A Stepwise Study on the Characterisation and Processing of South African Platinum Group Tailings

Rešoketšwe Martha Manenzhe

A thesis submitted to the Faculty of Engineering and the Built Environment, in fulfilment of the requirements for the degree of:

Doctor of Philosophy

at

the Centre for Minerals Research

Department of Chemical Engineering

University of Cape Town

in July 2023

"*The strongest argument of the detractors of mining is that the fields are devastated by mining operations … further, when the ores are washed, the water used poisons the brooks and streams, and either destroys the fish or drives them away … thus it is said, it is clear to all that there is greater detriment from mining than the values of the metals which the mining produces.*"

— Agricola, 1556.

PLAGIARISM DECLARATION

I know the meaning of plagiarism and declare that all the work in the document, save for that which is properly acknowledged, is my own. This thesis has been submitted to the Turnitin module and I confirm that my supervisor has seen my report and any concerns revealed by such have been resolved with my supervisor.

Rešoketšwe Martha Manenzhe

01 July 2023
On this date

ACKNOWLEDGEMENTS

I would like to express my sincerest gratitude to the following people, all of whom provided me with unlimited faith and support, and made this journey easier, fulfilling, and even enjoyable:

- A/Prof. Kirsten Corin and Dr Margreth Tadie, for their remarkable supervision, their patience, and the guidance that kept me focused and motivated. Thank you, too, for the well-roundedness of the partnership we enjoyed. It was insurmountably comforting to know that you saw me as a person first, and as PhD candidate second. It made all the difference in the world when I doubted myself, especially as a researcher. You were the compass that pointed north, always, and it is an experience I shall cherish for the rest of my career. May you continue to do for others what you have done for me.

- The laboratory staff at the Centre for Minerals Research: Kenneth Maseko, Shireen Govender, Refilwe Moalosi, Monde Bekaphi, Lorraine Nkemba, Gary Groenmeyer, A'isha Gierdien, Heather Sundstrom, Dr Lisa October, Dr Malibongwe Manono, A/Prof. Bleinda McFadzean and Dr Andrea Molifie for always being available to show me not only the best way to go about things, but where to find free food in the building on certain days, and for giving me a lift to campus on the cold, wet mornings I didn't have my car. But mostly, thank you for creating the wonderful working environment you have done. Ours is a rare and beautiful community in academia.

- All of my peers at the CMR: Mahlogonolo, Ayanda, Taonga, Floyd, Morina, Naledi, Avuyile, Liseka, Matimba, Chris and Jawaad; for all the wonderful chats, both academic and trivial. It has been an absolute pleasure sharing the lab with you. And my extended chemical engineering family: Tracey, Vuyi, Lerato (Motsepe), Naseeba, Catherine, and, I'm sure I'm forgetting a few people; I'm sorry about that. I haven't slept well for a long while now. Only after this thing has been submitted, will I know my left from my right, and recall all the acts of kindness I took for granted in my exhausted state.

- My parents, Moti and Lebohang Manenzhe, who, if asked what I do for a living, might be inclined to say, "Well, she's trying to make the world a better place, isn't she?" This is not hubris on my part; my parents truly believe the best about me, and it is the love and confidence they show and instil in me, that carries me when all else fails.

- All of my Ancestors, even those whose names I shall never know.

- My brothers, Kgotso, Thato and Mohau Manenzhe, for always being wonderful friends, and for never once asking, "So what are you going to do after this?" And of course, my uncle Matome Ramothwala, for promising me a trip to Victoria Falls as a graduation gift, which gave me the final push to dredge through this cold and dreadful winter, and reach, with shockingly genuine hope, the culmination of five years of hard work.

- My friends: June, Deepti, Apollonia, Mubanga, Diksha, Seabela, Audrey, Sabo, Nonto, Lerato (Mogoatlhe), Akshay, Elisabeth, Esther, and Brigid and Caitlin, and everyone who ever had to listen to me complain and cry and wallow in self-pity and doubt. You efforts were not in vain, it turns out. Here I am, submitting. No one is more shocked than me.

- Sibanye Stillwaters and Impala, for providing the tailings samples used in the study. And the institutions of the Centre for Minerals Research and the University of Cape Town.

- And Selina. Always.

LIST OF PUBLICATIONS AND PRESENTATIONS

Abstract accepted: Manenzhe, R. M., Corin, K. C., Tadie, M., 2023. A Stepwise Study on the Characterisation and Processing of South African Platinum Group Tailings. *In The 11th International Flotation Conference (Flotation '23)*, to be held on 6-9 November 2023. Cape Town, South Africa.

Manenzhe, R. M., Tadie, M., Corin, K. C., 2021. A Review on the Processing of South African PGM Tailings. *In IMPC 2020: XXX International Mineral Processing Congress*. 18-22 October 2020. Cape Town, South Africa

Manenzhe, R. M., Tadie, M., Corin, K. C., 2021. A Review on the Processing of South African PGM Tailings. *SAIMM Minerals Research Showcase*. 11-12 November 2019. Cape Town, South Africa

SYNOPSIS

The endurance of the mining industry has led to the near-depletion of some of the most processible ore types. This has resulted in a unique challenge that necessitates unique innovation for the industry. Firstly, existing technologies are increasingly geared towards improved efficiency in processing lower grade ores. Secondly, ores that were previously processed with older, and in some cases, inefficient technologies, have emerged as potentially viable solutions that would help maintain concentrator capacities.

On the other hand, as the industry has endured, so has its waste accumulation. Tailings dumps continue to grow, and continue to pose various environmental issues. But although they are a waste product, tailings also have several merits to them. They are already mined and readily available, and reprocessing them immediately addresses two conundrums i.e. how can the industry source alternative ores, and how can it deal with the steady accumulation of waste?

It is expected that as a result of their initial processing from so-called fresh ores, and their stay in their respective dumps, the tailings will be altered or tarnished. The surface properties of their compositional minerals will be oxidised and layered with other compounds that might hinder their interaction with flotation reagents such as collectors and hence, hinder their flotation response, presenting a challenge for their proposed reprocessing. More obviously, as they are a waste product, their grades will be far lower than the fresh ores that produced them.

Numerous studies aim to elucidate the viability of the metallurgical reprocessing of tailings. However, this flurry of innovation thus far extends to the vast stretches of the Witwatersrand dumps, and thus, to gold. The issue with processing other tailings types then becomes threefold. Is there enough value in the dumps to justify tailings beneficiation? What beneficiation method would be suitable? Would the method yield economically viable results?

This study acquired three bulks of PGM tailings to investigate these questions. The first bulk was Merensky, the second was UG2, and the third was a deslimed version of UG2 in which a portion of denser minerals were separated out. For the sake of convenience, the bulks are referred to by their shorthands throughout the thesis. Merensky became MER, the normal or raw UG2 became UG2R, and the deslimed UG2 became UG2D.

The study conducted the investigations along two lines: first, by characterising the tailings, and secondly, by floating them. The first characterisation step was a full elemental and mineralogical analysis that quantified the amount of valuables as well as gangue minerals; this was done via XRD

and QEMSCAN. The second step was to determine the degree of oxidation by using qualitative, in-situ experimental methods; these are EDTA extraction and oxygen reactivity.

It was hypothesised that EDTA extraction would measure the concentration of secondary and oxidised materials on the mineral surfaces; and oxygen reactivity would measure the demand of oxygen in each tailings, and therefore the tailings' capacity to react with species in the pulp phase.

The qualitative methods have only ever been used for fresh ores, and have shown to be reliable in predicting and/or explaining the flotation behaviour of those ores. They have never been used to predict an/or explain the flotation behaviour of an ore material that has already been processed, and is therefore very low grade, and oxidised. If they are as viable for tailings as they are for fresh ores, they would determine different EDTA extraction indices and oxygen demand constants.

QEMSCAN and XRD provided the different concentrations of the different minerals across the tailings, and showed that some minerals were present in one tailings but not the other. For instance, MER contained the highest fraction of chalcopyrite, as well as the highest fraction of sulphides. UG2R and UG2D each had more than ten times the fraction of chromite seen in MER. MER, on the other hand, had more pyroxenes, plagioclase and amphibole.

It was expected that these differences in composition would be the cause of the different extraction indices and oxygen demand constants. The robustness of both methods thus had to be tested. This was done by altering each of the tailings and testing whether the extraction indices and oxygen demand constants would change. The surface and composition alteration was induced with ultrasonication and desliming. The study thus answered the question: can the EDTA extraction and oxygen reactivity methods detect when a change has occurred on the mineral surfaces of the same tailings?

The tailings were then floated, and it was here that the question of economic viability was assessed. For the concentrators from which MER, UG2R and UG2D were collected, a reprocessing venture would be deemed economically viable if 30% of the copper present in the tailings was recovered. The flotation performance was thus analysed with copper recovery as the primary positive indicator. Nickel behaviour was also tracked in case of any supporting elucidations, and also because pentlandite is the primary PGE-carrier for Merensky and UG2.

The tailings were floated with DOW200 as the frother, SIBX as the collector, and CMC as the depressant. The results showed that the presence of the depressant resulted in very low solid quantities being recovered to the concentrate. In fact, less than 2% of each tailings was recovered, and less than 10% of the present copper (and therefore chalcopyrite) was extracted.

When the depressant was removed from the reagent scheme, recovery of the solids improved to 10%, but the copper yield was still below 30%. So, the collector dosage was increased under the fundamental assumption that the hydrophobicity of the valuables would be improved, and in this way, the efficiency of separating the hydrophilic gangue from the valuables would also improve. The plan worked, and UG2R finally achieved the industrial objective of recovering 30% of the present copper. While MER and UG2D failed to do the same, their performance was also at its best under these conditions, with each tailings yielding roughly 23% copper recovery.

In an effort to improve floatation, the tailings were cleaned via ultrasonication and desliming. These cleaning methods both had a detrimental effect on copper recovery. However, nickel (and therefore pentlandite) behaviour improved, showing that while the methods were disadvantageous to one mineral, they were favourable to another, and they might be useful for a study that uses a different metal as its positive performance indicator.

The study also showed that MER, UG2R and UG2D have different copper EDTA extraction indices. UG2D had the highest index, followed by UG2R, and then MER. The copper minerals associated with UG2D can therefore be concluded to be more oxidised than those associated with UG2R and MER. Moreover, UG2D was the least reactive to oxygen, having an oxygen consumption rate constant of 0.113 min^{-1} when compared to 0.198 and 0.152 min^{-1} for UG2R and MER, respectively. Ultrasonication and desliming decreased each of these constants, indicating that when cleaned with the chosen methods, the mineral surfaces became less reactive to oxygen.

And so, it was concluded that of the investigated tailings, UG2D was more oxidised than the other two, reacted the least with oxygen, and yielded the lowest copper recoveries. When UG2R achieved the highest reactivity with oxygen, it also yielded the lowest copper extraction index and the highest copper recovery. Overall, nickel behaved contrary to copper.

STATEMENT OF ORIGINALITY

The existing majority of tailings research concerns the reprocessing of gold tailings for residual gold recovery. Although South Africa has an abundance of PGM tailings, research into their processing has concerned the recovery of chromite and iron. There thus exists an archival gap concerning the potential reprocessing of PGM tailings for other products, copper among them. Further, the characterisation of PGM tailings remains largely unelucidated. How much value is in them, whether it can be recovered, and how to recover it, are questions yet to be answered.

The novelty of this study is two-fold. In the first case, it explored the use of techniques that have previously been used to qualitatively assess the electrochemical qualities of fresh ores. In this study, EDTA extraction and oxygen reactivity were, instead, used for analysis of Bushveld Igneous Complex (Merensky and UG2) tailings. The study showed the following:

- EDTA extraction and oxygen reactivity can be applied in qualitatively assessing the electrochemical quality of Merensky and UG2 tailings.
- When the mechanical methods of ultrasonication and desliming were used to alter the tailings, EDTA extraction and oxygen reactivity were able to detect change in the tailings, and yield distinct electrochemical indicators.
- The study therefore showed that EDTA extraction and oxygen reactivity can be used as analysis techniques beyond the natural state of the tailings, i.e., after artificial alteration.
- Each tailings contained a natural concentration of dissolved oxygen that, when the tailings were altered, changed along with the alteration. Tailings with higher natural concentrations of oxygen reacted more readily with it, and yielded higher consumption rate constants.

Secondly, the study explored the use of batch/froth flotation in recovering copper from the aforementioned tailings. It showed the following:

- The depressant CMC was detrimental to overall flotation of the tailings, and specifically, to the recovery of copper.
- The collector SIBX, when used alone, had a positive effect on the flotation of the tailings, and more specifically, on the recovery of copper.

NOMENCLATURE AND ABBREVIATIONS

a	Mass transfer capacity coefficient
A	Resting oxygen concentration
BMS	Base metal sulphide
C1	First concentrate (with C2 being the second, C3 the third, etc.)
$CaCl_2$	Calcium chloride
CMC	Carboxymethyl cellulose
CMR	Centre for Minerals Research
Co	Cobalt
Cu	Copper
DO	Dissolved oxygen
DOW200	DOW froth 200
EDTA	Ethylene diamine tetra acetic acid
Fe	Iron
g	Grams
g/mol	Grams per mole
g/t	Grams per ton
kg	Kilograms
k_L	Mass transfer coefficient
k_la	Oxygen consumption rate constant
L	Litres
L/min	Litres per minute
m	Metres
M	Molarity
m^3	Cubic metres
MER	Merensky tailings
mg	Milligrams
mg/L	Milligrams per litres
min	Minutes

min^{-1}	Per minute
mL	Millilitres
mol/L	Moles per litres
Mt	Mega tonnes
mV	Millivolts
NaOH	Sodium hydroxide
Ni	Nickel
nm	Nanometres
NTU	Nephelometric turbidity units
ORP	Oxidation-reduction potential
oz	Ounces
Pb	Lead
PGE	Platinum group element
PGM	Platinum group mineral
QEMSCAN	Quantitative evaluation of minerals by scanning electron microscopy
ppm	Parts per million
rpm	Revolutions per minute
SIBX	Sodium isobutyl xanthate
t	Time
UCT	University of Cape Town
UG2	Upper Group 2 chromite ore
UG2D	Deslimed UG2 tailings
UG2R	Raw UG2 tailings
UV/Vis spectroscopy	Ultra violet-visible spectroscopy
µL	Microlitres
µm	Micro metres (or microns)
wt.	Weight
XRD	X-ray powder diffraction
XRF	X-ray fluorescence

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

1.1. Background

The mining industry has long been plagued by the vast amounts of waste produced from its primary operations (Bosch, 1987). Among the most prominent processes employed in extracting valuable minerals from bulk ores is froth flotation.

