytical devices, X-ray Micro-Tomography (XMT) and Automated Mineralogy. The latter one is based on a combination of Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) (Cnudde and Boone, 2013; Lin et al., 2016b; Sutherland and Gottlieb, 1991). An example of Automated Mineralogy equipment is the JKMRC's Mineral Liberation Analyzer (MLA, Fandrich et al. (2007)).

This chapter introduces the basics of ore texture and its importance for mineral processing. The fundamentals and limitations of XMT and Automated Mineralogy are also discussed alongside an introduction to digital image processing and quantification.

2.2 Ore texture

Texture encapsulates a variety of properties of the ore and, as such, it can be used as a synonym for a broad range of ore characteristics. A general definition for texture, given by Jardine et al. (2018), is that it is the spatial arrangement of the chemical and geometrical elements that constitute a particular ore. This definition allows for the description of the ore in terms of four different aspects (Navarra et al., 2018):

- Mineralogy: Mass fractions of different minerals present in the ore.
- Liberation: Distribution of minerals into separate particles as a function of particle size, exposure and degree of liberation.
- Texture: Distribution, shape and orientation of crystal grains within the mineral matrix.
- Mineral Chemistry: Correlations between the preceding aspects and the presence of elements of interest.

For the purpose of minerals processing, the engineering of obtaining separated minerals from the ore, mineralogy and liberation are of the highest interest (Zhang and Subasinghe, 2012). Whilst mineralogy cannot be controlled or changed, liberation is a key performance indicator for many mineral processing systems (Leißner et al., 2016b). Liberation relevance is due to the fact that a certain degree of liberation achieved by a process will set an upper limit to grade and recovery that a downstream process can reach (Carrasco et al., 2016). Liberation and mineralogy have a bijective relationship with the main two properties minerals processing engineers use, namely, mineral grade and surface exposure. Figure 2.3 shows a schematic of a fragment being sliced at a random location. The exposed area contains a grain of 2D area A_2 and gangue of area A_1 . This grain also presents an exposed surface in 3D, S_2 and an exposed length in 2D, L_2 . V_1 and V_2 correspond to the total 3D volume of the fragment and the mineral grain, respectively.

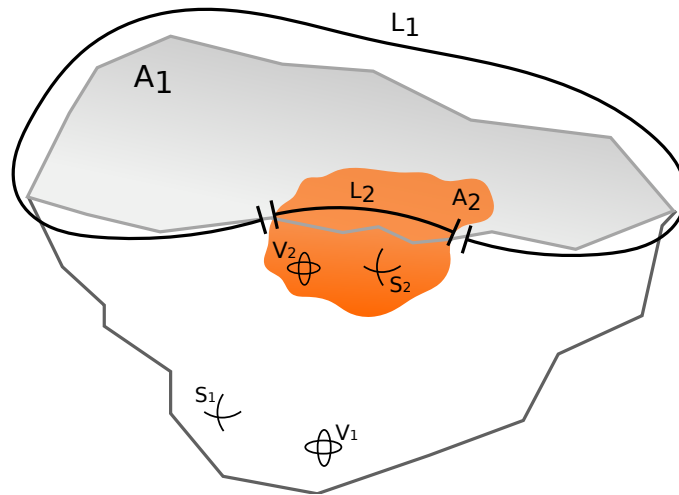


Figure 2.3: Definition of grade and surface exposure. Both are defined depending if the data is 2D or 3D.

Grade and exposure are then defined, in 2D and 3D, as follows. This analysis can be extended for each of the mineral phases, resulting in a set of mineral grade and exposure per mineral of interest.

$$\text{Grade}_{2D} = A_2 / (A_1 + A_2) \quad (2.1)$$

$$\text{Grade}_{3D} = V_2 / (V_1 + V_2) \quad (2.2)$$

$$\text{Exposure}_{2D} = L_2 / (L_1 + L_2) \quad (2.3)$$

$$\text{Exposure}_{3D} = S_2 / (S_1 + S_2) \quad (2.4)$$

The rest of this chapter will focus on the two main methods (XMT and SEM/EDS-based Automated Mineralogy) for assessing mineral grade and exposure, shedding light on the advantages/disadvantages, artefacts, limitations and new developments of each of them.

2.3 X-ray micro-tomography

X-ray Micro-Tomography is an imaging technique that produces 3D information of the interior for the object being scanned with a spatial resolution in the order of micrometres. As a tool for accessing the internal structure of samples, XMT has a wide range of uses. Examples of the wide range of applications include: cementitious materials (da Silva, 2018), porous media (Reynolds et al., 2018), lithium batteries (Pietsch and Wood, 2017) and geosciences (Cnudde and Boone, 2013). Concerning minerals processing, XMT is regarded as a non-invasive and non-destructive tool for delineating the internal structure of the fragment's texture (Lin and Miller, 1996). It has been used for assessing ore samples in terms of, for instance, their mineral liberation, fracture network, gangue porosity and grain size distributions (Charikinya et al., 2015; Dhawan et al., 2012b; Garcia et al., 2009; Ghorbani et al., 2011a). Stock (2008) reviews several applications, techniques and procedures of X-ray Micro-Tomography, including possible future trends like nano-CT, which is now starting to appear in the literature, as a tool to access nanometre-scale features. However, despite being a versatile tool, XMT images do not directly provide the mineralogy of the sample under study as, due to its fundamentals, only an attenuation map is obtained, with attenuation being a function of the density and effective atomic number of the material.

2.3.1 Fundamentals of XMT

Röntgen discovered X-rays in 1895, enabling non-destructive visualisation of opaque structures. Projection X-ray imaging uses the fact that in a small vicinity of the material under study, the attenuation of the passing ray can be related with the composition and density of the material (Stock, 1999), a phenomenon explained by the Lambert-Beer's Law via

Equation 2.5:

$$\frac{1}{I}dI = -\mu(x, E)dx \quad (2.5)$$

Where I is the intensity of the incident ray, $\mu(x, E)$ is the linear attenuation coefficient at the given position x and energy of the ray E . This first-order differential equation is represented in Figure 2.4, where the rectangle acts as the differential dx along the path of the ray crossing the sample.

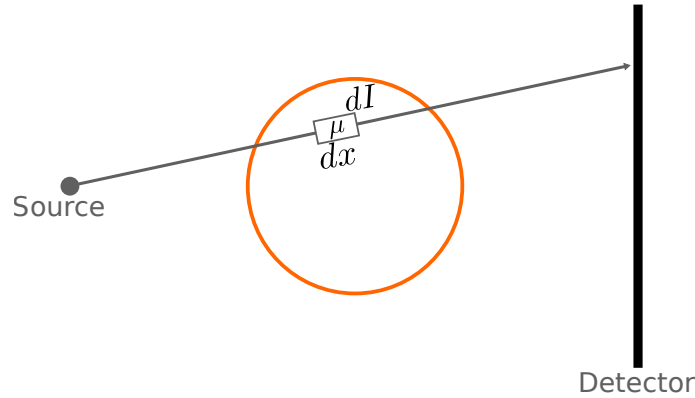


Figure 2.4: Schematic representation of Lambert-Beer's Law. Intensity of the passing ray decays exponentially with the distance travelled.

Integrating Equation 2.5 gives the final attenuation for the passing ray over its path ℓ :

$$\ln\left(\frac{I}{I_0}\right) = - \int \mu(x, E) d\ell \quad (2.6)$$

Equation 2.6 is valid for a monochromatic ray of energy E , but most X-ray sources produce a spectrum of radiation, yielding the more general form of Lambert-Beer's law:

$$I = \int I_0(E) e^{- \int \mu(x, E) d\ell} dE \quad (2.7)$$

The relationship between the attenuation coefficient with the energy of the passing ray is described by Equation 2.8 (Dyson, 1990). Where position dependant ρ and Z are the density and atomic number of the material, respectively. Energy dependant coefficients a and b describe the two main ways of interaction between X-rays and matter that are relevant at the energy levels of interest in XMT applications, namely Compton Scattering and the Photoelectric Effect (Lin et al., 2013).

$$\mu(x, E) = \rho(x) \left(a + b \frac{Z(x)^{3.8}}{E^{3.2}} \right) \quad (2.8)$$

For materials with more than one element, like minerals, an effective atomic number

can be calculated (Jussiani et al., 2016). A comprehensive database with the attenuation of 92 elements and the possibility of creating compounds via entering the chemical formula is available in Berger et al. (2010). Figure 2.5 shows how the attenuation coefficients of a set of minerals vary over a range of energy levels. Of interest is that chalcopyrite (most abundant copper mineral) and pyrite show a fairly similar attenuation compared to other minerals.

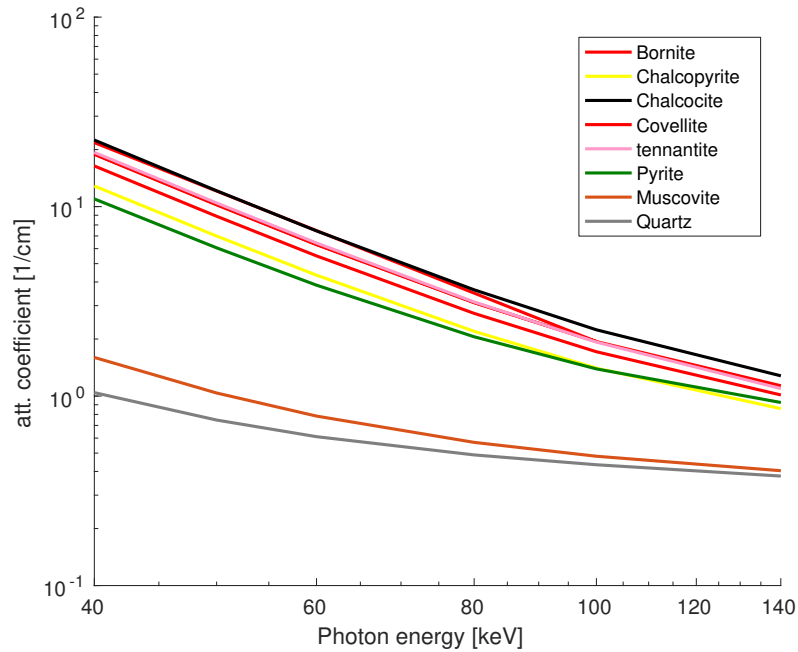


Figure 2.5: Linear attenuation coefficient of some minerals at different energy level, data from Berger et al. (2010).

The intensity of the passing ray is then measured by a detector comprised of a scintillator and a photo-sensitive array of sensors. The penetrating strength of the beam and the length of time the detector senses (exposure time) will set the number of counts measured and thus the signal-to noise ratio of the image. A balance has to be found so that the image does not appear under (too few counts) nor over (sensor saturation) exposed. The produced X-ray image is such that the level of brightness is related to the absorption of the material (Landis and Keane, 2010). The problem with these images, namely X-ray projections, is that information on the sample in the out-of-plane dimension is averaged, and hence lost. This can be overcome by taking a tomographic image of the sample, meaning, rotate the sample and obtain a set of 2D radiographic images so that the 3D internal structure can be inferred. Figure 2.6 shows a schematic representation of the tomographic process, it is worth noting that the number of sensors in the detector and the spatial resolution used will set the amount of the sample's volume scanned (known as field-of-view). Since the rotation is relative, in medical devices it is the detector that moves around the sample, whereas in the micro-tomography scanners used in this work it is the sample that is rotated, with the sensor kept stationary.

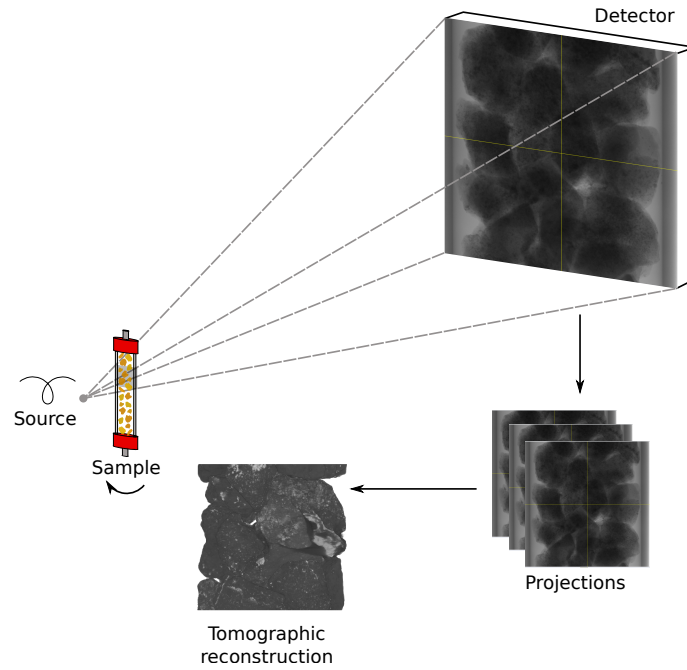


Figure 2.6: Schematic representation of a cone-beam X-ray scanner and the tomographic reconstruction.

The process of obtaining the 3D internal structure of the sample from the set of 2D projections is referred to as reconstruction and is done numerically and iteratively, normally using a Filtered Back Projection algorithm (Maire and Withers, 2014). In order to avoid undersampling the volume, and thus introducing numerical artefacts (aliasing), at least $q\pi/2$ projections have to be acquired; where q is the number of sensors in the detector horizontally (Kak and Slaney, 2001). Even complying to this restriction, the reconstruction introduces artefacts in the process due to the discrete number of rotations, differences in the sensors pixels and numerical tolerances.

Cone-beam tomography, shown in Figure 2.6, is one of the most used configurations in lab-scale scanners, but is not the only available configuration. Different tomographic setups in the industry and research facilities, with varying types of sources and beams, as depicted in Figure 2.7. Some of them are described below, with more detail in Wildenschild and Sheppard (2013) and Maire and Withers (2014):

- **Synchrotron beam-line:** A high energy beam from a synchrotron source passes through a monochromator and then hits the target as a parallel beam. This allows for the sample to be scanned in a relatively short time and with fewer artefacts. Because the beam is parallel, no magnification is obtained, thus, optical magnification is needed before the detector.
- **Fan-beam Micro-CT:** A lab-based configuration that lacks a monochromator, but includes a collimator that makes the beam have a linear fan shape, this creates a geometric magnification that will depend of the relative distances of the source, the sample and the detector, which consists of a linear array of sensors.

- Cone-beam MicroCT: Probably the commonest of all lab-based systems. The beam goes straight from the source to the sample, creating a cone shaped geometry. This allows the use of a 2D array configuration of sensors in the detector and the magnification of the sample depending its position relative to the source and detector.

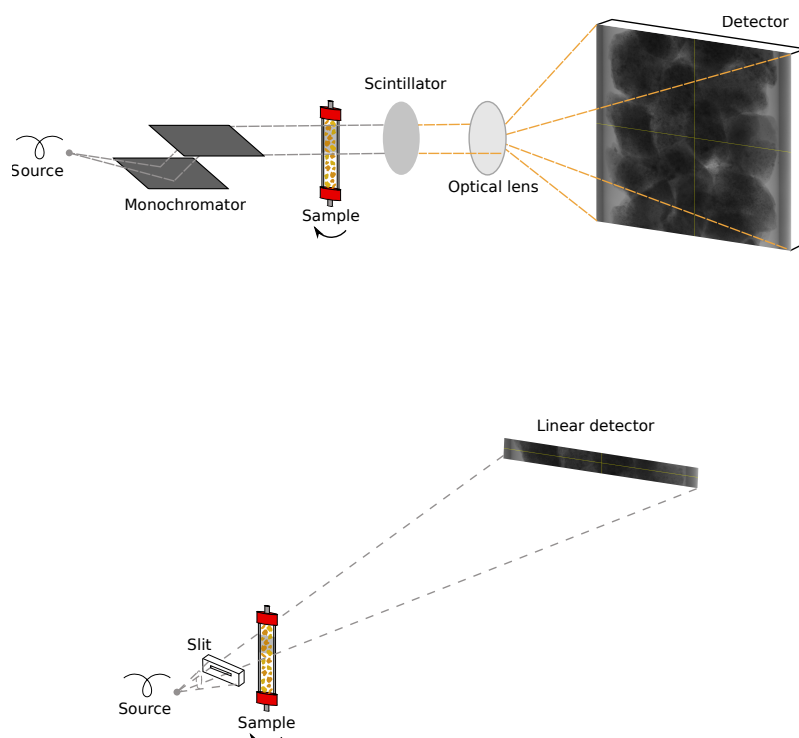


Figure 2.7: Schematic representation of other typical tomographic setups. Main differences are the presence (or lack) of geometric magnification and the nature of the beam (energy levels, monochromatic or polychromatic). Adapted from Wildenschild and Shepard (2013)

In lab configurations the maximum energy that can be reached by the equipment is normally lower than the one obtained in synchrotron sources. This implies longer acquisition times, but also in some cases better contrast between materials as their attenuation coefficient diverges more towards the low energy side of the spectrum (See chalcopyrite and pyrite in Figure 2.5). Since the differentiation between sulphide species in the ore is crucial to this work, a lab-based scanner is used instead of a cutting-edge synchrotron-based one. In this document, only a cone-beam XMT was the configuration used for scanning the samples.

2.3.2 Limitations and artefacts

The occurrence of artefacts is related to XMT limitations both in the acquisition and reconstruction procedures. A comprehensive list can be found in Davis and Elliott (2006) and Stauber and Müller (2008), with examples for lithium ion batteries and biological samples respectively. In the field of geosciences, Ketcham and Carlson (2001) presents a compendium of artefacts known to occur and the best practises for sample preparation,

acquisition and reconstruction in order to minimise the impact of these effects. In this document the commonest artefacts and limitations are covered in more detail, referring the reader to the above mentioned references for further information.

Beam hardening

As mentioned in Section 2.3.1, most X-ray sources produce a polychromatic beam, where even though a specific energy level is set in the device, a spectrum of energies is created. The average of the spectrum is referred to as the effective energy of the passing rays. The artefact occurs because attenuation is higher at the lower end of the spectrum (as previously shown in Figure 2.5), thus the effective energy of the passing beam becomes progressively higher as it passes through the sample. This effect is shown in Figure 2.8, where the effective energy of the original beam (in dark orange) becomes higher after passing through a sample (in light orange).

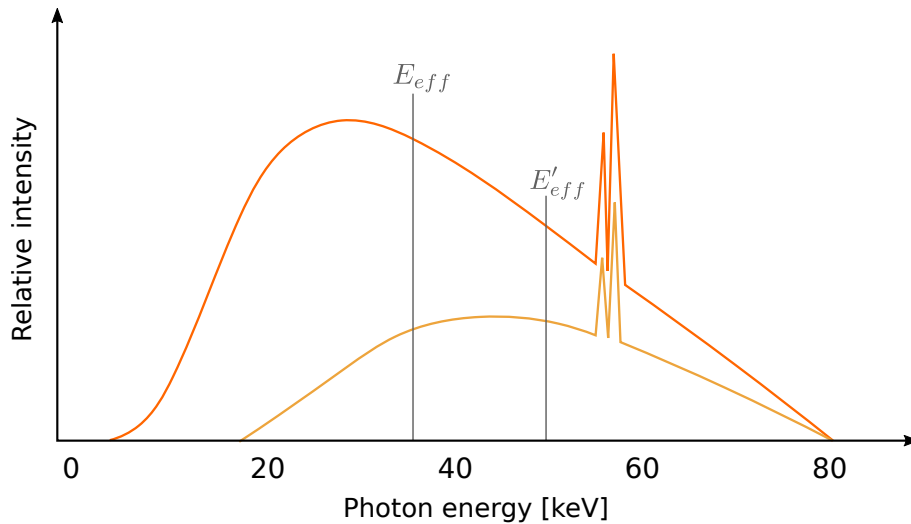


Figure 2.8: Beam hardening effect, the passing polychromatic ray becomes artificially more penetrating as it loses low energy components of its spectrum. Adapted from Stauber and Müller (2008).

The result of this effect is that the outer section of the sample appears brighter than its inner one, even though the sample's composition does not change. This is visible in the lower left corner example in Figure 2.9. Beam hardening can be avoided or reduced by filtering the lower end of the spectrum (Ketcham and Carlson, 2001) or via numerical correction (Davis et al., 2008; Hsieh et al., 2000).

Image contrast

The number of counts in the detector, and therefore the image intensity, depend on the intensity (or flux) of the beam and the exposure time. Since higher energy rays have more penetrating power and the attenuation coefficient being dependent on the energy applied,

the image contrast also changes with this parameter. For a one-material sample, the energy level can be optimised so the exposure time is minimised, without losing image contrast (Grodzins, 1983). The optimal value is highly dependent on the size of the sample: for a water-like sample of $100\mu\text{m}$ in diameter the optimal energy is 3.0 keV, but if the sample is 30 cm in diameter the optimal energy goes up to 1.0 MeV. This procedure might be of use if the beam is monochromatic and the sample is homogeneous in composition. If that is not the case, the optimal energy level is normally found by trial and error, with the aim being to maximise the contrast between different materials (achieved at lower energies) while minimising the scanning time (achieved at higher energies). Figure 2.9, obtained from Jussiani and Appoloni (2015), shows minerals scanned at different energies, it can be observed that the optimal contrast is achieved at different energies depending on the sample.

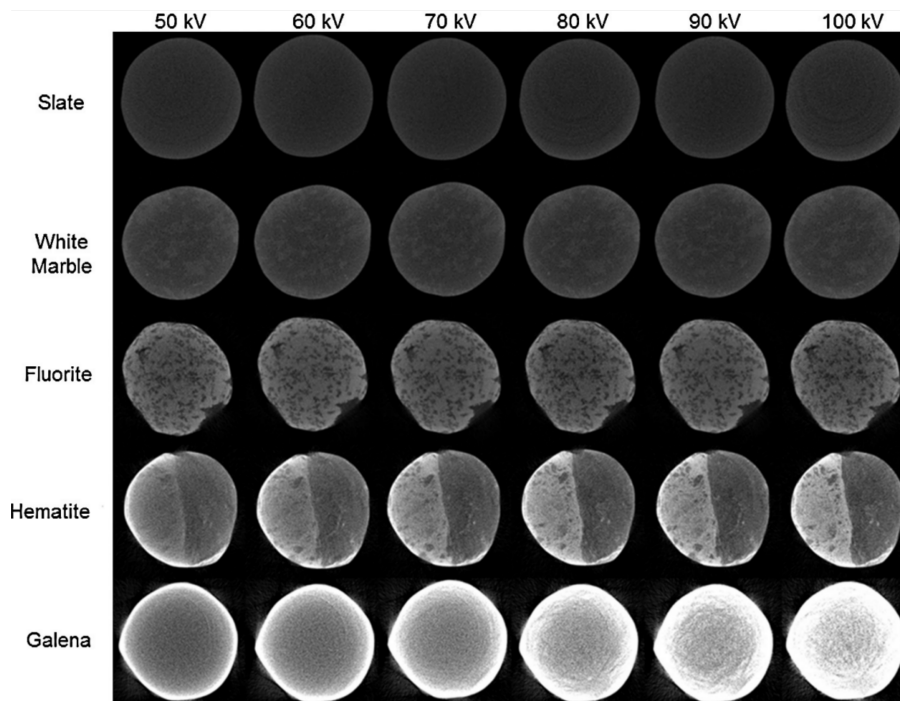


Figure 2.9: Contrast with energy, contrast is a complex function of the material and energy used. From Jussiani and Appoloni (2015).

Because the spectrum of the incident beam is unknown, the relationship between the image intensity and the sample's density and effective atomic number has to be calibrated. A minimum of two different energies are needed to determine parameters a and b from Equation 2.8. A wide range of known calibration standard materials of known density and atomic number can be used to have a robust calibration (Nguyen et al., 2018). This procedure is also known in the literature as Dual Energy (DE) tomography and allows for XMT images to discriminate materials by density and atomic number, improving its sensitivity and accuracy when trying to distinguish between materials with similar attenuation coefficient. Lin et al. (2013) used this for distinguishing different minerals from one another

and Teles et al. (2016) used DE for the estimation of porosity in rock samples of known composition. The main disadvantage of DE is that at low energies Compton scattering dominates, making the images less sharp. Long et al. (2009), for example, studied porosity in sandstone samples and found that the limiting factor for micro-porosity estimation is the resolution of the images.

Ring artefact

Due to differences in the sensitivities of the pixels in the detector arrays some might appear brighter than others for the same conditions. Due to the rotation of the sample, these differences produce concentric rings centred at the rotational axis of the image as shown by Figure 2.10. This artefact can also be caused by dust in the detector or the malfunction of pixels (Stauber and Müller, 2008).

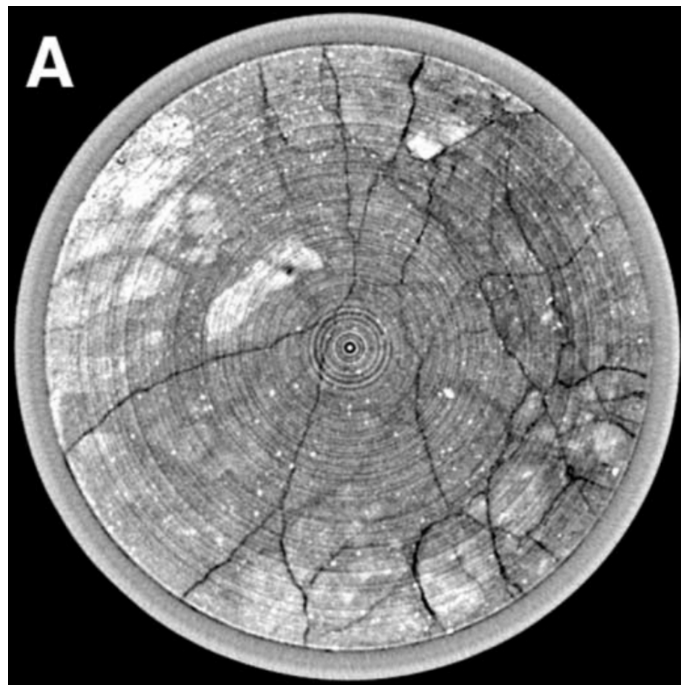


Figure 2.10: Ring artefact in a saproblite core appearing as concentric circles in the image. Example taken from Ketcham and Carlson (2001).

Correcting for this artefact will depend on the source of it. In the case of dust, cleaning of the detector should be enough. But, in cases of defective pixels or significant gain differences, the correction can be done by slightly moving the sample (or detector) in between projections (Davis and Elliott, 2006, 1997) or during post processing of the image (Schlüter et al., 2014).

Partial volume effect

Due to the discrete nature of the sensor, each voxel (3D version of a pixel) in the image represents the average attenuation of a certain subvolume in the sample. And since the voxel boundaries does not need to and in most cases does not match with the boundaries between different materials, the sharpness of the images gets reduced. Figure 2.11 shows a zoomed-in example of a mineral grain and how its boundary with the gangue gets diffused by the partial volume effect. Lines show different possible interpretations of the actual boundary, depending on the criteria used.



Figure 2.11: Partial volume effect, the boundary between the bright phase (grain) and the gangue gets blurred making hard to distinguish the actual location of the transition between the different minerals. From Le Roux et al. (2015).

Spatial resolution

Resolution may refer to either the image resolution (or magnification of the system) and the spatial resolution of the system. The first is a geometric relationship between the relative position of the source, the sample and the detector that yields the dimension that each pixel in the image represents, also known as pixel size, and expressed normally in $\mu\text{m}/\text{px}$ as it can be obtained by dividing the field-of-view by the number of pixels in the detector. The latter, spatial resolution, refers to a measure of how small can a feature be in order to be detected in the image. It is the result of the contrast between materials, the signal-to-noise ratio, the size of the X-ray source (spot size) and the added effect of other artefacts like partial volume effects; spatial resolution is normally expressed in micrometres (Judy, 1976). Similarly to optical systems, the spatial resolution can be calculated using the Modulation Transfer Function, defined as:

$$\text{MTF}(\omega) = \mathcal{F}\left\{\frac{d}{dx}\text{ESF}(x)\right\} \quad (2.9)$$

Where $\text{ESF}(x)$ is the edge spread function of an intensity profile perpendicular to an edge and $\mathcal{F}$ corresponds to the Fourier Transform. The resolution (R) is then defined according to the spatial frequency MTF_α that corresponds to an $\alpha\%$ of contrast loss.

$$R = \frac{1}{2\text{MTF}_\alpha} \quad (2.10)$$

Figure 2.12a shows the $\text{ESF}(x)$ of the edge between a mineral grain and the gangue of an XMT taken at a resolution of $16\mu\text{m}/\text{px}$. Figure 2.12b is the corresponding $\text{MTF}(\omega)$, where the 10% contrast loss has been identified. This value corresponds to a spatial resolution of $21.4\mu\text{m}$, contrasting to the original 16 micrometre pixel size represents a loss of 25% in resolution.

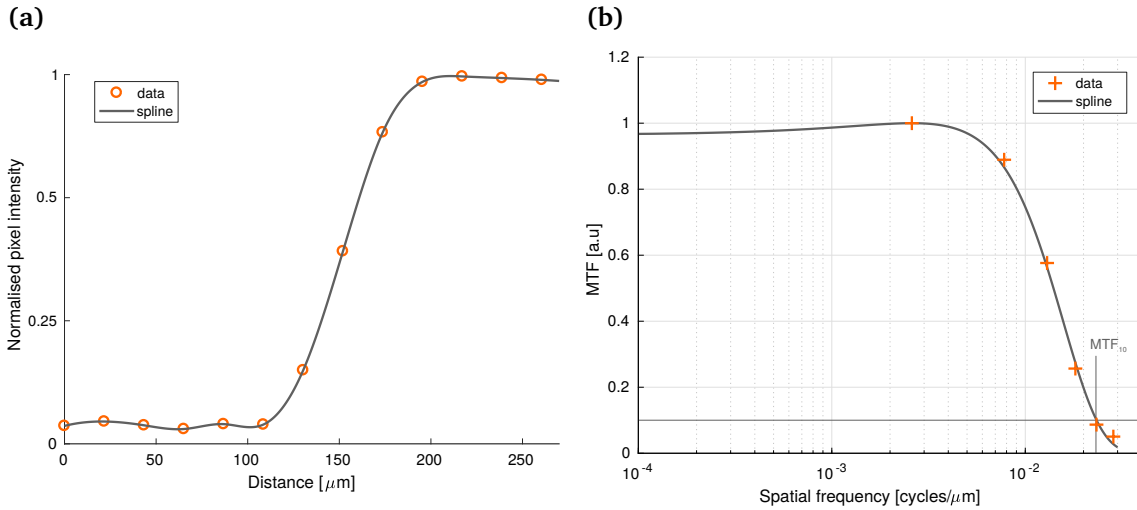


Figure 2.12: Edge Spread Function and the corresponding Modulation Transfer Function of a system, the MTF_{10} corresponds to a 10% contrast loss and a resolution of 21.4 micrometre.

The MTF_α is a function of the magnification and the power used, as this will affect the spot size of the source. Rueckel et al. (2014) studied the relationship between these variables and constructed a regression model linking them. The authors found that at small pixel sizes the achievable spatial resolution is heavily influenced by the spot size (power used). The importance of spatial resolution is due to the fact that it sets the minimum size of the features that can be assessed. Features below or near the spatial resolution will have a higher degree of uncertainty in their quantification. Lin et al. (2015) proposed a methodology for assessing the degree of uncertainty in the quantification of grain sizes, which consisted in performing repeated scans of the sample in order to quantify the levels of systematic and random error. Calibration procedures with standards that yield the accuracy of the quantification can also be performed, as in Fernandes et al. (2016), where

a porosity phantom (pack of glass tubes) is scanned so the porosity obtained analytically can be compared with the one calculated using the XMT images. All these calibrations or levels of uncertainty are system dependant, and as such they will change with the sample and scanning conditions used.

Temporal resolution

As in normal photography, the detector is open for sensing radiation for a length of time, known as the exposure time. The total acquisition time of a scan is equal to the product of the exposure time and the number of 2D projections used. A normal scanning time can easily be in the range of a few hours, which poses a limitation when trying to scan changing samples, as any movement during the acquisition will render the 3D reconstructed image blurred. Nevertheless, XMT has been used for monitoring dynamic processes (Menke et al., 2014, 2015). Figure 2.13 shows an example from Bultreys et al. (2016) where oil flow in a porous media was tracked over different time steps, separated by 12 s. Achieving this level of time resolution requires a highly penetrating beam, available at synchrotron facilities, where up to 270,000 frames per second can be acquired (Maire and Withers, 2014; Wildenschild and Sheppard, 2013). Special reconstruction algorithms can also be used to allow the sample to continuously rotate (Kazantsev et al., 2015).

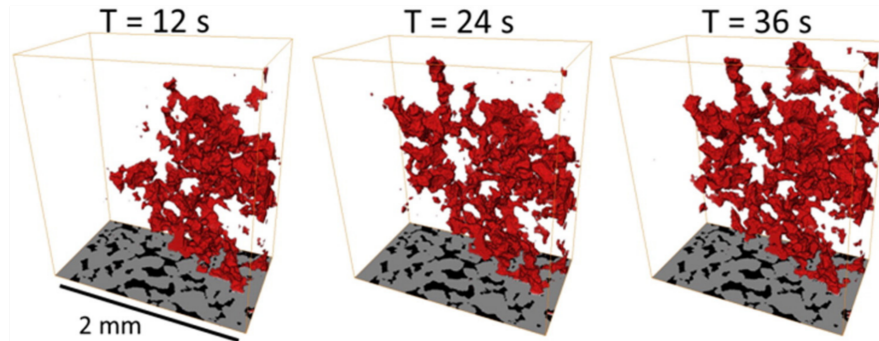


Figure 2.13: Dynamic X-ray Micro-Tomography of a drainage process showing the tracking of an evolving system, from Bultreys et al. (2016).

Depending on the application, this time constraint might be no issue, Lin (2015) for example, used XMT to assess the leaching process of copper ores, known to be a slow changing process that can take as long as months to be completed. All dynamic analyses can be performed either in an *in-situ* or *operando* experiment, the first one referring to scanning happening only before and after the changes have happened. The latter when scanning happens whilst the changes in the sample are happening.

2.3.3 XMT applications in minerals processing

As a versatile tool XMT has been used for a wide spectrum of applications in minerals processing and geometallurgy. It has become crucial for assessing and for quantifying the relationship between the ore's texture and the performance of different mineral processing applications (Kyle and Ketcham, 2015; Miller and Lin, 2018). This wide range is reflected in Figure 2.14, produced by Dhawan et al. (2012b) when reviewing the uses of XMT for hydrometallurgy.

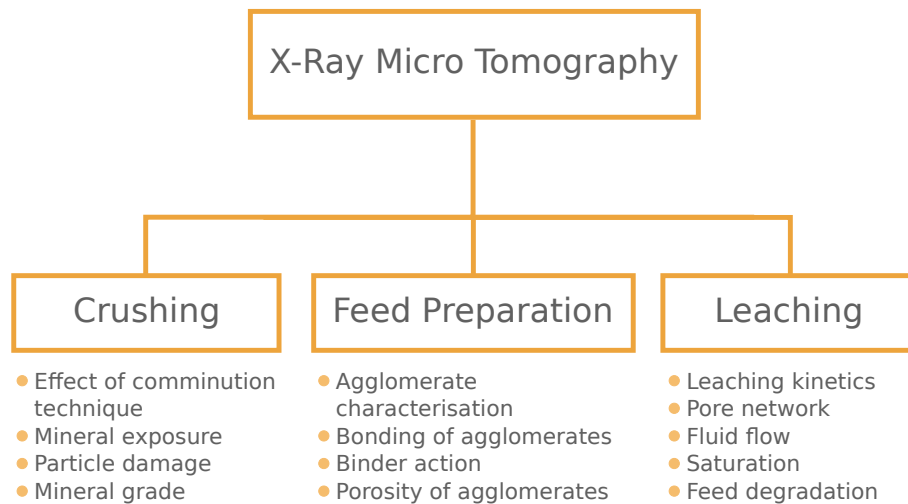


Figure 2.14: Uses of XMT in mineral processing applications, adapted from Dhawan et al. (2012b).

Textural information on the ore that is of interest in minerals processing, such as porosity, surface characteristics, grade and surface exposure can be obtained from XMT using imaging techniques. Videla et al. (2007) used histogram-based segmentation algorithms to classify voxels into gangue, chalcopyrite and pyrite. Results were validated by calculating the density of the samples and comparing these values with values previously reported in the literature. Ghorbani et al. (2011b) used dual energy scans to achieve mineral classification to determine the atomic number and density of different minerals with fairly different atomic number (14, 23 and 78), achieving good agreement with a traditional mineral liberation analysis. Jussiani et al. (2016) did it with known minerals with a much closer Z_{eff} (in the range 13-19). Effectively differentiating the constituent mineral phases in the ore is the first step towards a quantitative analysis of these systems.

When evaluating crushing of ores, the main aspect to be evaluated is the degree of liberation achieved. Garcia et al. (2009) analysed different comminution methods evaluating the amount of exposed grain surface created. The authors were able to quantify the ratio of specific inter-facial area before and after breakage. Results show that significant grain boundary fracture is achieved at low rates of energy dissipation, facilitating crack propagation at grain boundaries. This was later confirmed by Xu et al. (2013).

The link between an ore's quantitative textural information and performance of minerals processing systems is highlighted in the study of Miller et al. (2003), where the authors worked out the relationship between ultimate recovery in heap leaching and mineral exposure, building a predictive model based on the degree of surface liberation measured from XMT images. Ghorbani et al. (2013) used dual energy scans to quantify cracks formed after different crushing methods, showing that High Pressure Grinding Rolls achieve 10 to 15% more recovery of zinc than cone crushed ores due to the generation of micro-cracks. However, for copper ores Kodali et al. (2011) found that only oxides ores are affected by the amount of cracks generated, with the leaching of sulphide ores showing no statistical difference between the crushing methods. Parra et al. (2015) also used XMT to assess the leaching performance, this time using a synthetic leachable material, in order to test fracturing induced by blasting and its impact on leaching. Results showed that most of the fractures created were located along grain boundaries and no statistically significant differences in leaching performance between treated and untreated material was observed. This further emphasises the importance of mineral information, showing that the behaviour of a certain mineral under certain conditions does not represent a universal situation. Moreover, the link between an ore's texture and mineral processing systems can also work in the opposite direction, so the effect of processing the ore on its texture can be evaluated. Lin et al. (2005) tracked the packed bed porosity imaging over the leaching process and showed that porosity changed from 41% to 38% due to leaching and fines depositing in the bottom of the column. Simulations predicted a change in permeability of the bed from $1.4 \times 10^{-3} \text{ cm}^2$ to $4 \times 10^{-4} \text{ cm}^2$ after leaching. Also studying porosity, Zhang et al. (2018), assessed the effect that particle shape and gradation have on the packed bed's porosity. The authors found that the presence of fine particles account for most of the porosity, indicating that these are responsible for most of the water content in a packed bed.

Besides providing valuable quantitative information, XMT images can also be used as input for simulations platforms (Réthoré et al., 2011). Given XMT's voxelised nature some meshing based on the images might be needed depending on the numerical method used (Maire and Withers, 2014). Yin et al. (2013) used X-ray CT images to feed simulation models of fluid flow. Images were segmented and meshed in order to create the simulation domain from the real pore structure of the ore. However, results were not compared against real data. Lin and Miller (2005) used XMT images to capture, measure and analyse the shape of the rocks, developing a framework to create phantom rocks for simulation purposes. In a similar manner, Masad et al. (2005) used XMT to characterise particles by their surface properties (form, angularity and roughness). The authors tested their methodology on three different materials, and showed that XMT is a powerful tool that can be used to extract mathematical representations of the shape of particles for computational

modelling purposes.

In this thesis XMT images are used in many of these forms, to access and quantify textural related information, to study how the ore's texture evolves over the process and to feed simulation models.

2.4 Automated mineralogy

Quantification of mineralogy was initially performed using optical systems, which allowed for the discrimination of minerals based on their reflectance of visible light. This was later replaced by systems comprising an electron beam and X-ray spectroscopy, allowing for more reliable measurements and better discrimination between minerals. The use of Scanning Electron Microscopy (SEM) for quantitative analysis started in the mid 1970's with the development of the SEM-based CESEMI (Computer Evaluation of SEM images) at the Pennsylvania State University (Sandmann, 2015). However, it was after the development and commercialisation of the QEM*SEM (Quantitative Evaluation of Minerals by Scanning Electron Microscopy) in the 80's by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) that SEM-based analyses became ubiquitous in minerals processing (Sutherland and Gottlieb, 1991). The success of the QEM*SEM relied on its unsupervised analysis and the optimised operation of the Energy-Dispersive X-ray Spectroscopy (EDS, but sometimes also EDX), allowing for faster image acquisition and quantification compared to other competitors (Creelman and Ward, 1996). These developments led to the coining of the term 'Automated Mineralogy', referring to the use of an automatic system that measures mineral composition and texture by the means of an electron beam and X-ray spectroscopy. It was later, around the year 2000 that a competitor appeared, the Mineral Liberation Analyser (MLA), this time developed by the Julius Kruttschnitt Mineral Research Centre (JKMRC) (Fandrich et al., 2007). Around this time the QEM*SEM was re-branded as QEMSCAN (Gottlieb et al., 2000), and these days these two systems are the paradigm of Automated Mineralogy (Gu et al., 2014).

In this document the term 'SEM/EDS' is used to refer to any machine with both capabilities, like MLA or QEMSCAN.

2.4.1 SEM/EDS fundamentals

These SEM-based techniques require the sectioning of the fragments to expose 2D surfaces and therefore reveal their internal structure. Sample preparation involves mounting the fragments in epoxy resin capsules of about 30 mm in diameter. These resin blocks are then ground and polished in order to reveal an internal slice. In contrast to XMT this technique is thus destructive and invasive, but presents better image resolution and accurately clas-

sifies the different minerals in the sample. Figure 2.15 shows a schematic representation of the elements involved in an SEM/EDS system. Attention should be paid to both the Back Scattered Electron (BSE) and EDS detectors, which are the means by which the data is acquired (Bultreys et al., 2016).

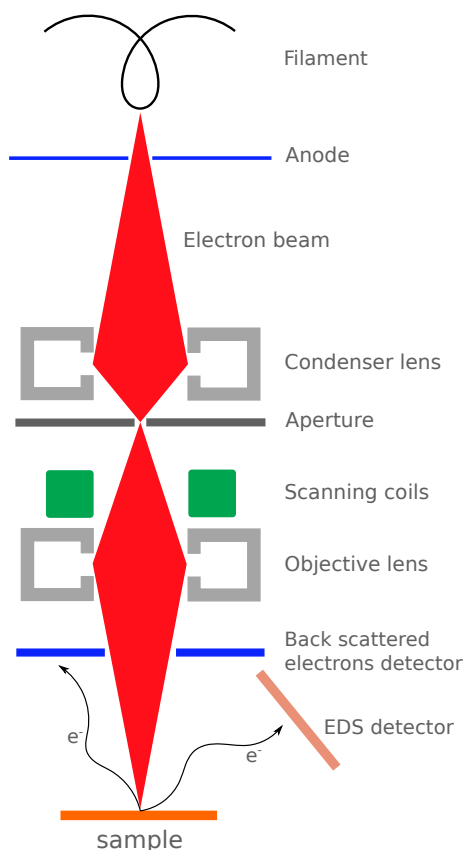


Figure 2.15: Schematic representation of an SEM and EDS machine. Adapted from Bultreys et al. (2016).

BSE analysis

The system can be programmed to automatically scan each sample, obtaining a BSE image that can have a resolution down to about 10 nm. To cover the whole sample, usually with a size in the range of millimetres, the machine follows a raster sequential process to produce a mosaic of scans. All the images collected are then stitched together to create a composite image (Bultreys et al., 2016).

The main objective of the BSE data is to create an image that will allow the machine to identify and separate each of the fragments in the sample. Additionally, BSE images are used to recognise in each of the fragments the different mineral phases according to their pixel value (Gu, 2003). Figure 2.16 shows an example of a fragment's phases after segmentation. The colours indicate individual regions detected, but not necessarily different minerals.

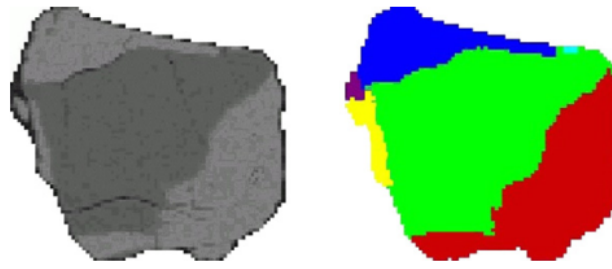


Figure 2.16: BSE image of a fragment and the corresponding phase segmentation according to image intensity. Colours indicate different regions, but not necessarily different minerals. From Gu (2003)

EDS analysis

With the information on the location of each region within each fragment, an X-ray analysis can be performed. This analysis consist of acquiring an energy spectrum that is later compared against a database so that the chemical elements of the sample can be determined. Figure 2.17 shows the sort of information that can be obtained from this analysis, where the brightness in each image corresponds to the abundance of the said element in the region. It can be observed that minerals that might have similar intensities in the BSE image (like pyrite and chalcopyrite) can be distinguished from one another by the EDS analysis.

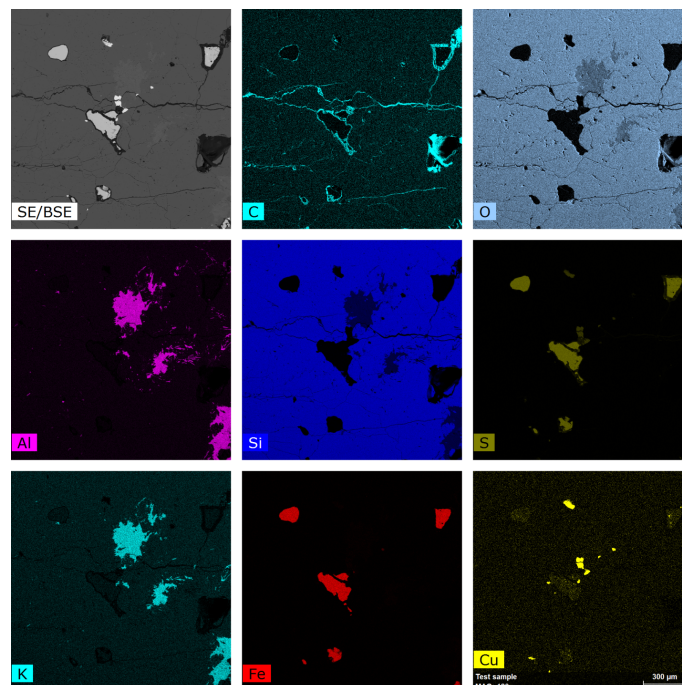


Figure 2.17: Element map obtained from MLA's EDS analysis. Chalcopyrite and pyrite have almost the similar brightness in the BSE image, but the latter lacks copper in the element map.

X-ray data has lower resolution than the electron beam, normally around 2 microme-

tres, and needs considerably more acquisition time in order to be robust. Therefore the MLA system allows this data to be measured in three different ways (Fandrich et al., 2007):

- Point: Takes only one measurement at the centroid of each region making it the fastest.
- Area: Rasters each region avoiding the boundaries.
- Map: Rasters the whole fragment regardless of the regions previously identified. It can take orders of magnitude more time than the other two methods.

Furthermore, the MLA system allows the user to create rules for combining these methods. An example is the Grain-based X-ray Mapping (GXMAP), where the user can set rules that, depending on the BSE region's image intensity, will trigger either a point-based or area-based X-ray analysis. This can speed up the process without losing resolution and confidence when assessing the mineral grains of interest.

2.4.2 Artefacts and limitations

Despite all the flexibility and high resolution achieved by SEM/EDS, there are limitations that cannot be avoided; the main one being the 2D nature of all measurements that pose a stereological bias in the quantification process.

Stereological correction

Stereology refers to the process of inferring higher dimensional (volumetric) information from data acquired at a lower dimensional domain (linear or areal). It implies solving the inverse problem of getting 3D data from 2D sections, but it also includes the relatively easier problem of using 2D projections (Sahagian and Proussevitch, 1998). Figure 2.18a shows a schematic of how the fragment's 3D information can get lost or skewed when section are used as measurements.

Stereological effects have been extensively studied and simulated in the literature (Chiaruttini et al., 1999; Mariano et al., 2016; Ueda et al., 2018). An example is shown in Figure 2.18b where the 2D size of particles is compared to their actual 3D size (given in both cases by the equivalent diameter). It can be seen that a particle's shape has a strong influence on how stereology affects the quantification of size, with 2D data providing in most cases an underestimation of the actual size.

Different approaches have been proposed for correcting for this bias, but most of them rely on the scanning of a considerable number of fragments, which depending on the sample size and texture, can be in the order of thousands (Ueda et al., 2016). The most used methods are based on assumptions about the particles' and grains' shape, which allows for

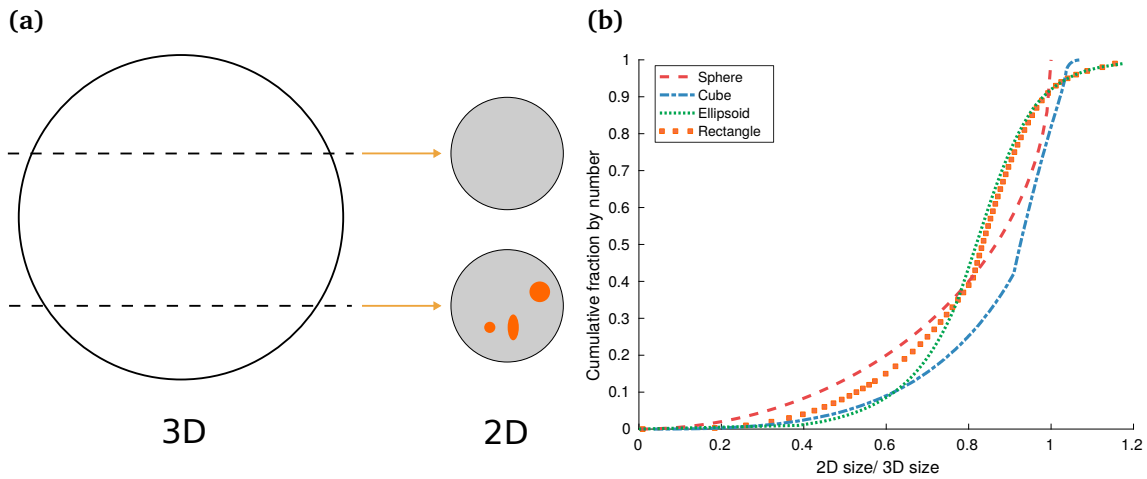


Figure 2.18: a) Stereological effect example, adapted from Ueda et al. (2018). b) Stereology on known shapes, adapted from Sahagian and Proussevitch (1998).

the use of probability kernels for transforming the grade distributions (linear and areal) into volumetric grade distributions (Fandrich et al., 1998; Gay et al., 2006; Jutzeler et al., 2012). These correction methods involve finding the solution to the following equation:

$$F(g_a|D) = \int_0^1 K(g_a|g_v, D) f(g_v|D) dg_v \quad (2.11)$$

where $F(g_a|D)$ correspond to the areal grade cumulative distribution, $K(g_a|g_v, D)$ is known as the transformation kernel and $f(g_v|D)$ is the unknown volumetric grade probability density function. All of these distributions are for a given particle size, or narrow range, D . The problem resides in finding a suitable transformation kernel and then solving the ill-posed inverse problem. Ore-specific (Fandrich et al., 1998) and generic symmetrical kernels have been proposed (King and Schneider, 1998), but a simple mineralogy is considered, typically with binary or tertiary systems (Lätti and Adair, 2001). Moreover, corrections have been only done for grain size and grade distributions, leaving other textural features like surface exposure without a known correction. Additionally, any correction found is heavily dependent on the ore used and cannot necessarily be extrapolated to another system (Maire and Withers, 2014). A real example can be found in Chapter 3, where 3D XMT images are used to estimate the ore-specific kernel in order to correct SEM 2D data.

Mineral identification

Converting from the X-ray diffraction spectrum to elements and later minerals, is also an inverse problem sensitive to noise, number of counts and partial volume effects among others. Procedures can be follow to avoid the effect of any of these issues, however that does not prevent EDS from failing or struggle to distinguish some mineral from one an-

other. Some copper sulphides in the chalcocite range, like spionkopite or digenite, are reported as chalcocite. Furthermore enargite, luzonite, tennantite, goldfieldite and colusite appear only as tennantite (Lee et al., 2011). This also happens in some iron minerals with similar atomic numbers and chemical composition like hematite and magnetite (Delbem et al., 2015). Calibration is essential, and sometimes chemical assays and/or X-ray diffraction measurements may be needed to corroborate the mineralogy provided by SEM/EDS (Lastra and Paktunc, 2016). This is because the analysis relies on the relative quantities of elements in the minerals, with some different minerals having very similar (or identical) chemical composition and can be especially problematic for minerals that have a composition range (i.e. where some substitutions can occur).

Artefacts

The main two artefacts in SEM/EDS are depicted in Figure 2.19. The first one occurring during reconstruction where the stitching of the sequential BSE images fails, highlighted in green in Figure 2.19a. The second artefact occurs during acquisition and has to do with the electrical conductivity of the surface. If the exposed area under analysis is not conductive, electrons from the beam will accumulate and appear as a bright zone in the BSE image (highlighted in Figure 2.19b). To avoid this artefact the resin mould has to be coated, after polishing, with a conductive material (Sandmann, 2015), with a carbon coating being the most commonly used.

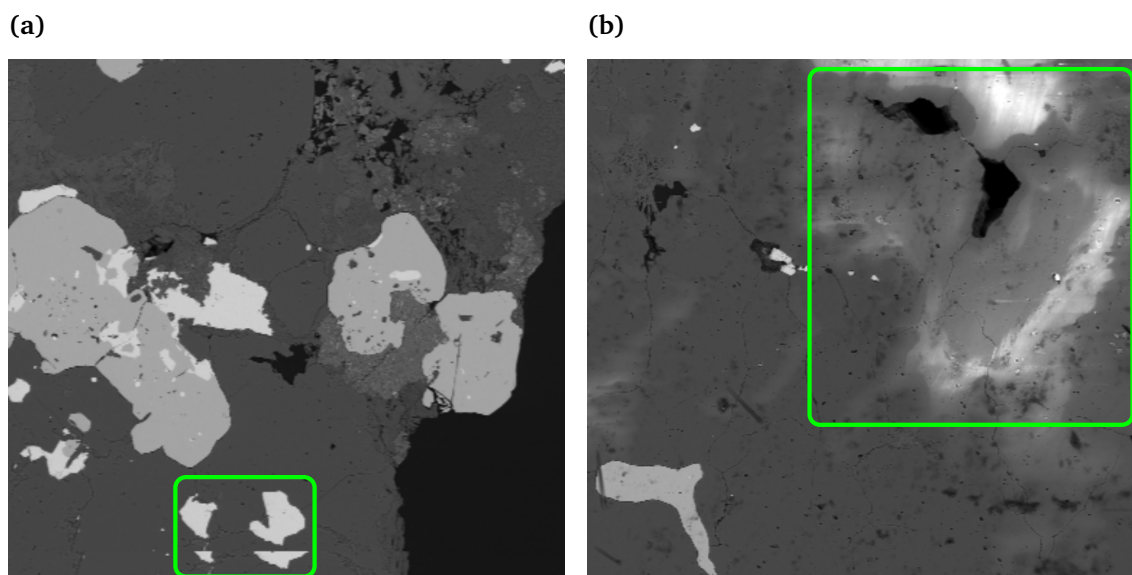


Figure 2.19: a) Stitching artefact, the lower end of the grains in the rectangle appear repeated near the actual location of the grains. b) Charging artefacts appearing as a bright diffusive area in the surface of the particle.

2.4.3 SEM/EDS in minerals processing

Since its beginnings Automated Mineralogy has been the gold standard method for assessing and quantifying an ore's textural properties (Wills and Atkinson, 1993). The significance of measuring liberation resides in the fact that the level of liberation of the valuable minerals from the gangue, normally carried out by comminution, limits the maximum possible grade for a given recovery in the downstream processes (Leißner et al., 2016b). Although several coefficients have been defined for liberation (Leißner et al., 2013; Mariano et al., 2016; Vallejos et al., 2018) and surface exposure (Leißner et al., 2016a), the method for quantifying them remains constant, being an SEM/EDS analysis. Currently, more than 160 SEM/EDS systems have been installed for measuring mineral liberation and mineral association (Lastra and Paktunc, 2016).

Ozcan and Benzer (2013) used Automated Mineralogy for assessing the degree of liberation generated by two of the main mechanisms used in comminution, namely, impact and compression. SEM/EDS provided reliable measurement of the particles' size and the degree of liberation. They concluded that the latter of the mechanisms provided a finer product with better mineral liberation. The two other mechanisms used in comminution, abrasion and shear, were not investigated. Little et al. (2015, 2017), on the other hand, assessed the effect of different mill types on particle shape and liberation. The aim was to understand how these may, ultimately, affect downstream processes' performance. The authors concluded that, for the specific ore and particle size used, both shape and liberation were predominantly a function of ore texture and not of the mill type. On the contrary, Liu et al. (2018) analysed the effect of different comminution flowsheets over mineral liberation, finding that this only depended on the final grinding mode. But, the authors also showed that the liberation achieved was unaffected by the crushing method used before grinding.

As mentioned previously in Section 2.2, comminution affects downstream processes setting an upper limit to how much the ground product can be separated or concentrated. Yin et al. (2017) investigated the effect of two different crushing methods on the ultimate leaching recovery. The authors used SEM-only images for quantifying and comparing the fractures generated in the ore. Results showed that HPGR crushers produced material that achieved consistently higher recovery compared to the one produced by the jaw crusher. SEM images provided valuable insights into what caused this increment in recovery, showing that HPGR crushing generates finer material with significantly higher levels of micro-cracking.

SEM/EDS can also shed light on the changes happening on the ore's texture along its processing changes that can hinder the process' performance. Ghorbani et al. (2013) studied the evolution of the mineralogy of particles being leached, showing that a mica

of jarosite was formed over the mineral of interest preventing the leaching solution from dissolving it. Furthermore, the analysis showed that certain mineral associations (pyrite and sphalerite) helped achieving faster leach kinetics.

Main issue with these analyses is the intrinsic stereological bias of automated mineralogy, something that in many cases is left uncorrected (Chiaruttini et al., 1999; Lastra and Paktunc, 2016). Correcting for this bias has been well studied, as mentioned in Section 2.4.2, though no clear correction exists for textural descriptors other than grain size and grade distributions (Lätti and Adair, 2001). Another issue is that SEM/EDS analyses are destructive as the sample gets sliced, preventing the re-imaging of the same particle.

2.4.4 XMT and SEM/EDS analyses

Going back to Figure 2.2 it can be seen that one of the main limitations in XMT is the entanglement between sample size and feature size. Thus, for a given spatial resolution the field-of-view is fixed and it can lead to sample sizes as small as 1.0 mm. This hinders the representativeness of the sample, especially for heterogeneous materials (Al-Raoush and Papadopoulos, 2010). Another main limitation is the lack of chemical information provided by XMT. SEM/EDS on the contrary does not suffer from these limitations, but provides only 2D information. The complementarity of both techniques in creating a more complete and multi-scaled dataset is thus apparent (Huddleston-Holmes and Ketcham, 2005). However, these techniques are frequently used separately over the sample so SEM/EDS provides mineralogy and XMT 3D connectivity information (Saif et al., 2017a). Thus, no quantitative cross information is created.

De Boever et al. (2015) proposed a workflow for working with these two image modalities. It consisted of scanning a low-resolution XMT scan of the whole sample, perform SEM/EDS analysis on the exposed sides and finally a high-resolution XMT scan of a sub-volume of the sample, as shown in Figure 2.20. De Boever et al. (2015) focused their discussion around the process of registering the images (see Section 2.5.1 for an explanation of image registration) and did not discuss how to obtain quantitative information from the fused multi-scale images.

This is persistent in the literature, where SEM/EDS is mostly used for a qualitative confirmation of the segmentation of mineral phases in XMT images (Ghorbani et al., 2011a). Lai et al. (2015) registered XMT and SEM/EDS images of Berea sandstone in order to guide the segmentation of different phases in the XMT images, but no quantification of the mislabelling is provided. Evans et al. (2015) also used SEM/EDS mineralogical information to corroborate the segmentation of pyrite from gangue minerals. In neither case was a quantitative assessment of the segmentation provided. In a different approach Van Geet et al. (2001) created a linear model for predicting and correcting the attenu-

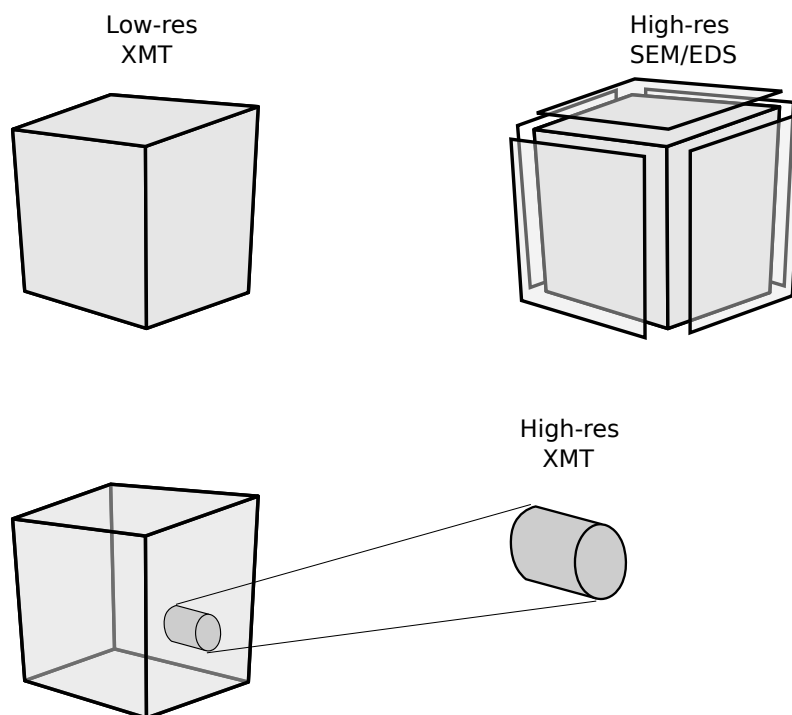


Figure 2.20: Workflow for combining XMT and SEM/EDS analyses, proposed and adapted from De Boever et al. (2015). A combination of low-resolution, high-resolution and SEM/EDS images of the same sample are used.

ation of XMT images according to the mineralogical content assessed with SEM images. SEM/EDS can also be used as a tool for helping resolve features below the detection level in XMT, as it can achieve higher resolution images. Sok et al. (2010), used high resolution SEM images to correlate local pore size and micro-porosity with the X-ray attenuation obtained from low resolution scans. This allowed for the creation of a proxy for unresolvable porosity in XMT images. Adding this calibrated micro-porosity to the macro-porosity readily measured in XMT created a good agreement between XMT and porosimetry data (35% and 36%, respectively). Another method for combining SEM/EDS is showing the same feature under study side-by-side in order to spatially correlate the occurrence of different phenomena. Charikinya et al. (2015) for example quantified the amount of fractures created by microwave treatment. SEM/EDS and XMT were used separately with the first used for analysing mineralogy and the occurrence of micro-cracks; the latter, being non-invasive, for quantifying porosity before and after treatment. The analysis of both sets allowed for correlating the creation of fractures with mineralogy, corroborating the presence of interphase trans-granular and grain boundary cracks.

On the side of multi-scale imaging, where a combination of XMT and SEM/EDS data is indeed used, Ma et al. (2016) presented a study using XMT and 3D Electron Microscopy that allowed for the assessment of the pore structure of samples ranging from 7.0 nm to 7.7 mm. Analysis was done at five different resolutions and provided valuable insights into the pore network, quantifying mineralogy, pore size and connectivity. Similarly, Saif

et al. (2017b) used a combination of XMT, SEM/EDS and FIB-SEM to analyse the pore structure of oil shales. Although upscaling is mentioned in their paper, the authors did not provide examples of this procedure, critical for overcoming the representativeness of the very small volumes scanned by FIB-SEM. Coletti et al. (2016) solved this issue by using ‘overlapping ranges’, so several direct and indirect techniques for measuring pore size can be combined in order to create a composite pore size distribution of the sample. A more complete review of multi-scale imaging is presented in Ma et al. (2017), with focus on shale rocks or in Bultreys et al. (2016) with focus on fluid transport in geological samples.

In summary, the main issues detected when using XMT and SEM/ED are: 1) the lack of a synergistic approach where both techniques can share information and 2) the lack of confidence levels or uncertainty bounds on the data collected. Chapter 3 introduces a methodology that addresses both issues by correlating quantitative information of features in both methods and analysing their statistics.

2.5 Digital image processing

Digital image processing consists of the use of computer algorithms applied to digital images. The aim of these algorithms vary from improving the image contrast, similar to what is done in photography, to obtain information about objects of interest. This is a key step in both XMT and Automated Mineralogy systems, it allows for the extraction and conversion of information in the form of an image into information in a format suitable for the user. An example is the calculation of the particle size distribution of a sample by obtaining the image area (or volume in 3D) of each particle scanned. This section will describe the different steps involved in the process of acquiring an image and obtaining the final quantification from it.

From Gonzalez and Woods (2006):

“An image may be defined as a two-dimensional function, $I(x, y)$, where x and y are spatial (plane) coordinates, and the amplitude of I at any pair of coordinates (x, y) is called the intensity or grey level of the image at that point. When x , y , and the intensity values of I are all finite, discrete quantities, we call the image a digital image.”

Figure 2.21 shows a schematic of the process of digitising an image. The object under study reflects radiation being emitted by an external source, radiation that is latter captured in an array of sensors, producing as an output a matrix where the value of each element, $I(x, y)$, correlates to the radiation intensity measured at each sensor. These elements are called pixels, or voxels when the image has a three dimensional shape $I(x, y, z)$.

Crucial in image acquisition and digitisation is the quantisation produced both in space locations and in intensity values. This two-fold sampling is controlled by the number of

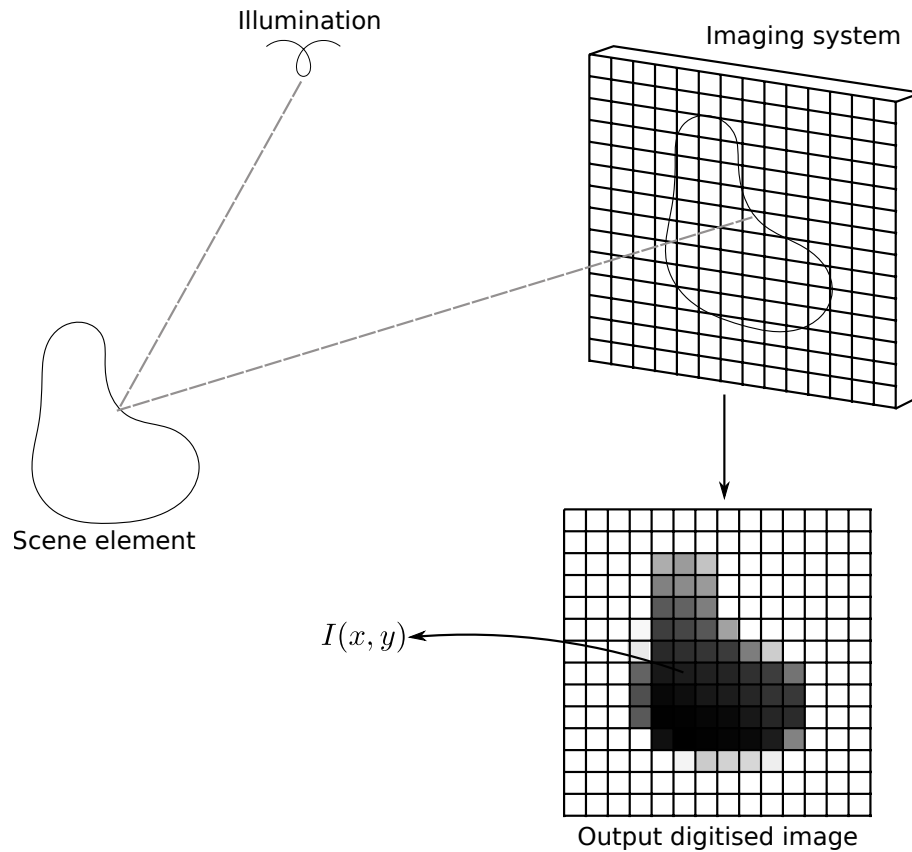


Figure 2.21: Acquisition of a digital image from an object. Digitising occurs when the continuum intensity of the sample is discretised by the finite number of sensors and brightness levels used. Adapted from Gonzalez and Woods (2006).

sensors and the data format used to store the data, respectively. Although more sensors are generally better, processing larger images takes considerably longer time and computing memory, especially in the case of 3D images. In the case of the data type used to store the data, the limitation is in the resolution of the Analog-to-Digital Converters in the detector, normally being 16 or 24 bits (65,536 and 16,777,216 possible values, respectively).

Digital image processing is the application of any operation that modifies the value of each pixel in the image. These operations are normally grouped and categorised depending on their objective and the kind of input/output that they take/produce. The main groups, as identified by Schlüter et al. (2014), are pre-processing, segmentation, post-processing and quantification. A traditional image processing workflow is depicted in Figure 2.22, with the steps being divided into these main groups.

2.5.1 Imaging fundamentals

The fundamentals of digital imaging and the basic procedures will be described in this section, leaving many advanced operations and topics out, for which the reader is referred to Gonzalez (2017) and Solomon and Breckon (2010). For the sake of brevity the adjective digital will be dropped in subsequent discussions, with all images assumed to be digital

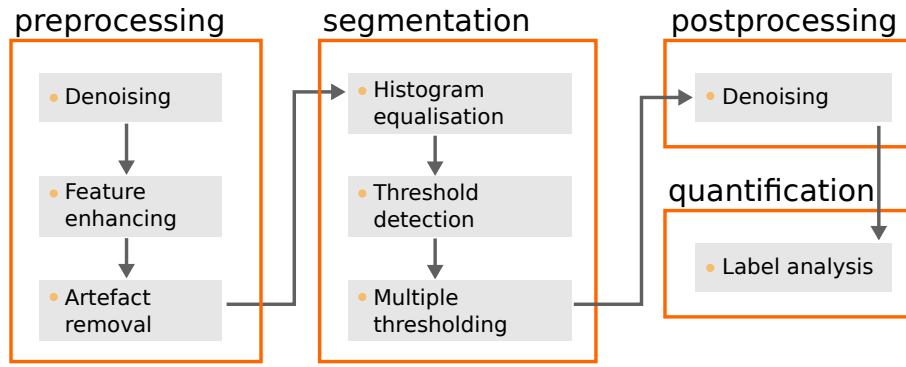


Figure 2.22: Generic image processing workflow. Adapted from Schlüter et al. (2014).

unless otherwise stated.

Image representation

Although images are no more than intensity values arranged in a matrix, there are several ways of representing them on a screen or paper. Figure 2.23 shows an example where black was assigned to the value 0, grey for 0.5 and white for 1. This relationship is arbitrary, but normally a bijective relationship is used, so increasing image values correlate to increasing lightness values in the 2D visual array. Furthermore, this relationship can include the rendering of some values with a transparent colour, normally done in 3D images to isolate the object under study from the surrounding air (Landis and Keane, 2010).

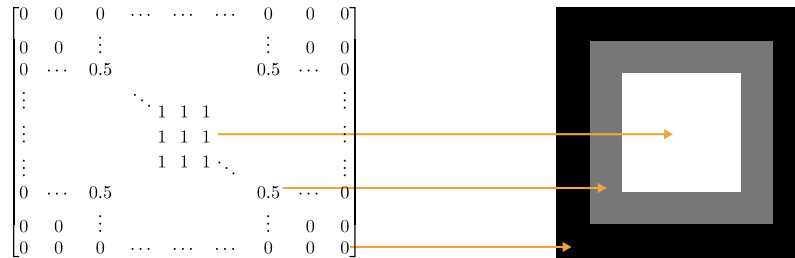


Figure 2.23: Image representation from a 2D array to a visual intensity array.

Pixel relationships

For many of the operations on the pixels, a definition of neighbourhood is required. When the image is in 2D, a pixel p with coordinates (x, y) has four neighbours (vertical and horizontally), defined by the following coordinates:

$$N_4 = \{(x + 1, y), (x - 1, y), (x, y + 1), (x, y - 1)\}$$

When including the diagonals, the neighbourhood includes eight coordinates, defined as:

$$N_8 = \{N_4, (x + 1, y + 1), (x + 1, y - 1), (x - 1, y + 1), (x - 1, y - 1)\}$$

These can be extended to 3D adding a third coordinate z . The corresponding N_6 (all six faces), N_{18} (N_8 on each plane) and N_{24} (including diagonals) neighbourhoods can be defined. These neighbourhoods are the cornerstone of the definitions of connectivity, regions and boundaries; all of which will be covered in later sections.

Image transformations

Although many of the operations in image processing focus on modifying the intensity values, a subset of them are used to change the spatial relationship between the pixels (Gonzalez and Woods, 2006). These spatial transformations, if they are linear, can be expressed in terms of matrices as shown in Figure 2.24. The matrix T performs a translation in space by (t_x, t_y) , a rotation of coordinates clockwise by θ and a scaling of both axes by s_x and s_y , transforming the original image on the left to the one in the right. It is worth noting that this process introduces some artefacts or changes to the original dataset due to the discrete nature of the coordinate system and the pixel intensity. The most noticeable of these effects is the blurring present in the transformed image.

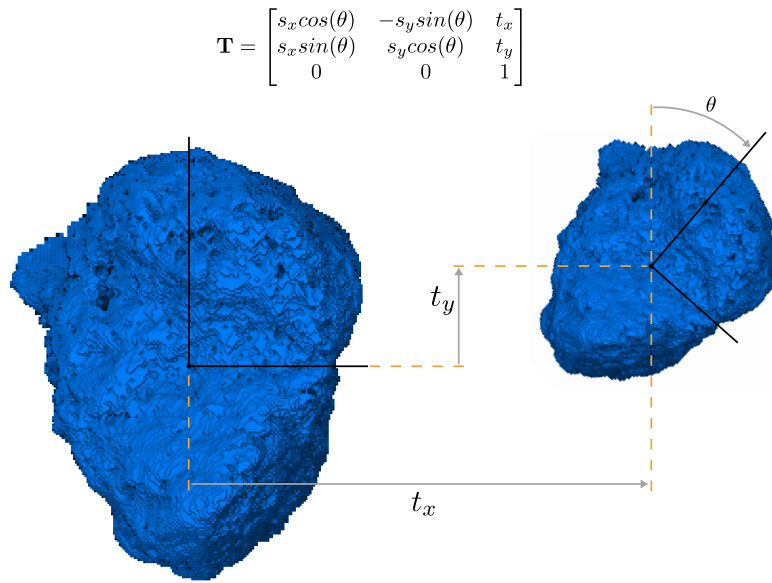


Figure 2.24: Rigid transformation of an image. The relationship between the two images, the model and the transformed one, is a matrix with 5 parameters for a 2D image.

The inverse problem of finding the transformation that relates two images is called registration. It is widely used in image processing to match two or more images of the same object taken at different times, where the object might have moved relative to the image acquisition system or to match two images of the same object taken with different equipment. The inverse problem is solved as a minimisation problem where a measure of similarity between the model and registered image has to be defined (El-Gamal et al., 2016; Studholme et al., 1999).

2.5.2 Preprocessing and data filtering

Image acquisition is subject to noise and artefacts, for instance as described in Sections 2.3.2 and 2.4.2 for XMT and SEM/EDS respectively. Although some precautions can be taken to prevent them from happening, most of the time some processing needs to be done to remove or mitigate their effect. This processing aims to remove the effect of noise and artefacts with the least possible impact on the details in the image (Schlüter et al., 2014). Filtering therefore consists of changing the intensity value of a pixel depending on the intensity value of its neighbouring pixels (normally N_8 in 2D and N_{24} in 3D). Computationally this can be an expensive process to perform, as some images might have millions of pixels and non-linear operations are needed for some filters. Figure 2.25 shows an example image presenting high levels of noise and ring artefacts (label b) and how the noise and artefacts got removed (label g) by applying a non-local means filter (Buades et al., 2008) on it.

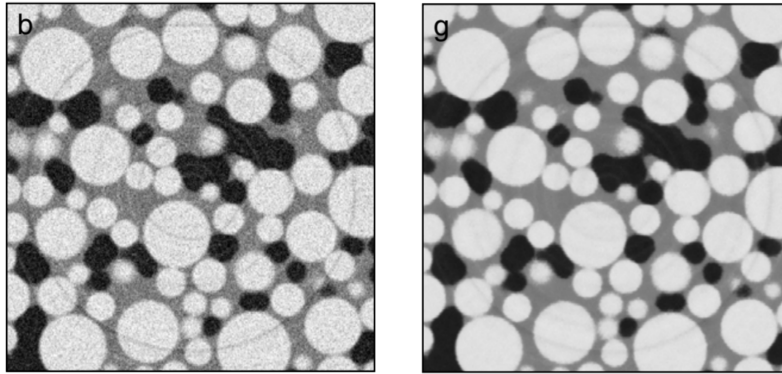


Figure 2.25: Non-local means filtering shows good performance at de-noising the image and removing ring artefacts. From Schlüter et al. (2014).

The filtering method will strongly depend on the type of noise and artefacts in the image (Wildenschild and Sheppard, 2013), as well as the computational resources available, as for instance, non-local means uses orders of magnitude more resources and time than a simple linear filter (Saif et al., 2017b). This difference is due to the extra computations that non-local means filters performs in order to decide whether to include each of the neighbouring pixels into the calculation. While it comes at a computational cost, the non-local means filter is generally edge preserving, where many other filters will blur edges (Menke et al., 2014; West et al., 2018).

2.5.3 Thresholding and segmentation

After an image has been filter, restored and/or enhanced the features of interest can be separated from the rest of the image. This process is called segmentation, consisting of assigning each voxel into groups or classes depending on their image intensity (West et al.,

2018). The resulting image is a labelled image, as shown in Figure 2.26. The grey-scale image is converted so that each colour in the new image corresponds to a phase present in the material. The effect of using a non-local means filter is also shown, allowing for better segmentation by homogenising the intensity values in the image without diffusing edges between phases (edge-preserving smoothing).

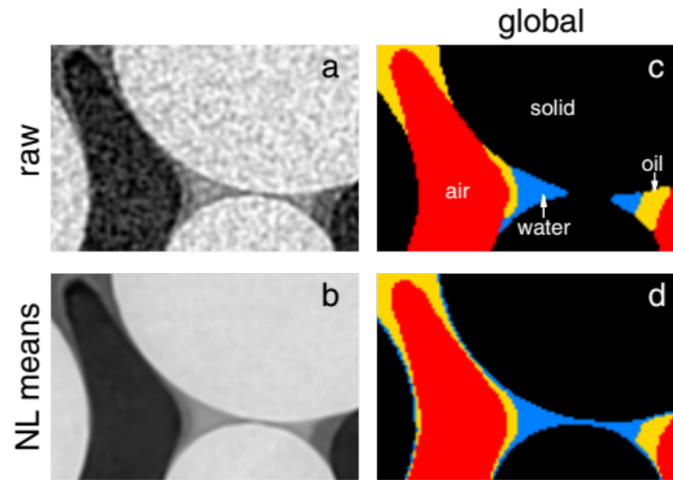


Figure 2.26: Thresholding and segmentation. Preprocessing the image allows for better segmentation. From Schlüter et al. (2014).

Because the image intensity is correlated to the attenuation of a region, segmentation can be performed simply by setting thresholds (Maire and Withers, 2014). This process consists of grouping pixels with similar grey values into classes. It can be done globally or locally, with the choice depending on the image (Le Roux et al., 2015). Global thresholding implies that the value selected to separate the phases is chosen regardless of the local variations in intensity within the image, whilst local thresholding takes into account the neighbouring characteristics of the image (Roche et al., 2010). Thus, global thresholding can be very sensitive to artefacts in the image, such as beam hardening, if they are not accounted for or previously dealt with in the processing workflow (Maire and Withers, 2014). On the other hand, local thresholding can lead to segmented images with artificially disconnected regions (Roche et al., 2010). The choice of one over the other will vary case to case depending on the image's quality and the variable that the user is looking to quantify.

2.5.4 Quantification

Once the images have been segmented into categories, each of their elements can be quantitatively analysed (Pietsch and Wood, 2017). This process involves the calculation of several descriptors of the data, namely, volume, length, area, roundness, just to name a few. It is worth noting that given the discretised nature of digital images many of these descriptors, especially length and surface area, can be influenced by the resolution used

(Maire and Withers, 2014). An example of this influence was presented by Shearing et al. (2012), showing that the quantified porosity of a solid oxide fuel cell was positively correlated with the resolution used. It is also worth noting that the analysis can be done in either 2D or 3D, as is shown by Figure 2.27, obtained from Ebner et al. (2014), where the authors scanned a sample of graphite material using XMT. The authors managed to segment the pore space from the graphite matrix, enabling them to calculate the porosity and tortuosity of the sample in 3D, in-plane (IP_1 and IP_2) and through-plane (TP).

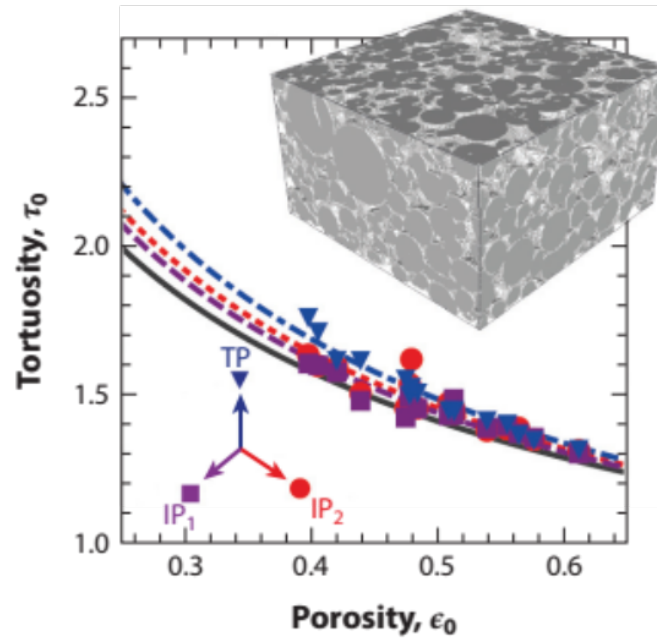


Figure 2.27: Quantification from images allows for extracting quantitative descriptors like porosity distributions. Image from Ebner et al. (2014)

2.6 Conclusions

The minerals processing industry is facing a technological challenge as the demand for metals rises alongside a decline in the head grade of the ore. This challenge calls for a better understanding of the relationship between the ore's properties and the performance of mineral processes. A quantitative description of both is thus crucial.

Imaging techniques have allowed for the quantitative analysis of the ore's texture at different scales, from the tens of microns to the tens of centimetres. X-ray microtomography gained popularity in recent years as an alternative to Automated Mineralogy due to its 3D, non-destructive and non-invasive measurement of the samples. Faster acquisition has also allowed for the dynamic analysis of *in-situ* and *operando* experiments, adding time as a fourth dimension. This technique has allowed for the analysis of mainly structural or geometric information such as particle size, porosity, tortuosity and density. Although not readily measured, basic mineralogical information can be obtained from

XMT analyses if good contrast between mineral phases is achieved, either by using low energies or a dual-energy approach. It is worth noting that the chosen method is highly dependant on the ore under study.

Automated mineralogy analyses, based on electron microscopy and energy-dispersive X-ray spectroscopy, are the gold standard of mineralogical analyses, as mineral composition is readily obtained. Besides mineral information, SEM/EDS provides measures of particle size, grade, porosity and liberation. These analyses though, are destructive and invasive and cannot be used *in-situ* nor in *operando* experiments. Furthermore, SEM/EDS analysis occurs only in 2D and stereological corrections have to be implemented. However, corrections have only been studied for size and mineral grade and not for surface exposure, a key factor in mineral processes such as flotation.

Moreover, even though there is a clear benefit for combining XMT and SEM/EDS analyses, no agreement in the literature has been found on how to combine these two imaging techniques. Chapter 3 deals with this issue, presenting a methodology that allows for extending mineral analysis in XMT via the synergistic use of SEM/EDS. The methodology also provides a framework for assessing and quantifying the uncertainty and biases occurring in both imaging techniques.

Chapter 3

3D Quantification of ores for minerals processing

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3.1 Introduction

As shown in Chapter 2, imaging of mineral samples has become the standard method for quantifying mineral texture. More importantly, imaging techniques have allowed textural characteristics to be related to the performance of mineral processing systems (Kyle and Ketcham, 2015). Applications include liberation processes such as milling (Leißner et al., 2016a), recovery processes such as flotation (Jordens et al., 2016; Tungpalan et al., 2015) and heap leaching (Naderi et al., 2011). The two main analytical devices used for imaging the internal structure of mineral ores are X-ray micro-tomography (XMT) and Automated Mineralogy (Cnudde and Boone, 2013; Lin et al., 2016b; Sutherland and Gottlieb, 1991), with SEM/EDS being the more routinely used.

XMT is a non-invasive and non-destructive tool that has been used for assessing ore samples in terms of, for instance, their mineral liberation, fracture network, gangue porosity and grain size distributions (Charikinya et al., 2015; Dhawan et al., 2012b; Garcia et al., 2009; Ghorbani et al., 2011a). For example, Miller et al. (2003) studied the relationship between ultimate recovery in heap leaching and mineral exposure, building a predictive model based on the exposure measured from XMT images. However, as discussed in Section 2.3.2, despite being a versatile tool XMT images do not directly provide the mineralogy of the sample under study, which is a major drawback for geological and mineral processing applications (Lin et al., 2013).

Automated Mineralogy, on the other hand, is currently the standard analysis tool used in minerals processing to obtain mineralogical information of the ore. This equipment, based on a combination of Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) measurements, are widely used for the majority of mineral assessments (Fandrich et al., 2007). SEM/EDS analysis requires sectioning of the fragments to expose 2D surfaces to reveal the internal structure. In contrast to XMT this technique is thus destructive and invasive, but presents better image resolution and classifies the different minerals present in the sample by a composite of electron microscopy and X-ray data. Moreover, since SEM/EDS-based analyses provide only 2D information, stereological corrections are advisable when size and mineral liberation quantification are performed (Fandrich et al., 1998).

As previously discussed in Section 2.4.4, there is a clear benefit of combining both techniques. XMT provides the 3D biased-free information whilst SEM/EDS can help with the assessment of mineralogy and the detection of smaller features with its higher resolution. Thus, SEM/EDS mineral classification can be defined as the ground truth when compared to XMT threshold-based classification. In terms of quantifying size (particle or grain) in 2D, SEM/EDS presents a better contrast and resolution than a 2D XMT slice, meaning that it can also be taken as the ground truth. Is when doing a 3D quantifica-

tion that XMT provides a better measure than SEM/EDS. The latter can only provide an inferred measure in 3D and thus XMT is the ground truth regarding this kind of analyses. This chapter presents a methodology that allows for the combination of both imaging techniques so that quantification can be performed in a calibrated manner, also allowing for the quantification of its uncertainty levels.

3.2 Combining XMT and SEM/EDS

Although co-existing for some decades, XMT and SEM/EDS analyses have not been used together on a regular basis. Furthermore, there is no standard methodology on how to combine them in a synergistic manner. Frequently SEM/EDS is used to show side-by-side the same feature under XMT analysis corroborating mineralogy segmentation (Evans et al., 2015; Huddleston-Holmes and Ketcham, 2005; Lai et al., 2015) and to help quantifying unresolvable features at XMT resolution (De Boever et al., 2015; Lai et al., 2015; Sok et al., 2010; Van Geet et al., 2001). Similarly, XMT has been used to assess the performance of stereological corrections for grade and particle size obtained from SEM/EDS data (Gay et al., 2006; Jutzeler et al., 2012) or to convey 3D information on connectivity in pore networks (Ghorbani et al., 2011a; Saif et al., 2017a).

In this chapter we propose a novel methodology for quantifying mineral information by combining information from XMT and SEM-based assessments using a grain-by-grain approach. We demonstrate how SEM-based mineral information can be used to calibrate XMT image segmentation to provide quantitative 3D mineralogical data. In addition, the XMT 3D information is used to assess stereological effects in SEM images, providing a method for easily generating ore and mineralogy specific stereological corrections. The novelty of the proposed methodology is that it allows the confidence bounds in the mineral segmentation and classification to be assessed, important considerations if these methods are to be used for quantitative analysis. It is worth noting that the methodology can also be used in a pore-to-pore manner, or any other feature that can be segmented and tracked over both imaging modalities.

The methodology is tested on copper sulphide ore fragments containing mainly chalcopyrite and pyrite in a quartz gangue matrix. The reason for choosing this ore is because chalcopyrite and pyrite are commonly associated with one another and yet are notoriously difficult to distinguish from one another in XMT images due to their similar X-ray attenuations.

3.3 Materials

3.3.1 Ore

For this study a typical porphyry copper ore with a grade of 0.8 wt% copper was used. Table 3.1 summarises the mineral composition as obtained from SEM/EDS assessment in a FEI Quanta 600i SEM/MLA. The analysed fragments consisted of crushed ore in the 8.0 mm to 12.2 mm size range. Modal mineralogy showed that the main non-sulphide gangue mineral is quartz, with pyrite being the main sulphide constituent, though it is considered a gangue mineral as the copper containing minerals are the species of interest. The main copper mineral is chalcopyrite, though accompanied by a range of other copper containing species.

Table 3.1: Main mineral composition of the ore sample. Main minerals are primary copper sulphides, pyrite and a gangue consisting of mainly quartz.

Mineral type	Weight %	Specific gravity	ID
Copper containing species	2.13 ± 0.47		
Chalcopyrite	1.25	4.1	CuFeS ₂
Tennantite	0.48	4.65	Cu ₆ [Cu ₄ (Fe, Zn) ₂ As ₄ S ₁₃
Bornite	0.25	5.06	Cu ₅ FeS ₄
Covellite	0.136	4.6	CuS
Chalcocite	0.011	5.5	Cu ₂ S
Pyrite	7.00 ± 2.74	4.95	FeS₂
Gangue minerals	90.69 ± 2.73		
Quartz	41.93	2.65	SiO ₂
Muscovite	39.81	2.76	KAl ₂ (AlSi ₃ O ₁₀)(Fe, OH) ₂
Other minerals	8.95		

3.3.2 XMT

A Nikon XTH 225 scanner was used to carry out the XMT acquisition. 37 fragments were analysed in total with 34 of them XMT scanned at high energy levels and lower resolution. The remaining three were XMT scanned at higher resolution and lower energy levels. The detector consists of a matrix of 2000 × 2000 detectors, which gave a linear resolution of approximately 9 μm to 16 μm for the size range of fragments used. The parameters used for the acquisition are listed in Table 3.2.

Using the database created by Berger et al. (2010), the linear attenuation coefficient can be plotted for different X-ray energy levels. Figure 2.5 shows this coefficient for the main minerals encountered in the samples studied in this work. There is a significant gap in attenuation between the quartz and the sulphide minerals. Note that although quartz was the main gangue mineral in these samples, the other non-sulphide gangue species also

Table 3.2: Scanner conditions for XMT scans.

Parameter	Value	
	Low Energy	High Energy
Volage	50 kV	89 kV
Current	137 μ A	117 μ A
Filter	None	1 mm Al
Exposure	2 s	0.708 s
Projections	2001	
Resolution	8.9 μ m/px	16.1 μ m/px

have much lower X-ray attenuations than the sulphide species. Segmentation difficulties arise when attempting to distinguish between the pyrite and chalcopyrite as their X-ray attenuation values are very similar to one another. It can be observed, though, that at lower energy levels the gap in the attenuation between these minerals is larger.

However, the fraction of photons that are able to pass through the sample decreases with energy. As the signal-to-noise ratio depends on the number of photons detected, lower energy scans need longer exposure times. For the ore used, good contrast and a reasonable acquisition time was achieved using an energy level of 50 kV at 137 μ A with a 2 s exposure time.

3.3.3 Automated mineralogy

A FEI Quanta 600i SEM/MLA machine was used to analyse all fragments. The sample preparation involved mounting the fragments in 30 mm blocks using epoxy resin. The prepared sample blocks were then polished using the Struers Tegrapol polishing machine to a diamond finish of 1.0 μ m. Carbon coating was also performed using the Quorum Q150R carbon coater to prevent electron charging of the exposed surface, avoiding image artefacts created by electrons being accumulated in sections of the ore. Figure 3.1 shows a schematic of the slice exposed for an example fragment; depending on the surface of the fragments, a slice 150 μ m to 250 μ m deep was exposed.