Froth flotation is a fundamental metallurgical technology that produces a majority of the world's copper, lead, nickel, zinc and other industrially valuable metals (Leja, 1982; Rao, 2004). It also produces approximately 88 000 tonnes of waste from nearly 90 000 tonnes of ore per day (GRID Arendal, 2017). Thus, only 2% of all excavated ores end up as value products; the remainder 98% end up as mine wastes. The United Nations Environment Programme (2002) estimates that a typical copper concentrator processes 125 tonnes of ore to produce one tonne of copper, meaning the efficiency of a typical copper plant, on a throughput basis, sits at an even lower 0.8%.

Thus, as a natural by-product of their operations, mines tend to have an abundance of tailings.

Various issues are inherent to tailings. Firstly, they tend to be toxic. Secondly, and more obviously, their sheer quantities make them tedious to dispose of (Wills and Finch, 2016).

On the other hand, several aspects about them, make tailings retreatment an attractive prospect. These are, as summarised from Bosch (1987), Breytenbach (2016), Buys et al. (2004), Janse van Rensburg (2016), and Ebben and Carlson (2019):

- The continued decline in ore grades, leading to a reconsideration of the potential value contained within tailings.
- The overall rise in the rand price of precious metals such as gold, platinum and palladium, as well as an increasing demand for these metals for various applications.
- The continued improvement in extractive technologies, leading to more efficient processes at relatively lower costs.
- The easy access to readily mined materials, as well as the reduced operational risk inherent in traditional mining. In addition, tailings reprocessing offers a potential for reduced operational costs because, in comparison to a process that has to start by excavating its ore and taking it through the various sizing and classification steps, tailings reprocessing is less labour-intensive. As a result, it also has the potential to be less energy-intensive.
- The increase in value of properties made available for development after tailings removal.

- A growing focus on sustainability, meant to alleviate the environmental challenges presented by tailings handling and storage.
- The potential for minimising environmental issues such as acid mine drainage.

There is thus a necessity for tailings reprocessing, and thus, a need to examine the practicality of such an undertaking. Naturally, the first point of concern is: is there enough value in mine tailings to warrant using them as a source of industrially valuable metals? In the case that there *is* value, how can it be measured, and how can it be extracted, given that the initial metallurgical processes exerted on the ore did not recover this fraction.

Lastly, do different mine wastes require different prospecting or reprocessing methods? If not, are there fundamental metallurgical concepts that can be developed, and subsequently used as a guide on the feasibility of reprocessing a given mine waste bulk? How can these concepts be developed, and how robust are they?

Current studies primarily focus on the recovery of gold, from gold tailings. They also tend to opt for reprocessing methods such as leaching, which, although already widely used for low grade ores, requires the handling and disposal of acids and acidic bulks (Trujillo et al., 2011). For concentrators that process their ores solely through flotation, it may require the installation of equipment that is not already part of the plant.

The prospecting of other types of wastes, e.g., platinum group mineral (PGM) tailings, remains largely unelucidated. For South Africa, a leading exporter of PGMs, this is a missed opportunity. The Bushveld Igneous Complex in the northern region of the country hosts the largest known reserve for PGMs (Hudson Institute of Mineralogy, 2023). In 2018 it produced approximately 70% of the world's platinum (NS Energy, 2019). This makes South Africa the biggest producer of PGM tailings. Not only does this present a potential for the recovery of residual PGMs, but for associated base metal sulphides (BMSs) too. Among the most prominent BMSs, are chalcopyrite (a copper mineral) and pentlandite (a nickel mineral).

The question then becomes: in the case of a reprocessing effort, is it possible to recover either the PGMs or BMSs, or both? Furthermore, is it possible to do so using a relatively benign method, or a method that is already available on any given typical concentrator, such as a flotation cell?

The questions posed by the study can be separated into two categories at this point. The first category addresses the overarching concept of tailings processing as a whole, while the second addresses, more specifically, the reprocessing of PGM tailings via a readily available, and

comparatively benign method, like froth flotation. The study proposes that in answering the second category, the first can also be elucidated.

1.2. Problem Statement

The endurance of mining as the primary source of metals has resulted in mine quarries becoming increasingly deeper with time, and tailings quantities growing. As a whole, the deeper quarries yield lower grade ores, necessitating more rigorous, and often, more expensive methods in order to maintain economically viable concentrator capacities (Bosch, 1987; Janse van Rensburg, 2016).

Moreover, the measured concentrations of metals such as zinc, copper, chromium and nickel in tailings dumps are reportedly higher than the threshold concentrations typically observed in natural soils (Eco Partners, 2011; Yale Environmental, 2015). Small changes in conditions such as pH and bulk potential could result in the mobilisation of these metals, resulting in another negative legacy of mining – acid mine drainage (Rösner and van Schalkwyk, 2000).

So, it has become necessary to consider alternative ore sources, and on the other hand, deal with the issue of the ever-accumulating waste. The reprocessing of tailings fits both objectives.

Although tailings are a waste product that has, in theory, been stripped of the value they once contained, industrial inefficiency dictates this not be true (Bradshaw et al., 1998; Stepanov and Stepanov, 1998). Thus, the tailings present an attractive prospect by being already mined, and being easily accessible (as they are generally located close to concentrators); and as such, they can be processed for the extraction of residual value.

1.3. Objectives of the Study

This study therefore aims to answer the questions posed in Section 1.1. More specifically, it aims to achieve the following:

- Firstly, to characterise selected South African PGM tailings for possible reprocessing.

The characterisation methods will be made with two key considerations in mind: tailings are low grade, and they have endured weathering. The characterisation methods must therefore be able to quantify any differences in grade or weathering, or both. This gives way to the next two objectives.

- To determine the ability of laboratory methods in characterising low grade ore materials.
- To determine if mitigating the tailings' weathered state will change their characterisation.

- Fourthly, the study aims to use a lab-scale reprocessing method with the aim of gaining understanding of any potential plant-scale performance.

Bearing in mind the practical considerations outlined in Section 1.1., the lab-scale method that will be assessed is froth flotation. This necessitates the next two objectives.

- To determine whether the qualitative characterisation of any tailings bulk can be used to predict its flotation performance, or explain it.
- To determine if mitigating the tailings' weathered state will change their flotation performance.

1.4. Scope and Limitations

This study recognises that PGM tailings reprocessing is a largely unexplored practice. As such, the practical aspects, especially the experimental design, could not be approached traditionally. For instance, in characterising the tailings, it had to be determined whether the proposed methods were able to detect any differences in the samples. In the case that they were unable to, alternative methods would need to be found and tested, and so forth and so forth. A similar thing can be said about using flotation. That is to say, is it possible to float tailings? If not, what is the alternative?

This meant the study had to be adaptive. As a starting point, a simple factorial was used. The design would be amended and refined based on the practical restrictions of the work, such as an instrument simply not being able to read a measurement when it went beyond a certain threshold.

The study further recognises that flotation is a complex process with numerous interacting factors (summarised in Figure 1.1. (Klimpel, 1984)). The focus will be on chemical parameters, specifically, the effect of collector and depressant variation.

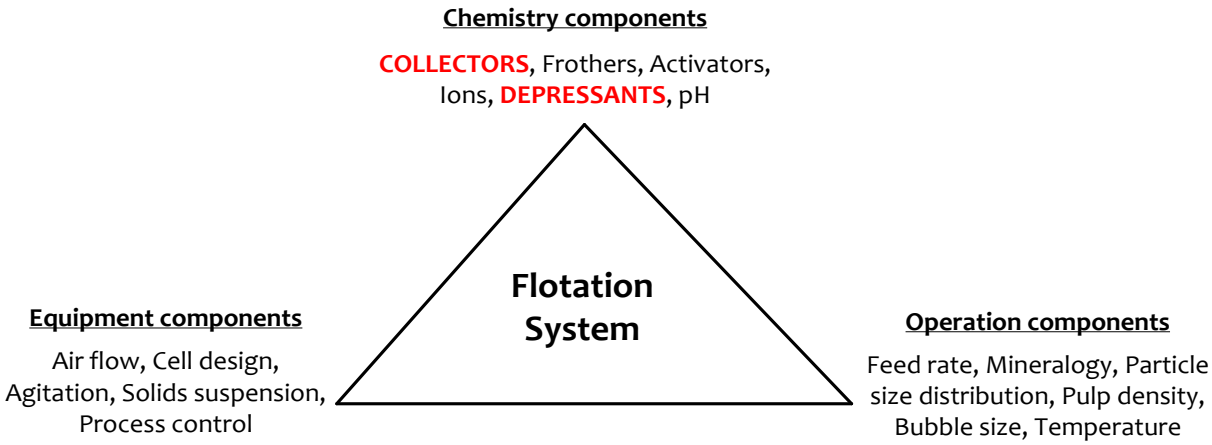


Figure 1.1: The different integral components that affect flotation systems, adapted from Klimpel (1984)

Chapter 4 contains the full details of the practical iterations that were carried out. An overall summary of the study's scope is illustrated in Figure 1.2.

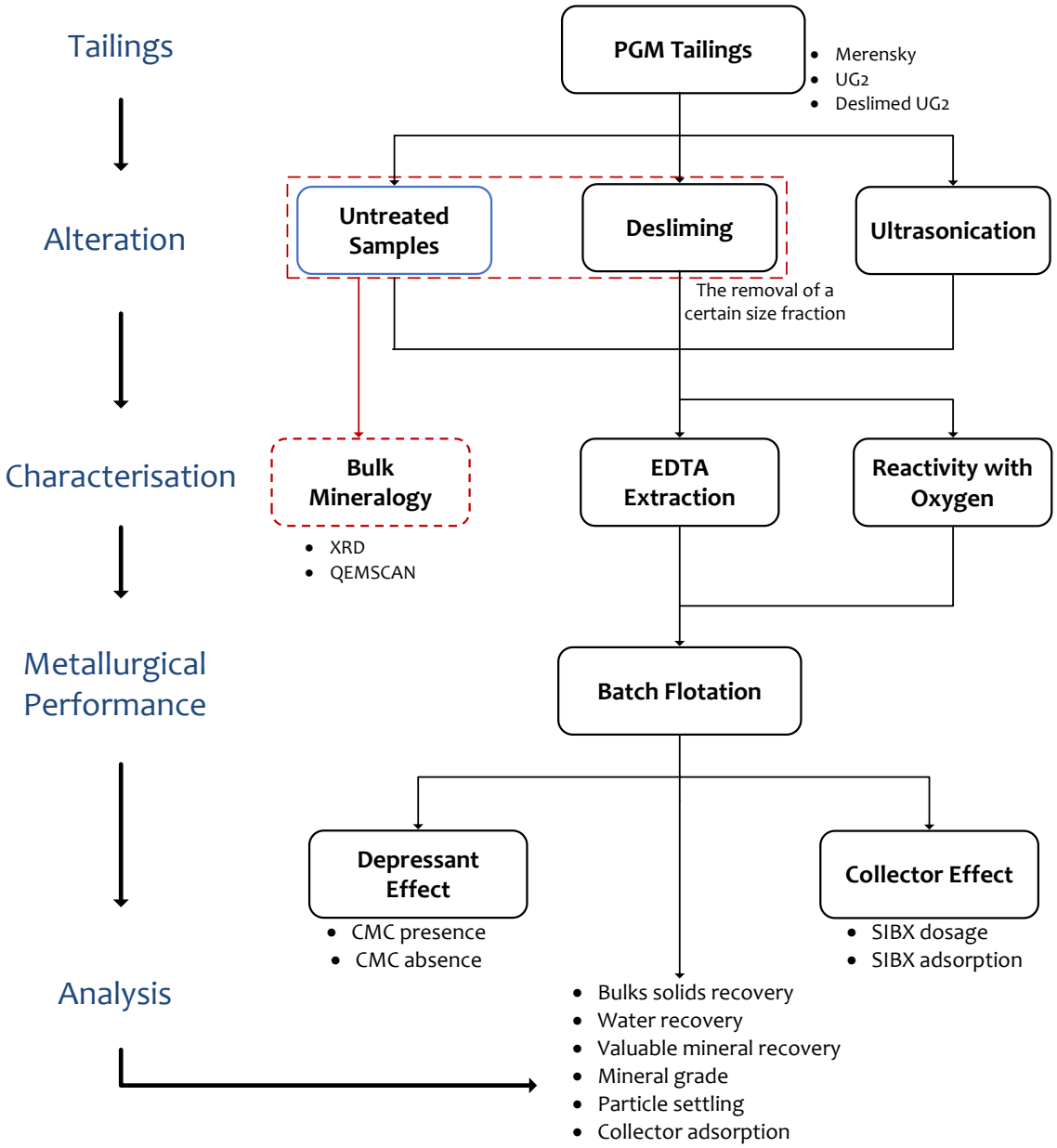


Figure 1.2: A summary of the study

1.5. Thesis Statement

The study aims to characterise Merensky and UG2 tailings, and to process them via froth flotation with the aim of recovering copper and nickel.

2. LITERATURE REVIEW

2.1. The Fundamentals of Froth Flotation

Froth flotation was first patented in 1877; in the decades since, it has become the most dominant technology used to process sulphide minerals and extract some of the most industrially significant metals – among them being copper, nickel, zinc and lead (Bunyak, 2000; Leja, 1982; Rao, 2004).

In a typical extraction flowsheet, a bulk ore containing various minerals of differing commercial value is crushed and ground to give appropriately sized and liberated particles. The particles are subsequently suspended in water, treated with flotation reagents, and the cell aerated (Finch, 1995; Ghosh, 2012; Harris, 1982). Whether inherently, or by way of their surfaces being altered by the added reagents, the various particle species in a flotation cell traditionally have different surface properties, and it is this difference that is exploited by the process of froth flotation to separate the valuables from the commercially valueless (Klassen and Mokrousov, 1963).