A combination of a standard Back Scattered Electron (BSE) and a Grain-based X-ray Mapping (GXMAP) measurement methods (Fandrich et al., 2007) were performed in the SEM/MLA, at a resolution of 2.25 μ m per pixel.

3.4 Calibrating thresholding in XMT with SEM/EDS images

After XMT scanning, all the fragments were ground and polished to expose a section of their interior for analysis within the FEI Quanta 600i SEM/MLA machine. Figure 3.2 shows

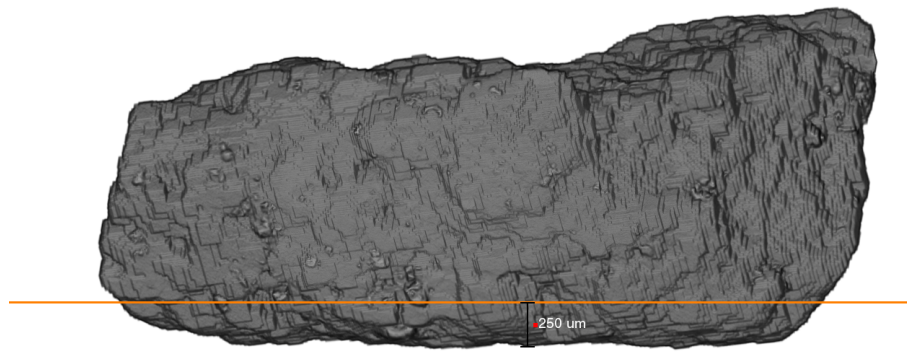


Figure 3.1: Example schematic of fragment's polished sectioning. Fragments were polished to different depths as shown in the figure by the orange slice.

a region of interest in which the results from the three imaging modalities are compared. The low energy XMT image in Figure 3.2a, the BSE image from the SEM in Figure 3.2b, and a mineral map based on a combination of the SEM and EDS measurements in Figure 3.2c. It should be noted that the XMT image represents a virtual 2D slice through a 3D data set (2D-XMT), while the other two images are inherently 2D data. It can be seen that the SEM BSE image has better contrast and looks sharper than the XMT image, this is mostly due to the higher resolution used in SEM/EDS. Nevertheless, the difference between pyrite (green in the mineral map) and copper minerals (pink and red) is also apparent in the XMT image at the energy level used.

For the low energy XMT scans the pixel intensity histogram, depicted in Figure 3.3 for a particular fragment, shows clear peaks for some of the phases of interest. The two main peaks are due to gangue and the air and porous media in the particle. At higher intensities there are slight undulations in the histogram due to the presence of pyrite and the copper minerals, though these are not nearly as distinct as the other peaks. The methodology of using the SEM-based data to set the thresholds between these phases, as well as quantifying the resultant uncertainty in the classification, is the main focus of this Section.

3.4.1 Methodology and algorithm

In order to use both imaging modalities one must take into account the destructive nature of SEM/EDS analyses, thus, XMT images have to be acquired beforehand. The steps of this procedure can be described as follows:

- 1 Fragments are individually scanned in the X-ray Micro-Tomography scanner using the settings reported in Table 3.2.
- 2 Gangue matrix and bright phase are together segmented from air, using the Otsu algorithm (Otsu, 1979), setting the image intensity for the surrounding air and internal porosity to zero. This can easily be done as the contrast between air and the

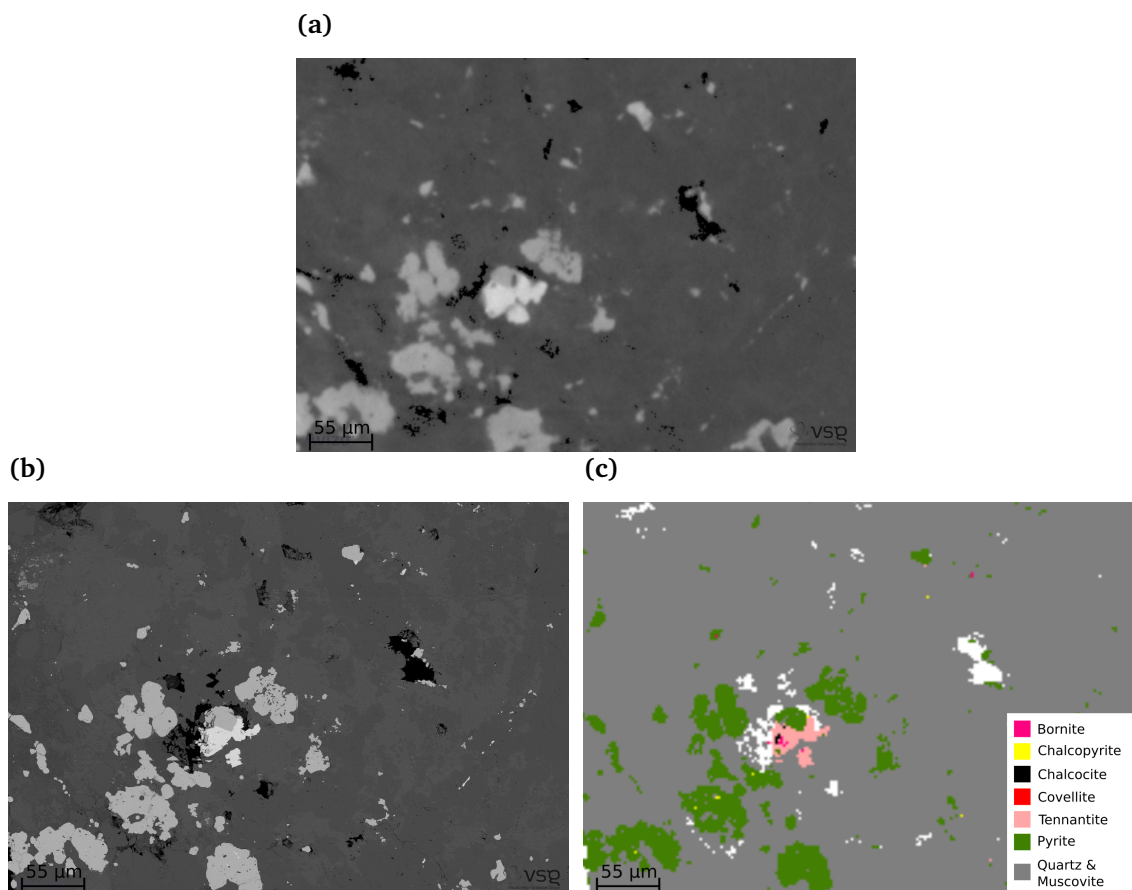


Figure 3.2: Region of interest of one example fragment. Contrast between gangue, pyrite and copper bearing minerals is apparent in both modalities. a) low energy 2D-XMT image, b) BSE image and c) Mineral map showing classification given by the SEM analyser.

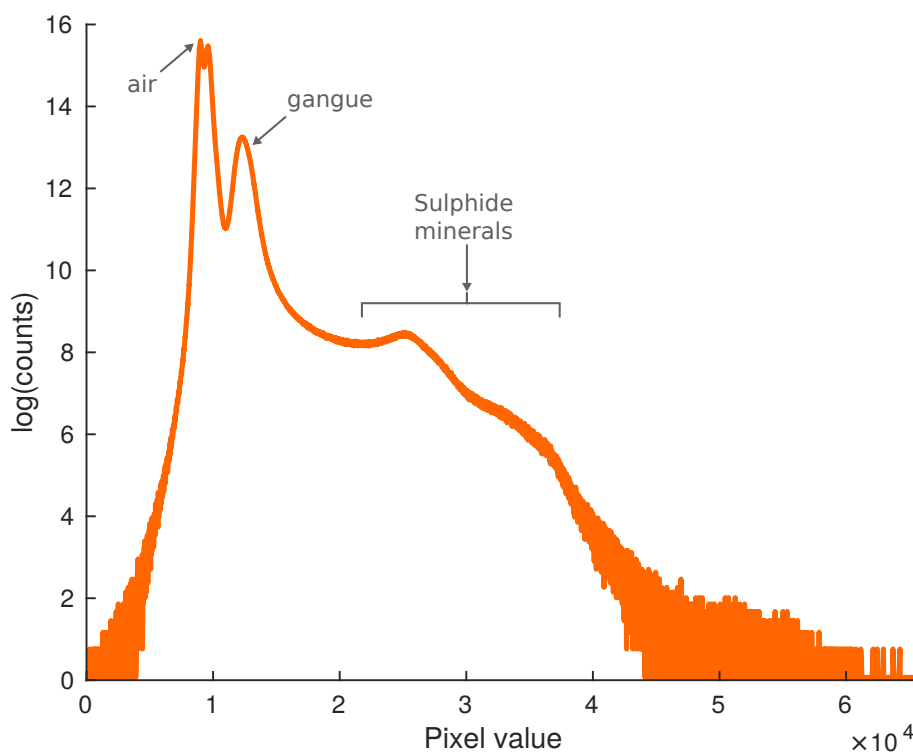


Figure 3.3: Example histogram of one XMT scan. Peaks from the key materials present in the sample are apparent, including air, gangue and sulphide minerals.

rest of the phases is apparent (see Figure 3.3).

- 3 The bright phases (pyrite and copper minerals together) are segmented from the gangue using the maximum entropy global thresholding algorithm for each fragment (Kapur et al., 1985). The binary mask obtained is then labelled using a connectivity algorithm, with an 8-connected neighbourhood, to identify individual grains.
- 4 Fragments are then scanned in the SEM machine after a grinding and polishing procedure as described in Section 3.3.3.
- 5 Porosity is segmented in the BSE image of the sections in the same manner as described in step 2. In the case of BSE contrast between air and the rest of the phases is even more apparent (see Figure 3.5a).
- 6 Minerals of interest (pyrite and copper minerals) are segmented from the mineral map image, in order to produce a binary mask for each mineral of interest. These are subsequently labelled as in step 3.
- 7 The XMT 3D volume is registered (see Section 2.5.1) into the segmented BSE image so that a rigid motion transformation is obtained. The similarity measure used was the normalised mutual information to account for the difference in contrast between the two modalities.
- 8 The motion transformation is used to align the XMT grain labelled mask (step 3) into the grain labelled mask (step 6), so that individually identified grains can be tracked over both images.

The algorithm used for tracking grains over the XMT image and the mineral image (step 8 of the above process) is based on the grain tracking algorithm developed by Lin (2015) and extended significantly to incorporate the SEM-based calibration. Lin's algorithm can be summarised by Figure 3.4. The main objective of the algorithm is to match the labelling of mineral grains appearing in a reference image to the ones in a subsequent image. This is done by taking the grain-labelled reference image (Figure 3.4a) and comparing it against the grain-binary segmented image from a different scan (Figure 3.4b). All pixels appearing in both images are assigned with the reference image's label (Figure 3.4c). Those pixels that were not labelled, as they only appear in the subsequent image (Figure 3.4d), are assigned to their neighbouring pixel's label (Figure 3.4e).

One of the main limitations of this algorithm is that objects that were not detected in the reference image (due to them having a size close to the spatial resolution) are not considered in the analysis. This has to be noted as the SEM image has a higher resolution than the XMT scans and many of the grains appearing in SEM images will not appear in the XMT corresponding virtual slice. For this reason the XMT virtual slice is considered the reference image, so that grains appearing only in the SEM analysis are discarded. This

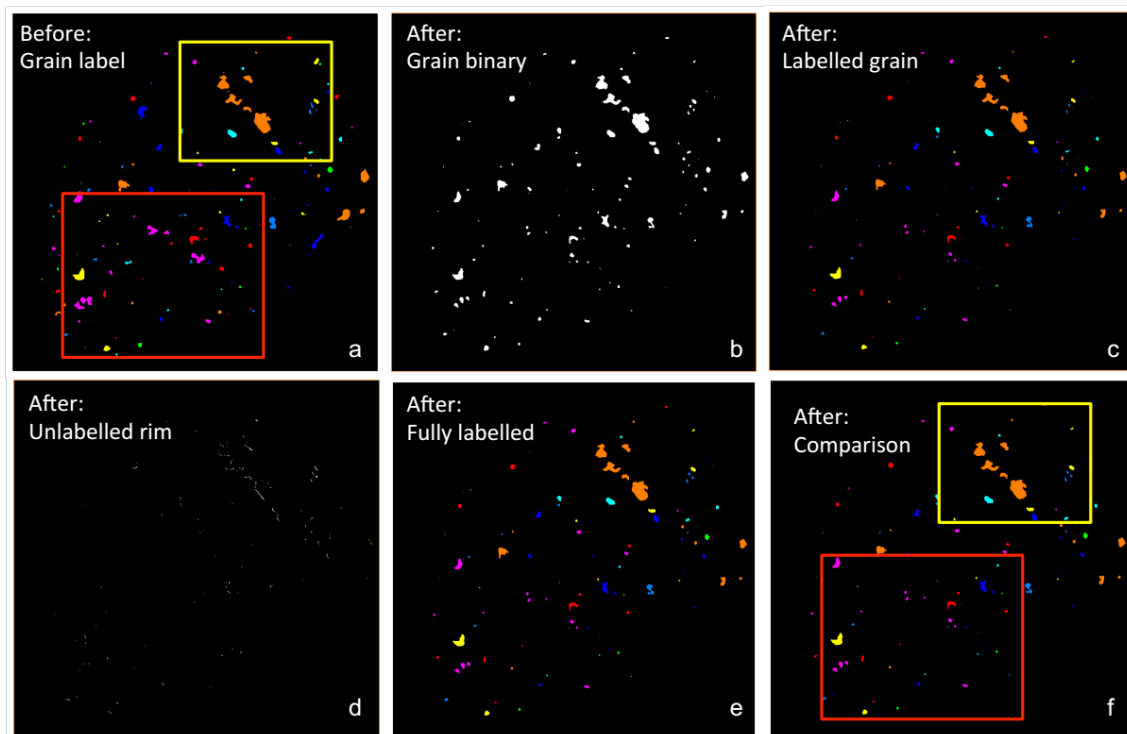


Figure 3.4: A slice through a 3D tomogram of an ore particle showing the different stages in identifying the same grains in different images. (a) Reference image with grains identified and labelled. (b) Mineral phase identified in subsequent image. (c) Mask based on reference image applied to subsequent image. (d) Unassigned rims not covered by the mask. (e) Labelled subsequent image with rims assigned to appropriate grains. (f) Comparison with reference highlighting regions. From Lin (2015)

algorithm runs in a combination of routines in both Avizo® and Matlab®. The first being used to segment and label the images and the second to perform the grain tracking algorithm (Figure 3.4c-e). A point to be stressed is that only the labelled images are transformed and matched, the original images (3D XMT, BSE and GXMAP measurements) are kept intact to avoid the introduction of systematic errors due to the registration process (mostly blurring, as covered in Section 2.5.1). This, however, is not the case for the virtual 2D XMT image, where the slice has to be created from the XMT 3D volume using registration algorithms. Figure 3.5 shows the BSE image of an example fragment slice along with the mineral map provided by GXMAP and the registered XMT grain labelled mask over the same BSE image. A good correspondence between all images can be observed.

The extended version used in this thesis makes essential changes so that the algorithm can work with images from different modalities and so that additional quantification can be obtained and combined. The main addition consisting of the mutual quantification of the grain area and the inclusion of grey image intensity of the XMT slice. A visual representation of the algorithm is shown in Figure 3.6. The flow chart shown there is applied to every individual fragment separately, but the grain quantification information is aggregated for posterior analysis.

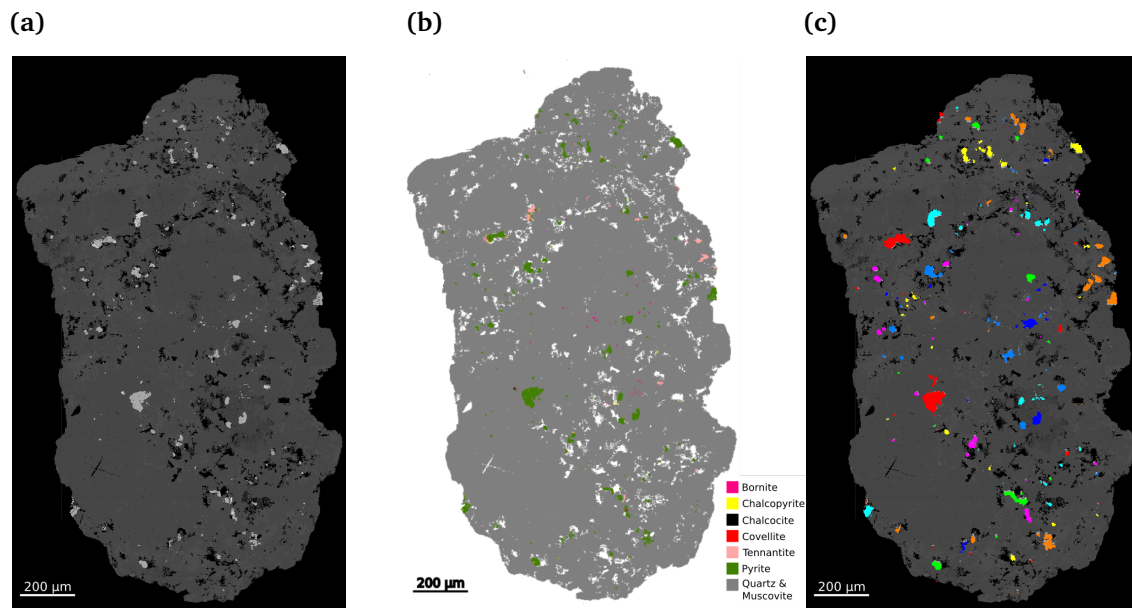


Figure 3.5: Registered slices from SEM and XMT analysis. The proposed grain tracking algorithm was applied to the SEM and XMT images to correlate information from each device. a) shows the BSE image from SEM, b) shows the mineral map from SEM and c) shows the XMT mineral label image overlapped to the BSE image, colours indicate the unique label number of each mineral grains.

After the algorithm has been applied to the ore samples, a grain-level database is created so that information about their pixel intensity, size and shape in XMT and BSE images, distance to the surface and mineralogy is made available. This database is used to study variability in grain size quantification by XMT, stereological effects in the grain size distribution obtained from SEM images and to calibrate a global threshold to segment the bright phase in XMT images so that pyrite and copper-mineral grains can be distinguished from one another. Figure 3.7a shows the pixel intensity histogram as obtained from the XMT, showing no obvious value for a threshold. It should be noted that unlike Figure 3.3 this histogram is only for the pixels in the XMT 2D slice corresponding to the SEM/EDS image. An appropriate threshold can be found by plotting all mineral grains according to their mineralogy as given by the EDS-based classification against their image intensity in the XMT low energy scan. Figure 3.7b shows this plot, where all grains in each category are sorted by their pixel intensity and plotted against the cumulative area. A global threshold can be set so that the level of misclassification leads to the grade indicated by the SEM/EDS analysis. It should be noted that this figure is plotted on the basis of the cumulative 2D area of the grains rather than the number of grains.

The label numbers in Figure 3.7b indicate situations where image artefacts affect the observed pixel intensity, and thus potentially influence the accuracy of the segmentation. Label '1' shows grains that have an average intensity that is lower, sometimes significantly, than the typical intensity of grains of that type. This is typically the result of the partial volume effect, where pixels at the grain-gangue boundary have an intensity lower than

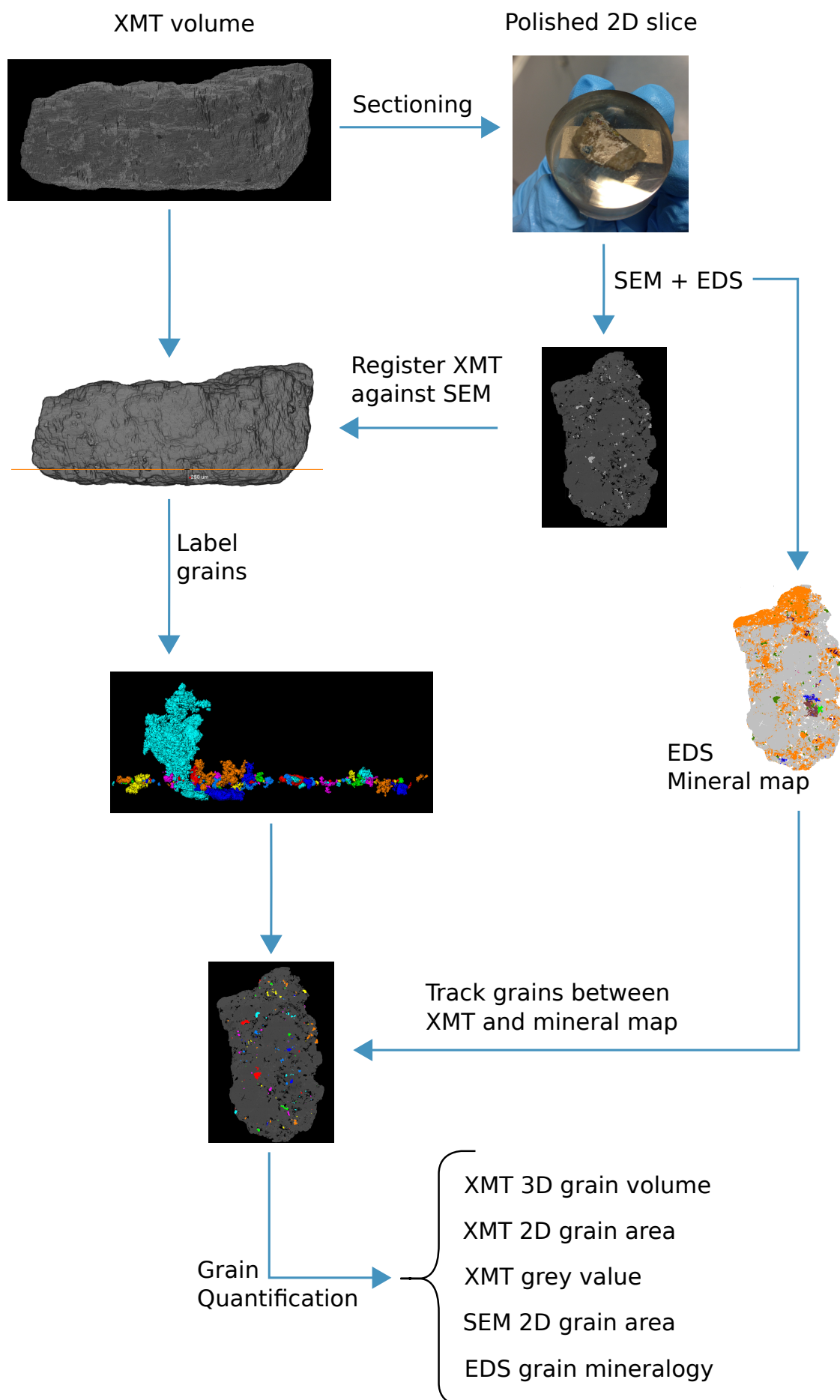


Figure 3.6: Updated grain tracking algorithm combining XMT and SEM/EDS images.

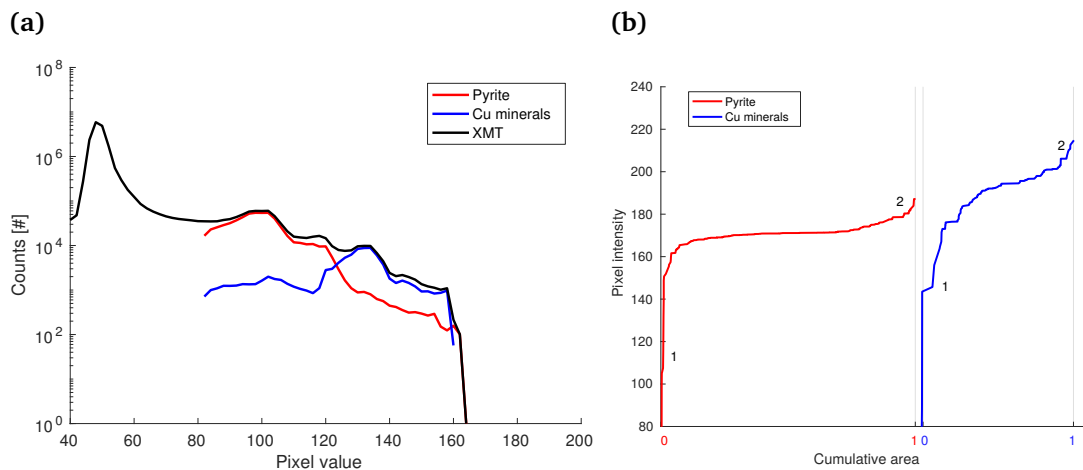


Figure 3.7: Tracked grains pixel intensity by mineralogy. a) image intensity histogram showing the XMT pixel value along with the respective histograms of pyrite and copper minerals grains for a particular fragment. b) pyrite and copper ores grains from all scanned fragments have been sorted by their pixel intensity so a global threshold can be set in order to achieve same composition given by the SEM analyser. Label '1' shows the result of boundary/partial volume effects, which lowers the grains' pixel intensity. Beam hardening causes variability in the grains' intensity with depth into the sample (label '2').

those in the interior of the grain. This artefact is critical in smaller grains where the boundary pixels constitute a large proportion of the total. This is why even though there are quite a large number of grains in these tails of the distributions, they do not contribute much to the total area. Beam hardening is an acquisition artefact that makes the measured intensity dependent on the position of the grain within the sample. This artefact is responsible for some of the subtler variability in the intensity of the grains within the same type (label '2') and, unlike partial volume effects, its influence is not restricted to small grains, though its effect can be reduced using a combination of filters and appropriate reconstruction techniques (Hsieh et al., 2000). For the copper minerals, another source of variability is that although chalcopyrite is the dominant mineral in this class, it is not the only one, with different copper minerals having different attenuations, though all of them higher than that of pyrite.

After obtaining the desired threshold from Figure 3.7 (an intensity of approximately 175 so that less than 10% of grains, by volume, are wrongly assigned), this value can be applied to all XMT volume images so that simplified 3D mineral maps can be obtained in which gangue, pyrite and copper minerals are identified. This curve also allows for the evaluation of the level of uncertainty and error in the classification of mineral phases as one can calculate the cumulative area that will be misclassified by a given intensity threshold. For the chosen value of 175, pyrite grains accounting for less than 10% of the total area (and thus volume when extended into 3D) are wrongly assigned as copper grains. Further detail on the statistics of the resulting classification is given in the following section.

3.5 3D Quantification and mineral mapping using calibrated XMT images

3.5.1 Mineral classification

Using the procedure described above, a global threshold that creates the same grade specified by the SEM modal mineralogy information was found. This threshold produces a misclassification, due to X-ray artefacts. This error can be quantified according to the grain size, as shown in Table 3.3, by grouping grains in size categories and evaluating the percentage of false positives (pyrite classified as copper) and false negatives (copper classified as pyrite). This is done after applying the desired threshold so the classification in XMT can be compared against the one provided by SEM/EDS. False positives are then defined as the grains that were classified as containing copper in the XMT scan, but were actually defined as pyrite grains by the SEM/EDS. Conversely, false negatives are copper grains in the SEM/EDS that were classified as pyrite in the XMT analysis. As expected, the miss-classification decreases with grain size, especially for the false negatives. This is because false negatives are mainly due to partial volume effects, which are strongly correlated with grain size. Conversely, a beam hardening effect is the dominant reason for the false positives, which show little size dependency.

Table 3.3: Mineral misclassification by size.

Size range μm	False positives (% of grains)	False negatives (% of grains)
< 25.3	7.62	7.85
25.3 – 53.1	10.32	7.94
53.1 – 82.5	6.90	0.91
82.5 – 124	9.33	2.3
124 >	10.42	0

Figures 3.8 and 3.9 show two typical fragments as examples; grey represents gangue, brown pyrite and yellow the copper mineral grains. Porosity is rendered transparent.

The information provided by this 3D mineral map adds a new dimension relative to all previous analyses done using XMT images alone. Now mineralogy can be associated with mineral liberation, grain size, grain shape, fracture, crack network creation, etc., all in 3D. Limitations of the methodology, however, are the result of limitations of both analytical devices. Critical ones are, having a large enough sample size in order to achieve statistically significant results, the resolution achieved by the XMT scan (heavily dependent on the particles size) and more minor consideration being possible mineral misclassification by the SEM/MLA scanner (Lee et al., 2011). Also, since only single energy level radiography is used, materials with similar attenuation coefficients will not be distinguishable from one another. For those materials, multiple energy radiography will be needed (Lin

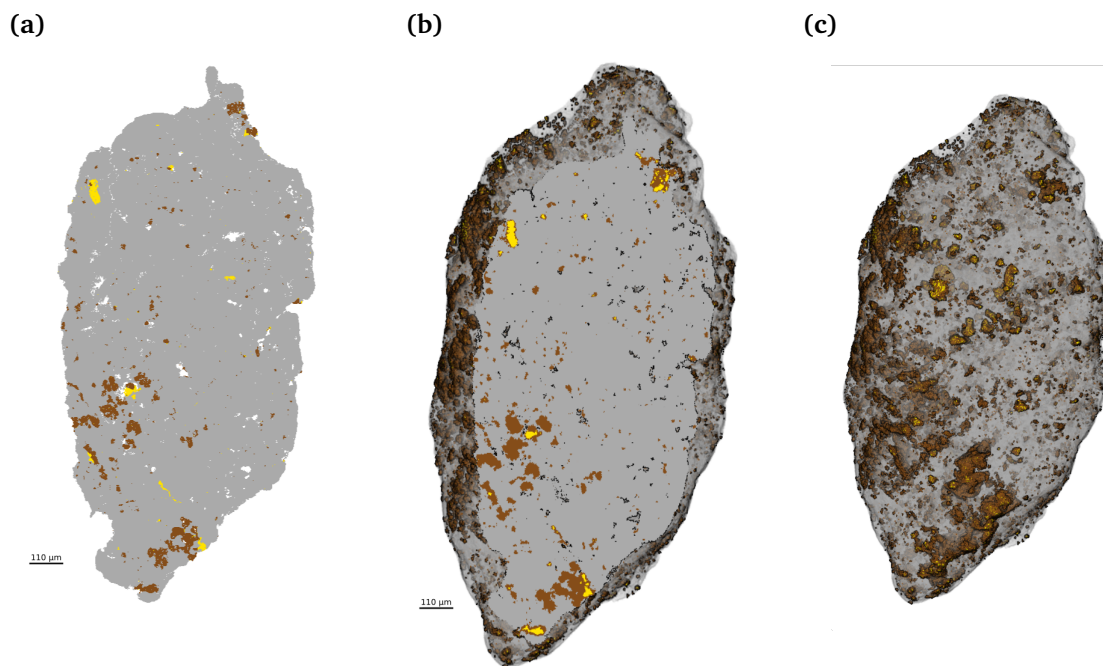


Figure 3.8: Resulting calibrated 3D mineral map. Applying the threshold found by Figure 3.7, a 3D mineral map distinguishing between gangue, porosity, pyrite and copper minerals is obtained. a) EDS based classification, b) same slice using the threshold found and c) the resulting 3D mineral map.

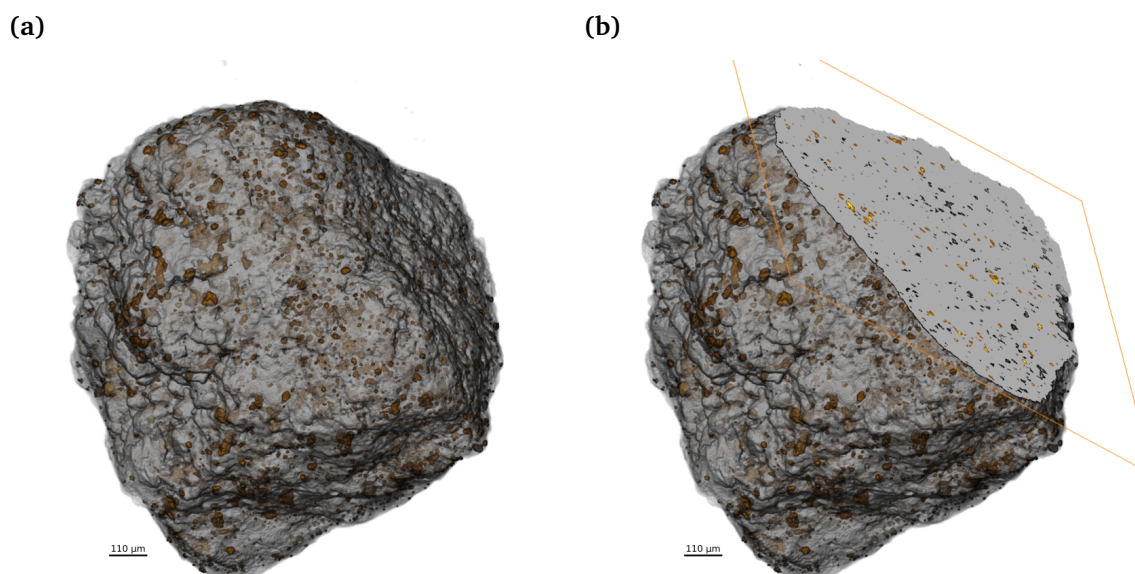


Figure 3.9: Resulting calibrated 3D mineral map and slice. Another example of the 3D mineral map obtained from SEM/EDS calibrated low energy XMT scans. a) rendered volume and b) virtual slice.

et al., 2013). Also, the methodology is bounded by the mineralogy presented by the SEM analysis and so it cannot distinguish between minerals that have not been identified in the SEM analysis. The combination of the XMT and SEM images does alleviate some of the sample size issues associated with using the latter method alone, especially with respect to grain scale information. This is because a slice through a fragment will only intersect a small fraction of the grains present, especially in systems such as the one examined in this

work where the grains are much smaller than the ore particles. By calibrating the XMT images, a far larger sample size of grains is available and thus less slicing of fragments is required. For instance, Table 3.4 shows the fractions of gangue, pyrite and copper minerals for the particles as obtained from the SEM analysis and compares them to the results obtained from the full volume using the calibrated XMT results.

Table 3.4: Mineralogy obtained from SEM and XMT. Proportion, by area or volume, of gangue, pyrite and copper minerals in the fragments scanned with low energy XMT. Differences show the statistical biased of SEM for a small sample size can be compensated with the 3D information given by XMT.

	SEM %	2D-XMT %	3D-XMT %
Gangue	95.47	95.69	96.74
Pyrite	3.07	3.17	2.49
Copper minerals	1.46	1.14	0.77

This shows that while the limited sample size exposed for the SEM analysis is useful for calibration and can provide an analysis for a far wider range of minerals, it can be misleading in terms of the actual particle scale variability, showing in this example an over representation of the presence of sulphide minerals (pyrite and copper minerals). This does not mean that XMT inherently provides a better analysis than MLA/SEM, but rather that by combining the two methods, the fragment scale compositional uncertainty associated with taking only a single slice through the fragment can be eliminated, which means that the combined methodology will inherently require the analysis of fewer fragments to achieve a statistically valid result than either of the methods on their own, due to the minimisation of the uncertainties associated with mineral misclassification in the XMT images and the limited number of grains intersected in a 2D section for the MLA/SEM. It is acknowledge that for a representative mineralogical study more than 34 sample need to be assessed to fully represent the variability of the ore under study, though the purpose of this work was to present a methodology and to study mineral grain scale effects, for which there is a statistically valid sample size (Evans and Napier-Munn, 2013; Lotter et al., 2018).

3.5.2 Grain size

After applying the tracking algorithm, only grains that appear in both modalities are considered, thus XMT is used in its 2D form. Using grains appearing in both modalities removes the bias created by the higher resolution achieved by SEM in comparison to XMT. For these grains, the grain size distribution by number is show in Figure 3.10a and by volume in Figure 3.10b. Grain's equivalent diameter is hereafter used as proxy for the actual mineral size and all size distributions are calculated by number unless stated otherwise.

XMT information is only obtained here from the virtual 2D slice and so no stereological effect is being assessed.

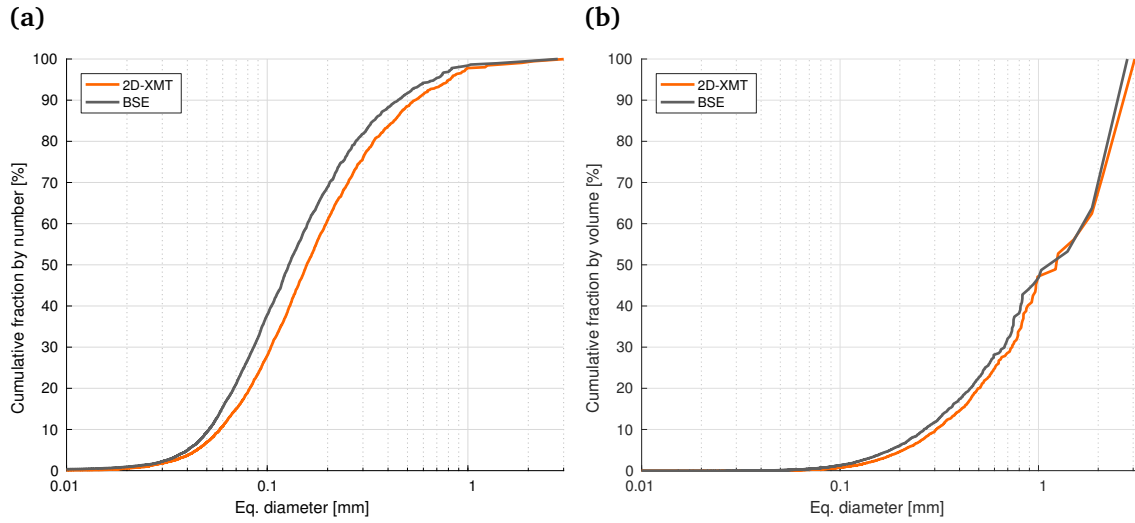


Figure 3.10: Grain size distribution of SEM slices and registered XMT slice after grain tracking. By considering only tracked grains, the effect of SEM detecting finer grains is removed, as only grains appearing in both modalities are considered.

It can be seen that in comparison to the 2D-XMT registered slice, SEM shows a grain size distribution with more fines, although this effect tends to disappear when considering the distribution by volume as fines contribute little to the total mass of the sample. As the linear XMT resolution is almost 8 times ($2.25\mu\text{m}$ compared to $16.1\mu\text{m}$) lower than in the SEM images, different effects start to have relevance like partial volume effects. Following what Lin et al. (2015) proposed for quantifying error in grain size and considering SEM as the true value for each grain size, we can study the error in XMT volume quantification. Figure 3.11a shows for each grain their size (equivalent circular diameter) given by the 2D registered slice in XMT and their size given by SEM. As expected, the error decreases with grain size. A linear fit to the data shows an intercept of $2.0\mu\text{m}$ and a slope of 0.79 ($R^2 = 0.92$), indicating the goodness of the fit. The intercept can be explained by the SEM resolution and a slope less than 1.0 indicates that XMT introduces a bias that makes grains appear to be bigger than they actually are. This mismatch can be adjusted by changing the threshold used to segment the sulphide grains from the non-sulphide gangue, though this would require adjustments away from that obtained using the Otsu algorithm.

Confidence limits of 95% can be used to estimate the precision of XMT when quantifying grain size. These bounds can be quantified by calculating the standard deviation of the relative error of XMT with respect to SEM. This means that the relative error in size ($\frac{\Delta A}{A}$) is calculated for each grain. Grains are then sorted by their size and the standard deviation of the relative error is calculated for sets of 150 grains, which is then plotted against the mean size of the sets. The resulting curve is shown in Figure 3.11b, showing that, for this particular case, grains larger than 0.5 mm in diameter present a random error

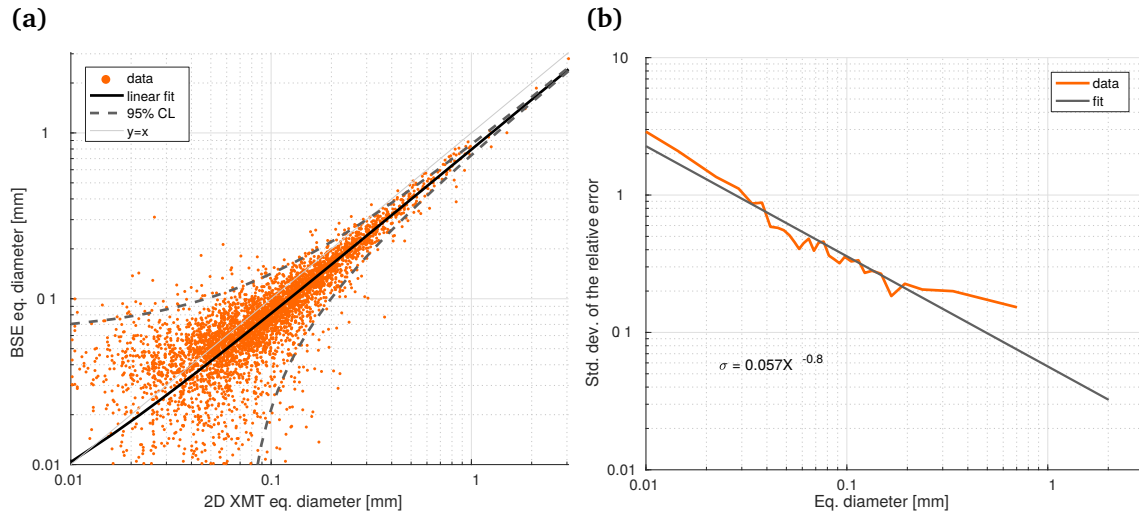


Figure 3.11: Assessing XMT error in grain size. After grain tracking, SEM grain segmentation can be used as a standard to assess XMT precision on measuring grain size. a) linear model fits the data with an R^2 of 0.918, a slope of 0.79 and an intercept of $2.0\mu\text{m}$. b) standard deviation of the relative error between SEM and XMT.

(uncertainty) of less than 10% in their quantified size at the given XMT resolution. The power law of -0.8 is to be expected, as it was shown in Lin et al. (2015) for the case of errors appearing in repeated scans of the same object. Lin et al. (2015) proposed that for a given grain volume V a small change in its boundary given by Δr will imply a fractional change in volume expressed by:

$$\frac{\Delta V}{V} \propto \frac{r^2 \Delta r}{r^3} = kV^{-1/3} \Delta r \quad (3.1)$$

where k is a dimensionless constant and the power law of $-1/3$ indicates an inversely proportional relationship with the grains radius. In the case of comparing the BSE and XTM slice to one another the analysis in the previous equation changes into its 2D form:

$$\frac{\Delta A}{A} \propto \frac{r \Delta r}{r^2} = kA^{-1/2} \Delta r \quad (3.2)$$

This suggest again an inverse proportionality between the fractional systematic error and the grains radius. The difference between the theoretical power law of -1 and the obtained -0.8 is due that the calculation of the standard deviation of the relative error corresponds to random and not systematic errors. But, similarly as was noted in Lin et al. (2015), the two errors can coincide in the power law that rules their effect. The final result of this procedure leads to the confidence bounds plotted in Figure 3.11a, allowing us to quantify the level of uncertainty when quantifying size using XMT without the need of an analytical phantom (Fernandes et al., 2016) or repeated scans (Lin et al., 2015).

3.5.3 Stereological bias

3D information on the tracked grains is also available for each of the grains present in both the XMT and SEM/EDS data. Table 3.5 shows the P20 and P80 obtained from the SEM assessment, the 2D registered XMT slice and the 3D XMT volume. Here the effect dominating the difference between the 2D and 3D data is the stereological effect. This effect makes the 2D grain size distribution, obtained from the slices, appear finer than the actual 3D size distribution as the slices will occur through random locations on the grains and not just at their full diameters.

Table 3.5: Grain size information obtained from the tracked grains. After tracking the higher resolution from SEM is corrected by only considering grains detected by both devices. The observed difference is mainly due to stereological effects.

	BSE	2D-XMT	3D-XMT
P20 μm	453.90	498.94	965.91
P80 μm	2283.21	2386.55	3777.99
Resolution $\mu\text{m}/\text{px}$	2.25	16.1	16.1

This effect has been studied before by performing the XMT imaging after the polishing of the fragments and without a grain tracking correction (Gay et al., 2006). This meant that only the average behaviour of the grains in the rest of the fragment and polished section were compared, rather than involving a comparison of exactly the same grains. In this study, XMT contains all the grain size information as polishing was done after scanning. Figure 3.12 shows the grain size distribution for the 2D-XMT and 3D-XMT versions of the tracked grains (left) and the cumulative distribution function of the stereological effect over the mineral grains. It is worth noting that, by using only XMT data (the 3D data and the virtual 2D slice through the data), the effect of higher resolution in SEM images, as well as the uncertainty in the grain size (Figure 3.11), is avoided and only the stereological effect remains as the source of difference.

Figure 3.13 shows the distribution of the size of 2D slices relative to the actual size of the 3D grains. The stereological effect for a number of other shapes are included for comparison (right; more shapes in Sahagian and Proussevitch (1998)). It can be seen that for the mineral grains, 90% appear smaller than they actually are and that their distribution differs significantly from that of the other shapes commonly used for these corrections (Gerlt et al., 2018). Also, size overestimation has a long tail, with grains appearing up to 3 times their actual size. As grain shape is ore and mineral specific, this relationship is key to the development of tailored stereological correction.

This information gives useful insight into the effect created by studying grain sizes based only on 2D images, and provides the necessary data for an ore-specific stereological correction for further studies with the same ore. Moreover, while a physical slice is

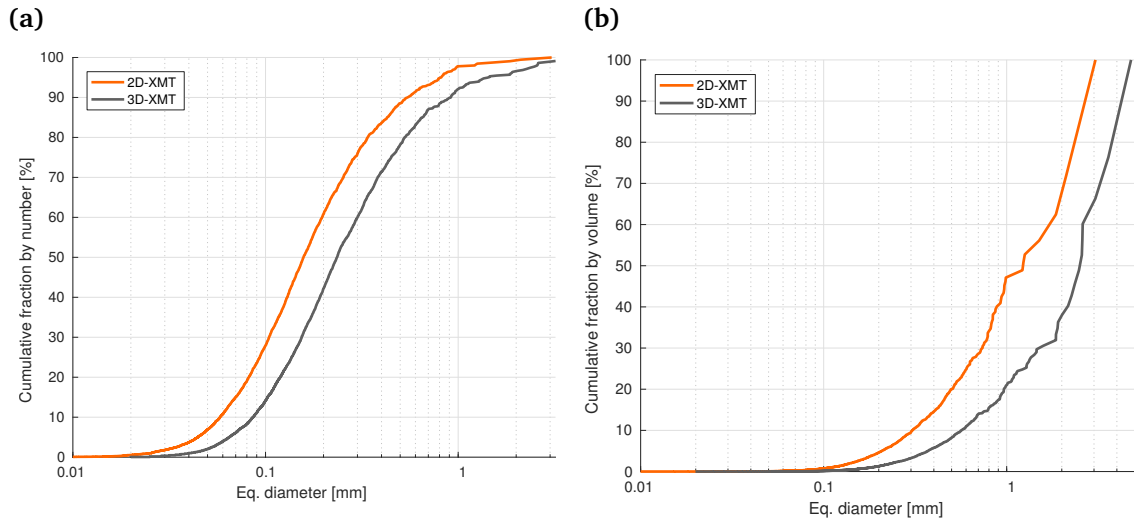


Figure 3.12: Stereological effect. Using the XMT 3D information of grain sizes, one can obtain the stereological effect of the 2D information given by the SEM slices. a) shows the grains size distribution of the 2D and 3D images, b) Same but by volume.