The valuables are usually hydrophobic (water-repellent), while the gangue minerals i.e. the commercially valueless, are usually hydrophilic (water-loving). When the cell is aerated, the hydrophobic particles attach to the air bubbles and float to an air-water interface known as the froth phase; here, they are recovered for further processing. The hydrophilic particles remain suspended in the slurry, and are collected as waste in the tailings (Ata et al., 2004; Bradshaw, 1997; Taggart and Hassialis, 1946). Figure 2.1 shows the basic components of a typical flotation cell.

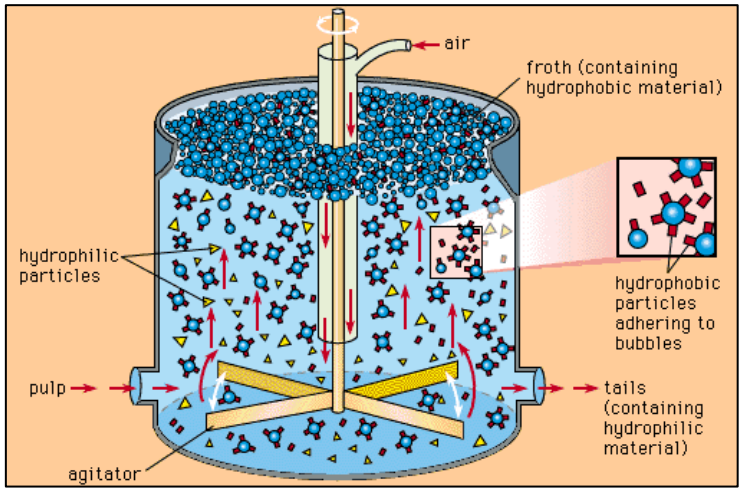


Figure 2.1: The basic components of a typical flotation cell (Encyclopaedia Britannica, 1998)

Flotation takes place in two distinct phases – the aforementioned pulp phase, and the froth phase. Finch (1995) summarises the overall process thusly: flotation performs two elementary functions: the recovery of mineral particles by attaching them to bubbles in the pulp phase, and the separation

of these bubble-particle aggregates from the slurry in the froth phase. However, complete separation of the valuable from the valueless minerals in the pulp phase is often unachievable.

Minerals report to the concentrate by one of two ways: true flotation or entrainment (Kawatra, 2009). True flotation is when hydrophobic particles attach to bubbles and float to the froth phase (Fuerstenau, 1984; Taggart and Hassialis, 1946). Entrainment is the mechanical carrying of particles through the movement of water from the pulp and into the froth phase. Unlike true flotation, entrainment is unselective (Ata et al., 2004; Wills and Napier-Munn, 2006).

Although some gangue minerals are naturally hydrophobic and therefore naturally floatable (Bradshaw et al., 1998), the majority of gangue minerals are hydrophilic and therefore unlikely to interact with the air-water interface. As such, they are carried to the froth phase in the following ways: by being entrained; by being locked to valuable hydrophobic particles; or by behaving as floatable-gangue composite particles (Becker et al., 2010; Corin et al., 2011).

To elaborate on the latter mechanism, and to use an example by Kawatra (2009): "*In the case of coal [flotation], much of the [gangue] pyrite consists either of sub-micron pyrite grains that are never liberated from the coal, or of pyrite particles whose surfaces consist primarily of coal, and therefore behave as if they were coal particles.*" In a similar way, valuable minerals can remain in the pulp as a result of being locked in hydrophilic particles, or behaving as composite particles. In this way, tailings can possess valuable minerals.

2.1.1. The Pulp Phase

To optimise the separation efficiency of the flotation process, specialised reagents that perform specific functions in enhancing the differences in mineral surface properties are used (Bulatovic, 2007; Dean and Ambrose, 1944). There are three primary classes of reagents. The first class consists of collectors, which are molecules added to the pulp phase to, ideally, form a hydrophobic layer on a specific mineral or group of minerals. The second consists of frothers, which are added to provide a stable liquid-air interface in the froth phase, such that the floated particles do not fall back into the pulp before being recovered in the concentrate. The third class consists of regulators, which are added to either enhance or hinder the adsorption of collectors to valueless minerals or groups of minerals (Garrels and Christ, 1990; Harris, 1982; Lovell, 1982).

However, flotation is exceedingly complex, and several interactions occur between the reagents. Moreover, each ore's minerals react differently to the interactions, making it difficult to quantify the precise behaviour of each reagent (Bradshaw et al., 1998; Wiese et al., 2006). For example, factors such as pulp potential, chemical composition and pH affect the efficiency with which collectors adsorb to minerals (Fuerstenau, 1982b).

2.1.2. The Froth Phase

The froth phase is the air-water interface where the floated minerals are recovered to the concentrate (Harris, 1982). If the froth is not stable enough, the floated particles can drop back into the pulp as a result of the bubbles breaking before the froth has flowed over the cell lip. If the froth is too stable, the entrained gangue will persist in the froth and be recovered to the concentrate (Kawatra, 2009; Slatter et al., 2009).

Additionally, as the froth ages, slurry drains from the froth, and a portion of the entrained gangue and valuable mineral particles weakly attached to their companion bubbles drop back into the pulp (Harris, 1982; O'Connor and Mills, 1995).

Thus, although froth flotation is a sturdy technology, as a result of a myriad of limiting factors in both the pulp and froth phase, it isn't entirely efficient. And as a result, it is not uncommon for valuable minerals to be lost to the tailings.

2.2. The Fundamentals of PGM Tailings

2.2.1. The Production of Tailings

The effluent resulting from the metallurgical processing of an ore is known as tailings. This is a waste stream that comprises the gangue minerals and metals, residual reagents, and unrecycled process waters (Engels, 2012; Knight and Haile, 1984).

The physical and chemical compositions of tailings dumps vary between sites. That is because of differences in the following: mineral composition that occur from ore to ore, different reagent schemes developed for treating each ore, and the degree of efficiency to which the valuables are extracted from each ore. Lastly, it is because of how the tailings are treated for/or prior to storage (Bicak and Ekmekci, 2012; Jones, 1987).

Relevant to this study are tailings produced from PGM and platinum group element (PGE) extraction, from the Bushveld Igneous Complex (BIC) of South Africa (see Figure 2.2 for the BIC's location and general profile of its reefs).

The BIC comprises the world's largest PGM reserves, the world's most productive PGM concentrators, and thus, it is the world's biggest producer of PGM tailings. Its principal concentrators, Merensky, Upper Group 2 (UG2) and Platreef produce an estimated cumulative 740 Mt of fresh tailings per year (Anglo Platinum, 2009; Vogeli et al., 2011; Mohamed et al., 2016). The BIC therefore presents a unique opportunity for PGM tailings reprocessing.

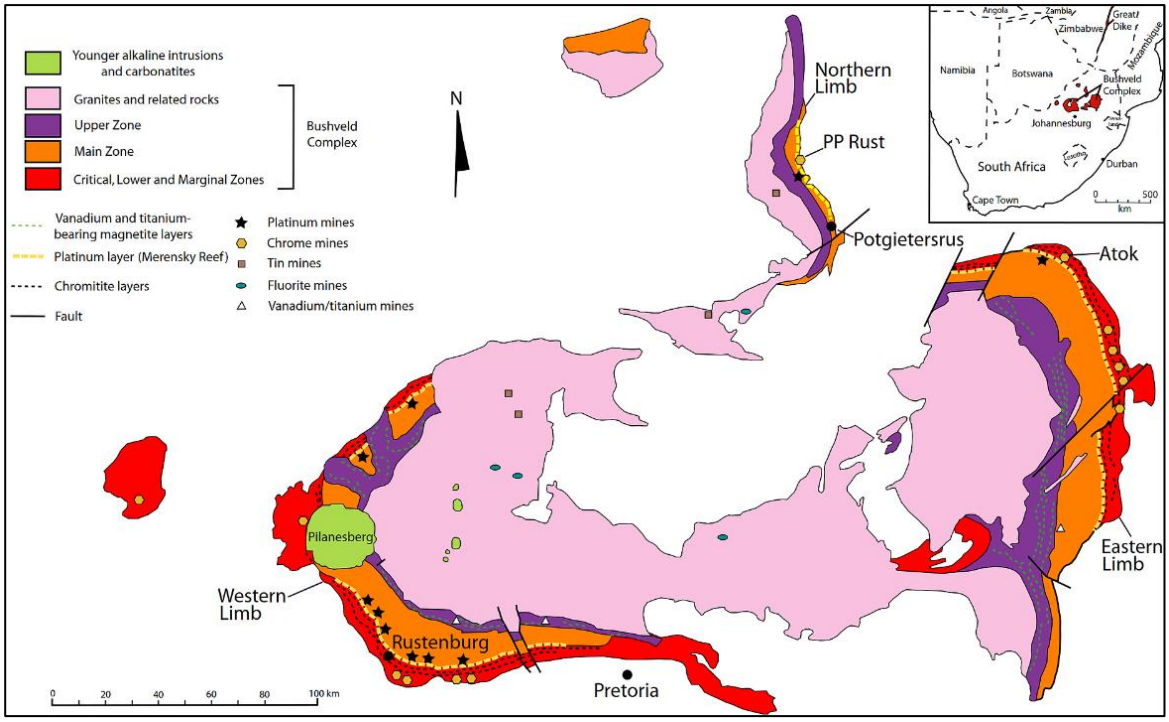


Figure 2.2: The Bushveld Igneous Complex, adapted from Hudson Institute of Mineralogy (2023)

2.2.2. The Chemical State of Tailings

Studies such as Letseli et al. (2018) have noted the processing of minerals from the earth's crust to significantly accelerate the progression of their weathering. At the point of their storage, tailings are primarily altered as a result of two processes. The first contamination results from the addition of flotation reagents (which alters the mineral surface properties). The second results from reactions that commence as soon as the minerals are excavated and react with oxygen (Ebben and Carlson, 2019; Engels, 2012).

As some of these minerals are sulphur-bearing, in contacting them with air and water, and in milling them into smaller sizes, thus increasing their surface area, their proneness to oxidation and hydroxidation is increased (Rao and Natarajan, 1989).

2.2.2.1. The Effects of Froth Flotation and Preceding Steps on Processed Ores

All mineral beneficiation begins at the quarry, with comminution. Grinding plays a significant role in mineral surface alteration (Kelebek, 1993; Klassen and Mokrousov, 1963). The grinding media affects such central factors as pulp chemistry conditions, and therefore, the flotation of sulphide minerals (Greet et al., 2004). Most sulphides are more electrochemically noble than the media used to grind them, and upon contact, a galvanic couple is generated between the media and minerals. This results in electrons flowing from the less noble to the nobler elements i.e. from the media to the minerals (Subrahmanyam and Forssberg, 1995)

In a typical context i.e. that of milling an ore and subjecting it to flotation, this corrosion of media results in a reduction of dissolved oxygen at the mineral-water interface. In turn, this results in two unideal consequences. The first is a reduction in the oxygen available for collector adsorption, and hence a limited chance for induced hydrophobicity. The second is thus: as the media is corroded, the debris precipitates onto the minerals and forms metal hydroxyl complexes, which are hydrophilic in nature and further, impair collector adsorption. In both scenarios, the flotation of the valuable mineral is very likely to be limited. And in both scenarios, valuable minerals may be lost to the tailings (Fuerstenau, 1982b; Guo and Yen, 2005; Kawatra, 2009; Owusu et al., 2013).

As flotation is so intricately entwined with, and so heavily reliant on the differences in the surface properties of minerals, in this way, surface oxidation becomes an inherent quality that influences flotation efficiency; in particular, as it affects chemical reactions occurring at the mineral surfaces and thus rendering the surfaces either hydrophobic or hydrophilic (Kelebek, 1993).

Minor oxidation positively influences the flotation of all principal sulphides of an ore; this, as a result of hydrophobic sulphur species being produced on the mineral surfaces. However, excessive oxidation impedes sulphide flotation; this, as a result of, instead, the production of hydrophilic ferric hydroxides (Becker et al., 2010; Kelebek 1993).

Weaved into this, is the effect of mineralogy, more precisely, the influence of the electrochemical reactivity of minerals on flotation. These have been noted to strongly affect the pulp chemistry by controlling such factors as redox potential (Eh) and dissolved oxygen (DO) (Kirjavainen et al., 2002; Owusu et al. 2013).

So, when considering tailings reprocessing, factors that should be anticipated to strongly influence the degree of process efficiency include, but are not limited to, tailings mineralogy and oxidation.

2.2.2.2. The Bulk Composition of South African PGM Tailings

PGM tailings are mostly comprised of host gangue minerals i.e. silicates and oxides, and sometimes, they are further comprised of trace amounts of economically valueless sulphides – pyrite and pyrrhotite. But as a whole, South African PGM tailings compositions are controlled by original ore compositions, which fall under three main categories (Table 2.1) (Vogeli et al., 2011).

Table 2.1: Main PGM ore types, characterised by their reefs of origin, adapted from Nel et al., (2004); Vogeli et al. (2011)

Reef	Dominant host mineralogy	Predominant gangue minerals
Merensky	(Ca-Mg-Fe) Silicates	Pyroxene, feldspar, olivine, chromite
UG2	(Cr-Al) Silicates; Oxides	Chromite, pyroxene, feldspar
Platreef	(Ca-Mg-Fe) Silicates	Amphibole, feldspar, pyroxene

Of these, the Merensky Reef is the most prominently mined for the production of PGEs, with UG2 being the second-most mined. Of the minerals comprised in the ores, pentlandite, which can contain up to 12.1 wt.% Pd, is the main PGE-carrier. As such, optimising the flotation of pentlandite tends to result in increased PGE recoveries (Vermaak, 2005). In fact, for Merensky ores, PGMs are known to be contained in sulphide mineral particles, and are therefore strongly associated with sulphides. The recovery of PGMs is often achieved by optimising the recovery of sulphides (Cawthorn et al., 2002; Letseli et al., 2011; Nel et al., 2004).

2.2.2.3. The Mineralogical Composition of South African PGM Tailings

PGM ores are regarded to be low grade since their Pt-Pd content averages between 2 to 5 g/t. Mill product (or flotation feed) figures therefore tend to closely approximate the produced tailings. Considering present beneficiation methods, older technologies are fairly rudimentary, and because of this, older tailings are likelier to have higher valuables concentrations (Vogeli et al., 2011).