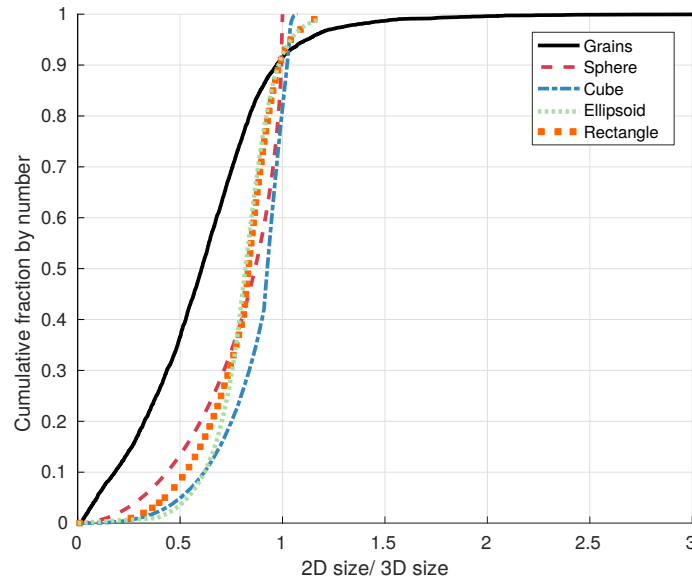


Figure 3.13: Cumulative probability distribution function of the error in size for the mineral grains and some convex shapes.

required to perform the SEM-based calibration, virtual 2D slices can be traced over the 3D data from XMT to provide a statistically robust stereological correction. Correction that consists in solving the inverse problem given by a variation of Equation 2.11 (Spencer and Sutherland, 2011):

$$F(s_a) = \int_0^S K(s_a|s_v) f(s_v) ds_v \quad (3.3)$$

where $F(s_a)$ correspond to the areal size cumulative distribution, $K(s_a|s_v)$ is the transformation kernel (see Figure 3.13) and $f(s_v)$ is the unknown volumetric size probability density function. In order to solve the inverse problem of finding $f(s_v)$ given $F(s_a)$ one must take an optimisation approach, as the problem is ill-posed (Fandrich et al., 1998;

King and Schneider, 1998). Equation 3.4 shows that the objective is to minimise the difference between the measurements and the model provided by the kernel $K(s_a|s_v)$ with

$$\begin{aligned} & \underset{f(s_v)}{\text{minimize}} \quad \|F(s_a) - \int K(s_a|s_v)f(s_v)ds_v\| \\ & \text{subject to} \quad f(s_v) \geq 0, \forall s_v. \end{aligned} \quad (3.4)$$

The above problem must be discretised in order to be solved numerically, and thus the integral becomes a matrix multiplication of the discrete versions of $f(s_v)$ and $K(s_a|s_v)$. Also, in order for the solution to achieve the smoothness expected for a distribution regularisation terms are added (King and Schneider, 1998). The resulting problem is then:

$$\begin{aligned} & \underset{f_v}{\text{minimize}} \quad \|F_a - K f_v\| + \lambda \sum_i f_v^i \ln f_v^i \\ & \text{subject to} \quad f_v^i \geq 0, \forall i. \end{aligned} \quad (3.5)$$

Figure 3.14 shows the correction of a BSE slice using Equation 3.5. For this case, 20 size classes were used and the ranges of the classes were chosen so the 3D distribution is evenly split. Discrepancies in the mid-sized grains can be observed, but good agreement between typical indicators, such as P20 and P80, can be observed.

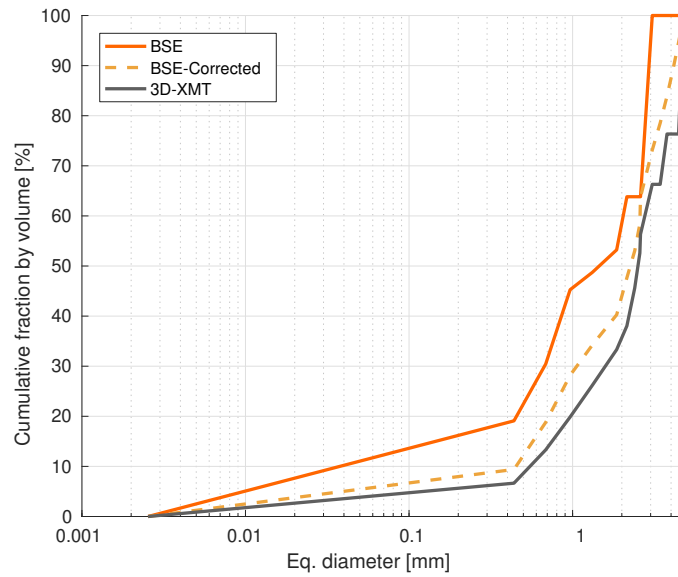


Figure 3.14: Stereological correction of area grade using an ore-specific kernel obtained from XMT scans.

The values of the P20 and P80 of the original and corrected BSE analysis along the actual 3D size is summarised in Table 3.6. Similar to what it can be observed in Figure 3.14, the correction tends to correct better the distributions in the coarser section.

In practice this correction can be used by scanning the same sample that is going to be assessed via SEM/EDS, in that manner a tailored 2D-to-3D correction can be obtained for the sample. In case the sample has already been mounted in resin for SEM/EDS analysis,

Table 3.6: Results of the stereological correction of BSE images using the transformation kernel found by combining XMT with SEM.

	3D-XMT	BSE	BSE Corrected
P20 μm	965.91	453.90	720.87
P80 μm	3777.98	2283.21	3526.75

the methodology can still be used, although at expenses of more XMT scans, via scanning the mounts one by one. This allows for also a tailored correction.

3.6 Conclusions

Although being highly complementary, SEM/EDS and XMT analyses are rarely combined, but rather used separately as tools for quantifying different features of the ore. A methodology for combining XMT and SEM images so that more detailed mineral information can be obtained from the 3D XMT images has been presented. The methodology uses a tracking algorithm that matches both imaging modalities at the mineral grain level. Tested in copper sulphide ores, the methodology allows the acquisition of a 3D segmented images of ore fragments where copper minerals, pyrite, gangue and porosity are differentiated. Segmentation thresholds are calibrated using the SEM automatic mineral classification, whilst the XMT grain size quantification error is also evaluated. SEM 2D image-based grain size distributions can also be corrected for stereological effects using the 3D information of the grains in the XMT volume. The importance and novelty of the proposed stereological correction resides in the fact that it is tailored to the ore under study. This ore-specific correction does not need to make assumptions on the shape of the grains or particles in order to construct the transformation kernel and makes possible a more precise correction without the need of sectioning a large number of particles, reducing thus costs and time.

The proposed methodology differs from previous work with XMT and SEM in the way in which data from both devices is combined so that information from one can be transferred to the other at the level of the individual grains rather than at an averaged macroscopic level. This novel approach allows the confidence limits and uncertainty in both the mineral classification and grain scale quantification to be assessed. Applications of this methodology are presented in Chapter 4 for assessing leach kinetics and in Chapter 5 for quantifying mineral liberation and surface exposure.

Possible limitations of the methodology are the presence of minerals with similar X-ray attenuation coefficients, making them harder to be segmented only using a low energy scan. For cases like these, a dual energy, or even multi-energy, radiography technique might be necessary. The use of a combination of multiple energy XMT scans and SEM information is thus the logical progression of this work.

Chapter 4

Assessing and quantifying leach kinetics

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4.1 Introduction

Chapter 2 stressed the fact that minerals processing is facing the challenge of having to deal with ever decreasing mineral grade. And although technological developments, such as froth flotation at the beginning of the 20th century have allowed for the treatment of some of these low-grade ores, some ores are still regarded as uneconomic (Wills and Napier-Munn, 2005). Heap leaching has positioned itself as the key for making economically viable the processing of such low-grade ores (Petersen, 2016). It benefits from having comparatively lower capital and operational costs compared to traditional processing that requires milling (Dhawan et al., 2012a). However, even after decades of development since it started working at industrial scale, heap leaching continues to suffer from limitations such as low recoveries and long extraction times (Ghorbani et al., 2016). Final recoveries can vary from 30% for harder to leach sulphides to almost 90% for easier oxides in operations that extend from a couple of month to more than a year (McBride et al., 2012a). This mineralogy-dependant performance added to time and space requirements are the main drawbacks of heap leaching.

Modelling and simulation have been widely used as design and prediction tools to overcome these drawbacks. Usually, complex phenomenological or empirical models based on first principles are used to accurately capture the process behaviour and make predictions in order to address design and/or operational issues (Gálvez et al., 2012). The main challenge when modelling heap leaching is capturing the massive range of length scales, from the chemical reactions occurring at the grain scale to the operational variability at the heap scale. Chemical reactions occur at the scale of microns whilst heaps can easily have millions of tones of ore in heaps that reach kilometres in length and tens of meters high. For more than 30 years the approach in the literature to address this challenge is to make strong assumptions and simplifications of the processes happening at the grain and particle scale. However, these assumptions have often proven to be unrealistic and misleading in terms of understanding the processes happening at this scale (Ferrier et al., 2016; Taylor et al., 1983).

In this thesis we will focus on the processes occurring at the particle scale, where reactants from the surrounding fluid need to be transported through the rock's internal porosity towards the mineral surface and dissolved metal species need to be transported out. By using X-ray micro-tomographic images of actual rocks, information such as internal porosity, existence of fractures, grain distance to the surface and size of grains can be used as an input to simulation models. Based on what was originally proposed by Lin (2015) several of the assumptions made in the models typically used to predict behaviour at this scale can be lifted. These assumptions range from assuming specific sizes and shapes for the grains to assuming that certain processes happen at a much faster rate

than others so that a quasi-steady-state regime can be used. In Chapter 3, Figure 3.13, we demonstrated that analytical shapes and sizes for grains is unrealistic with regards of the representation of the ore's texture as their shape kernel deviates considerably from the one exhibit by the grains. The limitations of validity for a quasi-steady-state simulation will be cover in Section 4.7.1. An extension of the methodology proposed by Lin (2015) is covered in this Chapter, where using the methodology of combining XMT and SEM/EDS introduced in Chapter 3 allowed us to account for the effects of mineralogy on the leach kinetics. An updated and improved simulation environment is introduced in Section 4.6 so that the assumption of quasi-steady-state can be lifted and tested against a fully dynamic simulation. This simulator dynamically models the chemical reactions of different minerals and leaching reagents, achieving higher prediction performance than the original version in Lin et al. (2015).

This chapter continues as follows, first an introduction to heap leaching and its current challenges is given, later the experimental setup is described in detail and followed by the presentation of an improved methodology for quantifying leach kinetics. This is followed by the description and formulation of a leaching simulation model at the particle scale. The chapter ends with conclusions and future work in this area.

4.2 Hydrometallurgy and heap leaching

4.2.1 The hydrometallurgical extractive path

Hydrometallurgy has gained momentum in the mining industry over the last few years mainly because of its capacity to process low grade ores in a more cost-effective way compared to other extractive methods such as concentration (Habashi, 2005; Petersen, 2016). This more competitive approach is due mainly to the use of heap leaching to extract the minerals from the ore (Ghorbani et al., 2016) and the possibility to avoid energy intensive processes like milling. Heap leaching typically uses a much larger particle size, with a P80 in the range of 12–25 mm compared to the 50 to 90 μm required for liberation plus concentration. As depicted in Figure 4.1, hydrometallurgy differs from traditional extractive methods after the primary crusher, a concentration circuit is shown faded alongside. In heap leaching after primary crushing, the ore goes to a second and third stage of crushing, then to an agglomeration drum where the fines created in the previous stages are attached to the coarse particles to facilitate percolation in the following stage, while simultaneously ensuring liberation. The agglomerates are then stacked in heaps that are irrigated with an acid solution (raffinate) on the top. The leaching solution reacts with the minerals so they can be transferred from the grain (solid state) into solution (liquid state). Finally, drained liquid from the heaps, known as the pregnant leach solution

(PLS), is collected and sent to the solvents extraction unit, where the metal of interest is striped from the acid solution. The recovered acid solution goes back to irrigate the heaps, creating a closed circuit. Striped metal is afterwards electro-won as meal sheets. This is an additional advantage of heap leaching as mines not large enough to justify the construction of a smelter can sell metal rather than lower value concentrates.

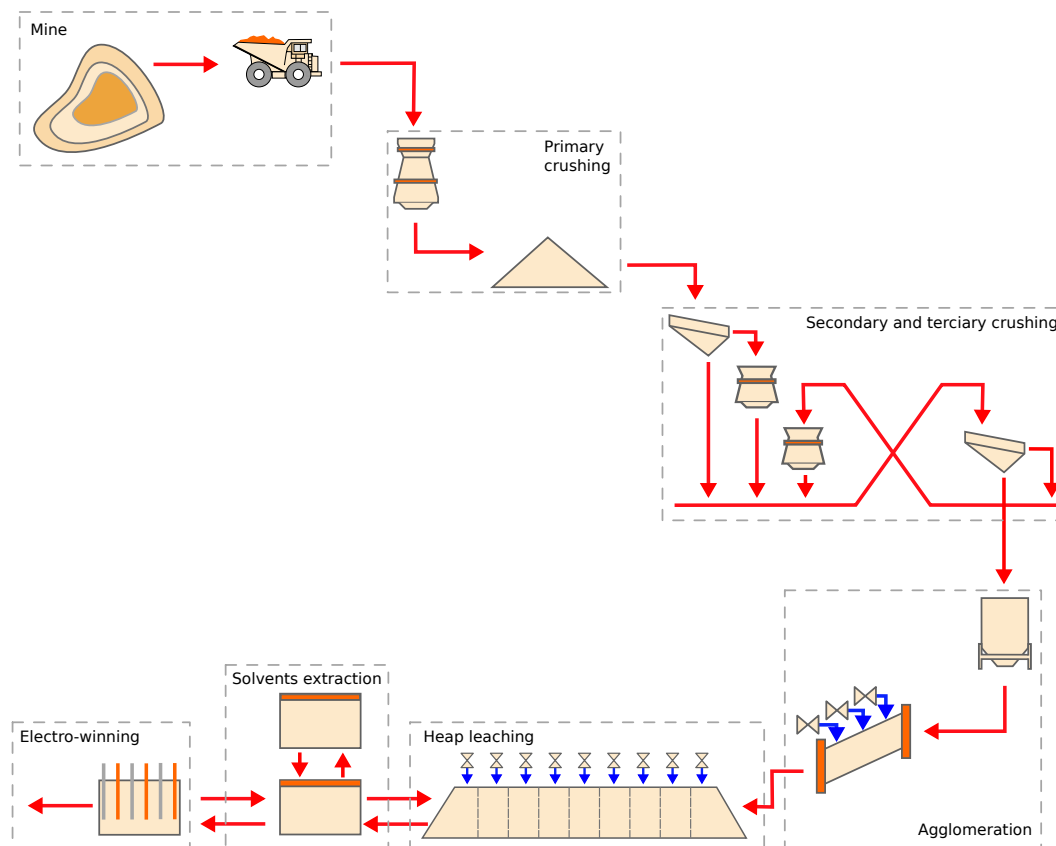


Figure 4.1: Flowsheet of a typical hydrometallurgical extraction circuit. Heap leaching is one of the key process involved, being the one that transfers the metal from the solid phase (ore) to the liquid phase (leaching solution).

Alternative leaching circuits can be used depending on the characteristics of the deposit. For example, dump leaching can be used for a low-cost operation with uncrushed ore (Run of Mine), where grades are not high enough to justify the additional crushing and agglomeration stages (Domic, 2001). Other hydrometallurgical paths use other percolation methods, like vat leaching or a milled stage followed by tank leaching for high-grade oxides. Heap leaching, though, remains the main hydrometallurgical method due to its simplicity and low capital costs (Ghorbani et al., 2016). Operation will also vary according to the mineralogy of the ore. For example, sulphide minerals require the action of bio-catalysts (bacteria) in order to accelerate the leaching process; a factor that is not present when treating oxides as that leaching is purely chemical (Jafari et al., 2018; Richter et al., 2018).

4.2.2 Heap leaching operation and fundamentals

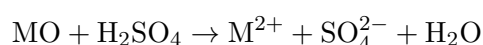
Heaps tend to be several hundreds of metres in horizontal extent and tens of meters high, but have key processes occurring at the particle and smaller scales. This multidimensionality presents a challenge in terms of modelling, simulation, operation and control. Table 4.1 shows some of the factors that affect heap leaching performance, gathered from Bennett et al. (2012) and Brandl (2008).

Table 4.1: Factors affecting heap leaching performance. From Brandl (2008).

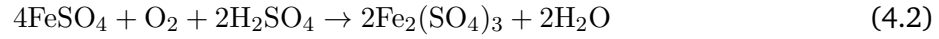
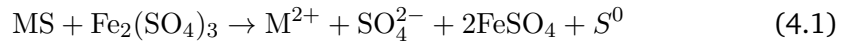
Factors	Parameters
Physicochemical parameters	Temperature, pH, redox potential, water potential, oxygen content and availability, carbon dioxide content, mass transfer nutrient availability, ferric ion concentration, light, pressure, surface tension, presence of inhibitors.
Microbiological parameters	Microbial diversity, population density, microbial activities, spatial distribution of micro-organisms, metal tolerance, adaptation abilities of micro-organisms.
Processing	Type of operation, pulp density, stirring rate (in case of tank leaching operations), heap geometry (in case of heap leaching), permeability, irrigation technology and pattern.
Properties of the minerals	Mineral type, mineral composition, mineral dissemination, grain size, surface area, porosity, hydrophobicity, galvanic interactions, formation of secondary minerals, porosity, gangue mineral.

Chemistry of heap leaching

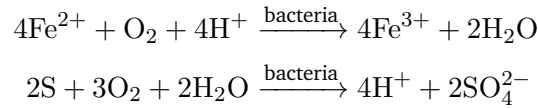
The chemical reactions involved vary with the ore being treated and the leaching solution used. Oxide minerals are the easiest to process as their leaching is purely chemical (Karthi, 2011). A generic reaction for a metallic oxide mineral (MO) is given below (Habashi, 1993), where it can be seen that sulphuric acid is used to dissolve it.



However convenient and fast-leaching oxide minerals are not of the highest interest as their abundance is much lower than that of sulphide minerals (Hernández et al., 2018). Leaching of sulphide minerals is more complex, requiring more steps as shown below:



During sulphide leaching the re-oxidation of Fe^{2+} into Fe^{3+} (Equation 4.2) can happen if enough oxygen is available, however its kinetics are very slow and need to be catalysed (Rossi, 1990). In an industrial operation re-oxidation of iron is desirable as it reduces the cost of needing to inject vast amounts of fresh Fe^{3+} in the feed solution so leaching does not enter into a reaction limited regime. Bacteria (ferrous-oxidising bacteria) can be used to catalysed such re-oxidation in a process known as bioleaching as, for primary sulphides, there is virtually no leaching without bio-activity (Richter et al., 2018). Other bacteria (sulphur oxidising bacteria) can help recover some of the acid being consumed. Bio-catalysed reactions are then as follows:



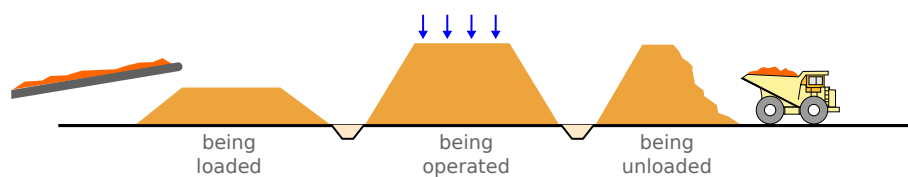
These reactions can be complemented with others originated from non-precious metals present in the ore, like in the case for the chalcopyrite–pyrite system (Nikoloski and O'Malley, 2018). Chalcopyrite is the commonest copper bearing mineral in the world and it is normally accompanied by pyrite (FeS_2) (Domic, 2001; Wills and Napier-Munn, 2005). Depending on the chemical conditions (pH, Eh and temperature) pyrite can be beneficial for the recovery of chalcopyrite, as it can act as an anode that allows for the oxidisation of the valuable mineral (Khoshkhoo et al., 2017). This thesis will concentrate in the case of sulphide minerals (specifically in the chalcopyrite–pyrite system) as it has more complexity and worse performance than oxide leaching, thus requiring better understanding.

Types of operation

Depending on the mineralogy, grade of the ore and free space available, heaps can be operated in two different ways, shown schematically in Figure 4.2. When mineralogy allows for shorter leaching times or there are space constraints on the size of the footprint heaps can occupy, then On/Off heaps are the choice. These heaps are continuously being loaded and unloaded, so that the footprint remains constant, but the valuable metal content still existing in the heaps is lost as waste when they are unloaded. The opposite case, slow leaching ores and when space is not a constraint, allows for continuous operation

of heaps, where instead of unloading the previous heap to make space, the new heap is loaded on top of the existing one.

On/Off Operation



Continuous Operation

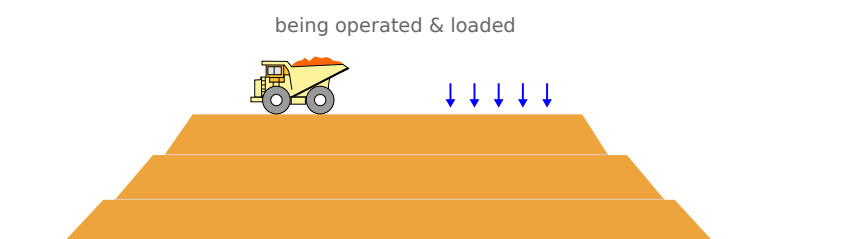


Figure 4.2: Types of heap leaching operations. Depending on space constraints and mineralogy heaps can be operated in two ways. Adapted from Lupo (2010).

4.2.3 Scales in heap leaching

Heap leaching can be seen as a transfer process in a multi-phase porous media where the metal is transported from the solid phase (mineral) to a liquid phase (leaching solution). Chemical reactions of the leaching reagent and the mineral grains occur at the micro scale (Figure 4.3d), whilst diffusion of the reagents and leachate happens at the particle scale (Figure 4.3c). Moreover, the chemical conditions experienced by each particle is a result of the meso scale process of fluid flow in the inter-particle porous media (Figure 4.3b) and ultimately the behaviour of the whole heap, or macro scale, is the result of the aggregate of all the particles been stacked (Figure 4.3a). This results in a multi-scale process with important phenomena occurring over scales of about nine orders of magnitude, going from microns to kilometres.

At the macro scale, the main processes are the transfer of mass and heat throughout the heap, but going down to the meso scale it is a combination of the inter and intra particle hydrodynamics together with reaction surface kinetics that governs the leach kinetics. It is normally at this scale that most experiments are carried out, using columns of various diameters (Petersen and Dixon, 2007). Down to the ore particle scale the main driver is the ore's texture (mineralogy and spatial distribution of grains and pores). These properties will ultimately define the grains' accessibility to the leaching solution (Rossi, 1990). And finally, at the micro scale temperature and the chemical reactions are the factors that influence leaching performance (Ghorbani et al., 2011a). This project focuses

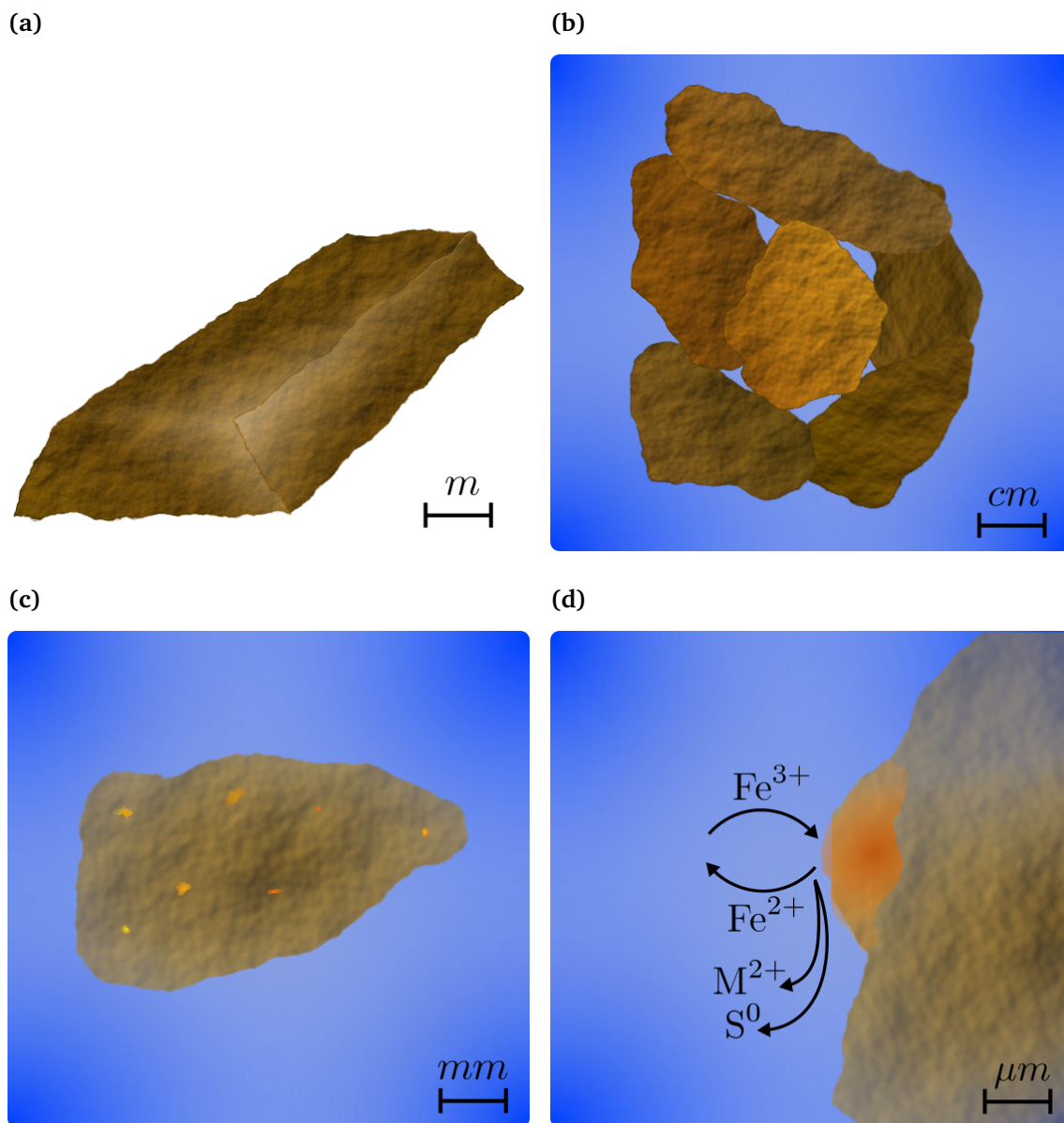


Figure 4.3: Spatial scales in heap leaching. a) Macro or operational scale: heaps can have hundreds of meters in extension, b) Meso scale: A group of particles create a porous media where the reagent flows, c) Particle scale: variabilities in their textural related properties play an important role, d) Micro scale: scale at which the chemical reactions occur, the dissolved mineral needs to be later transported out of the particle's matrix.

on the scales defined by single particles and a collection of them using packed particles in columns. These particles and the factors which influence leaching kinetics are investigated using XMT and simulation models.

4.2.4 The particle scale and its effect on the heap scale operation

Along with the complex set of chemical reaction happening at the grain scale, heap leaching also has important mass transfer phenomena that occurs at the particle scale. The metal already transferred into solution has to be transported from the internal porosity

of the rock towards the solution present in the porous media created by a group of particles (see Figure 4.3b-c). The importance of characterising particles being leached has been made apparent by Dhawan et al. (2012b). The authors summarised in their work the effects that particle size distribution has on heap leaching (see Figure 4.4). The wide spectrum of influences that a particle's size has on leaching makes an agglomeration stage necessary in most operations (Velarde, 2005). In which the fine particles are bound to larger particles, hence helping percolation within the heap not necessarily at the expense of surface exposure (Dhawan et al., 2013).

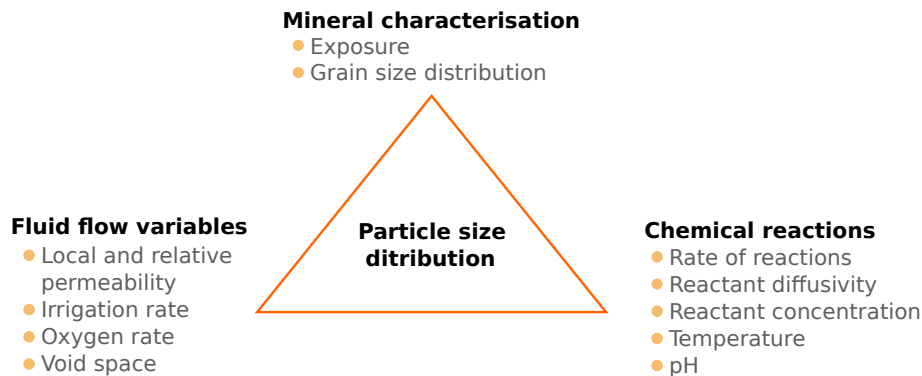


Figure 4.4: Effects of particles on variables involved in heap leaching performance, adapted from Dhawan et al. (2012b).

Although Dhawan et al. (2012b) focussed their study on the particle size distribution (PSD), many of the effects listed by the authors are also influenced by other particle properties, such as texture, mineralogy, extent of surface exposure, and others. The particle's texture and porosity plays a significant role in making the mineral grains accessible to the leaching solution. As it is not the objective to dissolve gangue minerals, the leaching solution needs to come into contact with minerals through the unreacted matrix via pores and fractures (Rossi, 1990). High pressure grinding rolls (Baum and Ausburn, 2011; Ghorbani et al., 2013, 2016) and microwave assisted technologies (Al-Harashsheh and Kingman, 2004; Al-Harashsheh et al., 2005) are two existing solutions to achieve better mineral exposure through enhanced micro fracturing.

The particle scale is also important as is at this scale that simulation models make use of apparent leach kinetics (Deng et al., 2015; van Hille et al., 2010). Apparent leach kinetics relate the concentration distributions at the meso-scale with the leaching rates. With these apparent kinetics depending on a combination of the inter-particle mass transport phenomena and the reaction kinetics occurring at the grains' surface (Dimitrijevic et al., 1996; Sun et al., 2015).

4.2.5 Heap leaching modelling

Simulating heap leaching has been a challenge since its early days, with authors applying different approaches and assumptions in order to overcome the hurdles. However, the objectives and roles of simulation have always been the same: assist the design, operational control and understanding of the processes and interactions occurring within the heap (Groznov, 2015).

To date several efforts have been made to model and simulate heap leaching processes. The first steps were taken during the late 70's, with the development of the Shrinking Core Model (SCM) presented by Levenspiel (1972) and the modelling of the mass transport of solutes in porous media by Bear (1988). Relying on these Dixon and Hendrix (1993) introduced one of the first heap models, assuming the heap to be a 1D plug-flow reactor where all the parameters are constant throughout the leaching cycle and particles are assumed spherical and mono-sized. A dimensionless description of the model allowed for sensitivity analysis to be carried out for scale-up parameter as well as the analysis of various leaching rate regimes.

With the introduction of Computational Fluid Dynamics (CFD) more complex multi-phase transport and fluid flow models of full scale 3D heaps became available (e.g. Bennett et al. (2012); McBride et al. (2018). McBride et al. (2012b) used a CFD simulation framework to integrate chemical reactions at the micro scale into the macro scale models and validated their results using data from a mining site. To model the heap, a multi-scale approach was used, where the micro-scale of grain dissolution was carried out using the SCM to calculate the reagent consumption and the mineral extracted. These calculations were used in a meso-scale 1D column model that simulates the fluid flow and mass transport equations. Finally, a set of 1D column models were grouped independently in modules to create what the author calls a 'process' heap model (McBride et al., 2012a). An updated and more comprehensive version of the proposed models can be found in McBride et al. (2018), where a 3D multi-species system is proposed. The problem with these comprehensive 3D models is that they are computationally expensive. All these macro/meso scale models still require of a model for the effective kinetics that result from the interaction of mass transport and surface rate kinetics occurring at the particle scale. The so called Shrinking Core Model is the most used approach as it provides a simplified version of these interactions (Cai et al., 2014).

This approach, although it has varied since first introduced, still assumes that each ore particle, supposed to be spherical, consists of an unreacted core that shrinks over time at rates that depend on the chemical conditions and diffusion processes (Bartlett, 1998; Liddell, 2005; MacQuarrie and Mayer, 2005). Figure 4.5 shows a schematic of the SCM, where it can be seen that there is a sharp boundary between the solid reactant and the

reagent (Reaction zone); the reagent has to diffuse through the 'ash' layer created by dissolved reactant (Levenspiel, 1972; Yagi and Kunii, 1955).

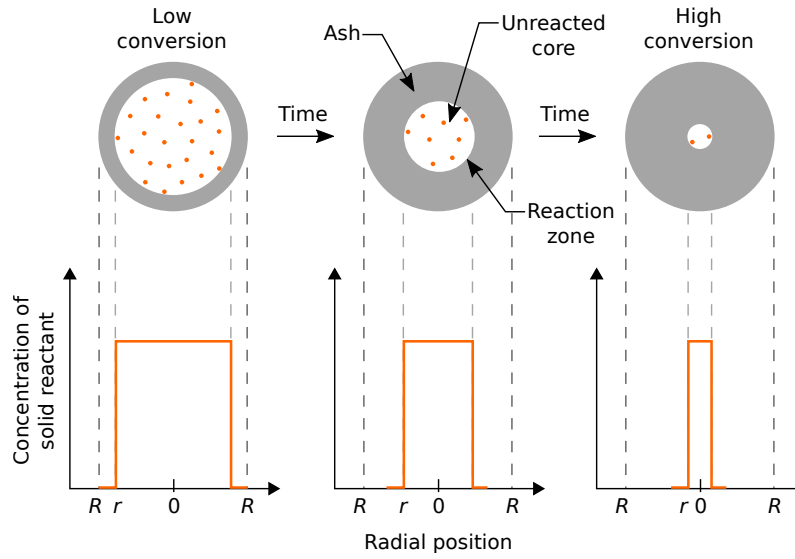


Figure 4.5: Shrinking Core Model representation, an unreacted core reacts with a front of reagent at a sharp boundary. Adapted from Levenspiel (1999).

The original SCM's assumptions translate into the following partial differential equation describing the evolution of concentration in the unreacted zone (Levenspiel, 1972; Yagi and Kunii, 1955):

$$\frac{\partial C}{\partial t} = \frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left(\xi^2 \frac{\partial C}{\partial \xi} \right), \quad (4.3)$$

where C is the concentration of reagent in the media, ξ is the dimensionless radius of the particle being leached (i.e. the radius of the particle divided by its initial radius). This equation can be, which is often the case, further simplified by neglecting the accumulation term $\partial C / \partial t$. For systems described by $aA_{liquid} + bB_{solid} \rightarrow products$, this can be done if the dimensionless group γ is less than 0.1 (Liddell, 2005; Taylor et al., 1983). This ratio is defined as:

$$\gamma = \frac{aC_a}{bC_b}, \quad (4.4)$$

where C_a and C_b are the molar concentration of the reagent and reactant, respectively. The partial differential equation becomes then an ordinary differential equation which form will depend on the assumptions regarding the surface rate kinetics (linear or non-linear) and the mass transport in the ash layer. SCM has evolved into more complicated formulations that allow for different leaching regimes to be modelled. Some models consider a polydispersed particle size (Li et al., 2015) or a reactant concentration profile that changes linearly in the ash layer (Velardo et al., 2002). Klauber (2008) and Naderi et al. (2011), after observing SEM images of leached particles proposed an SCM model

with 4-stages, that allowed for modelling the formation of a layer of S^0 around the particles, a known process that slows down the leach kinetics. A list of assumptions commonly found are in the Shrinking Core Models are:

1. Grains are spherical with a uniform size and distribution.
2. Reactive grains are evenly distributed throughout the particle.
3. Diffusivity and all other parameters are constant and uniform throughout the particle.
4. Accumulation terms are negligible compared to mass transport, so that a quasi-steady-state assumption can be made. There is a dimensionless group (Equation 4.4) to quantify this.
5. Grains consist of a single mineral type and react with only one reagent
6. Reactions are irreversible and first order in terms of the concentration of the reagent.

As pointed out by Ghorbani et al. (2011a) and made apparent with the recent use of XMT (Dhawan et al., 2012b), the first three assumptions rarely occur in real ore particles. Liddell (2005) presented an assessment of the applicability of the quasi-steady-state (QSS) assumption, noting that the early work of Levenspiel (1972) only focused on gas-solid reactions and that several papers had questioned the validity of this assumption in a heap leaching process. In more recent years Gbor and Jia (2004) extended this assessment by studying the effect of particle size distribution on the QSS assumption. The authors found that, depending on the coefficient of variation of the PSD, the Shrinking Core Model can lead to misinterpretations. As an example, they found that diffusion controlled regimes can also be interpreted as either reaction controlled or inner ash diffusion controlled regimes if mono-sized particles are assumed. Thus, the threshold proposed by Taylor et al. (1983) for γ might need to be revised, especially when relaxing some of the assumptions made in the simulations. Ferrier et al. (2016) compared three different versions of the Shrinking Core Models with experimental data so that the range of validity could be studied. The authors found that when leaching is in an intermediate regime (not reaction-controlled nor diffusion-controlled) the surface kinetics can be assumed to be linear without losing accuracy. However, in heap leaching, many reactions are not first-order so non-linear surface kinetics must be used (Kimball et al., 2010; Naderi et al., 2011; Williamson and Rimstidt, 1994).

The focus of this thesis is to access internal information about particles porosity and grain's mineralogy, size, shape and location in order to better inform models that allows for the relaxing of the set of assumptions generally made at this simulation scale. The information will be obtained using XMT scans with a modify version of the methodology proposed by Lin (2015) used to analyse the images, methodology described later on in

Section 4.4.

4.3 XMT applications in heap leaching

XMT has been successfully used to assess mineral grain's size distribution in 3D, to estimate the fraction of grains exposed to the surface of the particle (Miller et al., 2003; Reyes et al., 2018), mineral dissemination and leaching extent (Kodali et al., 2011; Yang et al., 2017) and, by using the correlation between the intensity in X-ray images and the density of the material, to estimate the mineralogy of the ore sample without destroying it (Reyes et al., 2017; Videla et al., 2007). Figure 4.6 shows the rendering of an ore particle scanned using XMT, the gangue minerals appearing grey and the sulphide mineral grains have been rendered orange.

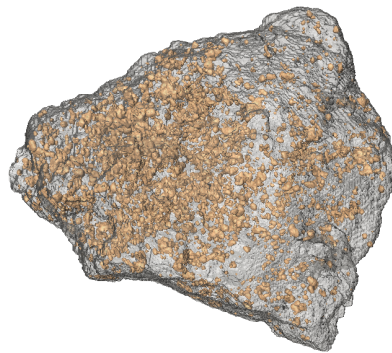


Figure 4.6: Reconstructed rock scan from X-ray micro-tomography scan. In transparent grey the rock and its internal porosity is shown along with the detected copper grains.

The benefits of XMT are not only in its capacity to delineate and visualise the internal structure of particles, but to also extract quantitative information, information that can be used to assess the outcome of several processes and their effect on the ultimate recovery or leach kinetics. Parra et al. (2015) used XMT to analyse the effect of blasting conditioning and fracturing on the leaching performance, showing the resulting effect to be less significant than the intrinsic variability observed in the leaching system. Other examples of internal porosity analysis can be found in Dhawan et al. (2012b), Yang et al. (2008) and Ghorbani et al. (2011b).

Dobson et al. (2017) introduced an experimental setup that allowed them to quantify mineral dissolution in-situ. The experimental setup was based on scanning the leaching columns throughout their leaching cycle so that changes in the volume of the mineral phase could be tracked. The dissolution was, though, only an aggregated result of the change in volume of all the particles in the field-of-view. Based on work by Dobson et al. (2017), Lin (2015) proposed a new methodology that allowed the authors to track the individual mineral grains and thus created a database of the rate of change of the size of the

mineral grains being leached as a function of both their size and position within the particles. The authors showed that measuring the leach rate over the initial leach period can be used to accurately predict the long term leach behaviour, thus potentially significantly reducing the time required to assess leach performance. Similar work has been carried out for studying the influence of spatial distribution of the ore particles and mineral grains (Fagan-Endres et al., 2017) and to assess leaching of agglomerates (Hoummady et al., 2017, 2018).

Also, XMT can be used as a tool to feed simulation environments, as the internal structure of the ore particles is readily obtained. Lin et al. (2016a) studied the leach kinetics of particles and used the measurements to calibrate a quasi-steady-state particle-scale simulator that used the same XMT scans of the particles as the simulation domain. Miao et al. (2017), on the other hand, focused more into the hydrodynamics using XMT 3D images to access the pore structure of a pack of particles, creating a dual-pore network comprised of the intra-particle pores (micro) and inter-particles pores (macro). Results showed the necessity of using dual-pore systems to capture the heterogeneity of the fluid flow within a leaching system and the importance of the model used for apparent leach kinetics that will link the effects happening at the micro scale with the ones at the meso and macro scale.

A limitation of the previous analysis though, is that although shape and chemical conditions have been accounted for in the assessment of the variability of the leach kinetics, the effect of mineralogy was not assessed. Our aim is to extend the analysis and methodology so that the effects of mineralogy on leach kinetics can be incorporated into the analysis. The focus of this project is to study leaching kinetics at the particle scale of a two specie system using a combination of XMT, SEM/EDS and an in-house dynamic simulation environment. The simulator uses the 3D XMT image of a particle as its domain so the particle's spatial and textural properties are readily available. A combination of 3D XMT images of the leaching column over its leach cycle and SEM/EDS analysis provides information about the variability of leach kinetics of each mineral specie; segmentation calibrated with SEM/EDS images using the technique described in Chapter 3. In this way, the assumptions stated in Section 4.2.5 are relaxed and a more comprehensive analysis of apparent leach kinetics is performed.

4.4 Experimental setup

The experiments involved the column leaching of ore samples from Kennecott Copper's Bingham Canyon mine (Rio Tinto, 2009). Leaching was carried out in 28 mm diameter and 190 mm height columns using 0.1M H_2SO_4 with $5 \text{ g L}^{-1} \text{ Fe}^{3+}$ (ferric sulphate) as the

leaching solution. Periodically over the course of 43 days of leaching, XMT images of the columns were obtained, along with chemical measurements. Individual rocks were segmented from the images and registered to the corresponding initial scan. Using image processing techniques the acquired raw data was later classified into three different classes: rock, pores and grains. The grain volumes were tracked over the different scans so that the change in volume could be used as a proxy for their recovery. Otsu and maximum entropy thresholding algorithms were applied to segment the rock from the air and the grains from the rock, as shown in Lin (2015). The mineral grains were individually tracked in order to study the leach rate dependencies on grain size and location within the ore particle.

The ore used in the experiments consisted of crushed ore particles, with a P80 of 10.44 mm, size normally found in heap leaching operations. The mineralogy of the ore, as obtained by the Mineral Liberation Analysis (see Table 4.2), revealed a copper grade of 0.8 wt% mainly in the form of chalcopyrite. The main non-valuable mineral species are pyrite and a quartz gangue matrix; for a more detailed composition please refer to Table 3.1. All these values are consistent with previous measurements using the same ore batch (Ilankoon and Neethling, 2013; Lin, 2015).

Table 4.2: Main mineral composition of the ore sample. Main minerals are primary copper sulphides, pyrite and a gangue consisting of mainly quartz.

Mineral type	Weight %	Specific gravity
Copper containing species	2.13 ± 0.47	~ 4.37
Pyrite	7.00 ± 2.74	4.95
Gangue minerals	90.69 ± 2.73	~ 2.70

Approximately 132 g of ore material was tightly packed in each column, as depicted in Figure 4.7a. Columns were operated in a controlled environment applying a constant fresh feed of leaching solution containing 0.1M H_2SO_4 (resulting in a pH of 1.1) and the leachate was not recycled (see Figure 4.7b). While the leaching is exothermic, the large specific surface area of the columns mean that typical internal heap temperatures cannot be maintained without additional heating. The columns were thus housed in an insulated incubator which was kept at a temperature of 60 °C, which is a desirable temperature for the ferric leaching of chalcopyrite (Córdoba et al., 2008; Liu and Granata, 2018) and consistent with previous leaching experiments (Lin et al., 2016a,b).

Emulating typical industrial operational conditions, fresh feed solution was pumped into the columns at a constant rate of $8 \text{ L h}^{-1} \text{ m}^{-2}$. Ferric ions are added with the feed in order to mimic the bacterial action present in real operation. The columns were operated at two different redox potential conditions, having one repeat for each condition, K10 being a repeat of K9 and K12 a repeat of K11. Table 4.3 summarises the conditions experienced by each column throughout the 43 days of leaching. This leach duration

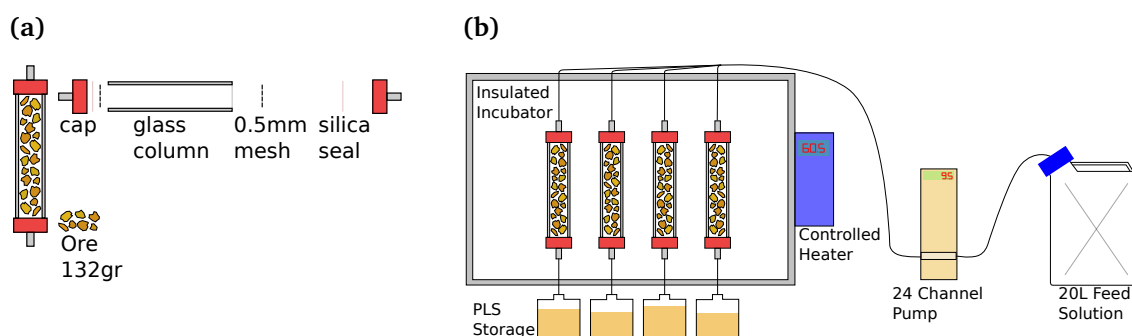


Figure 4.7: Experimental setup schematic. Four glass columns were used to leach the mineral sample in a controlled environment. Rate of fresh feed was kept constant throughout the experiment and the leachate was not recycled.

was deliberately chosen so that complete leaching is not reached, in order that SEM/EDS analysis can be used to identify the different mineral species, especially the sulphides, as the sample preparation for SEM/EDS is destructive.

Table 4.3: Column operation parameters. The four columns were operated in two different Eh conditions, with one repeat for each one of them.

Column	Ore	Flow rate L h ⁻¹ m ⁻²	Eh mV	pH	Temperature °C
K9	Sample K (0.8% Cu)	8	700	1.1	60
K10			—————		
K11			450		
K12					

Eh was controlled by the addition of ferric and ferrous sulphates, resulting in one feed solution with a nominal potential of 700 mV and another with 450 mV, both against a saturated calomel electrode. Figure 4.8 shows the regular measurements of the feed solution in terms of its pH and Eh. Stable values can be observed, however the high Eh solution did not reach its set value of 700 mV, achieving an average value of 650 mV. Ph was measured using a digital pH sensor (SevenGo Duo, Mettler Toledo).

4.4.1 Element analysis of leach solutions

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis was used for measuring the metal concentration in the leach solutions. An iCAP 6000 Series ICP-OES Spectrometer from Thermo Scientific was used for assessing the concentration of copper and iron. Four standards were prepared at different concentrations in order to calibrate the machine for each measurement. Concentrations of 5, 10, 20 and 50 ppm of both metals were used, along with a blank. Figure 4.9 shows an example of the calibration obtained for relating the counts inside the plasma chamber and the concentration of copper and iron in the sample. Goodness of the fit was above 0.9995 for each measurement

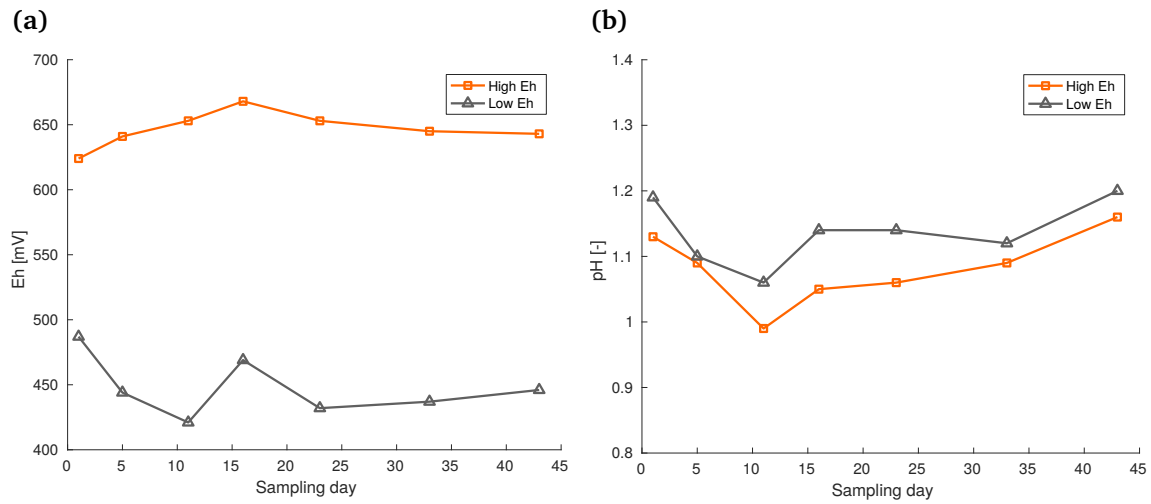


Figure 4.8: Eh and pH in the feed solution measurements show a stable feed solution, although the High Eh solution did not reach its intended design value.

and element, indicating the reliability of the procedure.

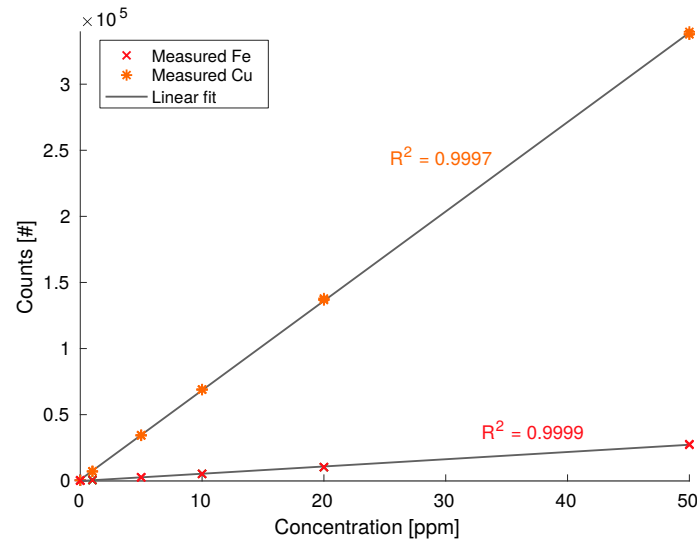


Figure 4.9: ICP-OES calibration, high linear correlation was obtained for the each element.

The sample preparation for measuring the leach solution consisted of creating 2 sets of diluted sample at 1:10 and 1:100 ratios. This was due to the high levels of iron present in the leachate, making the concentration fall outside the calibration region. The procedure's standard error, obtain by running 14 repeats, was 0.11 ppm for copper estimation and 8.2 ppm for iron. Figure 4.10a shows the results for the measurements of copper extraction. As expected the concentration in the leachate drops dramatically as the faster leaching grains (oxides, secondary sulphides and exposed small primary sulphides) get depleted, leaving only slow-leaching grains in the ore (primary sulphides and grains distant to the surface). Using the estimated initial content of copper in the ore an estimated recovery curve can be worked out (see Figure 4.10b). It can be seen that K9 and K10 behave similarly one to another, but a faster leaching behaviour can be observed in K12 compared

to its repeat K11. XMT will be used to determine if the discrepancy between K11 and K12 is due to feed variability, given this small sample size.

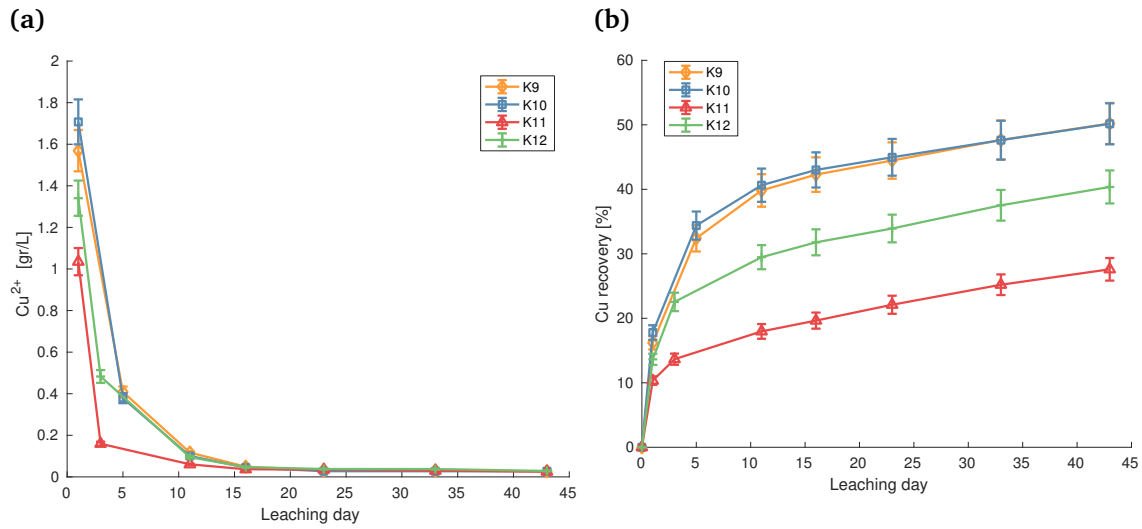


Figure 4.10: ICP-OES measurement of copper extraction shows the expected slow down heap leaching as faster grains get depleted. Recovery of copper per column is shown alongside in b).

The ICP-OES measurements for iron can be seen in Figure 4.11a. All columns show a similar iron content in the leachate, which translates into a similar pyrite recovery estimation as Figure 4.11b shows. This estimation assumes that there is no bacterial activity and thus all iron captured in the leachate must come from either dissolution of copper sulphides, pyrite and iron added into the system by the feed solution. The initial pyrite content for each column was estimated using the pyrite weight percentage in Table 4.2 and the ore mass packed. The pyrite recovery also assumes that chalcopyrite is the only copper mineral being leached and thus producing iron.

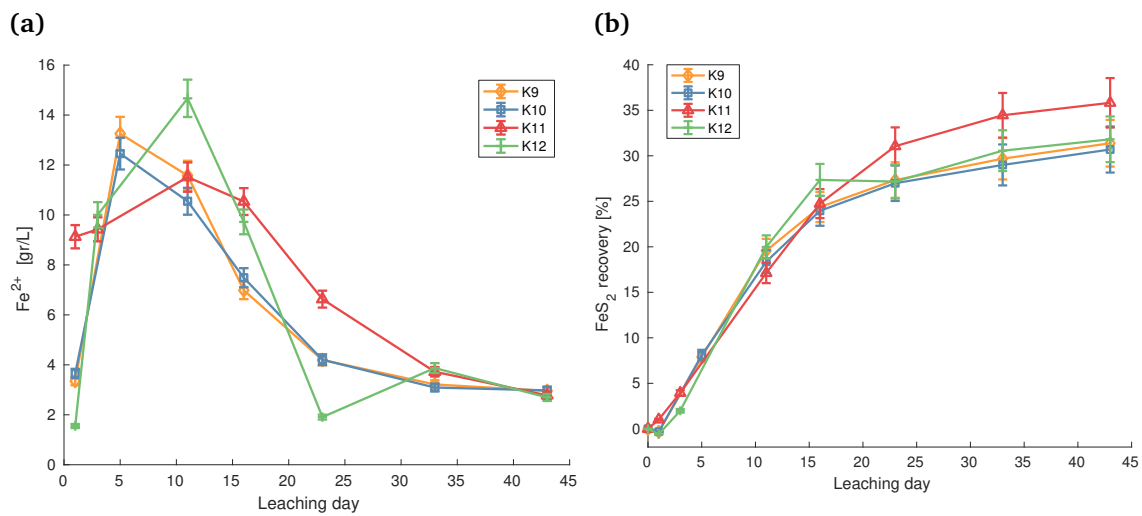


Figure 4.11: Iron extraction measured by ICP-OES and the worked out pyrite recovery. All columns show a similar behaviour regardless of the difference in their feed solution's Eh.

4.4.2 XMT measurements

Following a similar methodology to the one presented by Lin et al. (2016a), the columns were periodically removed from the incubator and imaged using XMT (See Table 4.4 for imaging schedule). This methodology allows for the creation of a 4D library of the individual mineral grains (3D size and position over time).

Table 4.4: XMT scanning imaging schedule. Each column was scanned at specific leaching end days.

Column	Scanning day							
K9	0	1	5	11	16	23	33	43
K10	0	1	5	11	16	23	33	43
K11	0	1	3	11	16	23	33	43
K12	0	1	3	11	16	23	33	43

All XMT scans were acquired in a Nikon XTH 225 scanner at an energy level of 89 kV, with 0.708 s of exposure time. A 1.0 mm aluminium filter was used to reduce the effect of beam hardening. The sensor consists of a matrix of 2000×2000 detectors, which results in a linear resolution of approximately $16.1 \mu\text{m}/\text{px}$ as the width of the glass column was set to fill the field-of-view. Considering the image contrast obtained, the effective spatial resolution is approximately $21.4 \mu\text{m}$ (see Figure 2.12 for the analysis). Due to the fact that it was the width of the column the axis that was set to fill the field-of-view, the complete height of the column falls out of it. In order to get the leaching behaviour along this axis, three different scans per column were used (see Figure 4.12). As can be observed, the volumes scanned were at the top, middle and bottom of the column. Occasional, as they are very time consuming, full height composite scans were carried out to localise the partial volumes relative to the whole column.

In Figure 4.12b the colour of each particle is coding the ability of the algorithm to distinguish each of the individual particles, so that they can be analysed separately. Figure 4.13 shows an example particle and the segmented grains before leaching and after 43 days of leaching.

Because only particle that were completely within the field-of-view were included in the analysis a total of 114 particles were assessed, which resulted in the tracking of 1.5 million individual mineral grains. However, considering the analysis in Section 3.5.2, it is known that a considerable error can be present in the quantification of grain size. Figure 3.11 shows that the variability in the quantification of size reduces drastically around 100 microns. Taking this into consideration it was decided to ignore from the analysis any grain with an equivalent diameter smaller than $90 \mu\text{m}$, this reduces the number of tracked grains to 1.2 million which is still enough for a statistically robust analysis. By tracking the change in volume of the grains, recovery can be calculated at different scales, for each

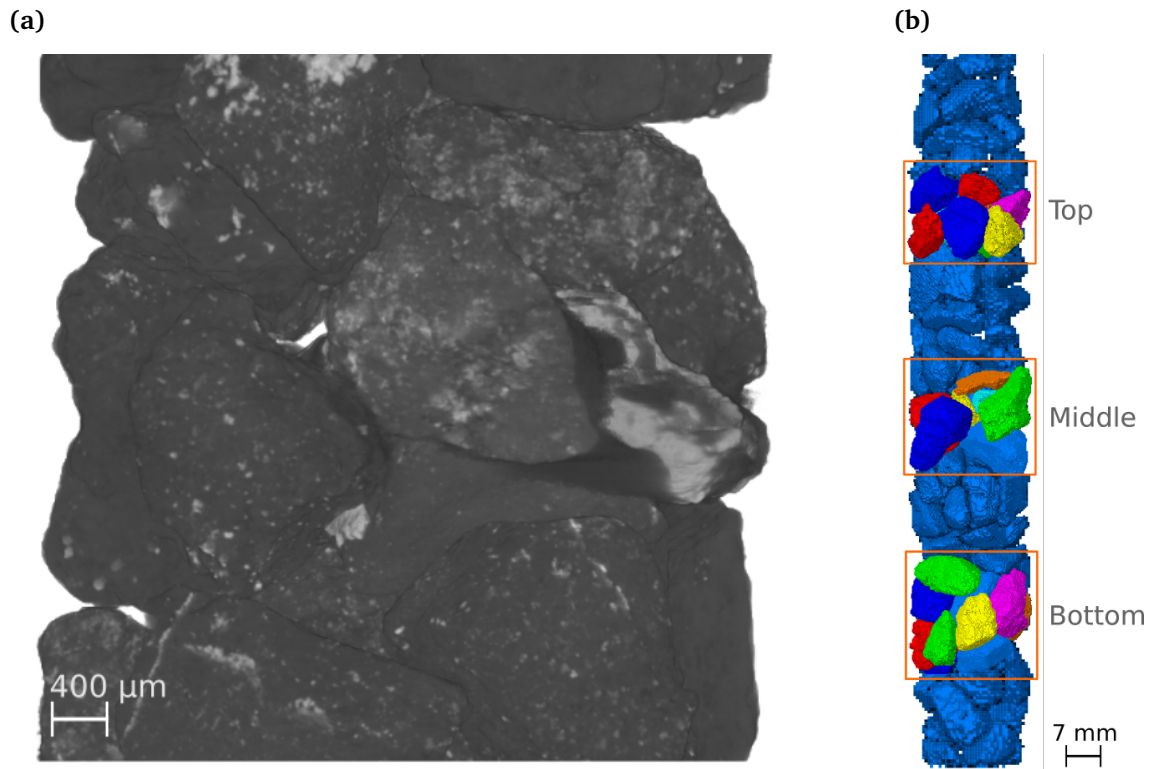


Figure 4.12: a) Example rendering of an analysed volume in a leaching column. b) Example of a whole-column scan with the columns' three scanned and tracked volumes over the leaching cycle following Table 4.4. Colour is coding the labelling of the individual rock particles.

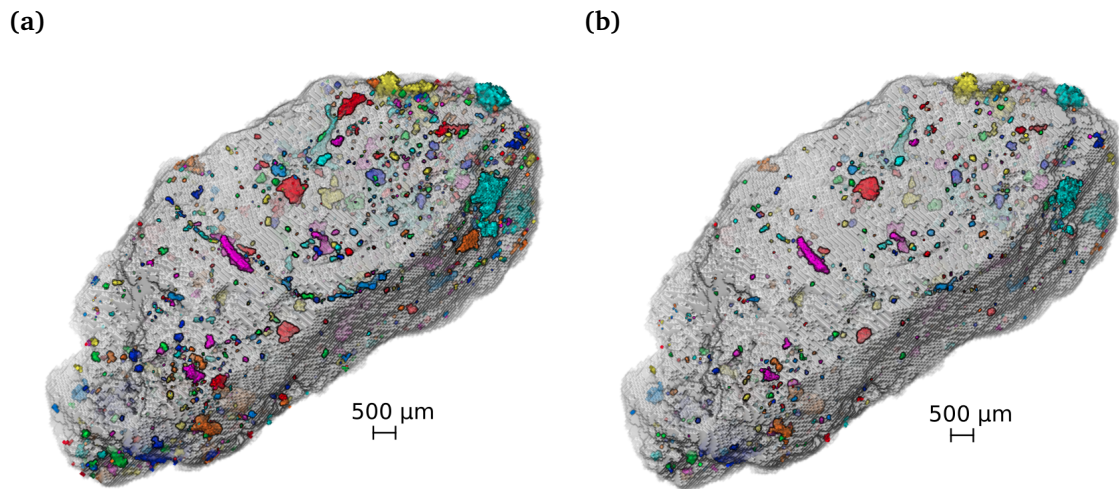


Figure 4.13: 3D XMT data from scanned particles. Using a tracking algorithms, volume of individual grains is tracked over the leaching process. Colour is coding the labelling of the individual grains.

grain, for each particle and for each column. Figure 4.14 shows the resulting recovery curve for each column, the error bars show the standard error of the method obtained by scanning a column twice (see Section 4.4.3), this error encapsulates both the uncertainty in the size of the grain and the random and systematic errors introduced by the XMT image processing analysis.

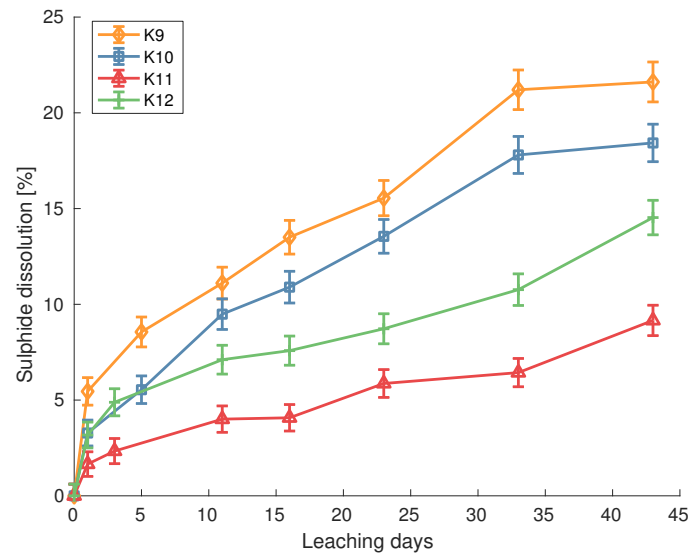


Figure 4.14: Recovery per column obtained via the XMT analysis, similar trend can be observed compared to the recoveries obtained via ICP-OES (See Figure 4.10b).

Since there is no distinction between pyrite and copper bearing grains in these initial analyses, recoveries obtained from ICP-OES and XMT will differ, as can be seen in Figure 4.15. Reasonable linear correlation is still present, however, with an $R^2 = 0.86$ and p-value < 0.01 . The linear fit indicates a bias between ICP and XMT of 7.25% and a correction factor of 2.34. The red dashed lines indicate the 95% prediction intervals. This plot indicates the need for distinguishing in XMT the different sulphides species.

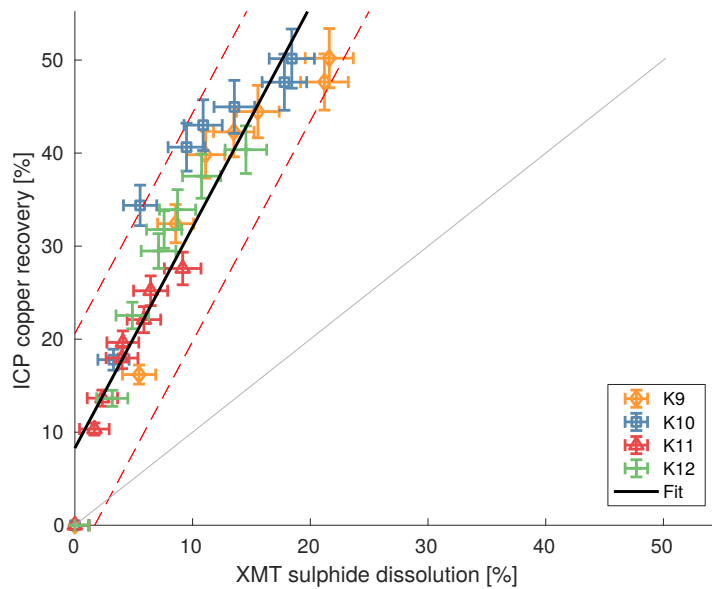


Figure 4.15: XMT versus ICP recovery per column. Section 4.5 looks into obtaining a mineralogy based recovery from the XMT images.

4.4.3 Statistical analysis

Using the XMT data, recovery can be analysed at the particle level, showing that the variability at this particular scale is considerably higher than at the greater column scale. This is apparent in Figure 4.16 where the recovery per particle, in column K9, is plotted against the particle's size and its relative position in the column (distance of the particle's center of mass to the column's centre). Statistical analysis shows that no correlation was found between the recovery experienced by the particles and its size (p-value > 0.3) and its relative position (p-value > 0.4). This is to be expected as the experiment was design using both a narrow particle size range and column diameter so the possible effects of these variables can be controlled for. In contrast, Fagan-Endres et al. (2017) used similar columns but with a wider particle size distribution (ranging from 0.25 to 16 mm) and results from XMT analysis showed the presence of preferential leaching at the column's wall. Smaller particles should leach faster, but the narrow particle size range used in our experiment means that the underlying variability overrides this effect.

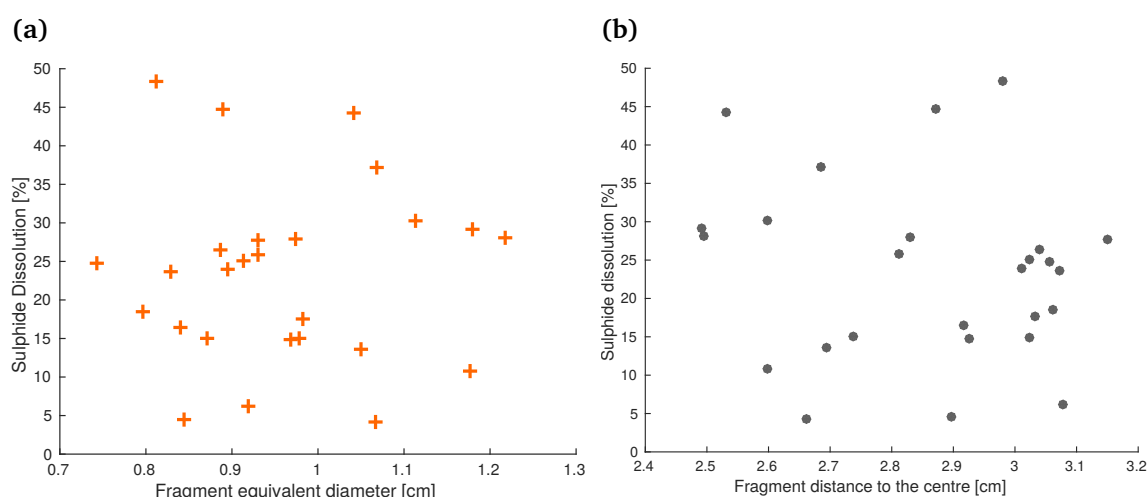


Figure 4.16: Recoveries for each particle in K9 against each particle's size and relative position in the column. No statistical correlation was found for any of the variables, showing that these were controlled by the narrow particle size distribution and column diameter used in the experiment.

Repeatability of the experiment can also be assessed by comparing particles leached in each column with its corresponding repeat. Figure 4.17 shows the distributions of the recoveries obtained at both chemical conditions (high Eh and low Eh). Combining K9 with K10 a total of 47 particles were analysed for the high Eh condition and combining K11 with K12 a total of 60 for the low Eh condition. A statistically significant difference was obtained between the two conditions using a t-test (p-value $< 1 \times 10^{-4}$). Conversely, no significant difference was found within each category (p-value > 0.1).

Measurement of uncertainty associated with the XMT analysis was studied by analysing the recovery obtained from different scans at the same stage of leaching. This is a test of

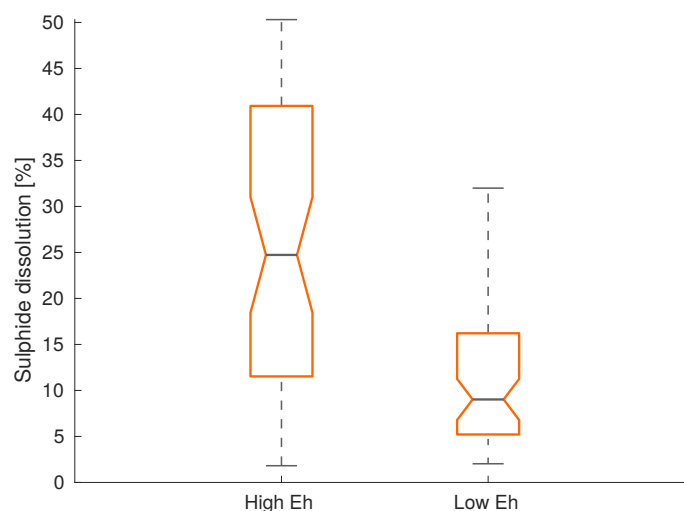


Figure 4.17: Distribution of recovery for each chemical condition (high and low Eh), statistical analysis shows a significant difference between the categories and no statistical difference within the categories.

the measurement uncertainty and is used to produce the error bars in the XMT measurements. As an example column K10 was scanned twice on the 43rd day of leaching and recovery with respect to the initial scan was calculated (see Figure 4.18). The difference between the repeats, when considering the recovery of the whole column, was 1.33%. When analysing the difference in recovery for each of the 12 particles analysed, the mean error is 0.85% with a standard deviation of this difference of 2.96%. A t-test failed to reject the null hypothesis of the mean value for the difference being different from 0 (p-value > 0.6). This makes us confident of the conducted experimental procedure and the imaging processing quantification used. One particle presents an error bigger than the rest of them, this is due to an error in the segmentation and separation of the particle from its neighbouring particle. The outlier was not excluded from the assessment of the repeatability as it represents an error that is not uncommon to occur in the system.

4.5 Leach rate kinetics quantification

After the 43 days of leaching, a two day rinsing cycle was carried out by feeding de-ionised water into the columns. This cycle is needed to recover any component that may have precipitated out and to halt the leaching process. The columns were then unpacked, with the particles labelled for subsequent identification, and dried. A set of 33 particles were selected from columns K9, K11 and K12 to be analysed under the electron microscope, a FEI Quanta 600i SEM/MLA machine. Samples were individually mounted in 30 mm blocks using epoxy resin and subsequently ground to expose a section of their interior. Polishing of the exposed slice was performed using a Struers Tegrapol polishing machine to a diamond finish of $1.0\mu\text{m}$. To prevent electron charging on the exposed surface,

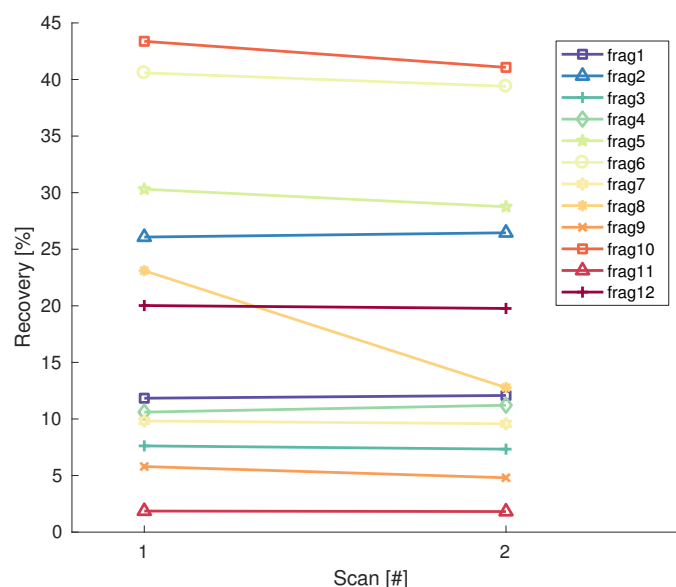


Figure 4.18: Assessment of repeatability and estimation of the error in quantifying recovery, done by repeating a scan.

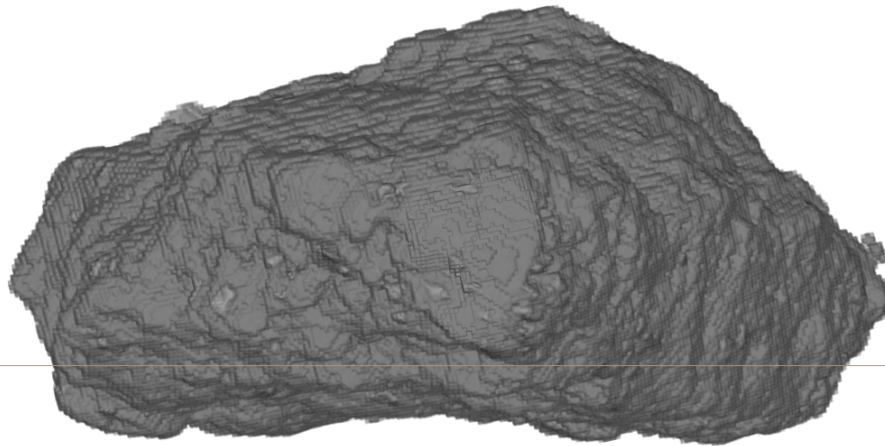
carbon coating was also performed. Figure 4.19a shows a schematic of the slice exposed for an example particle, depth of the exposed surface ranged from $150\mu\text{m}$ to $250\mu\text{m}$. This methodology is the same as that developed in Section 3.3.3 for the assessment of mineralogy.

Images of each block were processed using the MLA Dataview software. Figure 4.19 shows an example of a back-scattered electron (BSE) image along with the corresponding mineral map. These images were acquired at a resolution of $2.25\mu\text{m}$ per pixel. It is worth noting that the artefacts and possible misclassification visible in Figure 4.19c has no impact in the analysis as they happen in the gangue minerals. This is direct result of the method used to assess mineralogy (GXMAP, see Section 3.3.3) where detailed mineralogical information is measured only in the bright phase of the BSE image, i.e. sulphide mineral grains, with the system having problems distinguishing between gangue minerals such as Muscovite and Quartz.

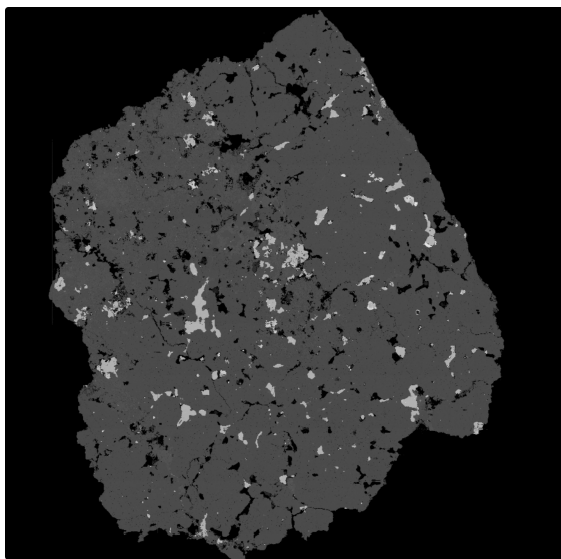
The modified version, introduced in Chapter 3, of the algorithm and method proposed by Lin (2015) for tracking individual mineral grains over different XMT scans was used to track mineral grains between the XMT and the SEM/EDS images. The method relies on matching the 2D BSE image from the SEM with a virtual slice in the 3D XMT volume, with the resultant geometric transformation being used to track grains on both images. A simplified step-by-step procedure is now described:

- 1 Mineral grains are segmented from the gangue in the XMT volume and the resulting binary image is labelled using a connectivity algorithm.
- 2 BSE images are registered, using an iso-scale rigid transformation, into the XMT volume in order to obtain a virtual slice through the XMT image that is equivalent

(a)



(b)



(c)

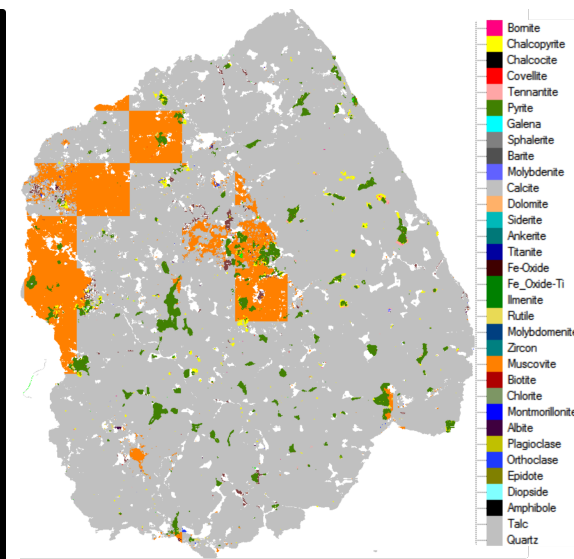


Figure 4.19: Example particle analysed using the SEM/MLA machine. a) Schematic of the exposed polished section, shown over the particle's 3D XMT rendering. b) Backscatter image obtained from the SEM. c) Mineral map obtained from the MLA analysis.

to the BSE images. The resultant geometric transformation is saved for later use.

- 3 Minerals are segmented from the mineral map image. The resulting binary image is also labelled as in step 1.
- 4 The corresponding geometry transformation is used to align the XMT grain labelled image (step 1) into the SEM grain labelled mask (step 3). Matching algorithms are used to track grains appearing in both images, and a unique label is given to those grains.

This methodology was published in Reyes et al. (2017), and a more detailed description can be found in Chapter 3. An example particle is shown in Figure 4.20, where a) corresponds to the virtual slice found in the 3D XMT volume that matches the BSE image shown in Figure 4.19a. The resultant labelled grain image is shown superimposed over

the BSE image in Figure 4.20b.

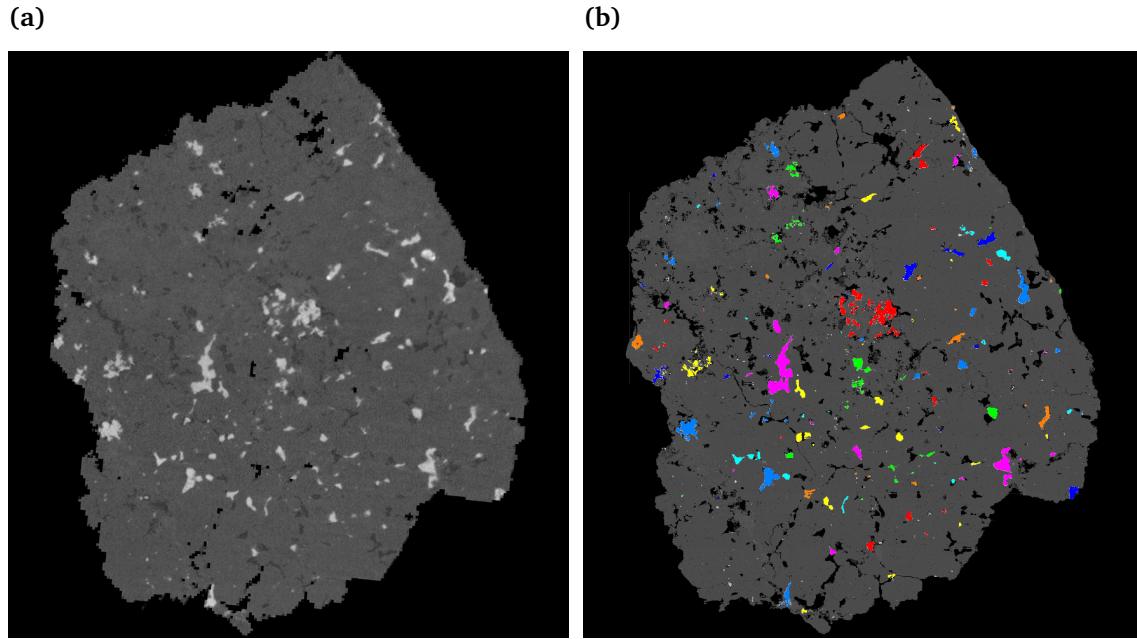


Figure 4.20: Example of grain tracking between XMT and SEM. a) XMT virtual slice found to match the corresponding SEM BSE image. b) Grains on both images are individualised and labelled, here shown superimposed over the SEM BSE image.

The result of this procedure is the addition of mineral information into the database described in Section 4.4. Although, since only 33 of the 141 particles were sectioned and only one section was obtained from each particle, the number of grains for which the mineralogy is known is only 4,712 (or about 0.4% of the total tracked grains).

As XMT images allow the tracking of individual grains in each particle, the surface reaction kinetic constant can be assessed individually for each scanned grain. Given the vast number of grains tracked (more than a million grains are tracked in this work), they can be grouped by their initial size and their distance to the particle's surface. The latter been defined as the distance from the grain's centre of mass to the particle's surface and as such, a proxy for mass transfer resistance. This allows for the decoupling of recovery (and thus leach kinetics) from the grain's size, shape and chemical conditions. Figure 4.21 shows the results for column K10 and K12, where it can be seen that, as expected, recovery is higher for smaller grains and for shorter distances to the particle's surface. An ANOVA test shows a statistically significant effect of distance and grain size (p -values $< 1 \times 10^{-4}$) on recovery.

Starting with a general version of a dissolution equation, without needing to define any particular order, the rate at which the mass (M) is being dissolved is given by:

$$\frac{dM}{dt} = -kAC^n, \quad (4.5)$$

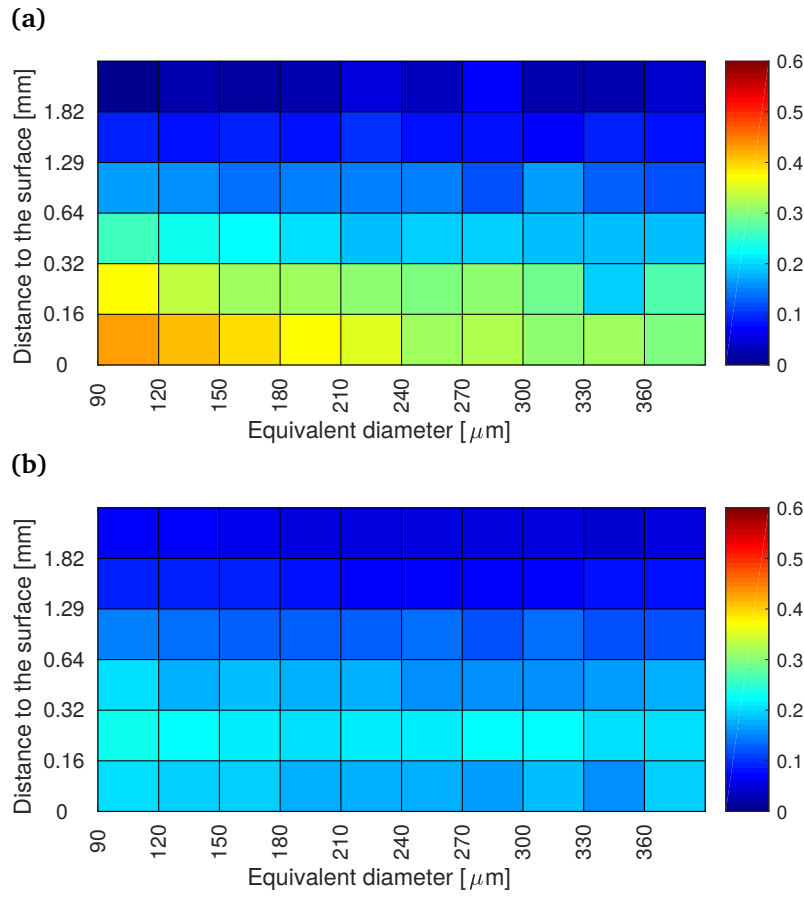


Figure 4.21: Sulphide dissolution measured at day 43 on each grain size and distance to the particle's surface category. a) High Eh column and b) Low Eh column.

Being k the surface rate kinetic constant, A the exposed area of the grain, C the reagent concentration and n the order of the kinetics (Lin, 2015). At any time t for a specific grain i of density ρ and shape factor α such that $A = \alpha V_i^{2/3}$, the dissolution from its initial size $V_i(0)$ can be expressed as:

$$\frac{dV_i}{dt} = -k_i \alpha / \rho V_i^{2/3} C^n, \quad (4.6)$$

Integrating this equation from 0 to a time t leads to Equation 4.7:

$$k_i = \frac{3\rho}{\alpha t \bar{C}} \left(V_i(0)^{1/3} - V_i(t)^{1/3} \right) \quad (4.7)$$

$$\bar{C} = \frac{1}{t} \int_0^t C^n d\tau \quad (4.8)$$

Where $\bar{C}$ is the average reagent concentration experienced by a grain up till time t . If distance is assumed to be a good proxy for mass transfer, then $\bar{C}$ should be similar for grains in the same distance to the surface category. Now, instead of analysing the specific individual value of the leach kinetics for each grain, which will require us to know the

value of the integral in Equation 4.8, the ratio between the grain i and the mean leach kinetic of it's size and distance category k_{mean} can be calculated.

$$\frac{k_i}{k_{mean}} = \frac{V_i(0)^{1/3} - V_i(t)^{1/3}}{1/N \sum (V_i(0)^{1/3} - V_i(t)^{1/3})} \quad (4.9)$$

Assuming that the leaching conditions are similar within the group allows us to cancel the integral and assuming that grains of similar size have similar shape factor α allows for that unknown also to be cancelled. The distribution of this ratio for all the grains is thus the intrinsic variability of the leach kinetics when shape, size and leach conditions have been accounted for. Figure 4.22 shows the cumulative distribution functions of this normalised apparent leach kinetic for each column, it can be observed that columns under the same leaching conditions exhibit similar distributions for the variability in their leach kinetics. Furthermore, when compared with the dissolution curves in Figure 4.14, it can be observed that even though there is quite a large variability in the ultimate dissolution achieved by the columns, repeats have a very similar underlying variability in their leach behaviour. The distributions also show that the columns leached at a higher redox potential present a broader range of variability in their leach kinetics, 13% of the grains are within $\pm 20\%$ of the mean leach rate. Whilst low Eh columns have a narrower variability with only 10% of the grains having a leach rate within $\pm 20\%$ of the mean. This might appear to be a small difference, but as it can be seen in Figure 4.22 the difference between the distributions for the high and low Eh is apparent.

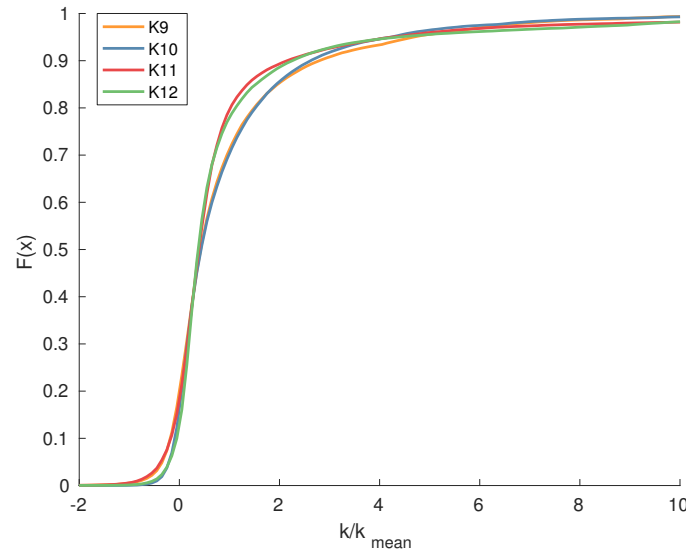


Figure 4.22: Cumulative probability distribution of the normalised leach kinetics. Columns under different leach conditions exhibit different leach kinetics, whilst repeats show similar behaviour.

As can be noted in Figure 4.22, there is a proportion of grains that are quantified to have a negative leach kinetic. This is mostly due to non-soluble mineral grains, thus, their volume remains unchanged over different scans, but due to systematic and random

errors in the XMT analysis (See Section refsec:grainsizequant a difference in volume is measured. To test this error the data from the repeated scan (Figure 4.18) can be used. Both scans are of the same sample, so one should expect the leach kinetics to be zero, as no volume change should occur between the scans. However, due to the random and systematic errors present when quantifying size, there a distribution can be found. Figure 4.23 shows that this error distributes normal centred at zero. That means that there is no bias introduced in the quantification of leach kinetics, but negative values are introduced, explaining what is seen in Figure 4.22.