Von Gruenewaldt and Hatton, in 1987, estimated that the tailings dumps of the chromium mines in the BIC contained approximately 400 000 oz of PGEs, and that an additional, approximate 38 000 oz is added to this bulk every year. The suggested mechanism by which the PGEs have "settled" there is as follows: though in low concentrations (~0.5 g/t), PGEs are known to be strongly associated with the chromitite layers of the Complex, with the PGMs predominantly occurring between chromite grains. The grain sizes are small such that, when the ore is washed, the PGMs become concentrated with the silicates in the tailings.

The mineralogy of a typical Bushveld Igneous Complex UG2 feed is as summarised in Table 2.2.

Table 2.2: The typical mineralogy of a Bushveld Complex UG2 mine feed, adapted from Nel et al. (2004)

Main mineralogy	Sulphide content breakdown	PGE content breakdown
0.1 to 0.2% sulphides; 22 to 24% Cr_2O_3 (or ~50 % chromite)	~50% pyrrhotite, ~35% pentlandite, ~10% chalcopyrite	45% platinum, ~25% palladium, 10% rhodium, 15% ruthenium

The speciation of PGMs hardly influences floatability responses, i.e. so-called fast-floating minerals are recovered in similar quantities to their slow-floating counterparts, though perhaps at different rates. Instead, such factors as association and grain size dictate metallurgical performance. As already mentioned, the recovery of PGMs associated with sulphides can be maximised by simply optimising base metal and iron sulphide flotation (Letseli et al., 2011; Nel et al., 2004). The grain size and association of Bushveld Igneous Complex PGMs is as summarised in Table 2.3.

Table 2.3: The overall grain size and association deportment of Bushveld Complex PGMs, adapted from Nel et al. (2004); Schouwstra et al. (2000)

Coarse	Associated with base metal and iron sulphides	Occurring on host mineral boundaries	Locked in silicates
5%	40%	30%	25%

Empirical findings have shown that the PGMs on host mineral boundaries are easily liberated during milling, while those locked in silicates are not easily liberated. The liberated minerals are easier to recover via flotation. In fact, because of the comparatively more rudimentary milling technologies before the 1990s, tailings of that era are likelier to have higher locked-PGM contents as these particles might not be sufficiently liberated (Nel et al., 2004). This suggests that depending on the milling efficiency, each tailings dump can contain a variety of PGM concentrations.

2.2.3. The Physical State of Tailings

The particle size distribution in a typical flotation cell is such that coarse particles are classed as being greater than 75 μm, and fine particles as being below 10 μm (Loveday and Brouckaert, 1995; Senior et al., 1995). This is because in order for the bubbles to be optimally attached to any given hydrophobic particle, their respective diameters must be compatible. If the bubble is large relative to the particle, the probability of contact is reduced as water flowing around the bubble can sweep off the particle before contact is made. If the bubble is small, its buoyancy might not be enough to lift the particle to the froth (Ghosh, 2012; Kawatra, 2009; Whelan and Brown, 1956).

Particles containing PGMs are highly disseminated and characteristically small. Their sizes generally average at 12 μm, and at most, rarely exceed 30 μm. As a result, extensive comminution is the (modern) industrial norm in the liberation of valuable minerals in these ores; and as a further result, the tailings are typified by small particle sizes comprised in a narrow range (22 to 66 μm) (Mohamed et al., 2016; Schouwstra and Kinloch, 2000; Schouwstra et al., 2000). Thus, it is expected that in reprocessing PGM tailings, one will deal with fine materials (most likely in the range 22 to 66 μm), and with the inherent challenges that come with dealing with such materials.

2.3. Basis for the Treatment of Tailings

2.3.1. Issues Associated with Tailings

The failure of tailings dams is well-documented. For example, upon its failure, the Los Frailes dam in Spain released nearly 4 million m^3 of acidic, heavy-metal bearing sludge into its surrounding environment. When it failed, the Mount Polley dam in British Columbia released nearly 24 million m^3 of sludge. It is estimated that a tailings dam failure occurs once every eight months. In each

case, the soil and surrounding natural water sources are contaminated, and massive flora and fauna die-offs occur (Ebben and Carlson, 2019).

Additionally, tailings concentrations of such metals as zinc, copper, cobalt and nickel, and in some cases, varying combinations of iron, aluminium and magnesium – tend to be higher than the threshold concentrations typically observed in unprocessed soils (Rösner and van Schalkwyk, 2000). In some cases, slight changes in pH and potential have been noted to induce the mobilisation of these metals, causing them to seep into the ground and ground water sources, potentially generating acid, resulting in acid mine drainage (Eco Partners, 2011; Janse Van Rensburg, 2016; Mohamed et al., 2016; Yale Environmental, 2015). For this reason, in a general sense, tailings are regarded as hazardous waste (Rösner and van Schalkwyk, 2000).

2.3.2. The Need for Alternative Ore Sources

The availability of higher-grade ores, as well as the difficulty inherent in processing lower-grade ores used to render the extraction of the valuable materials contained in tailings uneconomic. However, the continued decline in ore grades, as well as the continued improvement in extractive technologies, have seen the retreatment of tailings emerge as economically sound (Bosch, 1987; Letseli et al., 2018; Von Gruenewaldt and Hatton, 1987).

Hence, there is an industrial need to manage tailings. Although the issues associated with them are variable – with some being unique to specific sites – reprocessing tailings immediately addresses two issues, i.e., the possibility to produce a more benign product (by removing the sulphides), and the possibility to extract residual valuable minerals.

2.3.3. The Viability of Tailings Retreatment

No industrial metallurgical process is completely efficient, and as already demonstrated, this is no different with flotation. As some gangue materials will inevitably be recovered with the desired stream, some valuable minerals will, similarly, be lost to the undesired stream.

To demonstrate the practical feasibility of tailings reprocessing, the Golden Arc of South Africa has seen a surge of projects aimed at recovering the residual gold present in the tailings there. A Sibanye-Stillwater project estimates that as much as 175 tonnes of gold and 4 000 tonnes of uranium is present in the piles. In a separate project, Pan African Resources estimates that 19 tonnes of gold can be recovered. In yet another project, Metals X Limited estimate an annual yield of approximately 5 400 tonnes of tin and 2 200 tonnes of copper (Ebben and Carlson, 2019).

For the reprocessing of gold tailings, un-optimised flotation explorations have shown that simply using "*a standard sulphide flotation reagent suite*" can recover at least 60% of the gold and 50% of the

sulphides; with the current standard being that the re-dumped material contain at most 0.3% sulphides (Janse van Rensburg, 2016).

Hence, it is not unreasonable to deem tailings reprocessing viable. However, and especially where PGMs are concerned, the challenge comes in knowing the recoverable fraction of value contained in the waste piles. The 1987 prospector study by Von Gruenewaldt and Hatton is unique and solitary, and no further research has ensued from it. The value residing in PGM tailings piles remains unquantified and uncharacterised.

2.4. Proposed Methods for Characterising PGM Tailings

The surface properties of typical, so-called "fresh ores" are traditionally analysed ex-situ, on a laboratory scale. Usual methods for this include, but are not limited to: X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (IR), X-ray fluorescence (XRF), inductively coupled plasma mass spectroscopy (ICP-MS), and quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN). Through these methods, the chemical make-up of the comprised minerals can be approximated (Baker et al., 1991; Bicak and Ekmekci, 2012; Smart, 1991).

Depending on the project needs, each of the methods is used to determine different key parameters. For example, ICP-MS is used to determine the chemical composition of any given mineral, and XPS the atomic concentrations of elements on a mineral's surface (Fairthorne et al., 1997); i.e. they can be used to determine the concentration of, say, Al_2O_3, CaO, etc. in chalcopyrite (Moimane et al., 2019). On the other hand, QEMSCAN would be used to determine the average bulk mineralogy of an ore i.e. the amount of, say, pentlandite, pyrite, talc, etc. contained in an ore sample (Becker et al., 2010; Kalichini, 2015).

In summary, ex-situ methods directly determine the properties of an ore or mineral. But there is another class of surface analysis techniques which indirectly approximates ore and mineral properties. Usual methods for this include, but are not limited to: mineral rest potential, pulp redox potential, demand for dissolved oxygen, and a method that uses ethylene diamine tetra acetic acid (EDTA) to extract the oxidation products of sulphides (Baker et al., 1991; Bicak and Ekmekci, 2012; Smart, 1991). This in-situ category is preferred for industrial application as, by contrast, the ex-situ methods are time-consuming, expensive, require sample preparation that may cause changes to the ore, and are tedious to apply for a plant-like scale (Rumball and Richmond, 1996).

On the other hand, it is well documented that oxidising pulp conditions improve sulphide hydrophobicity by rendering the mineral surfaces sulphur-rich and non-polar, improving collector adsorption (Hintikka and Leppinen, 1995; Kirjavainen et al., 2002). Moreover, minerals such as

chalcopyrite are naturally floatable in oxidising pulps (Trahar, 1984). See equations 2.1. and 2.2. for the oxidation of chalcopyrite ($CuFeS_2$), where **x** approaches **1** for the outermost layers, and the iron atoms dissolve to leave a metal-deficient, sulphur-rich surface (Buckley and Woods, 1984).

$$CuFeS_2 + \frac{3}{4}xO_2 + \frac{3}{2}xH_2O \rightarrow CuFe_{1-x}S_2 + xFe(OH)_3 \quad 2.1.$$

$$CuFeS_2 \rightarrow CuFe_{1-x}S_2 + xFe^{2+} + 2xe^- \quad 2.2.$$

By contrast, reduced pulp potentials typically hinder xanthate adsorption; in extreme cases, they have been shown to render such floatable minerals as chalcopyrite, hydrophilic. The floatability of the coarse fraction can be restored by raising the potential through aeration or the addition of oxidants (Fuerstenau et al., 1968). Thus, the in-situ electrochemical properties of a slurry become significant in indicating an ore or mineral's amenability to flotation. Some studies have measured and used these properties to extrapolate the ores' readiness for flotation and, by extension, the bulk composition (Becker et al., 2010; Bicak, 2019; Bicak and Ekmekci, 2012; Owusu et al., 2013).

2.4.1. EDTA Extraction

Ore variability is a complex spectrum of variations in qualities such as grade, hardness and surface characteristics. Studies such as Bicak (2019) and Bicak and Ekmekci (2012) have shown that ore variability can be qualitatively determined by measuring the EDTA-extractive products of certain key metals present in the ore. The method determines the presence of, say, secondary copper minerals, and the surface oxidation of copper-bearing minerals. In fact, Bicak (2019) determined the presence of secondary and oxidised copper-, lead- and zinc-bearing in a low-grade ore.

Ethylenediaminetetraacetic acid (pictured in Figure 2.3), or EDTA, is an odourless and colourless acid that, upon its dissolution in water, and without reacting with metal sulphides, can form a complex with the oxidation products of sulphide minerals (Baumann and Wallace, 1969).

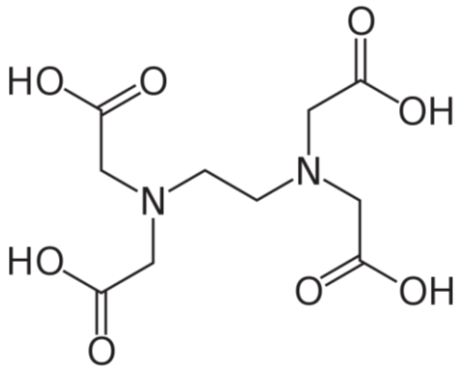


Figure 2.3: The molecular structure of EDTA, adapted from Zhao et al. (2016)

As summarised by Rumball and Richmond (1996), in a non-oxidising environment, at pH values between 7 and 11, EDTA can be used to "*selectively leach metal oxides, carbonates and sulphates from sulphide minerals when the sufficient time is given for the extraction.*"

When minerals come into contact with water, a polar substance, ions are transferred from the mineral and into the solution (Fuerstenau, 1982a). In a similar way, the oxidation products (metal oxides, hydroxides, carbonates, etc.) of sulphides can be leached into an EDTA solution. This is enabled by the molecular structure of EDTA, which has six strong donor atoms – two nitrogen and four oxygen atoms. Thus, strong metal-ligand interactions in the metal-EDTA complexes surrounding the metal cation in the complex are formed (Figure 2.4), achieving the maximal number of possible donor–acceptor interactions. The four carboxylate oxygens then establish a strong electrostatic attraction with the captured cation and stabilise the complex. However, beyond this, the precise mechanisms are little understood or explored in literature (Kovács et al., 2010).

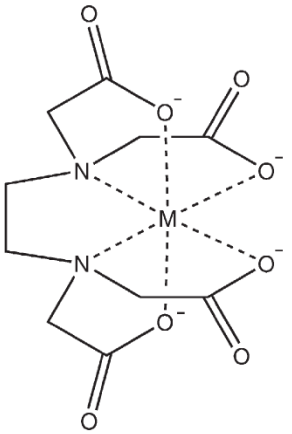


Figure 2.4: The structure of an EDTA-metal complex, adapted from Zhao et al. (2016)

The dissolution rates of minerals differ; for example, the dissolution of copper ions in EDTA, from chalcocite (Cu_2S), has been noted to be much higher than that of copper ions from chalcopyrite ($CuFeS_2$). Chalcocite therefore oxidises more readily than chalcopyrite in EDTA (Lascelles and Finch, 2002). Perhaps as an extension of this, different ores also show different degrees of susceptibility to oxidation (Rumball and Richmond, 1996). Pulp conditions, too, affect the rate of dissolution. Figure 2.5 illustrates the dissolution of copper and iron from chalcopyrite as a function of time at different conditions.

When the pH is increased from 5 to 9.5, and the mineral placed in nitrogen instead of oxygen, the amount of dissociating ions decreases. The formation of iron and copper hydroxides at the mineral surface creates a physical barrier that prevents further dissolution (Fairthorne et al., 1997). Although oxygen promotes the formation of hydrophobic species, further oxidation leads to the formation of metal hydroxides in solution, and they eventually precipitate on the hydrophobic

surfaces (Senior and Trahar, 1991). And so, as the chalcopyrite becomes more oxidised, it behaves more as ferric hydroxide than cupric hydroxide (Pugh and Tjus, 1987).