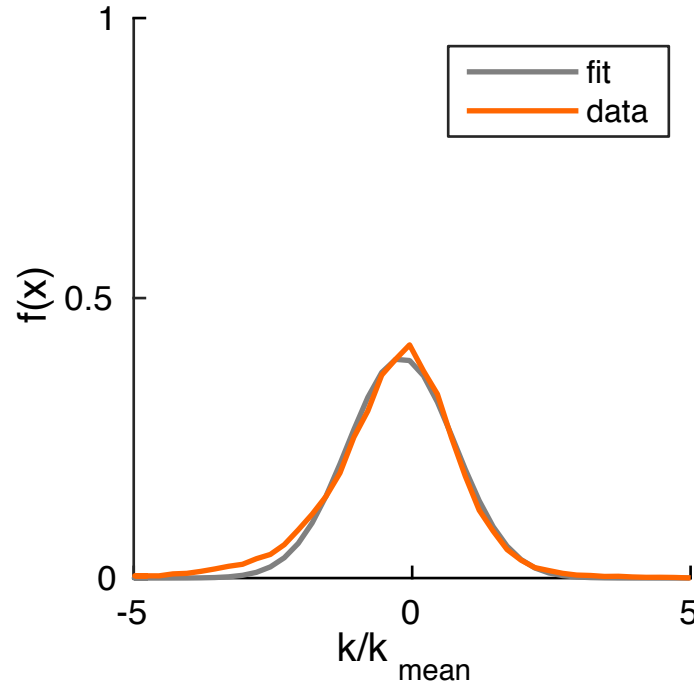


Figure 4.23: Probability distribution function of the error in the quantification of leach kinetics. As it can be observed, a normal distribution fits the data.

Using the tracked grains in both in the MLA and XMT analysis allows for the assessment of the effect of mineralogy as well as the once aforementioned size and distance. Figure 4.24 shows the leach kinetics obtained for K11, showing that copper bearing and pyrite grains experience considerable different distributions especially for slow leaching grains (below $k/k_{mean} = 1$). It is also important to notice that the copper bearing minerals present a bi-modal distribution (appearing as the step after $k/k_{mean} = 1.5$), whilst pyrite grains show a narrower mono-modal distribution. The former is to be expected as we are grouping different copper minerals into the same category, nevertheless it is noticeable that the methodology is able to capture this.

As it is useful to be able to represent this data using a formula. Previous research found that when particles were divided into classes according to size and distance to the surface, the kinetics within the class followed a gamma distribution $\text{gamma}(\alpha, \beta)$ (Lin et al., 2016a,b). Gamma's probability distribution function of the variable $x \in (0, \infty)$ is

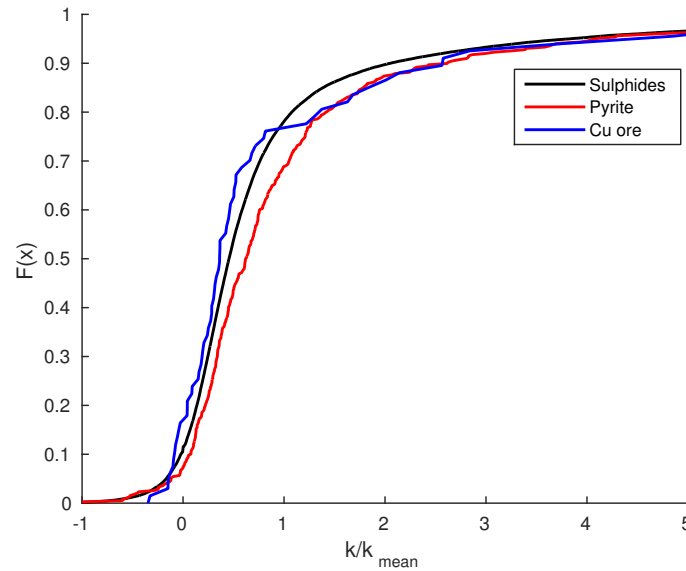


Figure 4.24: Distribution of the apparent leach kinetics distinguishing by mineralogy. As expected, the variability in the leach kinetics of copper minerals differs from the one showed by pyrite.

show in Equation 4.10:

$$f(x) = \frac{\beta^\alpha}{\Gamma(\alpha)} x^{\alpha-1} e^{-\beta x} \quad (4.10)$$

Where $\alpha, \beta > 0$ and $\Gamma(z)$ is the gamma function defined as:

$$\Gamma(z) = \int_0^\infty s^{z-1} e^{-s} ds \quad (4.11)$$

It was found that all size-distance classes had the same shape of this distribution, and therefore it was interpreted as representing the inherent variability of the surface kinetics for the whole column. An example of the distribution found for this particular system can be seen in Figure 4.25 where it can be observed that Eh conditions can influence the shape of the gamma distribution, having high and low Eh conditions considerably different values for the fitting parameters.

All this information about the variability of the leach rate kinetics can be used to better inform the calculation of the apparent leach kinetics when fitting to experimental data. Instead of fitting one average rate for all grains, this allows for not only fitting the overall performance of the leaching process, but to also represent the inter and intra-particle variability. The importance of this consideration is clear when observing the effect on the ultimate recovery. Figure 4.26 shows a constant rate leaching simulation and a simulation using a distribution of rate kinetics which mean value corresponds to the constant rate. Section 4.6 introduces a mathematical model that can accommodate such surface rate kinetics and Section 4.7 shows the performance of the simulations against the experimental data previously introduced.

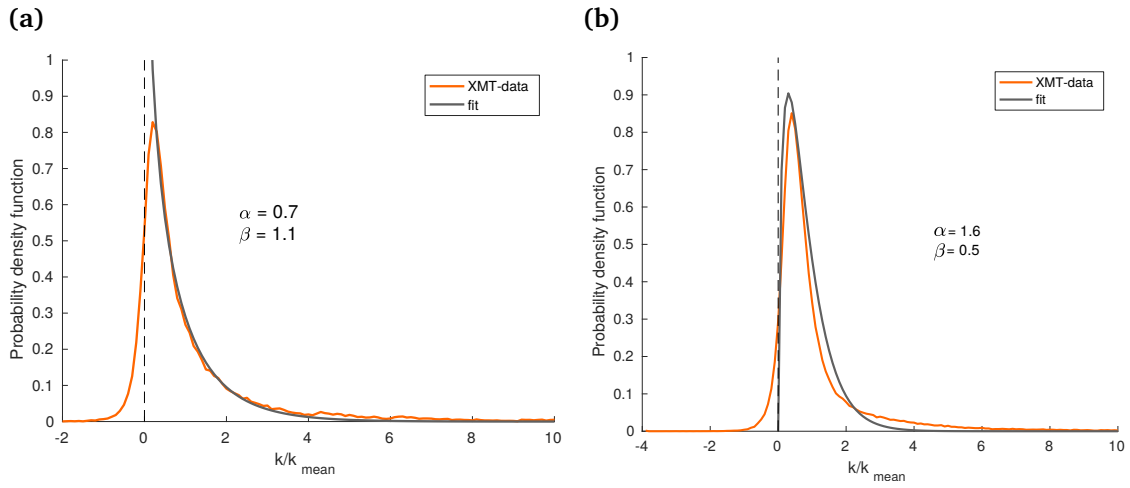


Figure 4.25: The leach kinetics variability show a gamma distribution, a) High Eh and b) Low Eh. Eh conditions showed to influence the fitting parameters, phenomenon that was not studied in Lin (2015).

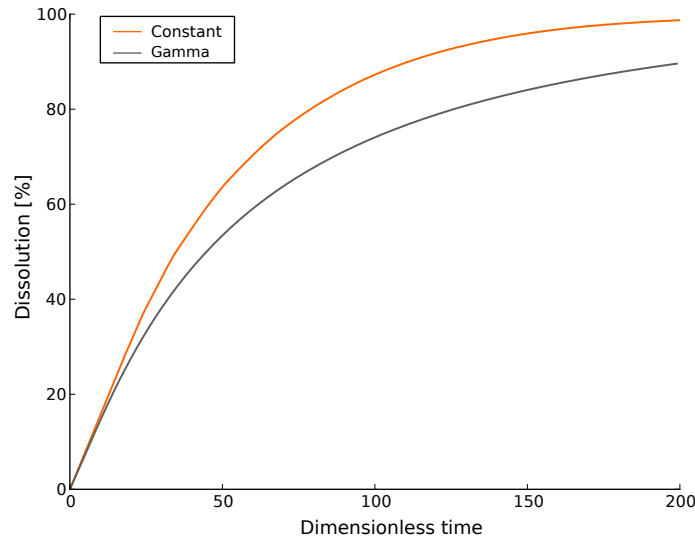


Figure 4.26: Simulated recovery for a constant rate kinetics and its distributed counterpart, as expected a distribution of surface kinetics achieves slower kinetics in the long run.

4.6 Mathematical model and implementation

For the modelling of the mass transport of solutes in porous media the well known convection-diffusion equation (Bear, 1988) can be used,

$$\frac{\partial(\phi s_{\alpha} C_i^{\alpha})}{\partial t} = \nabla \cdot (\phi s_{\alpha} \mathbf{D}(s_{\alpha}) \nabla C_i^{\alpha} - \vec{\mathbf{u}}_{\alpha}(s_{\alpha}) C_i^{\alpha}) + R_{\alpha} \quad (4.12)$$

where C_i^{α} is the concentration of solute i in the phase α , $\mathbf{D}$ is the effective diffusivity tensor of the media, ϕ is the porosity, $\vec{\mathbf{u}}_{\alpha}$ is the velocity of phase α , s_{α} is the saturation of phase α and R_{α} is a source/sink term that reflects the addition or removal of solute i . O'Kane et al. (1999) performed a set of experiments revealing the importance of linking

the transport equation with the multi-phase fluid flow in the porous media. Darcy's law (Equation 4.13) and Richard's equation (Equation 4.14) have become the standard for doing this, providing a framework to relate saturation in the medium (s_α) with capillarity pressure (h) for each phase.

$$\vec{u}_\alpha(s_\alpha) = -\frac{Kk_{r\alpha}(s_\alpha)}{\mu_\alpha} (\nabla p_\alpha - \rho_\alpha \mathbf{g}) \quad (4.13)$$

$$\rho_\alpha C(h) \frac{\partial h}{\partial t} = \nabla \cdot (\rho_\alpha \vec{u}_\alpha(s_\alpha)) \quad (4.14)$$

Where K is the absolute permeability of the porous media and $k_{r\alpha}(s_\alpha)$, p_α , μ_α , are the relative permeability, pressure and viscosity of phase α . $C(h)$ is the specific moisture capacity defined by $C(h) = \frac{\partial(\phi s_\alpha)}{\partial h}$. Most of the studies here reviewed differ in the technique used to solve this set of non-linear equations or how to deal with the source/sink term rather than proposing real changes to the core physics under these equations.

4.6.1 Hydrodynamics in porous media

When focusing on leaching at the particle scale, the transport processes can be modelled using Equation 4.15. This assumes that particles are nearly saturated. This is a valid assumption given that the particle's porosity is much finer than the inter-particle spaces, implying that capillarity forces will ensure particles are saturated or nearly saturated if they are in contact with external liquid.

$$\frac{\partial(\phi C_a)}{\partial t} = \nabla \cdot (\phi D \nabla C_a - \vec{u} C_a) \quad (4.15)$$

Given the dimensions of the capillary spaces within the particles it can be assumed that the transport is mostly diffusive, thus Equation 4.15 can be reduced to

$$\frac{\partial(\phi C_a)}{\partial t} = \nabla \cdot (\phi D \nabla C_a) \quad (4.16)$$

Equation 4.16 can be transformed into a QSS model by neglecting the accumulation term, leading to Equation 4.17. Both approaches are studied in order to assess the range of validity of the widely used QSS assumption.

$$0 = \nabla \cdot (\phi D \nabla C_a) \quad (4.17)$$

4.6.2 Chemical reactions and mass transport

Taking advantage of the voxelised nature of the XMT images, a finite volume approach was used to solved these equations.

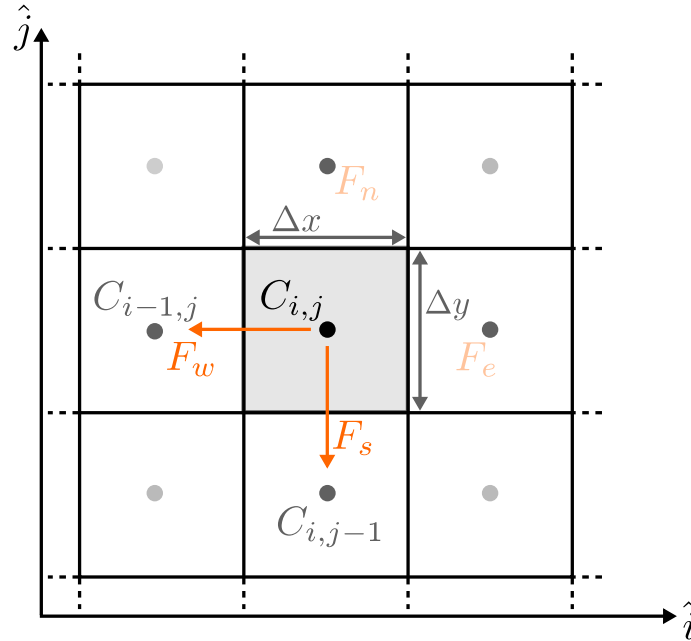


Figure 4.27: Finite volume method with a regular grid. The grid is obtained from the XMT voxelised volume.

The chemical reactions are modelled as boundary conditions for the fluxes at sulphide grain's surfaces, where first order surface kinetics are assumed (later on this assumption will be relaxed using non-linear surface reactions) using k_r as the surface rate constant, with units of length per unit time. Sulphide minerals are assumed to be impermeable

$$F_R = \vec{F} \cdot \hat{n} = k_r C_a \quad (4.18)$$

At the external boundary, a first-order mass transfer is modelled as follows, where k_e is the external mass transfer coefficient.

$$F_E = \vec{F} \cdot \hat{n} = k_e C_a \quad (4.19)$$

In order to avoid the grain voxels being binary in terms of recovery, a continuous fraction is used. This is modelled using the variable f , which is the fraction of the mineral within a voxel that has not been leached. Thus, the mass flow of reagent ($\frac{dM}{dt}$) into the grain is related to the copper output mass flow from the grain by the stoichiometric constants. Equation 4.20 shows this relationship, where a and b are the stoichiometric values for the reagent and reactant, respectively and C_b is the concentration of copper within the mineral phase.

$$\frac{df}{dt} = \frac{a}{b C_b \Delta x^3} \frac{dM}{dt} \quad (4.20)$$

The mass flow of reagent into the grain can be defined as the sum of the fluxes times the total area of the voxel.

$$\frac{dM}{dt} = - \sum_{\partial v_p} F \Delta x^2 \quad (4.21)$$

The fluxes correspond to the ones described in Equations 4.18 and 4.19 depending on the surface boundaries of the voxel.

For simulation convenience the governing equation and the boundary conditions are transformed into dimensionless forms. A dimensionless concentration, C^* is defined using the external reagent concentration as reference, thus,

$$C^* = \frac{C}{C_{ext}} \quad (4.22)$$

Fluxes are normalised by taking the diffusion flux as a reference, where L is the characteristic length scale of the rock.

$$\begin{aligned} F_D^* &= \frac{L}{\phi D C_{ext}} F_D = 1 \Delta C^* \\ F_R^* &= \frac{L}{\phi D C_{ext}} F_R = \frac{L k_r}{\phi D} \Delta C^* \\ F_E^* &= \frac{L}{\phi D C_{ext}} F_E = \frac{L k_e}{\phi D} \Delta C^* \end{aligned}$$

The above equations contain a dimensionless group, δ_1 , that represents the balance between diffusion and surface reaction. If $\delta_1 \gg 1$ the process is reaction controlled, and conversely if $\delta_1 \ll 1$, the process is diffusion limited.

$$\delta_1 = \frac{\phi D}{k_r L} \quad (4.23)$$

Taking these dimensionless fluxes and also the dimensionless time defined as $t^* = \frac{t k_r}{L}$ and substituting them into the grain dissolution equation creates another dimensionless group, δ_2 . This dimensionless group is the same as the γ defined by Taylor et al. (1983).

$$\delta_2 = \frac{a C_{ext}}{b C_b} \quad (4.24)$$

Table 4.5 summarises the dimensionless form of the governing equations and the grain

dissolution equation for the dynamic and QSS models.

Table 4.5: Summary of the governing equations of the system in a dimensionless form. Both, dynamic and QSS models have two dimensionless groups to represent the system.

	QSS	Dynamic
δ_1	$\frac{D}{k_r L}$	$\frac{\phi D}{k_r L}$
δ_2	$\frac{a C_{ext}}{b C_b}$	$\frac{a C_{ext}}{b C_b}$
Governing equation	$0 = \nabla_*(F^*)$	$\frac{\partial(\phi C^*)}{\partial t^*} = \delta_1 \nabla_*(F^*)$
Dissolution equation	$\frac{df}{dt^*} = \delta_2 \delta_1 \sum_{\partial v_p} F^*$	$\frac{df}{dt^*} = \delta_2 \delta_1 \sum_{\partial v_p} F^*$

4.7 Particle scale simulation based on XMT quantification 3D images

A parallel C++ program was written to solve the set of equation that arise from the discretisation of Equations 4.16 and 4.17. For the former an explicit forward Euler method was used to solve the partial differential equations. For the latter, the PETSc (Balay et al., 2014) C++ library was used to solve the linear system of equations using matrix inversion method. Not only for performance, but also to distribute the memory burden of simulating over the vast number of elements in an XMT scan (order of millions) a Message-Passing Interface Standard (MPI) was used to deal with the parallel execution. It is also important to note that the use of XMT images for the simulation implicitly allows for the simulation of a system with grains following a polydispersed size distribution, rather than the more commonly used mono-sized grains. To represent the gamma distribution of the surface rate kinetics the Boost C++ random number generator library was used (Schling, 2011), so that each grain gets assigned a random kinetic according to the distribution found in the system (shown in 4.25).

4.7.1 QSS vs Dynamic

Before calibrating and comparing the dynamic simulator against the experimental data from Section 4.4 a comparison with the quasi-steady-state simulator will be performed. This serves as an assessment of the validity of the QSS assumption and a sanity check for the development of the dynamic simulator.

To study the influence of the initial conditions on the simulations of the dynamic system were run with no reagent within the rock ($C^* = 0$), reagent within the rock equal to the external concentration ($C^* = 1$) and an initial concentration map equivalent to the steady-state of the QSS model ($C^* = qss$). Figure 4.28 shows these simulations along

with the previous QSS simulation and values for δ_1 and δ_2 . Figure 4.28 is also important because it shows one of the benefits of using dynamic simulation, especially for the case when the initial conditions were set to $C^* = q_{ss}$. In this case it can be seen that the dynamic simulation tally with the QSS model only at early time, but then shifts to a more reaction controlled regime. This is mainly because at the beginning grains with larger values of k_r are preferentially leached and a fast leaching regime can be observed, but later when these faster grains are depleted the systems shifts to a diffusion controlled regime. The QSS model does contain this shift in regime, but as it does not include the effect in the relative importance of accumulation the effect is less evident and can be misinterpreted. Gbor and Jia (2004) also discussed the misinterpretation of QSS results, but given their use of a single surface rate kinetics and mono-sized particles, the mechanism is subtly different.

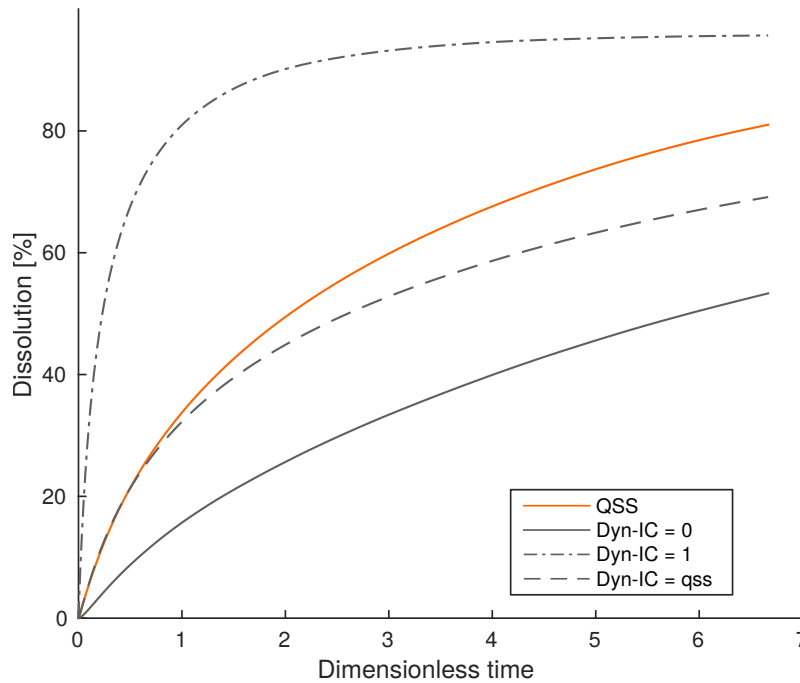


Figure 4.28: Comparison between dynamic simulation and QSS simulation with different initial conditions. If the initial conditions of the dynamic simulation are set to the first iteration of the QSS model both simulations are very alike, until the diffusivity takes control over the process and again QSS will overestimate the recovery.

The big impact of initial conditions on the kinetics hints that the inclusion of the leaching reagent in the fluid used to initially wet the ore could have benefits for the leach rate when in a strongly diffusion controlled system. Such benefits can be observed when the ore is pre-treated in an agglomeration drum before being stacked in the heaps. Agglomeration occurs in a sulphuric acid rich environment that cures the particles accelerating the posterior leach kinetics.

The effect of the second dimensionless group δ_2 was also studied. This dimensionless group was also introduced by Taylor et al. (1983), claiming that the QSS assumption is

valid for values of δ_2 lower than 0.1. Simulations where run using this value and differences were still appreciable. Figure 4.29 shows simulations with much lower values of δ_2 . The simulations agree with the behaviour found by Taylor et al. in that the difference between the models is reduced when δ_2 decreases, but is still appreciable at much lower values. This is probably due to the use of a distribution of surface kinetics. Results also agree with the notion that δ_2 defines how much slower the chemical process is compared with the flow in the porous media of the rock.

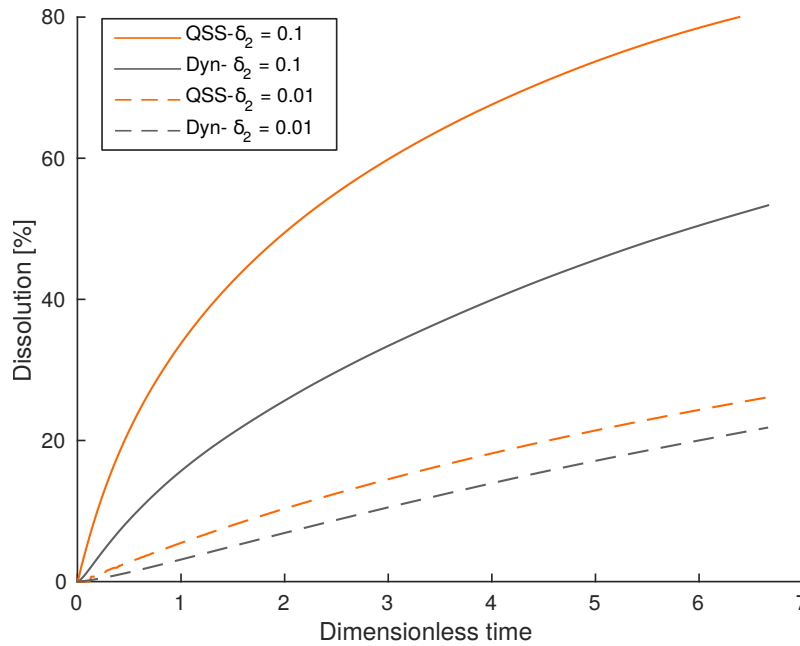


Figure 4.29: Comparison between dynamic simulation against QSS simulation with different values for δ_2 . Agreeing with Taylor et al. (1983) the models will tally better along the ratio δ_2 decreases. But the proposed threshold of 0.1 might not be small enough.

When using real data, obtained from experiments performed by Lin (2015) over a longer period of time (143 days) it can be observed that both the dynamic and QSS model show good levels of accuracy. This can be seen in Figure 4.30, where the result of the fitting and prediction (dashed lines) of both models are shown. The values for δ_2 in both simulations was set to 0.01, an appropriate value for models. On the other hand, the value of δ_1 was found by fitting the simulation to the first 53 days. Values of this parameters, the observed R-squared (R^2) and the root mean square error ($RMSE$) found for each model is shown in Table 4.6. Both models achieve good results, ($R^2 > 0.94$ and $RMSE < 5\%$), but some differences at late times can be observed.

Results in Table 4.6 show that in order to achieve similar results the value of δ_1 in each model has to be different, implying that, while QSS can fit the data, it can imply an incorrect regime. The observed effect is because of the accumulation term shifts the system towards a more diffusion controlled regime. This implies that in some cases the QSS assumption, even considering the particle size effect, may introduce a misinterpretation of the governing regime.

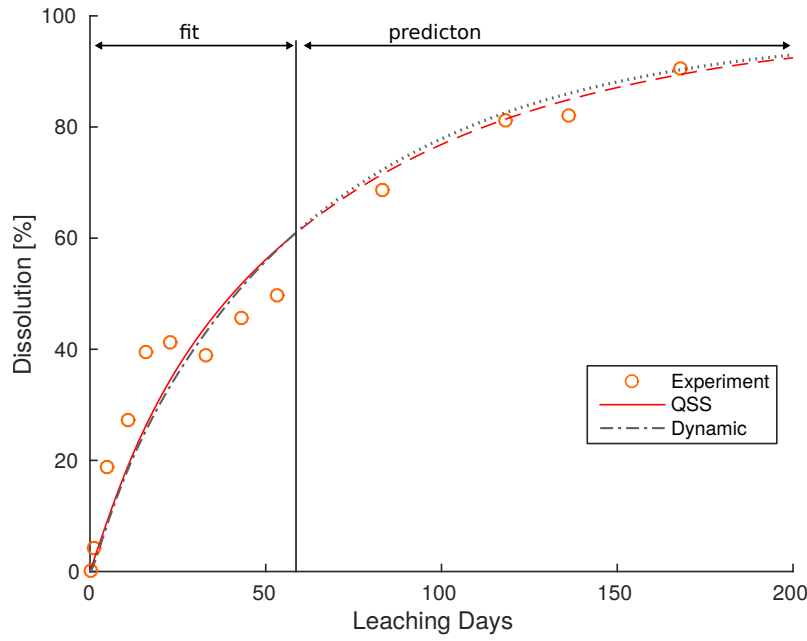


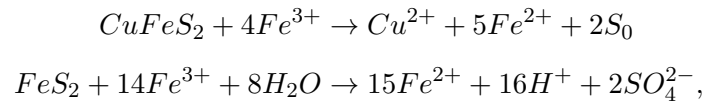
Figure 4.30: Dynamic simulation against QSS simulation in terms of predicting final recovery. Experimental data from Lin (2015).

Table 4.6: Fitting results for dynamic and QSS models. Both approaches achieve a good prediction of the experiment, but the lack of accumulation makes the QSS system look more reaction controlled than it actually is.

	δ_1	R^2	RMSE
QSS	10.0	0.948	4.398
Dynamic	6.67	0.942	4.920

4.7.2 Multi-species simulation

Taking into account the chemistry and mineralogy introduced in Section 4.4, a system with two mineral species (chalcopryrite and pyrite) and 3 reagents (sulphuric acid, ferric sulphate and ferrous sulphate) was implemented. Thus, the main chemical reactions being modelled are (Naderi et al., 2011):



Accumulation of elemental sulphur is neglected in this work, but it's a factor that will be consider in future work. Surface reaction coefficients were taken from the literature and are summarised in Table 4.7. For this reactions Equation 4.18 has to be modified to its non-linear form:

$$F_R = \vec{F} \cdot \hat{n} = k_r C_a^{n_a} \quad (4.25)$$

It is worth noting that the use of non-linear kinetics implies that the actual value of the concentration in the surrounding fluid has an impact in the kinetics, while that is not the case for a linear system, where all results get scaled by those values resulting in no effect on the kinetics.

Table 4.7: Rate kinetics for mineral species. Empirically derived rates of main chemical reactions obtained from Kimball et al. (2010) and Williamson and Rimstidt (1994) for chalcopyrite and pyrite, respectively.

Mineral type	Model
Chalcopyrite	$\frac{d[CuFeS_2]}{dt} = k_{r1} [H^+]^{0.8} [Fe^{3+}]^{0.42}$
Pyrite	$\frac{d[FeS_2]}{dt} = k_{r2} [Fe^{2+}]^{-0.4} [Fe^{3+}]^{0.93}$

An example slice of an idealised particle containing two spherical mineral grains (copper mineral and pyrite) is shown in Figure 4.31. The concentration of H^+ being consumed by copper minerals and produced by the oxidation of pyrite is shown, as well as the non uniform leaching of the grains pointing out again the unrealistic assumption of spherically uniform leaching in the SCM.

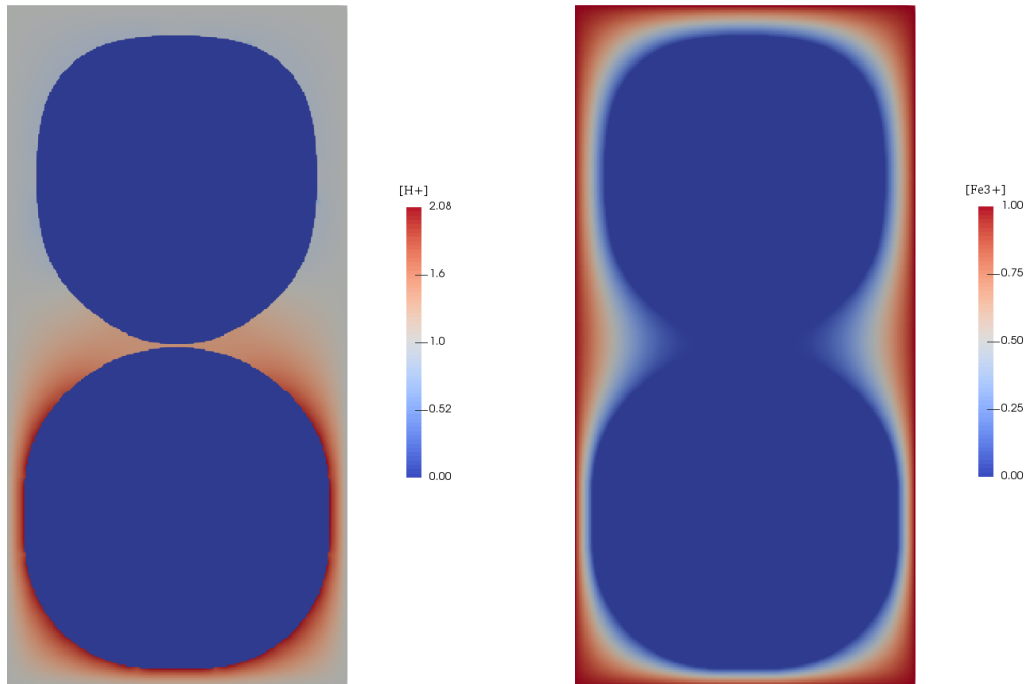


Figure 4.31: Example slice of the simulation of a copper mineral grain besides a pyrite grain. The production of Fe^{2+} by the latter hinders the dissolution of the former. See equations in Table 4.7.

This is further stressed when looking at the pattern of the concentration front entering the particle. As the ore texture is used as the simulation domain and some grains leach slower (or not at all), the concentration of the reagent does not follow a symmetrical front as can be observed in Figure 4.32, an example slice of a particle's concentration profile

mid-way the leaching cycle with grains at different stages of leaching. This shows that the simulator can represent the effect of the ore's texture on the leaching process and thus the inter-particle variability naturally occurring in heap leaching.

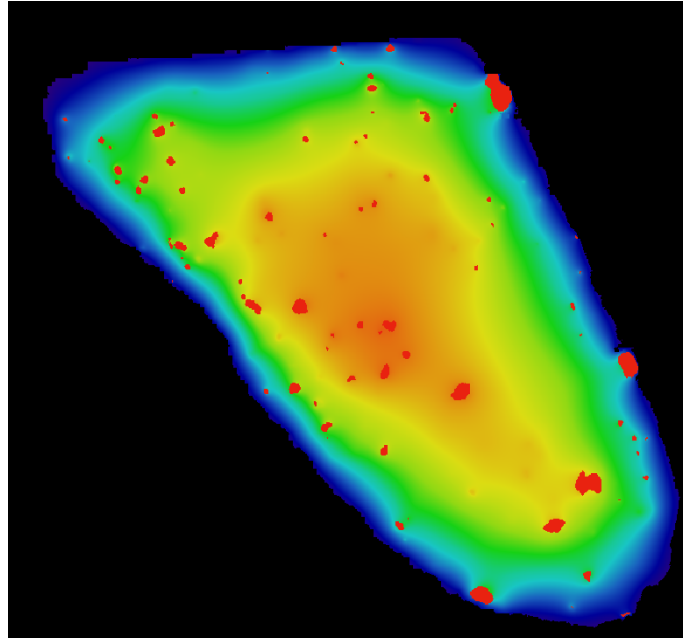
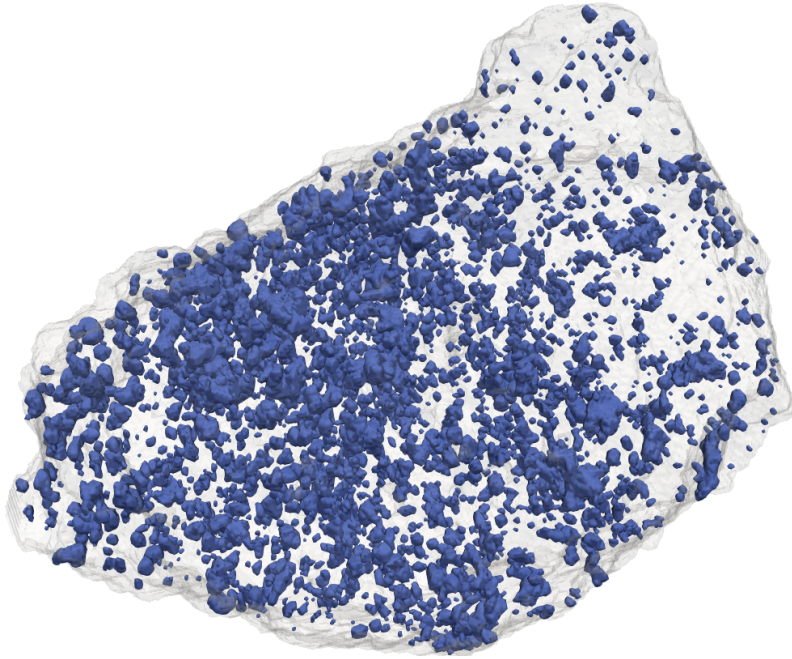


Figure 4.32: Example of the concentration profile inside the particle shows that some grains act as shields for the front to enter the particle, slowing down the leaching process of inner grains.

The effect of this asymmetrical leaching can also be observed when looking at the fluxes of reagent (Fe^{3+}) over the grains' surface. Figure 4.33 shows the initial stage of a particle before the leaching has started and leaching after some time (dimensionless time is used for simulations before calibration). It can be observed that some grains, although been at the particle's surface, do not leach as fast as some inner grains. This slow leaching grains shadow near inner grains and thus slow down their kinetics. It can also be observed that most high fluxes are located in the grain's surface that looks outwards of the particle, which is to be expected since the inner region of the particle has lower concentration values. Gangue and porosity type elements have been render transparent to allow the visualisation of the grains' surface.

Figure 4.33 also shows how the simulator tracks each grain's volume, so grain-type volume elements that have been totally leached can be replaced by a gangue-type element. This means that the permeability of the particle increases over the leaching cycle, emulating what it is known to happen in real leaching systems (Lin et al., 2005).

(a)



(b)



Figure 4.33: Grain-type voxels that are completely leached are replaced by gangue-type voxels increasing the particle's permeability over the simulation time. a) Initial condition b) Mid simulation time with fluxes rendered on the grains' surface.

4.7.3 Comparing simulation against experimental data

Using the early leaching data from each experimental column over the first 23 days the simulator parameters, namely the values for k_{r1} , k_{r2} and the gamma distribution's α and β , can be calibrated. Result of the fitting can be seen in Figure 4.34, where a good correspondence with experimental data can be seen, even for days later than 23.

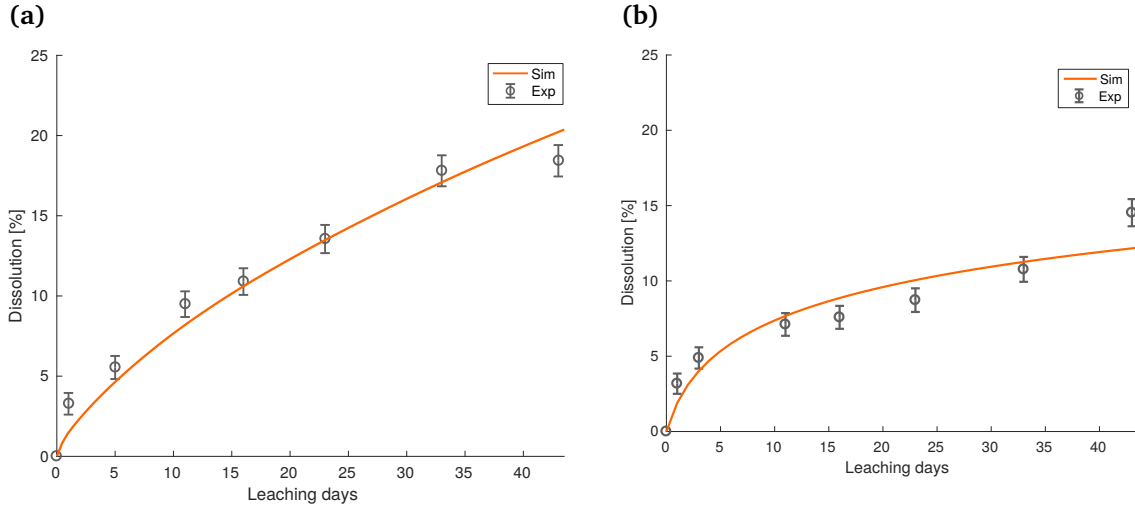


Figure 4.34: Calibration results for high (a) and low (b) Eh columns, good fit is achieved for the whole leaching cycle, even for later days which are out of the calibration set.

The simulator can simulate the data well with very few fitting parameters, but as the model is capable of simulating and tracking individual grains, a sub-classes assessment can be performed in order to investigate the distance to the surface and grain size dependency of the leach rate. Figure 4.35 shows the fitting of two different subclasses of distance and grain size. This figure shows that the models not only fits the average behaviour of the whole particle, but also how leaching depends on distance to the surface and the grain's size. Fitting is not perfect as the leaching rate of individual grains is assigned randomly from the measured representative distribution and not based on the actual grain-by-grain kinetics. This ensures a more generic fit instead of an overfit to the data.

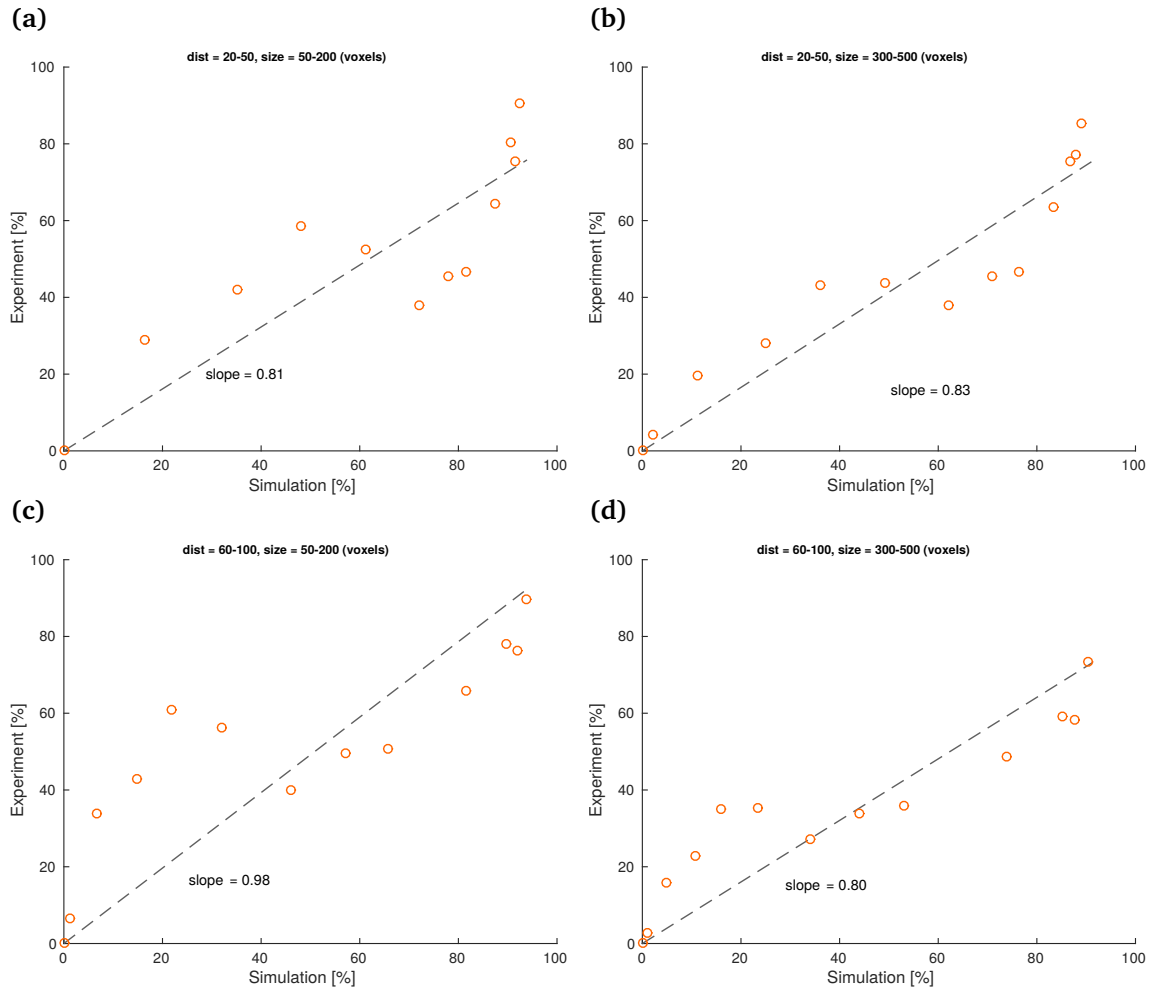


Figure 4.35: Fitting for distance and grains size subclasses. Simulation shows good fitting ($slope \approx 0.8$) for different subclasses of size and distance to the surface.

A Monte Carlo simulation is then carried out using different particles as simulation domain to take into account the inter-particle variability. Figure 4.36

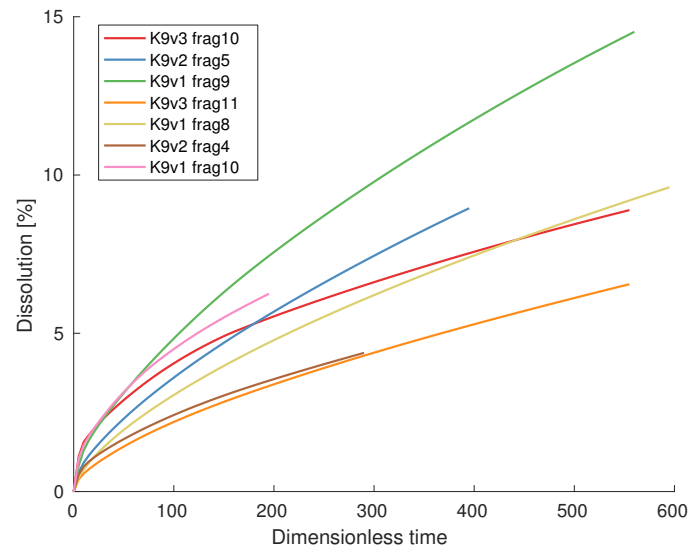


Figure 4.36: Simulation with different particles as simulation domain so the variability introduced by the particle's shape and porosity can be incorporated into the simulation.

At the same time different seeds for the random number generator are used to take into consideration the intra particle variability. Figure 4.37 shows the results for a high Eh and a low Eh column. The coloured area shows the 95% confidence interval obtained from the Monte Carlo simulation.

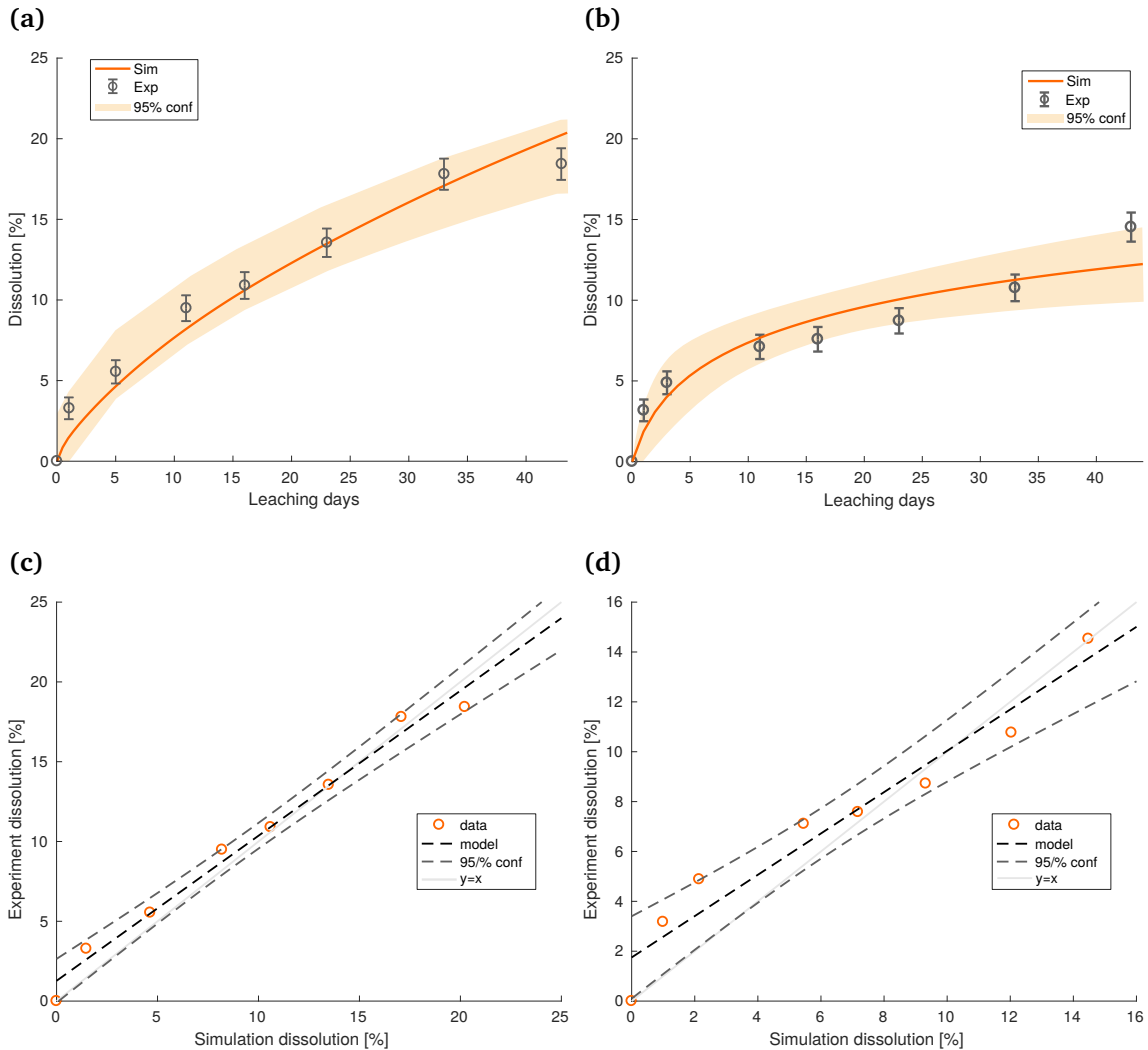


Figure 4.37: Simulation results. Using several particles and different seeds for the random number generator the behaviour of the dissolution can be assessed and presented with confidence intervals.