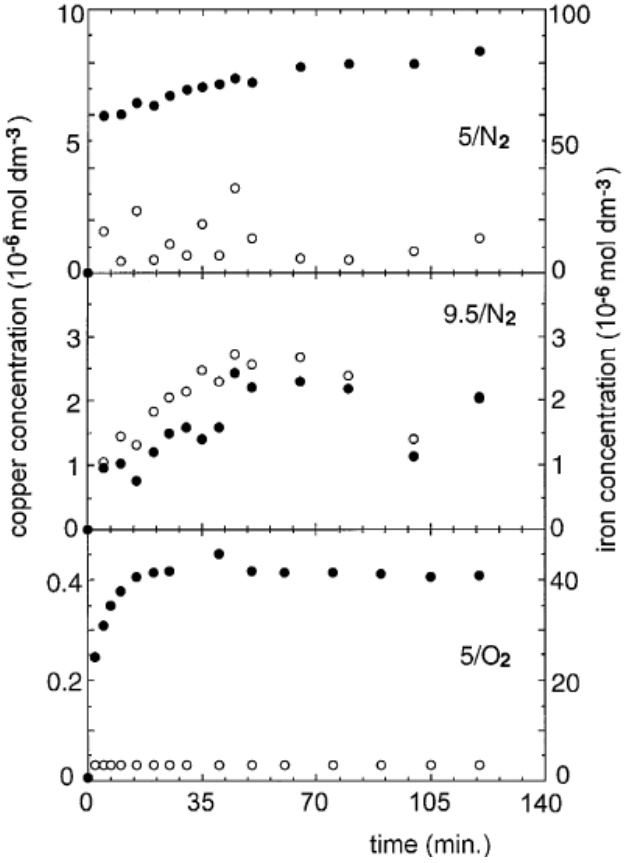


Figure 2.5: The dissolution of copper (the empty circles) and iron (the dark circles) from chalcopyrite in nitrogen and oxygen at pH values 5 and 9.5 (Fairthorne et al., 1997)

Thus, the extent and source of oxidation of sulphide minerals can be determined with certainty by using an EDTA solution to leach slurries comprising the relevant minerals, filtering the leachate, then analysing the filtrate for cations. The above is feasible provided there is enough EDTA to dissolve all oxidised metals that form more stable complexes with EDTA than the unoxidized metal of interest; that is, it is recommended to have excess EDTA. Rumball and Richmond (1996) achieved this by adding 25 mL of slurry to 250 mL of 3% w/w Na_2EDTA solution.

As different minerals dissociate at differing rates, a secondary variable in EDTA extraction is leaching time. Rumball and Richmond (1996) observed that for an oxidised Australian Pb-Zn-Cu ore, an hour was enough to extract most of the extractable lead and zinc, while iron dissolution required close to eight hours. It was thus necessary to set a standard leach time (of one hour) for practical reasons, and note iron dissolution as only a fraction (80%) complete. Also worth noting was the effect of collectors. Potassium amyl xanthate (PAX) was observed by Rumball and Richmond (1996) to increase the level of EDTA-extractable metals; this was attributed to, possibly, "*a PAX derivative solubilising some of the metal sulphide rather, than an increase in the level of oxidation.*"

2.4.2. Reactivity with Oxygen

The electrochemical reactivity of an ore can be elucidated by measuring the oxygen reactivity of that ore's slurry. Owusu et al. (2013) used this method in characterising two pyrites. A slurry sample is sealed in a continuously stirred, airtight vessel equipped with an electrode to measure the change in dissolved oxygen (DO) as a function of time. Air is then purged into the slurry at a set flow rate, and the decrease in DO concentration is measured at, say, 10-second intervals for 5 minutes. From this, the oxygen consumption rate constant ($\mathbf{k_La}$) is calculated using Equation 2.3 (where $\mathbf{DO_0}$ is the oxygen concentration at time $\mathbf{t = 0}$) (Becker, 2009; Becker et al., 2010; Owusu et al., 2013).

$$DO = DO_0 e^{-k_L a \cdot t} \qquad 2.3.$$

Since equal amounts of air are dosed for any given set of tests, higher remaining concentrations of oxygen at the end of a test indicate a lower propensity for the ore to react with oxygen, and vice versa. In oxidising conditions, the more reactive the ore, the lower the oxygen concentration at the end, and the higher the oxygen consumption rate constant (k_La). The differences in oxygen consumption rates of the respective samples are a result of differences in chemical and mineralogical composition, as well as electrochemical characteristics (Owusu et al., 2013). Figure 2.6 is an example of dissolved oxygen profiles of pyrites with different electrochemical qualities.

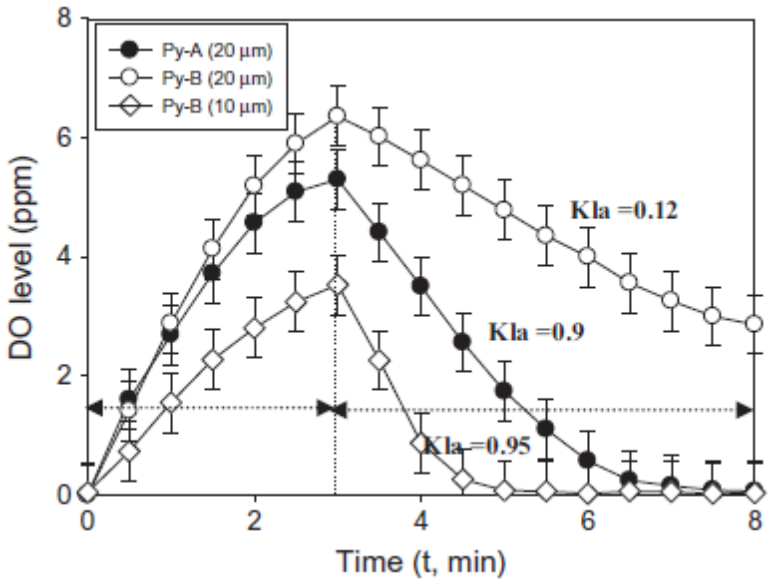


Figure 2.6: Dissolved oxygen levels as measured against time, for two pyrite samples (Owusu et al., 2013)

If the electrochemical reactivities of respective ore materials are demonstrated to be sufficiently different, their effect on pulp chemistry and flotation response can be quantified, with decreasing oxygen contents indicating the minerals' readiness for oxygen consumption (Göktepe and Williams, 1995). The ore material that is more reactive to oxygen is expected to induce more reductive conditions (or decreased Eh values). This leads to an impedance in the formation of

metal-deficient or sulphur-rich surfaces, and further, to decreased rates of collector adsorption to the associated valuable minerals (Buckley and Woods, 1984; Göktepe and Williams, 1995).

Better flotation is therefore expected for valuables that are associated with more reactive ore materials. In this way, a link between dissolved oxygen, pulp potential (Eh), and the flotation responses of the associated valuable minerals can be established. In fact, Becker et al. (2010) used the oxygen reactivity method in conjunction with microflotation tests to determine the behaviour of four different pyrrhotites. In this case, however, the less reactive pyrrhotite had the best collectorless flotation (i.e. natural flotation) recovery, while the most reactive had the poorest collectorless flotation response. It was further noted that the addition of collector (SNPX) resulted in reduced reactivity and therefore improved mineral recovery.

In considering the several relevant factors, it is therefore possible to determine a hierarchy of mineral reactivities, and to determine the parameters affecting each mineral's oxidation. Such factors include collector presence, aeration and conditioning time.

2.4.3. A Validation of the Characterisation Methods

The oxidation of sulphide minerals is exceedingly complex. The consensus in literature is that a holistic understanding requires a blend of surface sensitive ex-situ and in-situ techniques, with the results obtained from the techniques overlapping and complementing each other (Fairthorne et al., 1997). Ex-situ techniques include, among others, QEMSCAN, XRF and X-ray diffraction analysis (XRD). These can be used to determine the elemental and mineralogical compositions of an ore material (Becker et al., 2010), and therefore, of the tailings. Thus, the reliability of EDTA extraction and oxygen reactivity in tailings characterisation can be assessed. And so, while EDTA extraction and oxygen reactivity are expected to provide qualitative tailings profiles, QEMSCAN, XRF and XRD are expected to provide quantitative profiles by informing which minerals are present in the tailings, as well the deportment, associations, and liberation data of those minerals.

2.5. Proposed Methods for Processing the Tailings

One of the more attractive qualities about tailings, is that they are already available. It would be even better, if their reprocessing made use of tools that are also readily available. The ubiquity of froth flotation makes the technology a very desirable option. And so, whether tailings can float or not, becomes an important consideration to make. Section 2.1. has outlined the basic fundamentals of froth flotation, and highlighted the various points that either favour or hinder its efficiency. This section will therefore pick up from there, and delve even deeper into some of the most easily-applicable, and at the same time, effective factors and parameters that control the process.

The first category concerns chemical parameters, i.e. flotation reagents. The second category concerns the mineral surfaces, and whether their oxidation can be mitigated.

2.5.1. Flotation Reagents

Flotation reagents are used to optimise the degree of separation efficiency by enhancing the recovery of valuable minerals, and depressing that of the non-valuables. In order to function, reagents must have an active group that differs from the remainder of the molecule in its affinity for water or the mineral particle (Dean and Ambrose, 1944).

Specialised reagents have been developed to perform specific roles in enhancing the differences in mineral surfaces (Bulatovic, 2007). However, the minerals in each ore react differently to the various interactions that occur in flotation cells, making it difficult to quantify the exact behaviour of each reagent (Bradshaw et al., 1998; Wiese et al., 2006). Regardless of this, the fundamental reagent types maintain their core functional design, and are as follows: frothers, collectors and regulators. Regulators are further divided into activators and depressants (Lovell, 1982).

2.5.1.1. Flotation Collectors

Fuerstenau (1984) proposes that the efficiency of flotation separation depends on the degree of hydrophobicity achieved by the valuable particles, and that the hydrophobicity depends on the adsorption of the chosen collector onto the particle surfaces.

Collectors are heterogeneous molecules that contain an inorganic, active group, and a non-ionic, hydrocarbon chain. They are added to form a hydrophobic layer on a specific mineral or group of minerals (Dean and Ambrose, 1944). The inorganic group, which is polar and hydrophilic, adsorbs onto a mineral surface by attaching to it, and the hydrocarbon chain, which is orientated towards the water phase, renders the mineral surface hydrophobic, and subsequently attaches to an air bubble (Garrels and Christ, 1990; Lovell, 1982). Figure 2.7 illustrates the general molecular structure of a heterogenous collector.

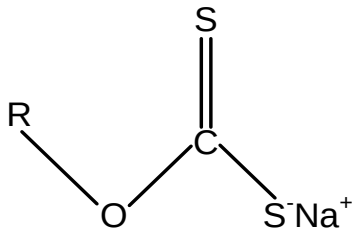


Figure 2.7: A heterogenous collector, where 'R' represents the hydrocarbon radical, adapted from Lovell (1982)

Collectors can be ionic, cationic or anionic. The anionic group is the most widely used, and can be designed for sulphide or oxide mineral flotation, thus belonging either to a sulphydryl or oxhydryl subgroup (Bulatovic, 2007; Dean and Ambrose, 1944). Dithiocarbonates (or xanthates),

dithiocarbamates, and dithiophosphates, all of which belong to the sulphydryl (or thiol) subgroup, are the most commonly used family of collectors in sulphide flotation (Rao, 2003; Lovell, 1982).

Xanthates, in particular, have a high selectivity for sulphides, and a general non-affinity for non-sulphide gangue minerals, and have thus emerged as the most important thiol family for sulphide flotation. Short chain xanthates are preferred because the large sulphide ion in the mineral (compared to the oxygen ion in oxide minerals) does not typically form hydrogen bonds. So sulphide minerals tend to be naturally less hydrophilic than oxygen-bearing minerals (Fuerstenau, 1982d; Lovell, 1982; Rao, 2003). Figure 2.8 shows common xanthate lengths and configurations.

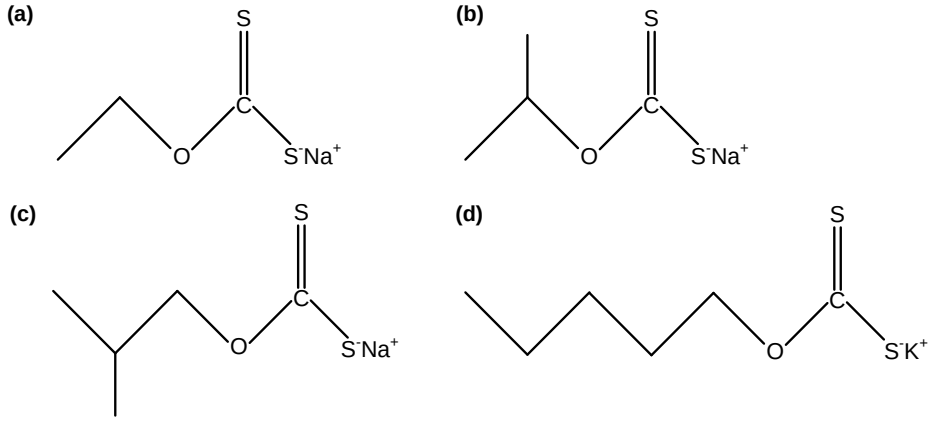


Figure 2.8: The structures of industrial thiols: (a) sodium ethyl xanthate (SEX), (b) sodium isopropyl xanthate (SIPX), (c) sodium isobutyl xanthate (SIBX), and (d) potassium amyl xanthate (PAX), adapted from Bulatovic (2007); Dean and Ambrose (1944); Lovell (1982)

Collectors are surface active compounds; but most, especially short-chain thiols, are not active at the liquid-air interface (Bradshaw, 1997). They typically coat mineral particles through multilayer chemical adsorption. The rate of the adsorption is fast, generally reaching a reversible equilibrium in seconds, and in fact, the initial stages of contact between the mineral and collector can be expressed with an exponential rate equation (Equation 2.4); where **a** and **β** are constants, and **q** is the collector adsorbed at time **t** (Finkelstein and Lovell, 1972).

$$\frac{dq}{dt} = \beta . \exp(-aq) \qquad 2.4.$$

Among such factors as pulp pH, hydrocarbon chain length and configuration (Fuerstenau et al., 1985; Plaskin et al., 1954), collector adsorption can be easily controlled or affected by changing its initial concentration in solution, therefore affecting flotation. For a given range of concentration, the degree of adsorption increases along with the dosed amount. The target mineral recovery is also expected to improve. Beyond the given range, the relationship reaches a plateau, and increasing the collector concentration will neither improve adsorption, nor mineral recovery. But beyond this point, increasing the concentration will impede mineral recovery (Wang, 2016).

An example of this relationship is depicted in Figure 2.9, with the adsorption profile of 8-hydroxyquinoline when contacted with wolframite.

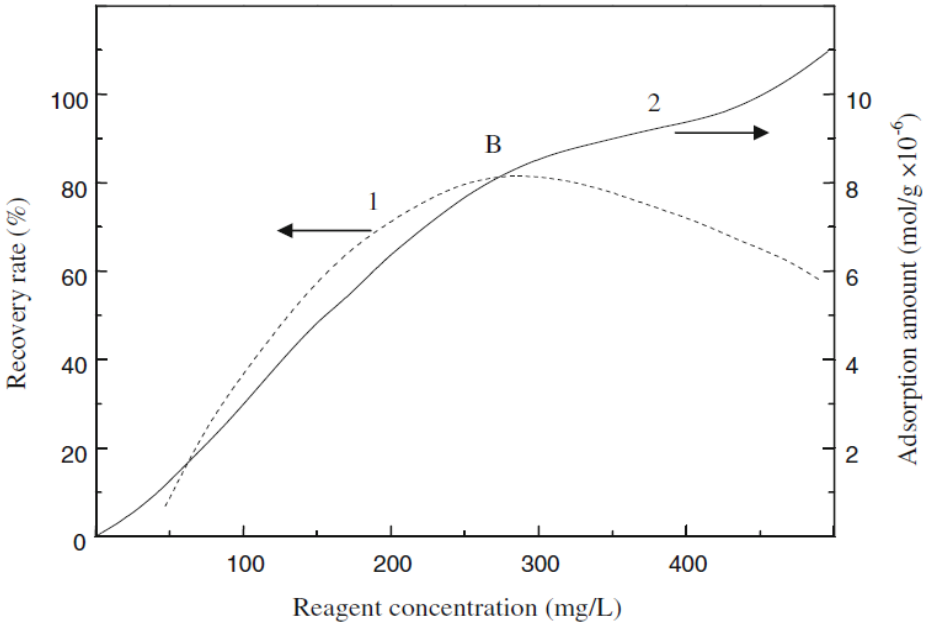


Figure 2.9: The adsorption profile 8-hydroxyquinoline as if affects the flotation recovery of wolframite, where point B represents a transitory plateau phase, adapted from Wang (2016)

Hadler et al. (2005) have also shown that the degree of SIBX adsorption onto the target minerals of a South African PGM ore was reliant on the initial concentration. When the initial dosage was increased from 10 to 25 ppm, the final surface concentration more than doubled (see Figure 2.10). Moreover, while the valuable mineral recoveries were not affected, higher concentrate grades were achieved at the higher dosage.

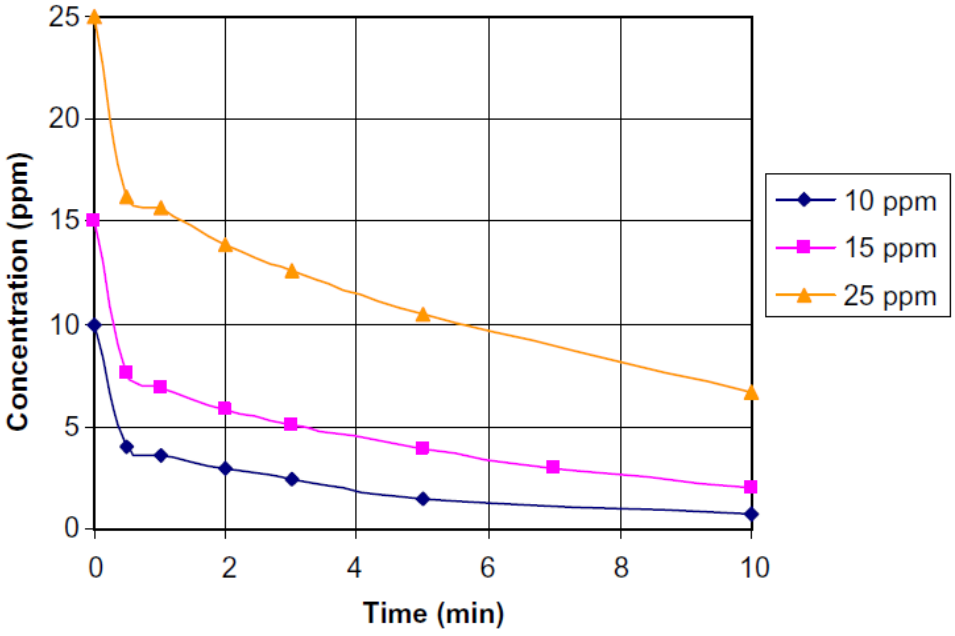


Figure 2.10: The adsorption profile of SIBX with a South African PGM ore, adapted from Hadler et al. (2005)

2.5.1.2. Flotation Frothers

Frothers are non-ionic, heteropolar, surface active molecules. They are used to provide a stable liquid-air interface so the floated particles do not fall back into the pulp before being recovered in the concentrate. In the pulp phase, they increase the dispersion of air through the cell, reduce the coalescence of individual bubbles, and decrease the rate at which bubbles rise to the froth phase, which then increases the possibility of bubble-particle contact (Harris, 1982; Lovell, 1982).

Various frother types (from acidic to basic) are used, but the most important group, is the neutral. Neutral frothers are effective in both acidic and alkaline ranges, and are therefore applicable in the flotation of both base-metal and oxidic ores, and for industrial minerals. Polyglycol ethers are the most widely used sub-group, with several variations being produced by different manufacturers (such as the Dowfroths produced by the Dow Chemical Company and the Aerofroths produced by Cyanamid) (Bulatovic, 2007; Koshdast and Sam, 2011).

The frothing ability and selectivity of polyglycol ethers depends on hydrocarbon chain and molecular weight of the frother. The higher the molecular weight, the more persistent the produced froths. However, more persistent froths result in reduced selectivity (Koshdast and Sam, 2011). As the frother concentration increases, bubble coalescence decreases until, at a specific concentration known as the critical coalescence concentration (CCC), coalescence stops; the phenomenon is illustrated in Figure 2.11. Stronger frothers have lower CCC values than weaker frothers (Cho and Laskowski, 2002).

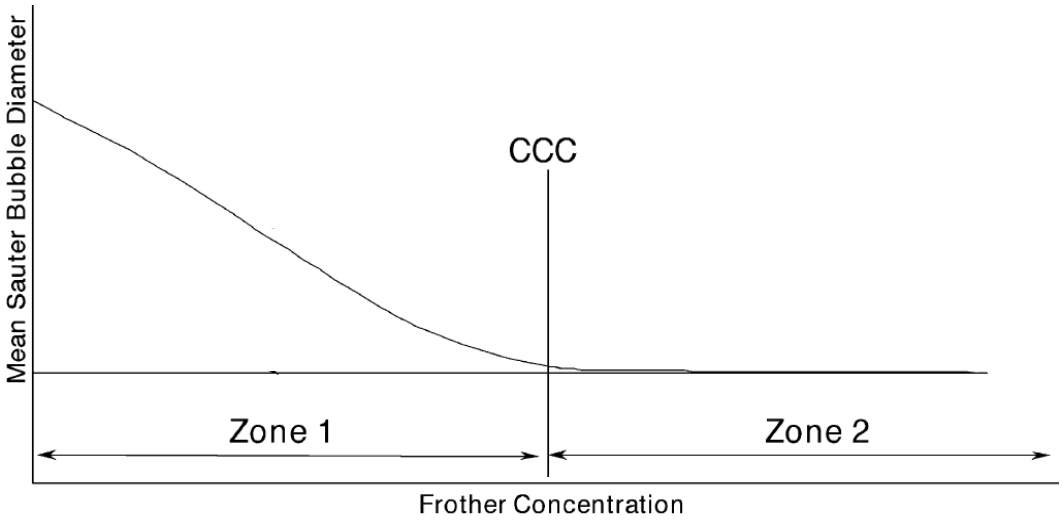


Figure 2.11: The effect of frother concentration on bubble size, adapted from Cho and Laskowski (2002)

The mechanisms of frother actions are not completely independent of other reagents in solution, and other chemical species in the froth phase. Additionally, they are not independent of factors such as type and size of the floated and gangue minerals (Lovell, 1982).

2.5.1.3. Flotation Modifiers

Modifiers are used to either enhance or hinder the adsorption of collectors to minerals. In cases where collectors fail to optimally interact with target minerals, activators, which are inorganic compounds, are added. Copper sulphate, which produces a Cu^{2+} ion, is used for the activation of sulphide minerals. Sodium sulphide (Na_2S) and hydrosulphide (NaSH) are used for the sulphidisation of tarnished oxide minerals and carbonates (Michaud, 2016).

To discourage the interaction of collectors with a given target mineral, depressants are used to, instead, enhance those particles' hydrophilicity. Depressants are also used to limit the flotation of such naturally floatable gangue minerals as talc (Becker et al, 2009; Bradshaw et al., 1998). Depressants can be either organic or inorganic, with the inorganic group becoming obsolete because of the toxicity of the compounds. Organic depressants (in the form of the modified polysaccharides – guar gum (guar) and carboxymethyl cellulose (CMC)) – are therefore the most commonly used for sulphide mineral flotation (Bulatovic, 2007; Michaud, 2016).

Organic depressants are natural or modified natural products with big molecular structures, and molecular masses above 10 000 g/mol^{-1}. Their molecular structures comprise numbers of strongly hydrated polar groups that give them their mineral-depressing quality (King, 1982). Figure 2.12 shows the partial molecular structure of CMC, and Figure 2.13 shows guar gum.

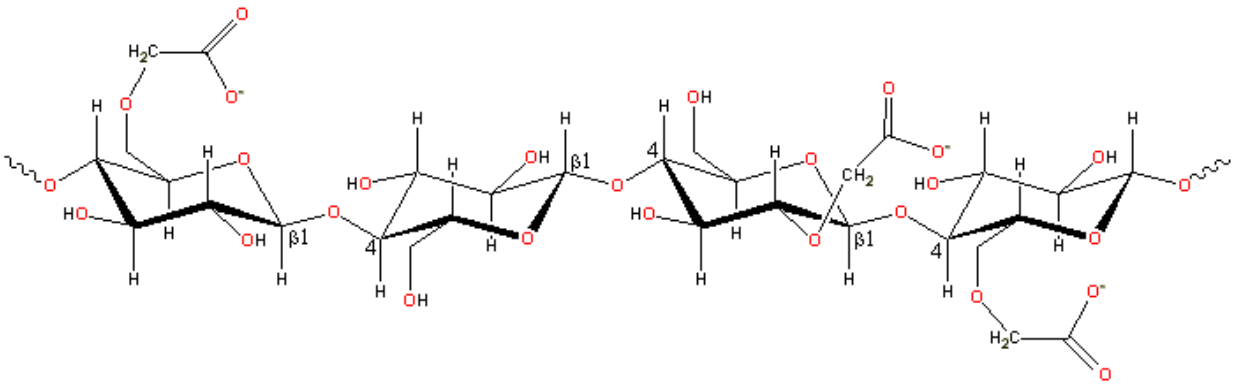


Figure 2.12: The partial structure of a CMC molecule (Chaplin, 2021)

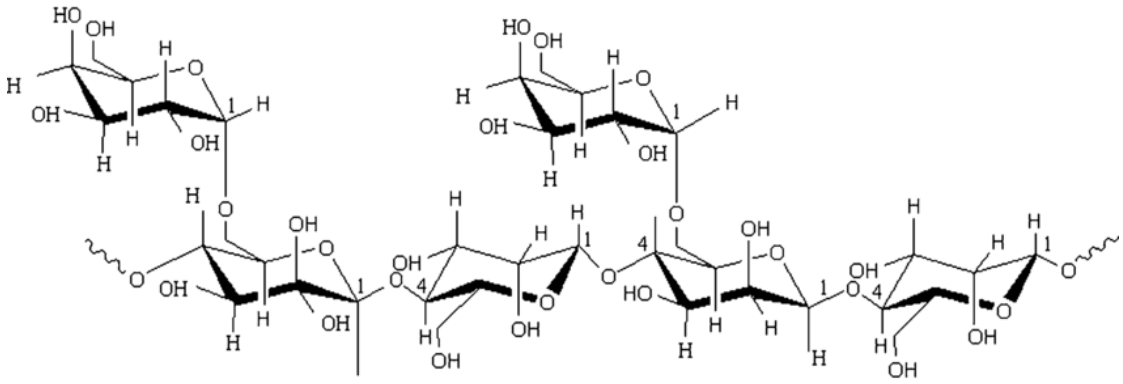


Figure 2.13: The partial structure of a guar gum molecule (Mugdil et al., 2014)

Depressants either disperse, like CMC, or they don't, like guar gum (Wiese et al., 2008). Dispersants complete their depressing action by preventing the coating of unwanted slimes, and therefore preventing the formation of hydrophobic species on the mineral surfaces. Although the mechanisms of depressant adsorption are not always well-understood, in some cases, depressants form large aggregates and complex with the collector present in solution (Shortridge et al., 1999; Pugh, 1989). CMC was chosen for this study as, along with guar gum, it is widely applied in the South African PGM industry to selectively depress siliceous materials, talc and orthopyroxene-talc composites (Becker et al., 2009; Wiese et al., 2008).

There are different types of CMC, and they are categorised according to active content and molecular weight. The active content is the fraction of CMC present in a given product. CMC types used for flotation are nor purified, and usually have an active content of about 70 wt.% CMC, with the remainder fraction being salt and glycolates. The molecular weight indicates the degree of polymerisation, with the viscosity of CMC in solution being proportional to the molecular weight (Burdukova, 2007; Shortridge, 2002).

The functional carboxymethyl group in CMC renders the molecule negatively charged when dissolved in solution, which also renders the particle surfaces CMC adsorbs onto, negatively charged as well. The particles therefore repel each other and disperse. Empirical evidence has shown that increased dispersion cleans slimes from the mineral surfaces more effectively, and in turn, reduces the floatability of naturally floatable gangue materials (Robertson, 2003).