When focussing on the mineralogy aspect of the simulation, measurements from ICP can be compared against the simulation. Figure 4.38 shows the simulation results for copper average extraction against the total sulphide extraction (copper and pyrite). Error bars show the variability, two standard deviations, expressed by the Monte Carlo simulation. The red line corresponds to the values obtained from the ICP analysis of the leachate and feed solutions. Good correspondence can be observed between simulations and experimental results.

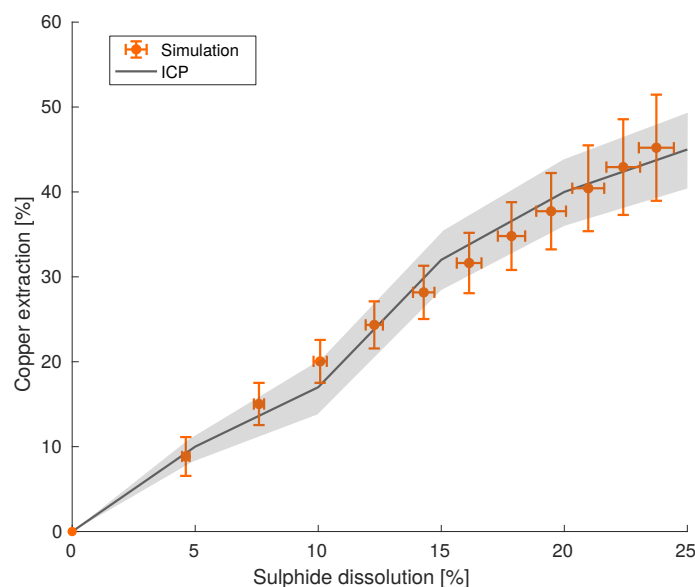


Figure 4.38: Extraction of copper compared against total sulphide dissolution as obtained from ICP and simulations. The trend obtained from experimental measurements is also observed in the simulations. Shaded area shows the uncertainty in the measured ICP recoveries.

4.8 Conclusions

The importance of lifting the most common used assumptions in the Shrinking Core Model were assessed, showing that the inclusion of variability in the rate kinetics and the ore's texture has a strong effect on the behaviour of the leaching process in later times. Considering these variabilities allows for not only a better fit of the ultimate recovery, but also provides a better explanation on the regime governing the system.

A new methodology to assess apparent leach kinetics, combining information provided by X-ray micro-tomography and scanning electron microscopy. Previous research showed the capabilities of XMT in assessing the variability in leach kinetics, although mineralogy influences were not studied. Linking SEM/EDS mineral information into the 3D structural data of the ore given by XMT provides a new insight into leach kinetics, generating a large database of leaching behaviour at the grain scale. Pyrite and copper bearing minerals showed different probability distributions, with copper minerals hinting a bi-modal distribution and pyrite a narrower mono-modal distribution. Although to be expected, this allows for assessing and quantifying for the level of difference between these minerals.

The result of this methodology is a new model for apparent leach kinetics, where the intrinsic variability of the kinetics is exposed and decoupled from leaching conditions, grain size and mineralogy. These new leach kinetics can be applied for scaling up models for improving prediction of the leaching behaviour and its ultimate recovery. The methodology was presented in a copper sulphides leaching system, but it can be applied to the leaching of other metals. This methodology can be used as a fast assessment tool that

could significantly reduce many months required in traditional experimental procedures to assess leach kinetics. Future work involves the use of the distribution in Figure 4.23 to correct for the errors in quantifying the leach kinetics of non-soluble grains that leads to negatives values.

A fully parallel dynamic simulator of the leaching process at the particle scale has been introduced. The simulator consists of a multi-species system where different mineral kinds are leached by a set of reagents, emulating the chemistry happening in a real leaching system. Using data directly obtained from ore samples by X-ray micro-Tomography and Mineral Liberation Analysis, apparent leach kinetics variability is analysed and decoupled from grain size, distant to the surface and mineralogy. This modelling and simulation allows for lifting many of the commonly used assumptions when simulating leaching at the particle scale, like shape and distribution of mineral grains and the presence of a quasi-steady-state regime. This latter assumption was tested comparing the dynamic simulator and the QSS version against experimental data of a long leaching experiment. Results showed that although both simulators fit the data and achieve accurate predictions of the late stage of the leaching cycle, the QSS simulator interprets the system as being in a more reaction-control regime than it actually is. This can lead to misinterpretations of the leaching regime and thus misleading the limiting factors that are hindering the process.

Using the dynamic simulator and using a Monte-Carlo-like simulation approach, experimental data was fitted in order to predict the leaching behaviour. Different particles were used as the simulation domain in order to take account of the inter-particle variability. The newly assessed apparent leach kinetics were used to take account of the surface kinetics variability. Simulations show good agreement with experimental results in terms of the recovery of copper and the interaction with gangue minerals like pyrite. Thus, the simulator can take into account the inter and intra particle variability of the leach kinetics, allowing for the accurate prediction of the leaching performance.

Future work involves using the simulator for predicting macro scale heap leaching behaviour and to adapt, if necessary, the methodology to allow for the assessment of the leaching of agglomerates and the simulation of the accumulation of elemental sulphur in the reaction zone.

Chapter 5

Assessing and quantifying liberation

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5.1 Introduction

Liberation is one of the two fundamental operations in minerals processing; the other being concentration (Wills and Atkinson, 1993). Its importance resides in the fact that it sets the maximum possible grade for a given recovery of downstream processes (Carasco et al., 2016; Leißner et al., 2016b). This limitation is apparent when plotting a grade/recovery curve as in Figure 5.1, for a given recovery, there is a maximum theoretical grade a mineral processing system can achieve. The extent of liberation, or shape of this curve, will strongly depend on the ore's texture, the equipment and the separation method used (Miller et al., 2009). Liberation is thus a key factor in the performance of mineral processing systems

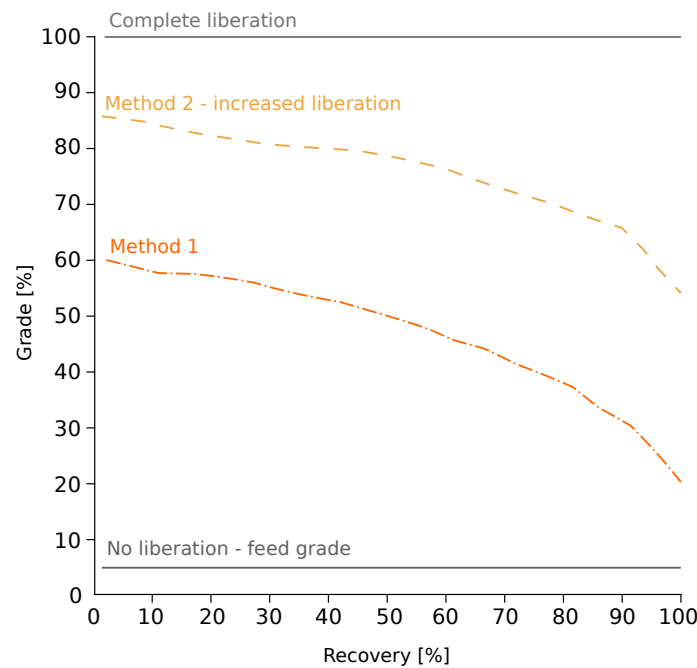


Figure 5.1: Illustration of a grade/recovery curve comparing two different liberation methods. Adapted from Miller et al. (2009).

Albeit a key parameter, there is no consensus on how to define liberation, and furthermore on how it should be quantified (Bérubé and Marchand, 1984). After breakage the ground particles will exhibit a liberation distribution, as shown in Figure 5.2, where some particles will contain only gangue minerals (liberated gangue), partial content of valuable mineral and fully liberated particles.

Initially Gaudin (1939) quantified this liberation distribution using the Degree of Liberation (DL). As shown in Equation 5.1, the Degree of Liberation of a sample of particles is defined as the mass fraction of free valuable mineral—particles that are composed of only valuable mineral—with respect to the total valuable mineral in the sample.

$$DL = \frac{\text{mass of free valuable mineral}}{\text{total mass of valuable mineral}} \quad (5.1)$$

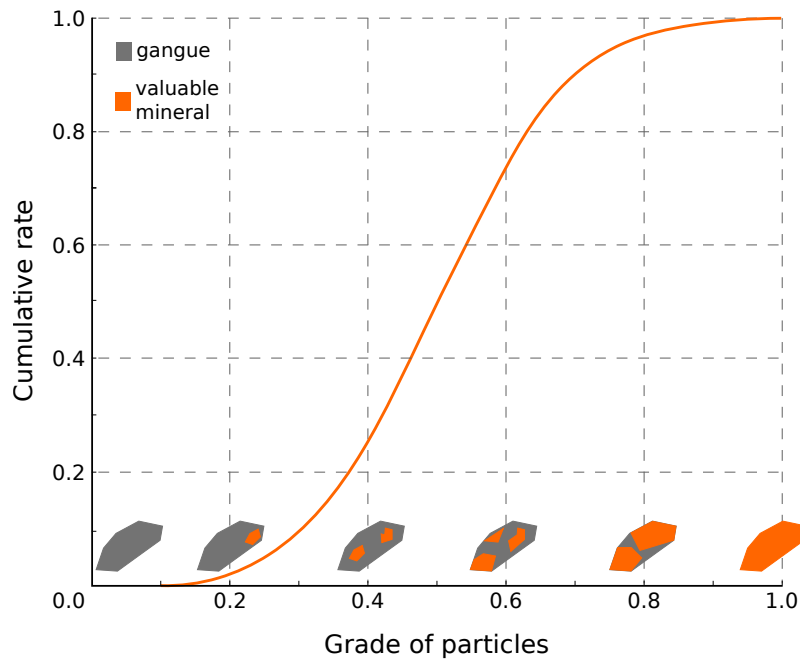


Figure 5.2: Schematic of a liberation distribution after grinding a sample. Upgrading is achieved via breaking the particles into smaller particles, where some might achieve full liberation.

This index, though, does not consider the possible upgrade achieved in not fully liberated particles (Vallejos et al., 2018). To account for this Bérubé and Marchand (1983) defined the Liberation Coefficient (LC). Equation 5.2 shows that this coefficient considers all particles containing the valuable mineral.

$$LC = \frac{\text{mass valuable mineral}}{\text{total mass of particles containing valuable mineral}} \quad (5.2)$$

Both of these coefficients describe single points of the liberation distribution (Leißner et al., 2013) and they do not consider the quantification of the surface exposure of the valuable mineral. In this document liberation is described and quantified using both grade and surface exposure (definitions of both introduced in Section 2.2). Calculating both grade and surface exposure for each particle in the sample, as shown in Figure 5.3, allows for the creation of a distribution of these descriptors. Being these distributions the quantification used to characterise liberation.

The inclusion of surface exposure into the quantification of liberation is because in concentration by flotation, performance depends heavily on the achieved surface exposure of the floatable minerals, with flotation being one of the most widely used separation technology in minerals processing (Wills and Napier-Munn, 2005). This is especially crucial for coarse particle flotation where the amount of available surface exposure is often the limiting factor. Furthermore, the relationship between liberation and surface exposure is a complex function of the mineral texture as liberation of the valuable minerals from the gangue is normally carried out by comminution (Mariano et al., 2016; Ozcan and Benzer,

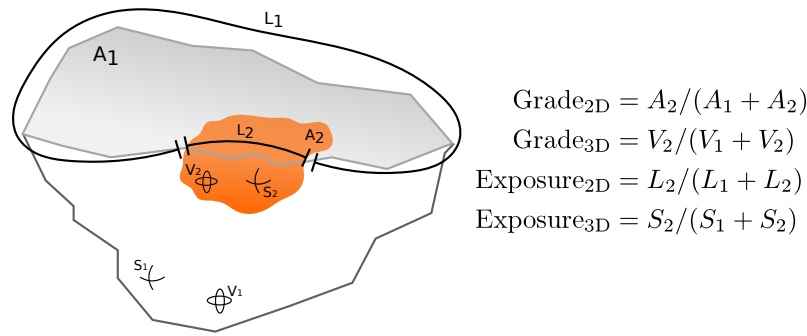


Figure 5.3: Liberation calculated as grade and surface exposure in both 2D and 3D.

2013; Yin et al., 2017).

5.2 Imaging quantification of liberation

Grade and surface exposure are commonly quantified using automated mineral analysers equipped with Scanning Electron Microscopy and Energy Dispersive X-ray Spectrometry analysis from particle's polished sections (Leißner et al., 2016b; Little et al., 2016). Little et al. (2015, 2017) assessed the effect of different mill types on the resultant mineral shape and liberation, with the aim of understanding how these parameters may affect flotation performance. The authors concluded that, for the specific ore and particle size used, both shape and liberation were predominantly a function of ore texture and not on whether milling occurs in a ball or stirred mill.

The main issue with this kind of analyses is that the intrinsically 2D nature of automated mineralogy techniques translates into significant stereological effects. Correcting for these effects is challenging as requires knowledge of grain shape, often erroneously assumed to be spherical or ellipsoidal (Sahagian and Proussevitch, 1998). Performing sequential polishing and scanning can account for this, but it is very time consuming and highly labour intensive (Lätti and Adair, 2001). Early attempts to correct for stereology were proposed by Miller and Lin (1988) using simulation tools to understand the relationship between 1D (linear grade) and 2D (area grade) information for estimating 3D (volume grade) distributions. Recent work using simulated ore has been proposed by Ueda et al. (2016), Van Der Wielen and Rollinson (2016) and Hilden and Powell (2017). On the other hand, Fandrich et al. (1998) and King and Schneider (1998) attempted to correct grade distributions using real ore. However, the method requires for narrow grade and size fraction distribution and was only validated in 3D by mass balance between the two assumed species. Zhang and Subasinghe (2013) presented an updated model that directly uses image analysis information in order to account for the ore texture and lifted assumptions that made previous models unsuitable for high grade ore. Yet again the models were not validated against real 3D measurements. In the case of surface exposure, to

the best knowledge of the authors there is still no correcting methodology.

As it has been shown in previous Chapters X-ray Micro-Tomography (XMT) is an imaging method that can non-invasively and non-destructively delineate the rock and the mineral grains in 3D. This provides an alternative method to directly image the full 3D particle, eliminating the need for stereological corrections and readily providing surface exposure (Miller and Lin, 2018). Garcia et al. (2009) for example, used XMT scans of particles to study interfacial area as a metric for assessing preferential breakage after compression, showing that low energy dissipation is the preferred way for creating grain boundary fractures. Grade can also be studied for simple mineral systems like in Lin and Miller (1996), where the authors used the information provided by XMT to obtain 3D grade distributions in a Sphalerite/Dolomite system. Using a two-level threshold and a connected components labelling technique authors were able to quantify the content of both minerals of interest. Miller et al. (2009) used an updated algorithm to construct grade/recovery curves and compared the results between the 3D and 2D information, showing that the latter overestimates the extent of liberation. This result contradicts the findings by Lätti and Adair (2001), reinforcing the importance of the effect that the ore's texture has on the results one can obtain. Recently, Wang et al. (2017) presented a methodology for the quantification of mineral grains surface exposure using XMT. The methodology includes image processing operations for compensating of known XMT and image processing artefacts. Here we proposed a similar approach to the one presented by Wang et al. (2017) with a more extensive assessment, incorporating particle size and mineral grade into the analysis. This allows for further understand the nature of comminution that is achieved for a given ore and its ultimate flotation response such as the existence of preferential breakage. A generic low-grade porphyry copper ore is used to show the methodology.

5.3 Materials and methods

5.3.1 Ore sample

A porphyry copper ore with a grade of 0.8 wt% copper was used to illustrate the capabilities of this method. Table 5.1 summarises the mineral composition as obtained from an MLA assessment of the larger particles before comminution. A total of 33 representative fragments were sliced, polished and scanned. These particles were representative of those subsequently crushed and were in the size range 8.0 mm to 12.2 mm. The main non-sulphide gangue mineral is quartz, with pyrite being the main sulphide constituent. Copper minerals are mainly chalcopyrite, though accompanied by a range of other copper containing species (see Table 3.1 for details).

Another representative sample of the fragments were crushed in four stages using a

Table 5.1: Main mineral composition of the ore sample. Main minerals are primary copper sulphides, pyrite and a gangue consisting of mainly quartz.

Mineral type	Weight %	Specific gravity
Copper containing species	2.13 ± 0.47	~ 4.37
Pyrite	7.00 ± 2.74	4.95
Gangue minerals	90.69 ± 2.73	~ 2.70

Fritsch lab jaw crusher Pulverisette 1. The crushed material was sieved into eight size classes (particle size distribution shown in Figure 5.4. The procedure involved the repeated crushing of different size intervals of material in order to have similar amounts of material in each interval. The material that remained about $212\mu\text{m}$ was not included in the analysis as this is beyond typical flotation sizes and we wished to investigate the XMT performance at finer sizes (we already know that it performs well with larger particles).

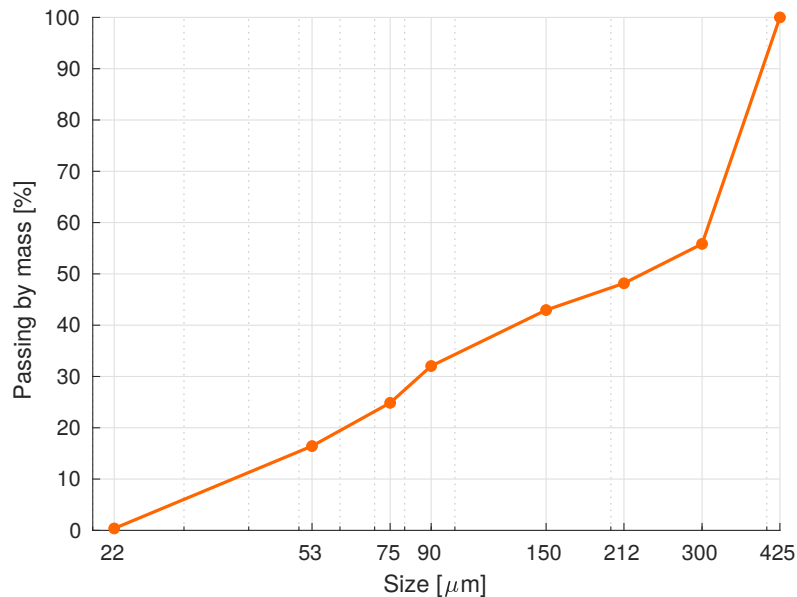


Figure 5.4: Particle size distribution of crushed ore. Sizes are $300\mu\text{m}$, $212\mu\text{m}$, $150\mu\text{m}$, $90\mu\text{m}$, $75\mu\text{m}$, $53\mu\text{m}$ and $22\mu\text{m}$.

5.3.2 XMT scans

Sample preparation for scanning was performed by taking representative samples of each size class via coning and quartering. These samples were placed in a 6.0 mm perplex column as shown in Figure 5.5. The width of the column plays a key role, as it defines the resolution of the images when the field of view is set as the column width. For this imaging equipment, the resolution is 1000th of the width of the field of view, which gave a voxel size of $6.21\mu\text{m}$ when imaging the whole column.

The sample was scanned using a Zeiss Xradia 510 Versa system. Three different energy

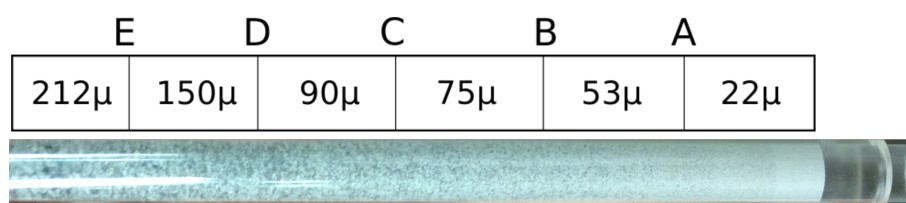


Figure 5.5: Sample preparation. Coning and quartering was used to sample each size class and placed in ascending size order in a 6.0 mm column.

levels (50 kV, 60 kV and 70 kV) were tested together with different resolutions (1.01 μm , 2.01 μm , 3.1 μm and 6.21 μm). This was done in order to ascertain the best scanning conditions, as well as the best compromise between accuracy and scanning time. High energy scans can be carried out more quickly than low energy ones, but result in less contrast between different sulphide minerals, while lower resolution scans allow larger sample sizes to be scanned in a given time, but contain less spatial information. It was found that for this particular ore the highest energy level provided a good contrast between the gangue and the sulphide minerals. Spatial resolution was selected as the lowest value that provided no significant change in the results with a further increase in the resolution, so that scanning time is minimised and the number of analysed particles is maximised. A summary of all the acquisition parameters are listed in Table 5.2, where it can be seen that two spatial resolutions were used for this analysis. This optimum resolution and scanning energy combination will vary with the ore type being studied, being especially dependent on the mineral texture.

Table 5.2: Scanner conditions for X-Ray XMT scans.

Parameter	Value
Voltage	50, 60 & 70 kV
Power	4, 6 & 8 W
Filter	none
Exposure	1 - 2 s
Projections	2001
Resolutions	1.01, 2.01, 3.1 & 6.21 μm

To minimise the data collected time the column sample was scanned such that two size classed fitted into a single field of view, thus allowing data for all size intervals to be obtained from four scan volumes. This can be observed in the slices shown in Figure 5.6, all scanned at 70 kV and 6.21 μm per pixel resolution.

It was found that for this particular ore the highest energy level provided a good contrast between the gangue and the sulphide minerals. The highest resolution was used when scanning particles bellow 53 μm , while for coarser ones 6.21 $\mu\text{m}/\text{px}$ was the preferred resolution. This optimum resolution and scanning energy combination will vary with the ore type being studied.

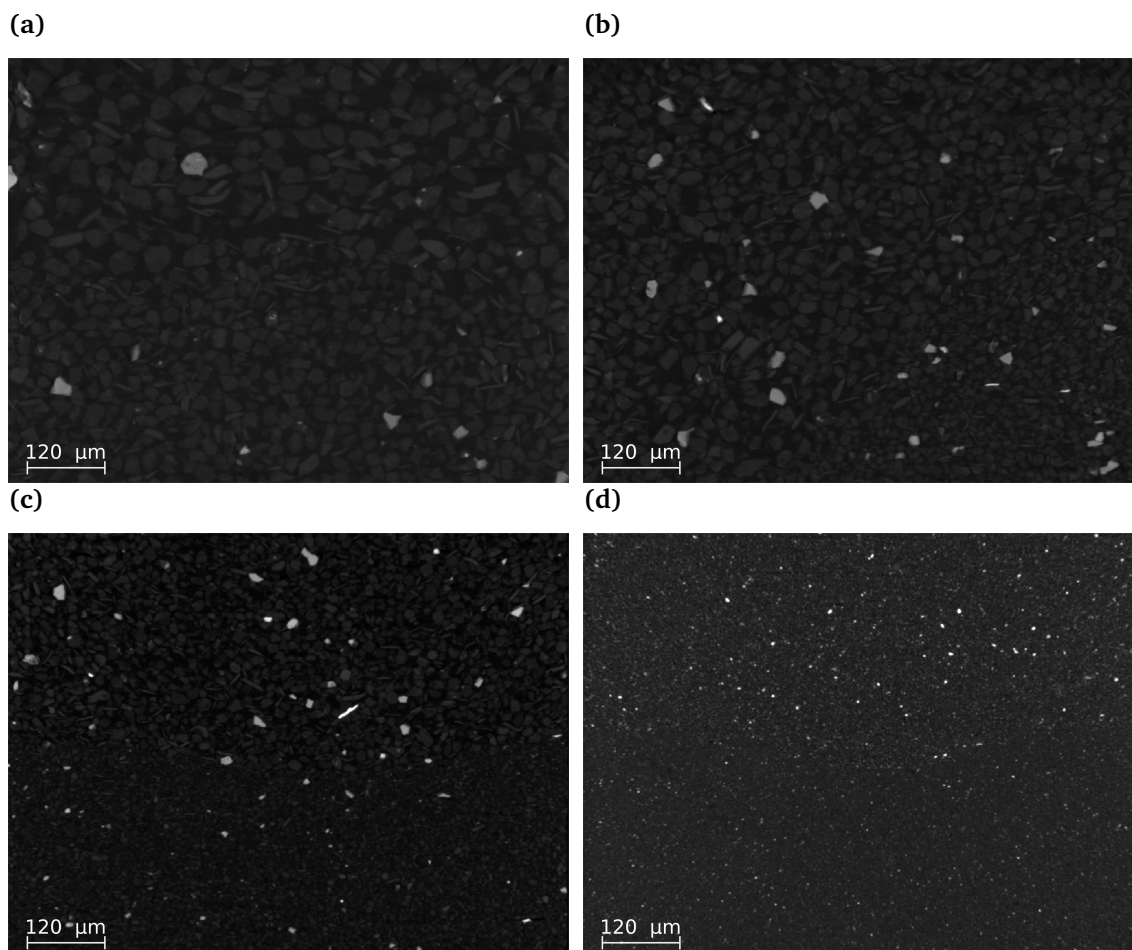


Figure 5.6: Sample slice of acquired images. Scanning regions were selected so two different size classes fit in. Good contrast can be observed between gangue and metallic material (the reader is referred to the digital version of this document for better contrast).

5.3.3 Image processing

Handling of the images and the post-processing was performed in a combination of Avizo® and Matlab®. After cropping the image to remove the column, a global threshold was found that segmented the fragments from the air in between them. Object separation algorithms were then used to identify each individual fragment and to assign a unique identifier to each of them. Figure 5.7 is an example of the resulting 3D label image.

A similar procedure was then carried out to identify each of the sulphide mineral grains in order to obtain a 3D image where each fragment is individually identified together with each of the mineral grains it contains. Figure 5.8 shows a rendering of an example volume, where gangue is shown in a transparent grey colour and sulphide grains are rendered according to their unique label numbers.

The next stage of the data analysis was to calculate the surface area of each of the particles, as well as the exposed surface area of each of the grains that intersects the particle surface. In order to obtain the exposed surface, a distance map for the particle is firstly calculated, which indicates the distance of each voxel to the air phase. This map can

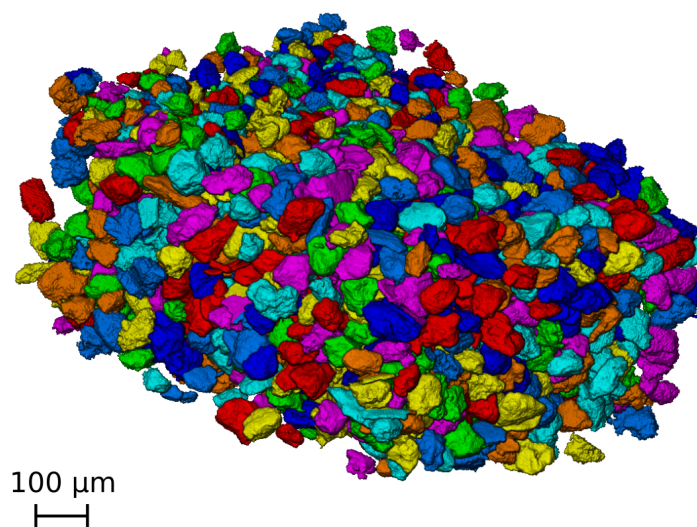


Figure 5.7: Segmented fragments. Fragments are separated from one another and a unique label number assigned to each of them.

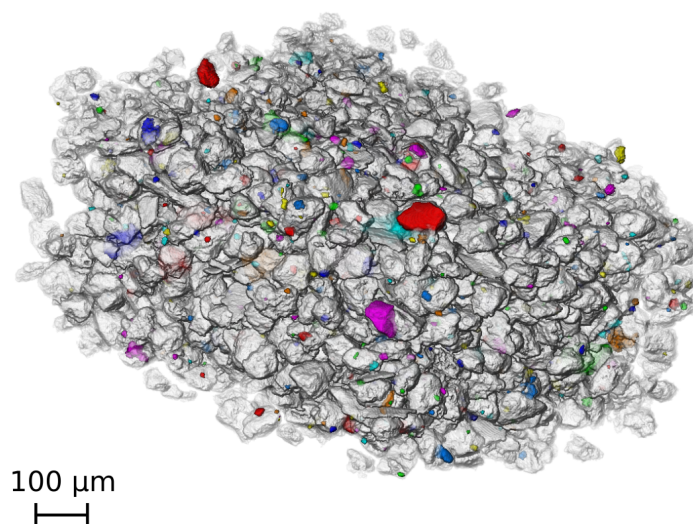


Figure 5.8: Result of image post-processing. Gangue is rendered transparent to show internal grains coloured according to their unique assigned label. Some partially and completely liberated grains can be observed.

thus be used to obtain those voxels that are directly adjacent to the air (zero distance), together with both the particle and mineral grain ids associated with these voxels. In this way, the surface exposure of the whole particle and the mineral phases within it can be obtained. This can be done in a 2D (perimeter exposed) and 3D (surface exposed) fashion. The measured volumes, surface areas, and lengths of the particles and sulphide grains can then be used as the basis for analysing the grade and liberation distributions of the samples.

Because XMT is able to scan a volume of packed particles, a substantial number of them can be analysed in a single scan. For the size classes examined, the total number of particles tracked is nearly 20,000, with approximately 70% of them being fully liberated gangue. The smallest particles, with less than 100 voxels in volume (around 12 μm in

diameter) were discounted from the analysis due to the high uncertainty in their quantification (as pointed out by Lin et al. (2015)) and because they will have been misclassified as small particles belonging to the bigger size classes. Table 5.3 details information on the number of particles scanned in each size class and the proportion of them, by mass, that are liberated gangue. As expected, this proportion increases as the particle size decreases.

Table 5.3: Number of tracked particles for each particle size category.

Size class	# Particles	Mass fraction of liberated gangue
B (53-75 μm)	6831	0.82
C (75-90 μm)	5550	0.67
D (90-150 μm)	4057	0.66
E (150-220 μm)	2731	0.61

5.4 Results

Three different energy levels were tested at a resolution of $6.21 \mu\text{m}/\text{px}$. Figure 5.9 shows an example slice of a scan of section B of the column scanned at 50 kV and 70 kV. No significant difference was apparent in the scans, and therefore the highest energy was later used for the other scans as it minimises the scanning time and increases the sharpness of the images. The reason for testing the lower energy level is that the difference in X-ray attenuation of the minerals of interest tends to increase with decreasing energy.

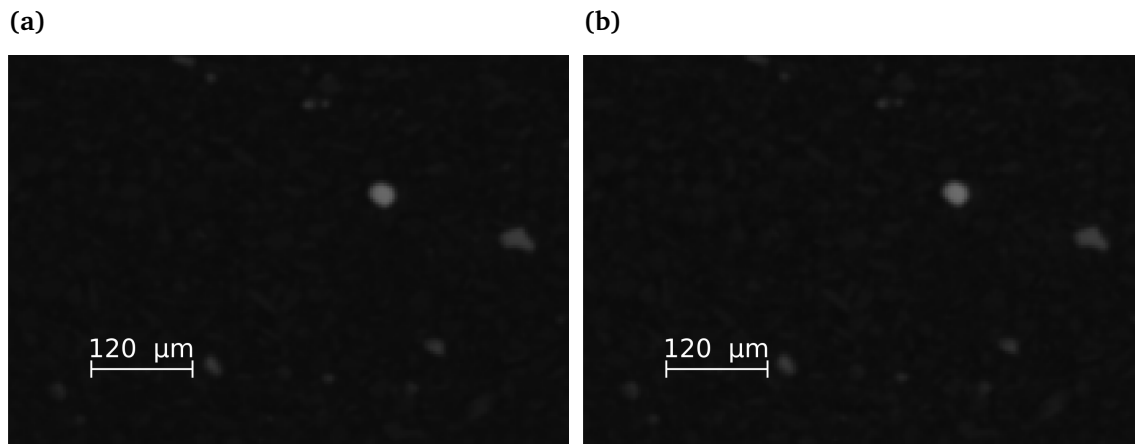


Figure 5.9: Different scanning energy levels. (a) 50 kV and (b) 70 kV. No significant difference was observed and therefore the highest energy level was used in later scans as it minimises the scanning time.

Having the energy level set, three scanning resolutions were tested. Fitting the whole column in the field of view sets the resolution at $6.21 \mu\text{m}/\text{px}$. Higher resolutions implies that only a region of interest of the core of the column is scanned. Figure 5.10 shows an example slice of a scan of section C at resolutions of $2.01 \mu\text{m}$, $3.1 \mu\text{m}$ and $6.21 \mu\text{m}/\text{px}$. As expected, higher resolutions mean a crispier image, but a smaller sample size. Better contrast between the gangue and the surrounding air is also achieved at higher resolutions,

but no significant improvement can be observed going from 3 to 2 $\mu\text{m}/\text{px}$.

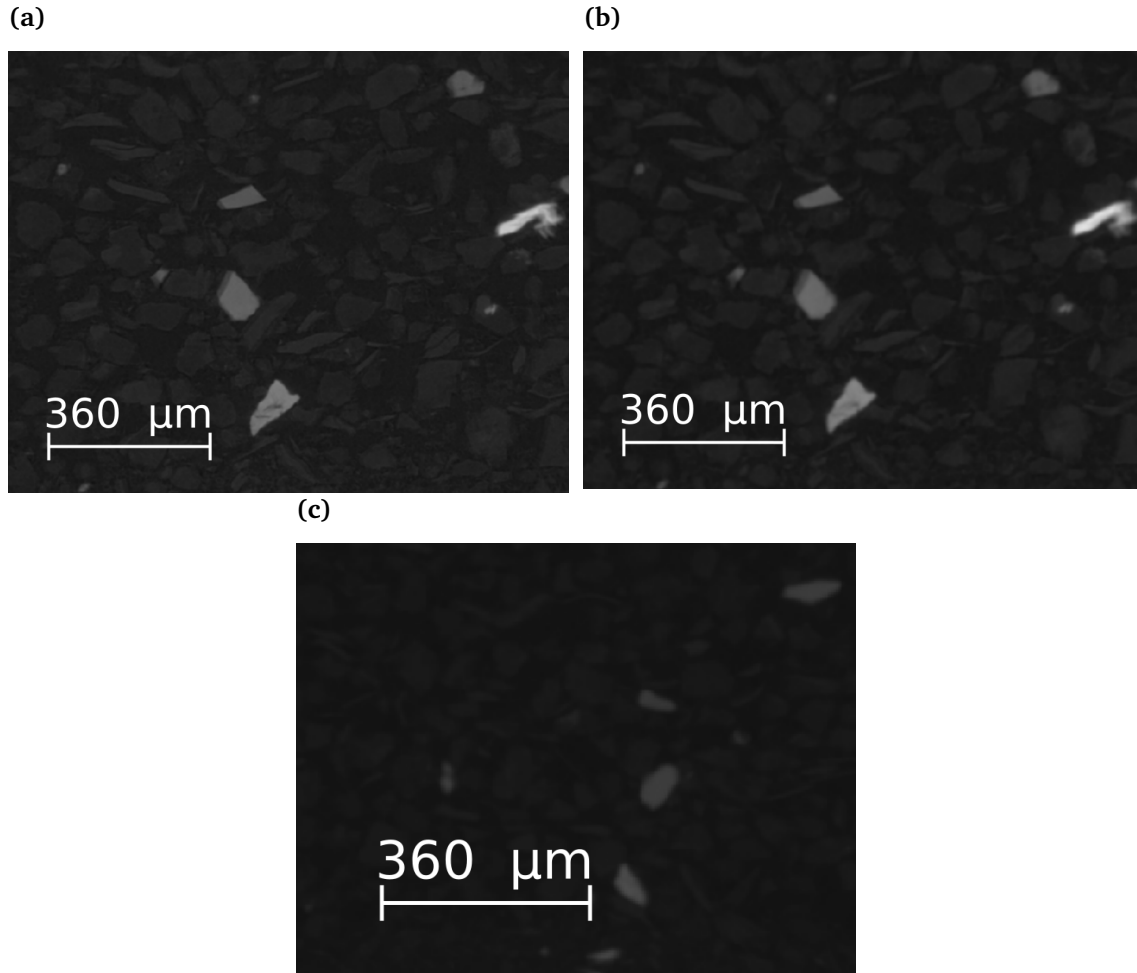


Figure 5.10: Result of image post-processing. (a) 2.01, (b) 3.1 and (c) 6.21 $\mu\text{m}/\text{px}$ resolution. No significant improvement can be observed between the highest two resolutions. Conversely, significant blurring is observed at the lowest tested resolution.

5.4.1 Grade quantification

Considering all possible slices through every fragment, the distribution of grade in 2D and 3D must coincide. Figure 5.11 shows how this distribution changes depending on the particle's size, considering classes C (75 – 90 μm), D (90 – 150 μm) and E (150 – 220 μm). As expected, the finer the fragments, the more liberated material can be found in the form of high grade particles. A composite created by weighting the data according to the mass fraction in the crushed product is also included.

5.4.2 Surface exposure quantification

In the case of surface exposure, even considering all possible slices per fragment the 2D and 3D data differ. Figure 5.12 shows how 2D data does not converge to the 3D surface exposure, this is observed at all sizes studied. This shows that it does not matter how

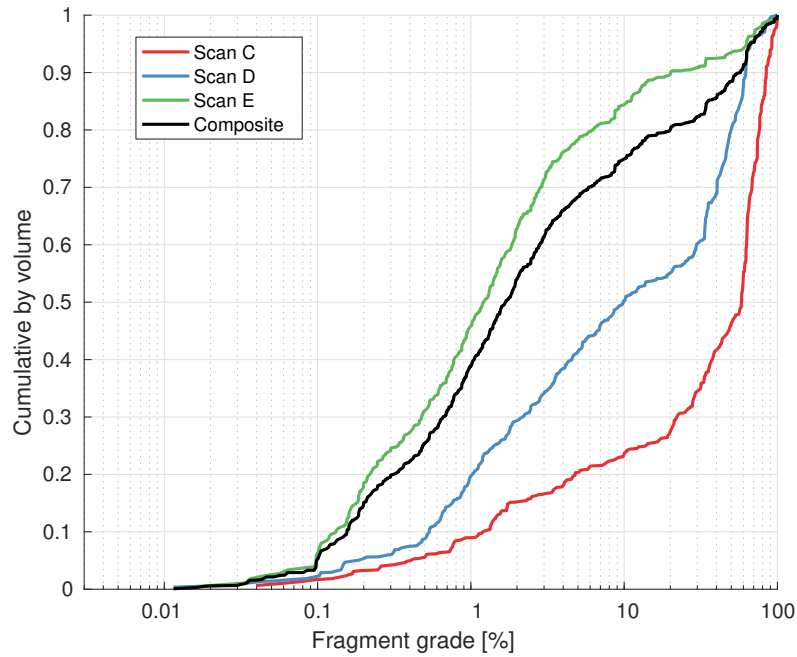


Figure 5.11: Grade quantification at different fragment size. As expected, grade increases with a decreasing fragment size. Scan C 75 – 90 μm , Scan D 90 – 150 μm , Scan E 150 – 220 μm .

many particles are analysed by means of 2D slices, it cannot compensate for the loss of 3D information. While stereological corrections for particle and grain size distribution are possible as long the grain shapes are known, they are notoriously difficult to carry out for surface exposure. Wang et al. (2018) only corrected for liberated gangue category

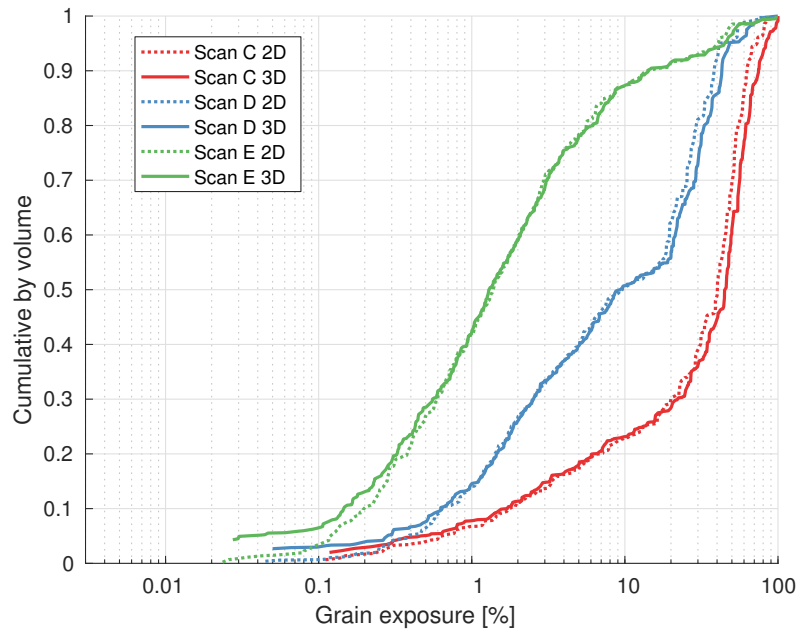


Figure 5.12: Exposure quantification at different fragment size. Similarly to grade, liberation improves with a decreasing particle size. Scan C 75 – 90 μm , Scan D 90 – 150 μm , Scan E 150 – 220 μm .

As it analyses a 3D volume, XMT can be used to simultaneously measure a large number of particle fragments. Even though a large proportion of the particles in this sample

consist of liberated gangue (over 70%, by number), there are still sufficient particles (1552 individual particles) for those that contain sulphides to be divided into a number of categories based on both the diameter of the fragments and their grade, with sufficient grains in each category to obtain not only a statistically valid mean, but also a distribution. Category boundaries for both parameters were chosen so that a similar amount of sample is present in all of the combinations (note that fully liberated gangue was excluded from this analysis). Figure 5.13 shows a chequerboard plot of the average surface exposure for each combination of fragment's grade (by volume) and size (e.g. for fragments with a size between 50 and 64 μm and a mineral grade between 20 and 50%, the expected level of exposure will be around 25%). As expected, surface exposure is strongly correlated with grade (p-value < 0.01). Conversely, for this particular ore and crushing procedure, there is only a weak influence of the particle size on the grains' surface liberation for a given fragment grade (p-value > 0.10). A strong influence of particle size on surface liberation for a given grade would be indicative of preferential fracture. A slight indication of preferential breakage can be seen at the higher grades where finer, high-grade particles have a higher surface exposure than the coarser particles.

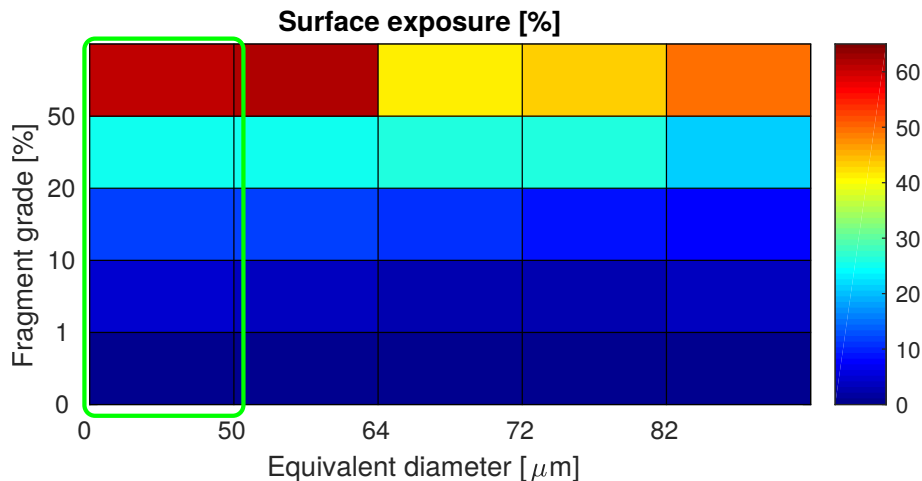


Figure 5.13: Surface exposure as function of fragment's size and grade. Grade, as expected, shows a strong correlation with the surface exposure of mineral grains. The size of fragments is only weakly correlated.

The variability of surface exposure in each of these categories is also of interest as a reasonable degree of surface exposure is required for good flotation performance and therefore even if the average surface exposure is sufficient for good flotation performance, losses in the category could still be experienced if there is a significant amount of material with exposure much less than the average. Figure 5.14 shows this surface liberation distribution for each of the categories highlighted within the green rectangle in Figure 5.13 (5 grade classes with particles in the size interval 22 μm to 50 μm). It can be observed that most categories show comparatively narrow distributions, which translates into an average liberation that is representative of the behaviour of most of the particles in the

category.