2.5.2. Mineral Surface Cleaning Methods

Section 2.2. has outlined the fundamentals of tailings surface alteration. This section will therefore pick up from there, by exploring some of the most easily-applicable, and at the same time, effective methods of cleaning mineral particle surfaces. The study acknowledges that surface cleaning methods can be either chemical or mechanical (Michaud, 2018); however, in the interest of tightening the scope, only mechanical methods will be considered.

2.5.2.1. Ultrasonication

The slime coatings on minerals particles, and their effect, can be mitigated by using mechanical methods such as hydrocyclones and ultrasonication (Oats et al., 2010). Ultrasonication of a slurry either before or during flotation, has been demonstrated by various studies to remove fine, ultrafine or oxidised coatings from the minerals particles. With the surfaces clean, the collector adsorbs on the target minerals more efficiently and as a result, the recovery of valuables is increased (Aldrich and Feng, 1999; Celik, 1989; Djendova and Mehandjiski, 1992).

Ultrasonication removes coatings by generating ultrasonic waves, which in turn generate bubbles that oscillate along waves, then after a few wave cycles, deviate from the regime. Bubble expansion causes pressure elevation and compresses the inertial forces, and so, the bubbles collapse. This collapse generates a fluid microjet near the mineral surfaces, and the force removes fine particles and other coatings on the surfaces (Videla et al., 2016). Two methods are used to ultrasonicate flotation slurries (see Figure 2.14 for an illustration).

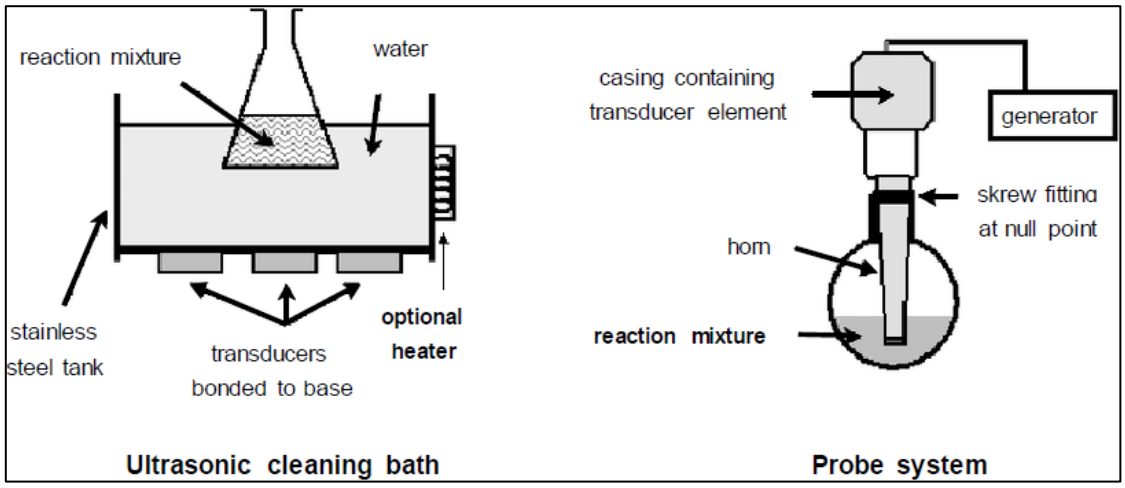


Figure 2.14: Laboratory methods for the ultrasonication of flotation slurries (Mason, 2003)

In the first method, the slurry is placed in an ultrasonication bath, and the ultrasonic waves are generated from the bottom of the bath. In the second, a probe is immersed in the slurry, and the waves are generated from the probe tip. Probes are preferred for small slurry volumes (50 – 200 ml), while baths can be used for large volumes (Aldrich and Feng, 2004; Mason, 2003).

2.5.2.2. Desliming

Another mechanical method of removing slime coatings from mineral particles, is desliming, which entails the removal of fine particles through gravitational or size-based separation (Michaud, 2018). The particle size distribution of an ore material plays a vital role in the efficiency of froth flotation (Maksimov et al.; Yehia et al., 1999). Optimal flotation rates and mineral recoveries tend to be favoured in the middle particle size region. There is an upper and lower particle size limit beyond which, flotation becomes increasingly impeded, eventually reaching a region in which no flotation can happen (Phiri et al., 2019; Trahar, 1981).

These size limits are different for every ore material, but in general, particles in the intermediate range (-50 to +10 µm) float faster than fine particles (-10 µm), at the same surface coverage of the hydrophobic collecting species. The critical surface coverage required for the flotation of fine particles, is more than double that required for intermediate particles (Crawford and Ralston, 1988). The general agreement is that as particle sizes decrease, flotation behaviour becomes more

impeded, or less efficient. However, the decrease in particle size is necessary as it liberates valuable minerals. The danger comes when the ore is ground so fine, it becomes a powder, and it becomes difficult to physically process (Phiri et al., 2019).

Desliming can be done by sieving (or screening), or it can be done by elutriation. Sieving simply requires a screen of a given size, where particles that pass through the screen are the undesirables and are therefore discarded. The particles retained on the screen are then floated. Depending on the system parameters, capacity and objectives, screening can be replaced by using a hydrocyclone and setting a specific cut size on it (Possa and Lima, 2000; Yang et al., 2022). Elutriation is a logistically more demanding method, and it takes into account, not only the sizes of the particles, but their shape and sedimentation density as well (Tiemann and Betz, 1979).

Desliming has the major disadvantage that, if the valuables have been ground fine and have small grain sizes, as tends to be the case for PGE and PGM ore materials, there is a higher risk of discarding them with the undesirable stream (Mohamed et al., 2016; Schouwstra et al., 2000).

2.6. A Consolidation of the Literature Review and Relevance to the Study

The near-depletion of high-grade ores, among other factors, has necessitated the consideration of alternative PGM sources. Various factors in the metallurgical processing of ores result in valuable minerals being lost to the tailings. Hence, this study proposes PGM tailings as an alternative PGM source. However, there is a dearth in literature on any methods, whether in-situ or ex-situ, that are used to characterise PGM tailings and thus quantify the value present in them.

While ex-situ methods have been demonstrated to be efficient in directly determining the compositions of various ores, in-situ methods have been demonstrated to be efficient in determining the weathering of sulphide minerals and sulphide-bearing ores. The focus is on sulphides as, for ores like Merensky, PGMs are closely associated with sulphides, and a long-standing industrial practice has been to indirectly optimise PGM recovery by targeting sulphides.

Of concern to this study are Merensky and UG2 tailings, which are classed – for the purpose of this study – as oxidised sulphides. This study further equates ore weathering to surface oxidation, and infers the definition by Senior and Trahar (1991), that the oxidation products of sulphide minerals occur on the mineral surfaces as precipitated hydrophilic species such as metal oxides and hydroxides known to decrease the collectorless floatability of these sulphides. This study therefore proposes that the characterisation of PGM tailings be the first step in processing PGM tailings for the recovery of residual PGMs. For practical reasons, the chosen methods for surface analysis are in-situ; they are EDTA extraction and oxygen reactivity.

Tailings characterisation, in this context, therefore entails the following:

- The mineral and elemental composition of Merensky and UG2 tailings, as determined by QEMSCAN, XRD and XRF. Of particular interest, are the concentrations of base metal sulphides, and more specifically, the concentrations of chalcopyrite and pentlandite.
- The degree of oxidation of the chalcopyrite and pentlandite in the tailings. Since the study is concerned with the recovery of copper, and secondarily, with the recovery of nickel, it aims to use the EDTA extraction method to determine the degree of oxidation of the copper-bearing and nickel-bearing minerals in Merensky and UG2 tailings.
- The readiness of Merensky and UG2 tailings to react with oxygen.

Once the tailings are characterised, the study will employ froth flotation for the recovery of copper and nickel, as it is a sturdy technology that has been proven to be industrially viable in the processing of other tailings (gold). Further, the intricacies regarding weathering and the mitigating measures, where flotation is concerned, are fairly well-understood. This study therefore proposes the development of an in-situ technique, that can be correlated to mineral characteristics and in turn, be used to predict the flotation behaviour of the relevant tailings.

With personal correspondence as a reference, a reprocessing venture for the tailings in this study would be deemed economically viable if 30% of the present copper is recovered.

3. RESEARCH HYPOTHESIS

3.1. Hypothesis

Different ores are comprised of different minerals of varying concentrations, and different minerals have different surface properties that are differently reactive when processed. Thus, the respective wastes (or tailings) from these ores will have experienced varying degrees of weathering. The study thus posits the following hypotheses for different PGM tailings:

- EDTA, a compound that can form complexes with the oxidation products of sulphide minerals, will, in extracting these products, determine the extent of oxidation of the Cu, Ni and Fe species. Tailings with more pronounced oxidation will have higher EDTA-extractive indices than those with lower oxidation; this is because tailings with more pronounced oxidation are coated with more products of weathering.

- The electrochemical reactivity of differing tailings can be used to determine the extent of the tailings' oxidation. Tailings with more pronounced oxidation will consume lower amounts of dissolved oxygen, resulting in lower oxygen reactivity constants. Less oxidised tailings will produce higher reactivity constants; this is because their fresher surfaces will consume more oxygen, and as a result, induce more reductive pulps and therefore lower the relevant pulp potential values.

3.2. Experimental Plan to Test the Hypothesis

The study will test the hypothesis by investigating the following:

- The validity of using the EDTA extraction and oxygen reactivity methods to determine the degree of weathering (or oxidation) of selected South African PGM tailings.
- The validity of using the EDTA extraction and oxygen reactivity methods to quantify the recoverable fraction contained in South African PGM tailings.
- The efficiency of the EDTA extraction and oxygen reactivity methods in characterising the differences in weathering (or oxidation) of selected South African PGM tailings.
- How the oxidation of the tailings effects the recovery of the value minerals, and whether the oxidation can be mitigated.
- The batch flotation of the selected South African PGM tailings.

4. MATERIALS AND METHODS

Three tailings were received from concentrators in the Bushveld Igneous Complex. The Merensky tails were acquired from Impala. Two UG2 tails were acquired from Sibanye-Stillwater; one was raw (or normal), and the other was deslimed. In this context, desliming entails the removal of fines and a fraction of the silicates. The desliming process was performed at the concentrator by plant personnel and equipment, prior to delivery of the sample to UCT. For the purpose of this study, shorthands were used to refer to the tailings. The shorthand for the Merensky sample is MER; that for the raw UG2 sample is UG2R, while that for the deslimed sample is UG2D.

4.1. Tailings Sampling and Preparation

Representative samples were provided by the respective mine sites. Samples were taken from a selection of points around the tailings storage facilities to ensure representativity. The samples were received at UCT in sets of 20 kg buckets. Each tailings was first homogenised by pouring onto a containment tray (roughly 1.5 m x 1.5 m) and mixing manually, with a spade. Once this was done, a second homogenisation step was carried out, using a rotary riffle splitter. The second step produced 1 kg aliquots. The aliquots were sealed in plastic bags prior to use.

4.2. Background to the Experimental Design

Studies such as Newell et al. (2006) have shown that artificially oxidising sulphide minerals (chalcopyrite, pentlandite and pyrrhotite) beyond a certain timespan (121 days), is akin to inducing a reactivity plateau on them. In other words, when these minerals were exposed to oxidation conditions in a controlled, laboratory environment, there came a point where continuing with the exertion of the conditions did not significantly alter the mineral surfaces any further. And this was only over a matter of days. The tailings used in this study sat within mine dumps for longer periods.

The first step in characterising them was to determine whether the chosen methods were suitable. For example, let's say the EDTA method can extract the oxidation products of copper, nickel, iron, etc. from the tailings. Does that reveal anything meaningful or unique about the tailings, or are the extracted values purely coincidental? In other words, is the surface still reactive enough to yield useful information? And if the surface conditions of the same sample were changed, would the EDTA method be able to detect this change, or would the extracted values remain the same? This gave way to the following consideration: not only did the pure samples have to be tested, samples whose surfaces were altered also needed to be tested. A simple surface alteration method, ultrasonication, was chosen for the reason that it is readily available, practical and commonly used

to clean mineral surfaces (Kyllönen et al., 2004). From this, a pseudo-matrix in which surface alteration vs. characterisation are the primary variables, could be constructed (Figure 4.1).

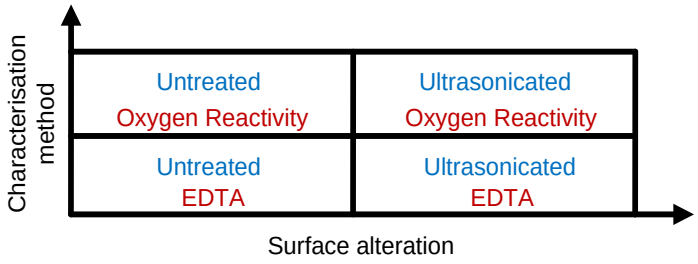


Figure 4.1: The variables for the characterisation of the tailings

The summary in Figure 4.1 was the first batch of tests, and whether anything would be amended, added or removed, would depend on the statistical reliability of the results. An if-then flowchart (Figure 4.2) was used in order to test the practicality of the proposed experimental design. The internal loops in the flowchart (zoomed in/isolated in Figure 4.3), formed the core of the experimental conditions, and are further expanded in Figure 4.4.