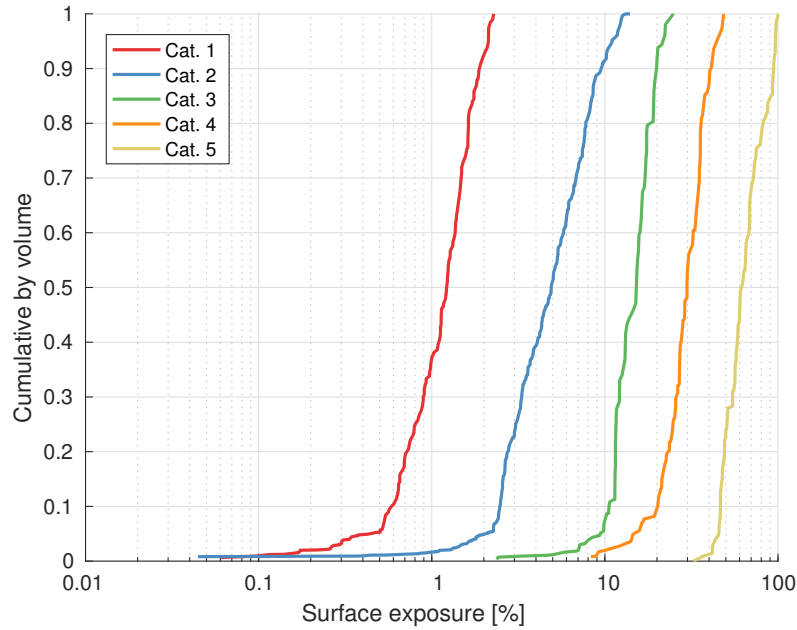
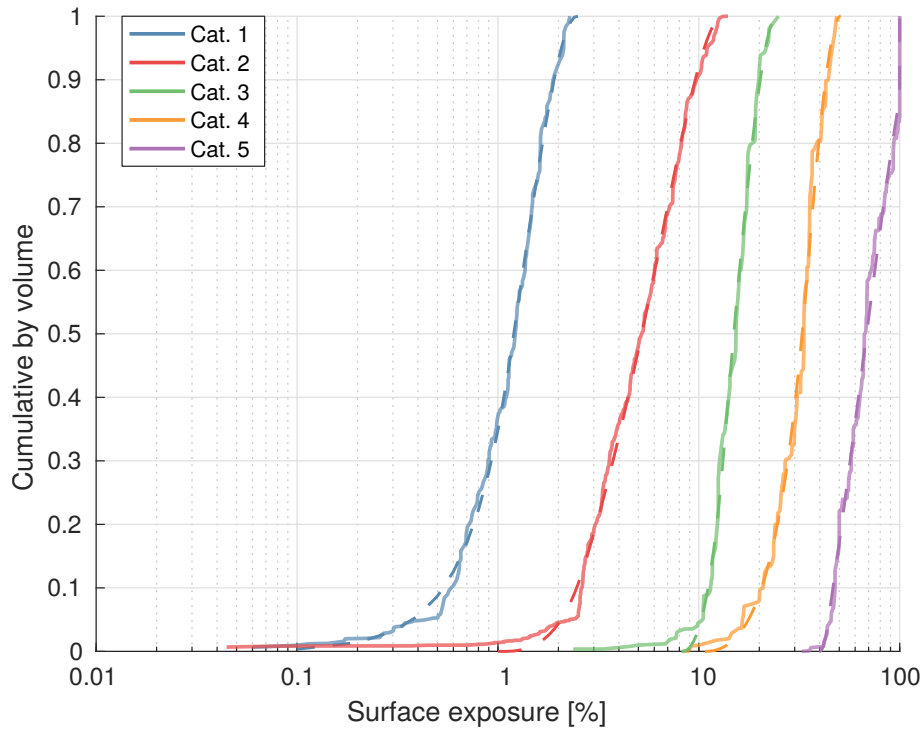


Figure 5.14: Example surface exposure within selected categories of grade and size. Categories highlighted in Figure 5.13 by a green rectangle are shown. These include particles in the $22 - 50 \mu\text{m}$ range with grades between $0 - 1\%$ (Cat. 1), $1 - 10\%$ (Cat. 2), $10 - 20\%$ (Cat. 3), $20 - 50\%$ (Cat. 4) and $50 - 100\%$ (Cat. 5).

This kind of information about liberation (measured as grade and surface exposure) as a function of particle size is key for the development of flotation models that can better represent the behaviour of the process and thus predict its outcome. Models like the one proposed by Vallejos et al. (2018), where the authors derive a model for the recovery of particles depending on their size and degree of liberation. Similarly this kind of assessment can be used to create flotation rate kinetics that are dependent on the particles' size, degree of liberation and surface liberation as in Jameson (2012) or Welsby et al. (2010). The data showed in Figure 5.14 can be fed into a simulation model by fitting a known probability distribution function. A triangular distribution is a simple way of representing the data by fitting the minimum, maximum and mode of each grade category, Figure 5.15a shows this fitting. Figure 5.15b shows the actual probability density functions of each category, showing the expected high variability in the high-grade particles. It is worth noting that this higher variability is partially due to the range of the grade categories, ranges that were chosen to evenly distribute the number of particles in each category so as to ensure a statistically representative sample.

The benefits of using this information to feed simulation can be demonstrated with a simple flotation model. Let's consider a model where only particles with a certain degree of surface exposure are floated and thus recovered, meaning that flotation is acting as a perfect selective process depending only on surface exposure. Figure 5.16 shows the amount of sulphide volume that is recovered for different threshold values for the surface

(a)



(b)

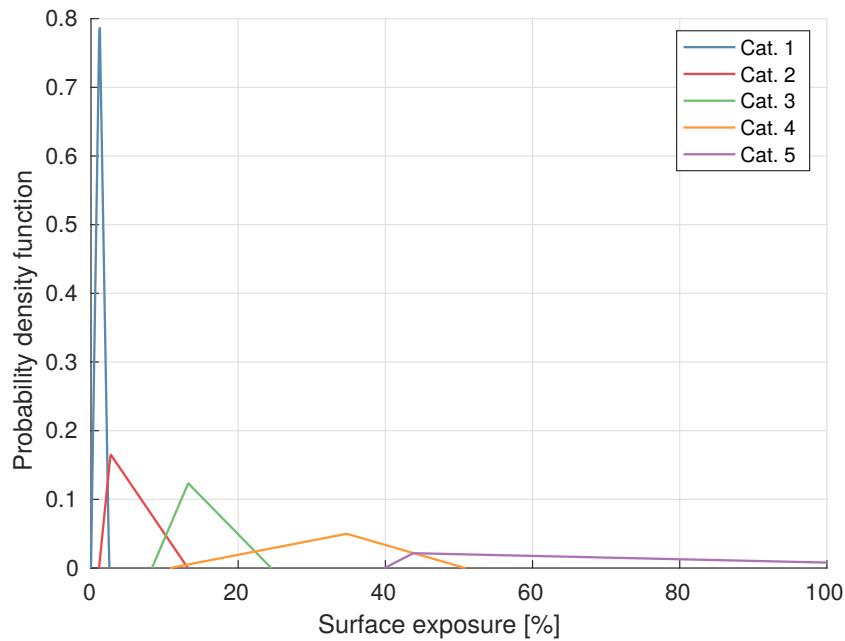


Figure 5.15: Surface exposure distribution for particle size and grade categories as in Figure 5.14 with triangular probability distributions showing a good fit (a). Cumulative distributions are shown in b) with a linear axis to better show the variability.

exposure. There are sufficient particles in the measurements that this effect can also be analysed for different particle size intervals. Behaviour remains mostly constant over size, except when crushing starts getting closer to the grain size, as can be seen with the $22\mu\text{m}$ to $28\mu\text{m}$ range. This is consistent with the grain size information from the uncrushed ore, where the mean grain size is $32\mu\text{m}$ and the P80 is around $100\mu\text{m}$ (all values given by

the automated mineralogy analysis used in order to produce Table 5.1 at a resolution of $2.25\ \mu\text{m}$).

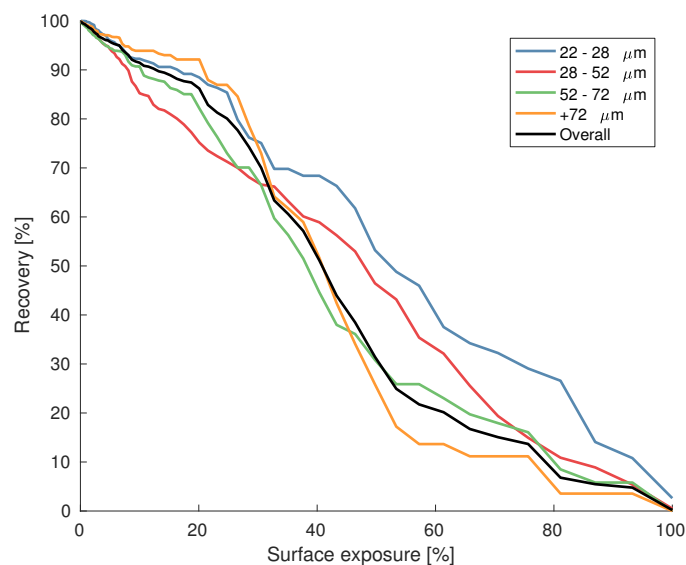


Figure 5.16: Recovery of minerals according to their surface exposure. As expected, recovery of sulphides goes down as the surface exposure threshold goes up, as fewer particles achieve that level of exposure.

Figure 5.17 shows the traditional grade-recovery curve (Miller et al., 2009) that summarises the boundary at which downstream processes can operate. The line is obtained by calculating the resulting mineral grade and recovery of sulphide when selecting all particles above a certain surface exposure. Thus, for 100% recovery the mineral grade of the feed is obtained (no selectivity), and when recovering only fully exposed particles a 100% grade is obtained at expense of nearly no recovery. An intermediate point is marked-up where it can be seen that in order to obtain 80% recovery and a grade of nearly 60%, a downstream process needs to select particles that have more than 20% of their surface as mineral grains.

The uses of this plot are twofold, first as a means to compare different comminution processes and secondly as a prediction tool for downstream processes performance when treating the product resulting from comminution.

5.4.3 Assessing stereological effects

Due to physical, time and budget constraints, when performing traditional SEM/EDS analysis no more than a couple of slices will typically be obtained from each fragment. Lack of full information about the 3D properties of the particles creates a sampling error that affects both the quantification of grade and surface exposure. By creating a fixed number of random virtual slices on each fragment these effects can be studied and analysed. Figure 5.18a shows the sampling effect for the quantification of grade when only one random slice is taken through each of the grains; in agreement with Miller et al. (2009) that

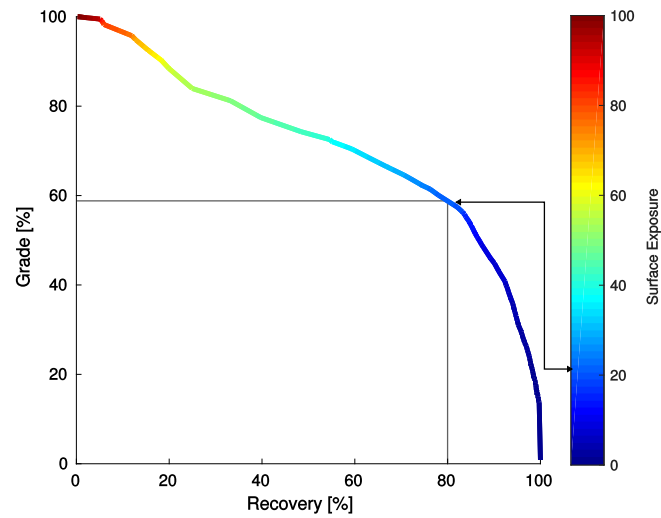


Figure 5.17: Grade-Recovery curve of the system as a function of surface exposure. Note that in this analysis grade corresponds to mineral grade, and not metal grade.

2D analysis overestimates the actual grade of the analysed ore. Increasing the number of slices per fragment makes the 2D grade converge towards the actual 3D value, as shown in Figure 5.18b. This gives an indication of how many more SEM slices would be required to give the same level of accuracy as obtainable from the XMT.

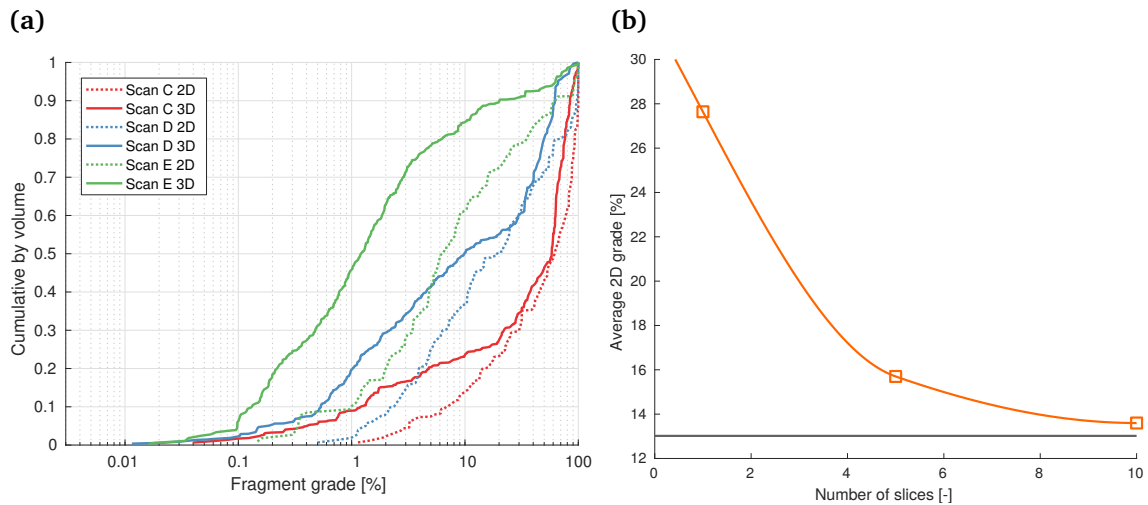


Figure 5.18: Grade 2D quantification affected by number of slices used. Lack of full 3D information creates a sampling error that can be overcome by increasing sampling size. Effect is apparent at any size class, with greater strength at the coarser particles.

In the case of surface exposure, there is not only a sampling error, but also an unavoidable stereological discrepancy when using 2D data. Even when using all possible slices, 2D liberation does not converge to the actual 3D exposure. Well known stereological effects prevent this from happening and its effect can only be overcome by creating ore-specific correction models. Figure 5.19a shows how the distribution of grain exposure is affected by both the sampling error and the stereological effect, making 2D analysis overestimate

the level of exposure experienced by mineral grains. Figure 5.19b-d shows parity plots for the 2D versus 3D surface exposure at different numbers of slices per fragment (1, 5 and 10 respectively). Figure 5.19b-d shows that there is a correlation between the 2D and 3D measured surface exposures of the individual grains, but that even when a comparatively large number of slices are taken through each particle, there is still a lot of scatter in the relationship, especially at lower surface exposures. This means that any grain level grade-liberation analysis undertaken based on 2D slices is likely to have significant errors associated with any distributions or correlations created, stressing the importance of correcting for this bias with methods like the one introduced in Chapter 3

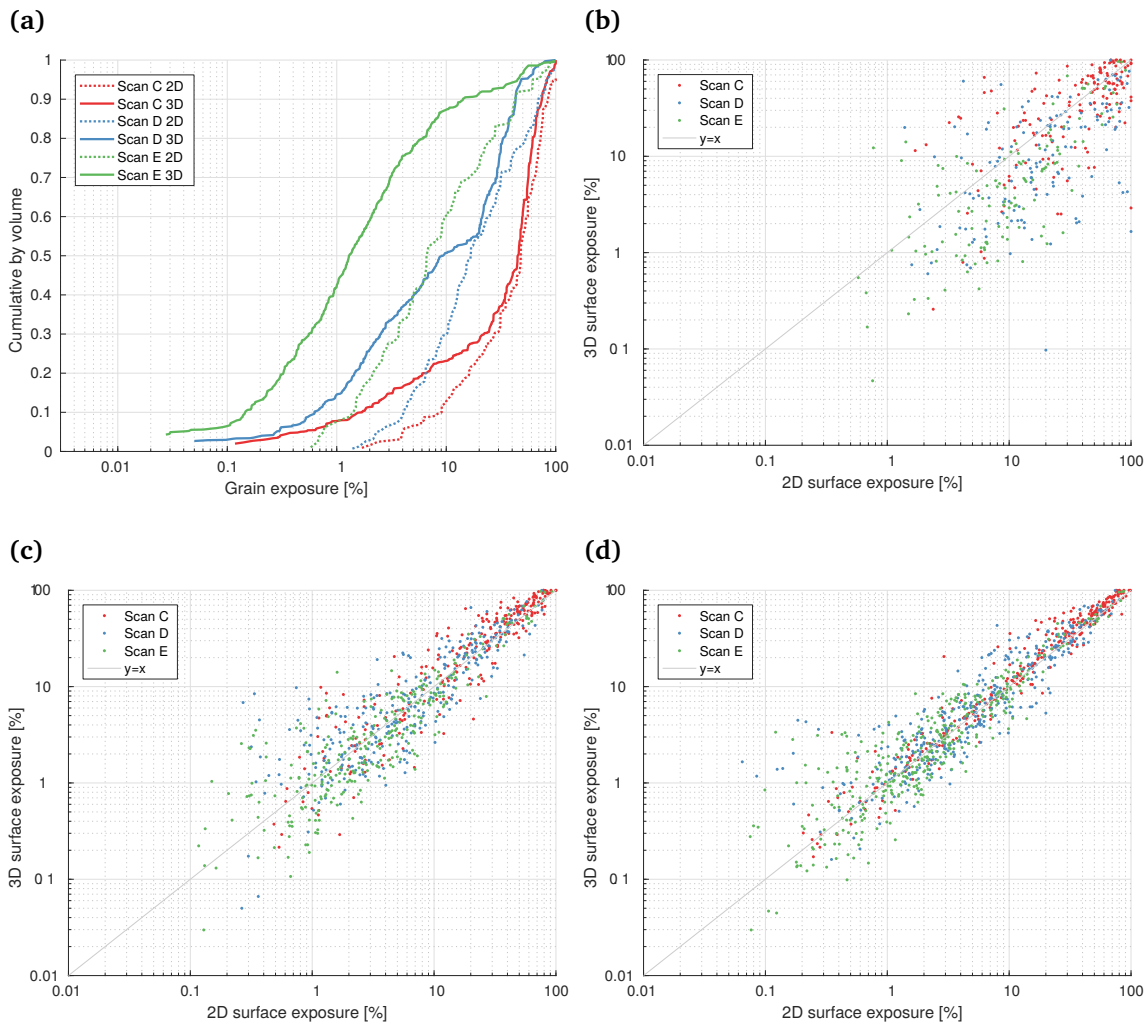


Figure 5.19: Surface exposure 2D quantification affected by number of slices used. Stereological effects are apparent at any size class, with greater strength at the coarser particles.

5.4.4 Assessing preferential breakage

Grain exposure can also be linked with the particle's grade and, as expected, there is a direct relationship between them. Figure 5.20 shows that there is a near linear correlation between the grade of a fragment and its surface exposure, though at lower grades the

surface exposed tends to be higher than the actual particle grade, while at higher grades the particles present a lower surface exposure relative to its grade. This implies that at lower grades there is a slight preferential breakage towards the grain phase and conversely at higher grades the effect is the opposite.

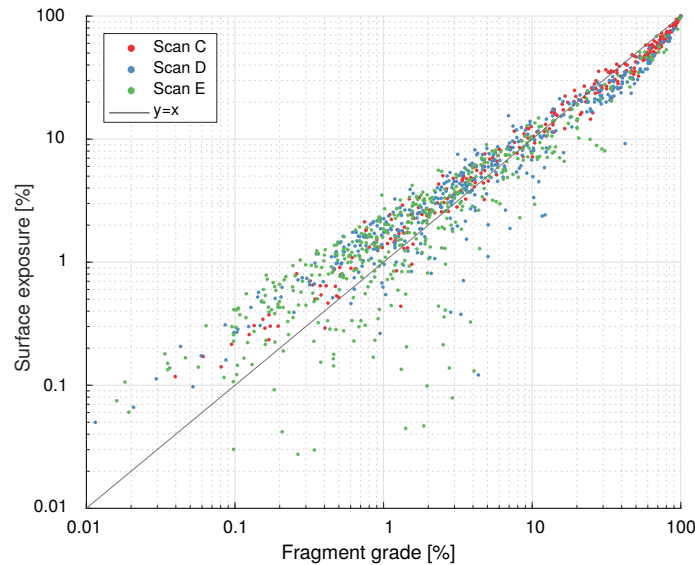


Figure 5.20: Surface exposure as a function of fragment's grade allows for assessing the occurrence of preferential breakage (deviation from $y = x$ line).

This preferential breakage towards the gangue at high grade particles is most probably related to the ore used and the crushing methodology. This data demonstrates how this type of investigation could be used to quantify the effect of different comminution techniques in terms of the extent of any preferential breakage experienced for a specific ore. This is important to quantify as preferential breakage can help or hinder the flotation response for a given particle size and grade depending on which phase the fractures preferentially occur in. Some proposed new comminution techniques, such as microwave assisted comminution and high voltage pulsed electrical comminution (Charikinya and Bradshaw, 2017; Kingman and Rowson, 1998; Little et al., 2016), rely on preferential breakage to achieve improved liberation at a given particle size and this effect is thus important to accurately quantify.

5.4.5 Assessing mineralogy

Because the ore is the same as the one used in Chapter 3, a threshold can be calibrated in order to obtain simplified mineral maps that distinguishing between the gangue, pyrite grains and copper containing grains. Applying this methodology allows the previous results to be extended in order to determine if there is a difference in the behaviour between pyrite and the copper containing sulphides in terms of liberation and surface exposure. Figure 5.21a and 5.21b show the distribution of grade and surface exposure (respectively) of the assessed particles with copper containing grains separated from pyrite grains. A

statistically significant difference can be observed for surface exposure (p -value < 0.05) where there is a worse surface liberation for the copper species than other sulphide containing species. Conversely, there is no statistically significant difference between the species grade distribution (p -value > 0.10).

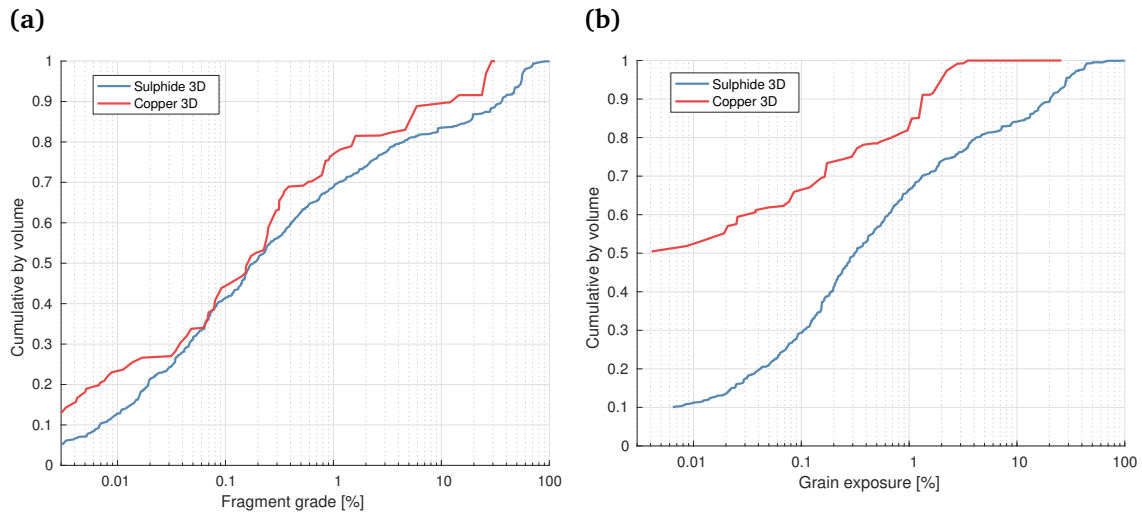


Figure 5.21: Fragment's grade and surface exposure distribution for pyrite and copper containing grains. Copper shows worse liberation performance than pyrite.

This implies that the copper grains are more likely to be surrounded either by gangue or other sulphide grains than the pyrite grains. This is reinforced by 5.22 showing a clear tendency for copper grains to have a lower surface exposure for a given particle grade. Meaning that, for this particular system of ore and crushing method, there is a preference for these grains to be enclosed by gangue and/or other minerals. This is undesirable and would have an adverse effect on any flotation response

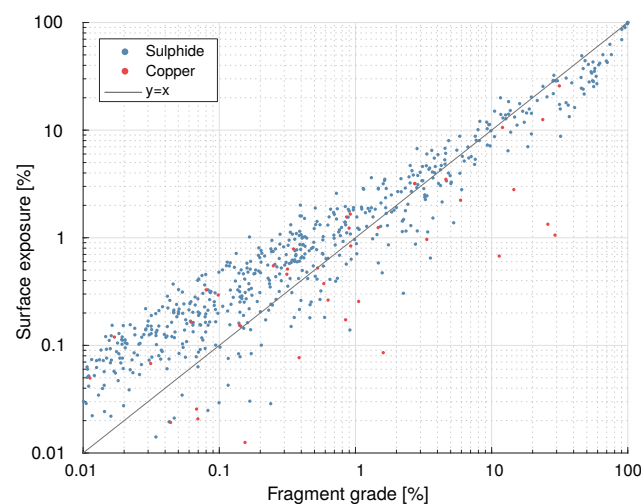


Figure 5.22: Exposure against fragment's grade for two different minerals

5.5 Conclusions

A methodology for assessing liberation in terms of grade and surface exposure using XMT has been developed and tested using a typical porphyry copper ore. X-ray microtomography has been shown to be a useful tool for assessing liberation in a non-destructive and more comprehensive way than can be achieved using traditional methods such as sectioning and scanning electron microscopy. Optimal acquisition parameters were obtained in order to minimise scanning time and to ensure that contrast between gangue and mineral phases were maximised, allowing for a simplified mineral map that distinguished between copper containing species and non-valuable grains (pyrite).

The stereological effect, present in traditional SEM/EDS analyses, was also studied. A significant effect in both the estimation of grade and surface exposure was observed. 2D data from XMT analysis was shown to overestimate average surface exposure of the particles, while at the same time requiring a significantly larger number of fragments to be included in order to converge to the same grade. More importantly, even when using all possible 2D slices, grain surface exposure, a key factor in flotation, does not converge to the actual 3D surface exposure experienced by the particles.

Surface exposure was also analysed for different fragment sizes and grades, showing a strong relationship with the latter. In the particular case of the ore and crushing method used, fragment size had no significant influence on surface exposure for a given grade. Furthermore, the ability to distinguish between copper ores and other mineral grains can also be used to analyse the mineral processing system in terms of preferential breakage, giving valuable insight about the efficiency of the crushing/milling process in liberating the surfaces of the valuable mineral for the specific ore (and ultimately texture) being crushed/milled. Information about the distribution of surface exposure for a given fragment size and grade and mineralogy can be used to develop more accurate probabilistic flotation models that can reflect the influence of comminution on flotation performance.

Chapter 6

Conclusions

The overall objective of this thesis was to develop methodologies for the complementary use of XMT and SEM/EDS imaging for the quantification of minerals processing systems. This document presented the methodology, including the development of new image processing algorithms, for achieving this. Furthermore, the techniques developed were applied to two different minerals processing applications.

The specific aims of the research program described in this thesis were the following:

- 1 Obtain a more detailed quantification of textural related properties from images by calibrating X-ray Micro-Tomography with Automated Mineralogy assessments.
- 2 Assess the level of uncertainty when quantifying mineral ores using X-ray Micro-Tomography.
- 3 Quantify and correct for biases occurring in Automated Mineralogy assessments by the use of X-ray Micro-Tomographic images.
- 4 Use quantification information to develop better simulation models of mineral processes for prediction and evaluation.

The fulfilment of each of these aims was described separately in Chapters 3 (items 1 and 3), 4 (items 2 and 4) and 5 (items 2, 3 and 4). The key outcomes from each chapter are summarised below.

6.1 3D quantification of ores

Despite being complementary in many of their measurements and limitations, XMT and Automated Mineralogy are rarely combined in minerals processing. In this thesis a methodology that allows for a synergistic combination of both modalities is introduced. This methodology enables the calibration of mineral identification in XMT images, which ultimately results in a three-dimensional mineral map, as shown in Figure 6.1, that distin-

guishes between porosity, gangue minerals, non-valuable minerals and valuable minerals. Successful tests on a typical porphyry copper ore, where distinguishing between pyrite and chalcopyrite is a well known problem, gives confidence that the methodology can be applied to other mineral systems.

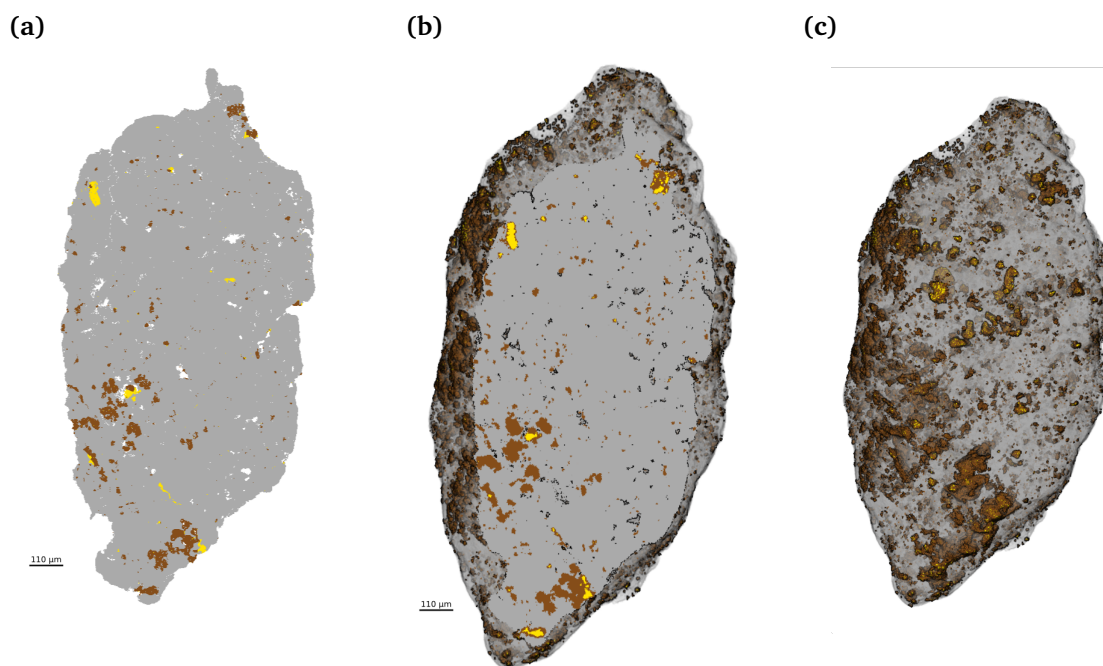


Figure 6.1: Resulting calibrated 3D mineral map. Applying the threshold found by Figure 3.7, a 3D mineral map distinguishing between gangue, porosity, pyrite and copper minerals is obtained. a) EDS based classification, b) same slice using the threshold found and c) the resulting 3D mineral map.

The methodology uses a grain tracking algorithm that matches mineral grains appearing in both XMT and SEM/EDS images. This allows for the quantification of the level of uncertainty when quantifying size, adding confidence bounds to the analysis. At the same time, this allows for the correction of well known biases and artefacts in SEM/EDS analyses due to its two-dimensional nature. Figure 6.2 shows how traditionally assumed shape models for mineral grains are far from the real case. Using the actual 2D/3D size distribution enables the possibility for a tailored ore-specific correction of these biases in SEM/EDS, without the need for performing labour intensive and time consuming tests.

In this case study it was possible to distinguish the pyrite from the copper sulphide species, but it was impossible to distinguish the different copper minerals from one another due to a combination of similar X-ray attenuations and the small number of grains of the minor copper species intercepted in the 2D sections. To overcome this limitation a combination of multiple energy XMT and possibly a higher number of sections might be necessary.

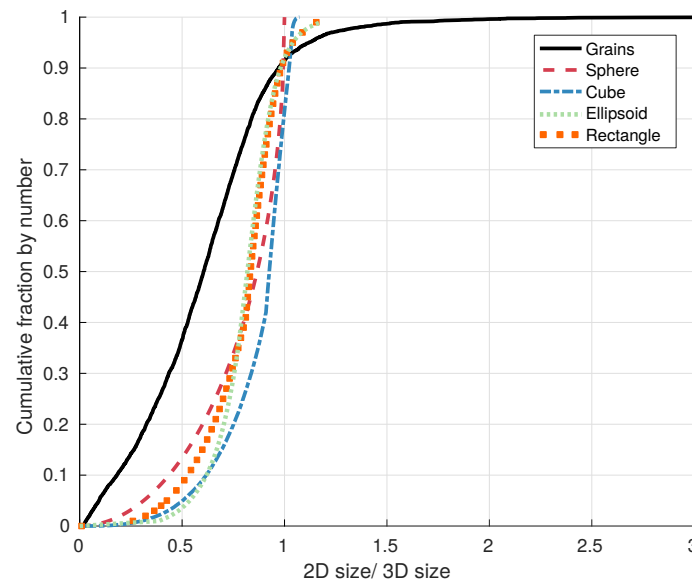


Figure 6.2: Cumulative probability distribution function of the error in size for the mineral grains and some standard convex shapes.

6.2 Assessing apparent leach kinetics

Apparent leach kinetics are the connection between the micro and meso/macro scale processes happening in heap leaching and, as such, they are vital for simulation purposes. Apparent leach kinetics depend on the intra-particle mass transport and surface rate kinetics of the chemical reaction on the mineral grains. Previous research had managed to study the intrinsic variability of these kinetics when they are decoupled from grain size (specific surface area) and distant to the surface (chemical conditions, mass transport limitation). In this thesis we have extended that assessment using the combined effect of periodic XMT scans and the mineralogical information from SEM/EDS measurements. The result of this assessment is the additional decoupling of mineralogy from the variability of leach rate kinetics. As is shown in Figure 6.3a, pyrite and copper bearing minerals present different distributions. These leach kinetics were used to feed a newly developed simulation environment that allowed for the modelling of a multi-species system with non-linear surface rate kinetics. This simulator uses the very same XMT scans of the particles as the domain for solving the mass transport and reaction equations. Results of the simulations are shown in Figure 6.3b against experimental data. It can be seen that the simulator fits both the recovery of copper minerals and also the dissolution of non valuable sulphides (pyrite). Simulations were carried out using different particles as the simulation domain in order to take into account the inter-particle variability.

The fully dynamic simulator was tested against the previously developed quasi-steady-state simulator. Results show that the assumption of a quasi-static situation might lead to a misinterpretation of the leaching regime. As can be observe in Figure 6.4, both the dynamic and the quasi-static simulations fit and predict the data with decent accuracy.

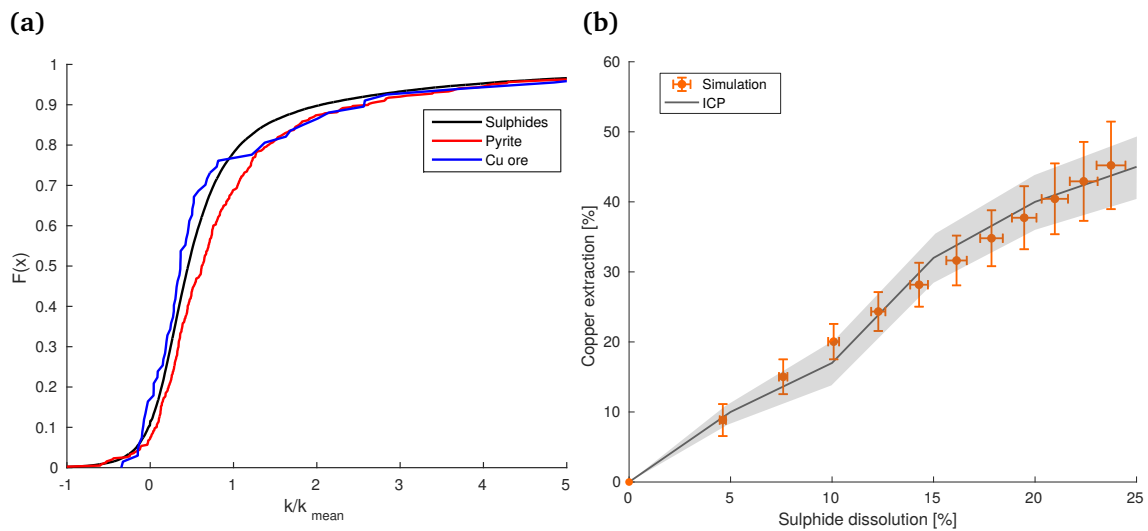


Figure 6.3: a) Distribution of the apparent leach kinetics distinguishing by mineralogy. As expected, the variability in the leach kinetics of copper minerals differs from the one showed by pyrite. b) Extraction of copper compared against total sulphide dissolution as obtained from ICP and simulations. The trend obtained from experimental measurements is also observed in the simulations.

However, the dimensionless group δ_1 on each simulation was observed to be different, with the QSS simulator indicating a more reaction limited regime. This misinterpretation could lead, in real heap leaching operations, to an erroneous operational decision on how to deal with the limitation, as a reaction limited regime might hint the need for a change in the chemistry of the reagents used, whilst a diffusion limited regime hints for the need of a change in the particle size distribution.

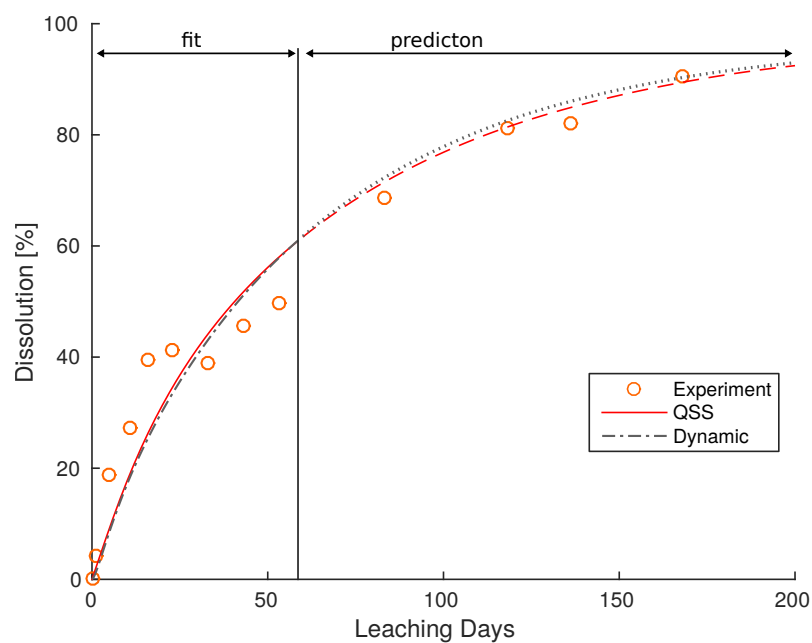


Figure 6.4: Dynamic simulation against QSS simulation in terms of predicting final recovery. Experimental data from Lin (2015).

6.3 Assessing mineral liberation

In order to demonstrate the benefits of obtaining a 3D mineral map like that shown in Figure 6.1, mineral liberation was assessed in Chapter 5. The 3D nature of XMT allowed us to relate, for the first time, particle size, surface exposure and mineral grade in 3D. This relationships enable us to quantify the occurrence of preferential breakage, as shown in Figure 6.5. The deviations of the particles from the $y = x$ line show either a preferential breakage towards the gangue (below the line) or mineral grains (above the line). The particular results are ore-specific and depend on the crushing method used, but the methodology is generic and can therefore be used for other ore textures and crushing/milling methods, so the occurrence of preferential breakage can be quantified. This is of importance for the industry, especially for the concentration of coarse particles as milling and grinding are a big part of the energy consumption in the processing of the minerals.

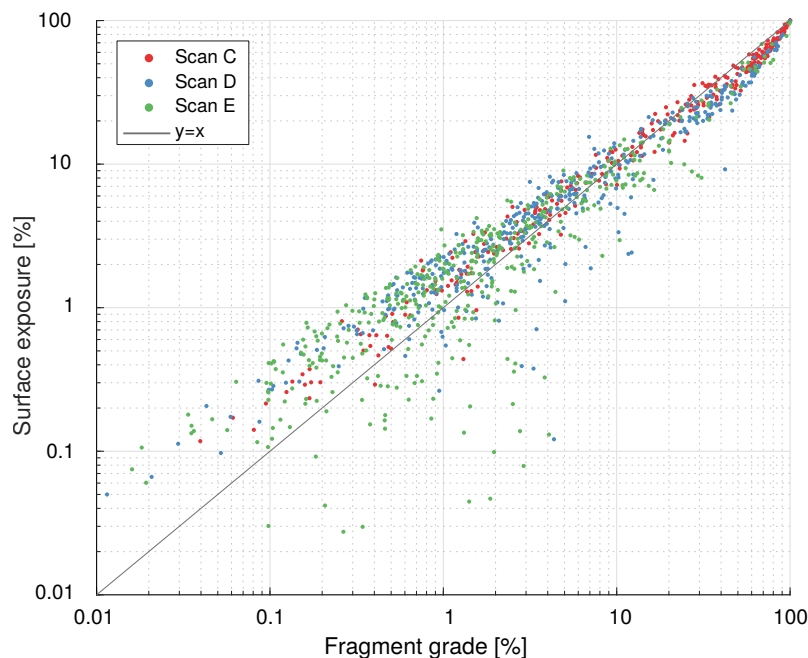


Figure 6.5: Surface exposure as a function of fragment's grade allows for assessing the occurrence of preferential breakage (deviation from $y = x$ line).

The 3D data set allowed us to assess the biases that Automated Mineralogy assessments introduced when quantifying for grade and surface exposure due to their 2D nature. We showed that even when using all possible 2D slices that constitute the 3D scan, the value for surface exposure still overestimates the real value. Mineral grade, on the other hand, converges and gets reasonably close when 5 or more slices are taken from each sample. This shows that no matter how many fragments are polished and scanned, surface exposure will be always overestimated.

Very much in line with of objective 4, we have shown that combining particle size, surface exposure and mineral grade can be used to predict the behaviour of mineral pro-

cessing systems. Figure 6.6 shows a typical Grade-Recovery curve, but in which we have enabled the possibility to predict the performance of a selective processes that depend on surface exposure, such as flotation. This curve can be constructed for more than one crushing/milling configuration so they can be compared according to the requirements of the metallurgist.

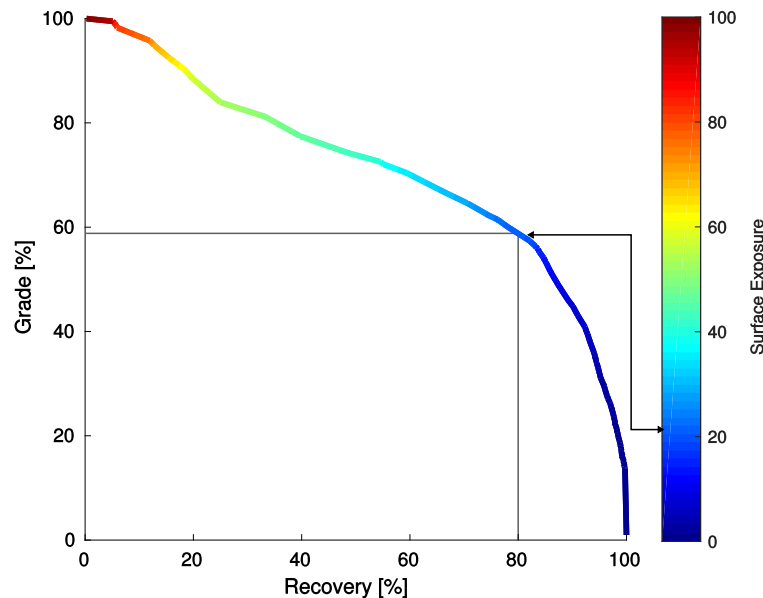


Figure 6.6: Grade-Recovery curve of the system as a function of surface exposure. Note that in this analysis grade corresponds to mineral grade, and not metal grade.

6.4 Future Work

1. **3D quantification of ores** Possible limitations of the methodology are the presence of minerals with similar X-ray attenuation coefficients, making them hard to be segmented using a single energy scan. Minerals with very similar X-ray attenuation coefficients and minerals with very low abundance in the sample might require a dual-energy or even multi-energy radiography approach. Thus, extending the methodology for combining multiple energy X-ray scans is the natural progression of the methodology.
2. **Quantifying leaching rate kinetics** The simulator uses an explicit formulation for solving the partial differential equations, which forces the use of many small time steps. An updated version with an implicit scheme will allow for faster simulations without losing accuracy.
3. **Quantifying leaching rate kinetics of agglomerates** Future work will consider extending the analysis of leach rate kinetics to agglomerates, as these are the most common particle system used in heap leaching. This poses new challenges in the

segmentation of particles as agglomerates are in itself a conjunction of particles of different sizes. Also, agglomerates will tend to degrade and move, making the tracking of the particles and grains much harder.

4. **Quantifying liberation** In this thesis the use of one or more slices was studied, showing that 2D mineral grade and surface exposure do converge to their respective real 3D value. However, these slices were chosen using sampling with replacement. It would be interesting to see the effect of sampling without replacement (technically one does not scan the same polished slice twice) and more importantly the effect of sequential slicing. It is possible that the latter show a faster convergence towards the 3D value.

Although a stereological correction for grain size and particle grade was shown in this thesis, the case of surface exposure was not considered. A logical continuation is to formulate a method to correct for the stereological bias in surface exposure, which to the best of our knowledge, has not been addressed yet.

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Appendix A

Publications

The work presented in this document has been published in the following Journal articles:

- Reyes, F., Lin, Q., Cilliers, J., and Neethling, S. Quantifying mineral liberation by particle grade and surface exposure using x-ray microCT. *Minerals Engineering*, 125:75 – 82, 2018.
- Reyes, F., Lin, Q., Udoudo, O., Dodds, C., Lee, P. D., and Neethling, S. J. Calibrated X-ray micro-tomography for mineral ore quantification. *Minerals Engineering*, 110:122–130, 2017.

And the following presentations at international conferences:

- Reyes, F., Cilliers, J.J., & Neethling S. J. Quantifying Mineral Liberation by Grade and Surface Exposure Using X-Ray microCT for Flotation Processes. In: *XXIX International Mineral Processing Congress*. Moscow, Russia. September 17–21, 2018. (winner of the Young Author Award)
- Reyes, F., Barker, D. B., Lin, Q., Neethling, S. J. Multiple Species Leaching Simulator at the Particle Scale. In: *Computational Modelling 17*. Falmouth, England. June 09–10, 2017.
- Reyes, F., Barker, D. B., Lin, Q. & Neethling, S. J. Assessing Apparent Leach Kinetics Using 4D X-ray micro-Computed Tomography. In: *8th International Seminar on Process Hydrometallurgy, Hydroprocess*. Santiago, Chile. June 15–17, 2016
- Reyes, F., Barker, D. B., Lin, Q., Neethling, S. J. Quasi-Static vs Dynamic Models for Predicting Heap Leach Kinetics. In: *Computational Modelling 15*. Falmouth, England. June 09–10, 2015.