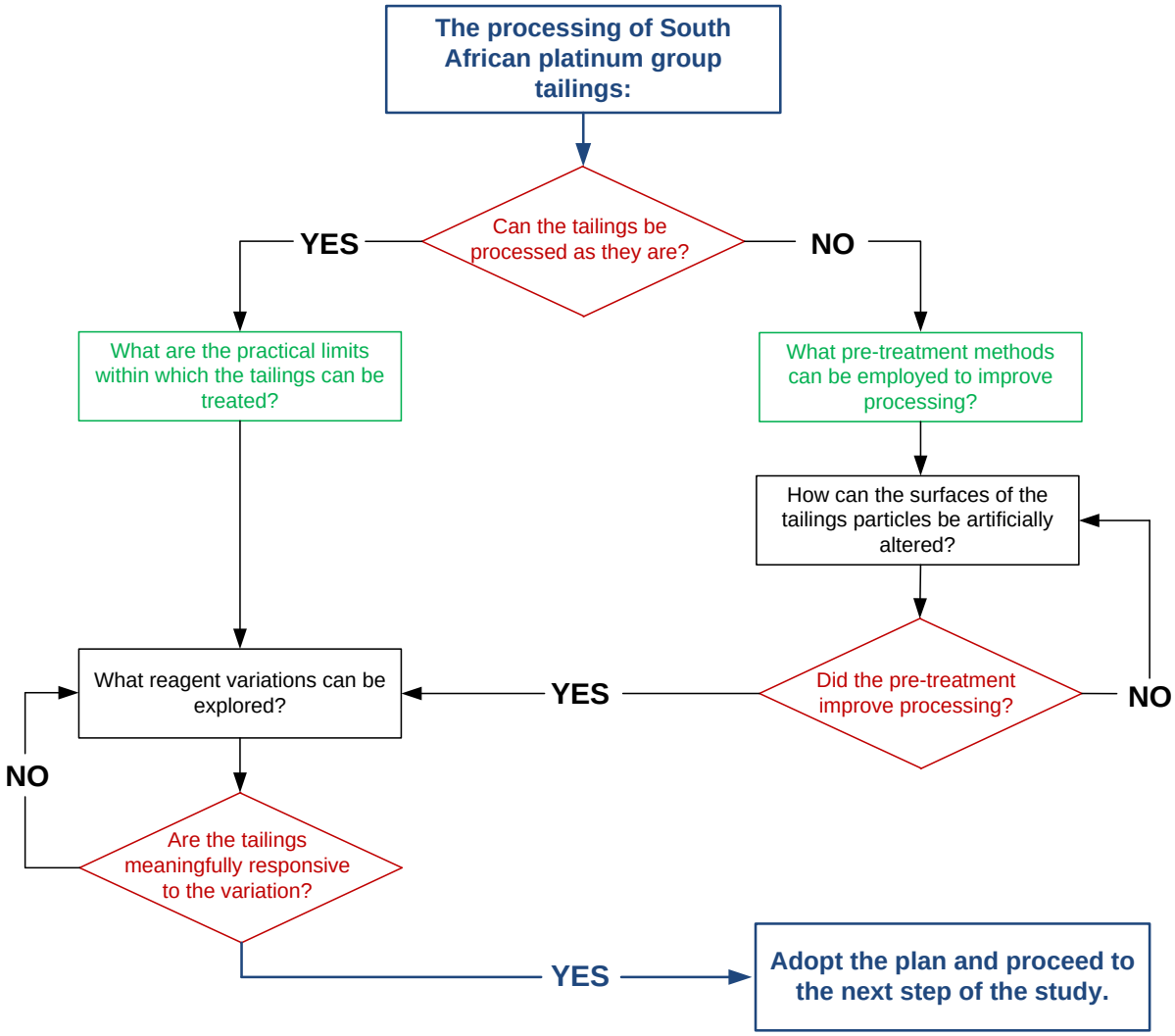


Figure 4.2: The flow chart followed in determining the practicality of the study

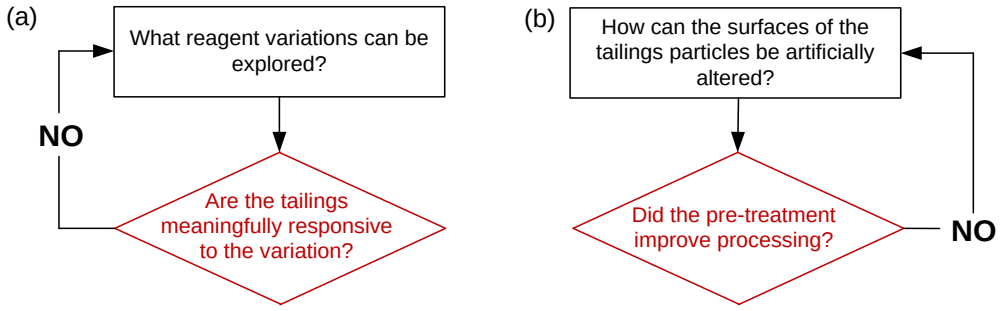


Figure 4.3: The internal loops on which the experimental parameters and variations were built; (a) the reagent variation loop, (b) the particle surface loop

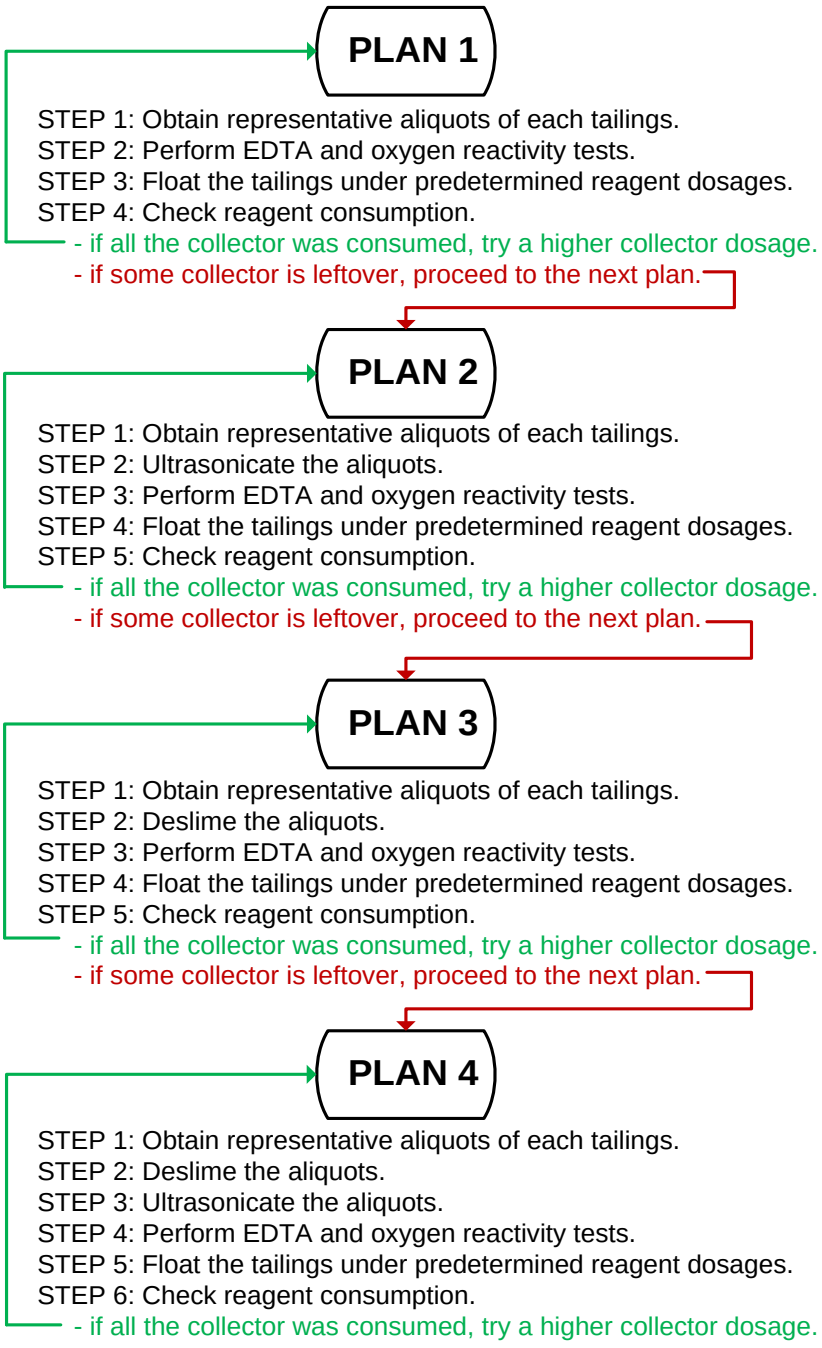


Figure 4.4: An expansion of the internal loops relevant to the study's experimental flowchart

4.3. Tailings Characterisation

4.3.1. Bulk Mineralogy

Quantitative evaluation of minerals by scanning electron microscopy (QEMSCAN) and X-ray diffraction (XRD) were used to determine the bulk mineralogical compositions of the tailings.

4.3.1.1. The QEMSCAN Procedure

Representatives of the 1 kg aliquots were riffled and split into 1 g portions using a quantachrome microriffler. An analysis block was then made from each sample; this was done by mixing the sample with resin and graphite, then curing them. The analysis blocks were checked for quality with an optical microscope. They were then polished and carbon-coated, and placed in a vacuum, where the QEMSCAN 650F (Figure 4.5) was used to analyse them.

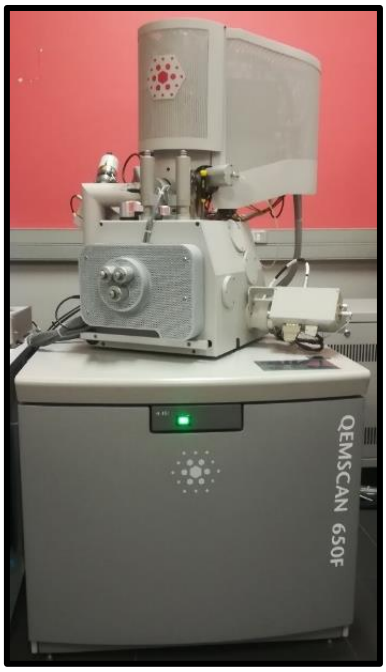


Figure 4.5: The QEMSCAN 650F

To gain an expansive understanding of the compositions, three analyses were carried out, i.e., bulk mineralogy analysis (BMA), particle mineralogy analysis (PMA), and specific mineral search (SMS).

4.3.1.2. The XRD Procedure

Samples were prepared for phase quantification in the following way: they were micronised in ethanol using a McCrone microniser to produce a homogenous particle size distribution. Powder XRD spectra were obtained using a Bruker D8 Advance powder diffractometer with a LynxEye detector and fixed divergence and receiving slits with Co-Ka radiation. The phases were identified using Bruker Topas 4.1 software (Coelho, 2007) and the relative phase amounts (weight %) were estimated using the Rietveld method.

4.3.2. EDTA Extraction

As outlined in Section 2.4.1., a 3 wt.% EDTA solution is required for the extraction tests.

4.3.2.1. EDTA Solution Preparation

In order to make 3 wt.% EDTA, 30 g of EDTA (powder) was dissolved in 1 L of distilled water, and placed on a magnetic stirrer to obtain a homogenous solution. The purity of the powder was approximately 98%. The pH of the solution was adjusted by adding NaOH pellets and stirring until it stabilised to 7.5. Each batch of solution was used within three days of being prepared.

4.3.2.2. Tailings Sample Preparation

The 1 kg bags were further split into 100 g portions, and then into 10 g aliquots.

4.3.2.3. Extraction Tests

10 g of tailings and 200 mL of EDTA solution were poured into a 300 mL beaker, sealed with parafilm, and magnetically stirred for 30 minutes. When this was done, the slurry was filtered using a Millipore filtration funnel fitted with 0.22 μm filter paper. The liquid filtrate was analysed for metal ions (Cu, Ni and Fe) present in solution.

The filter cake was also analysed for the same metal ions. The analysis method that was used is inductively coupled plasma (ICP) atomic emission spectrophotometry, using the Varian ES 730 ICP-OES Mars 6 Microwave Digester. A blank (not contacted with tailings) EDTA solution and distilled water were also sent for analysis, and used as reference solutions.

Once the metal ion content was determined, equations 4.1. and 4.2. were used to calculate the $\mathbf{E_S}$ values. $\mathbf{Es_{Ni}}$ indicates the surface oxidation of the nickel minerals in the tailings, $\mathbf{Es_{Cu}}$ indicates that of copper minerals, and $\mathbf{E_{SFe}}$ indicates that of iron (Bicak, 2019; Bicak and Ekmekci, 2012). The E_S values can thus be used to indicate the degree of the surface oxidation of the samples.

$$\mathrm{Es_{metal\ ion}} = \frac{\text{Concentration of metal ions extracted by EDTA (in mg)}}{\text{Concentration of metal ions in untreated tailings sample (in g)}} \quad 4.1.$$

$$\text{Where: Metal ions in initial tailings} = \text{Metal ions in filtrate} + \text{Metal ions in filter cake} \quad 4.2.$$

4.3.3. Oxygen Reactivity

The oxygen reactivity factors were determined using the method developed by Afrox (Afrox, 2008). The following key components were required: calcium water, medical grade oxygen, an oxygen metre, a 400 mL beaker and a magnetic stirrer.

Figure 4.6 shows the typical oxygen reactivity setup.

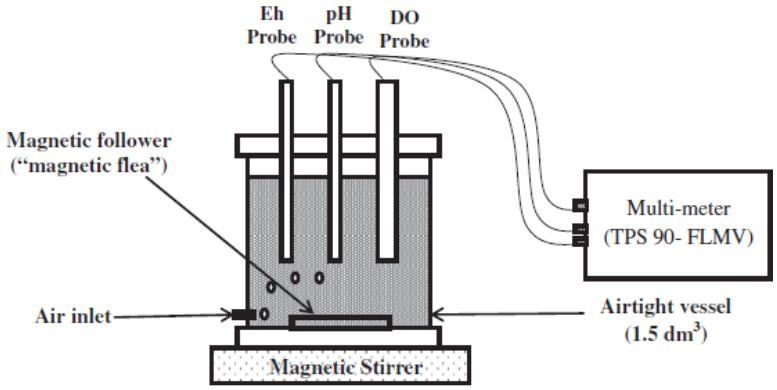


Figure 4.6: The typical setup for an oxygen reactivity test, adapted from Owusu et al. (2013)

For this study, a Hanna multiparameter probe (HI98194 for pH/EC/DO), capable of measuring the slurry Eh and pH too, was used in place of a single-purpose oxygen metre. The oxygen used was provided by Air Products at a purity of 99%.

4.3.3.1. Calcium Water Preparation

The calcium water was prepared by adding ~1.84 g of $CaCl_2$ to 5 L of distilled water to produce a 0.0033 M solution. Each 5-litre batch of solution was used within three days of being prepared.

4.3.3.2. Tailings Sample Preparation

The 1 kg tailings samples were further split into 100 g portions, and then into 10 g portions. Samples from splitter jars sitting opposite each other were then combined to produce representative aliquots of 80 g (see Figure 4.7 for an illustration of the process. The jars with the matching numbers correspond, and are combined into one aliquot). The remainder 20 g (jars numbered 4) was placed in a separate bag (for tests that would require a mass of 20 g or less).

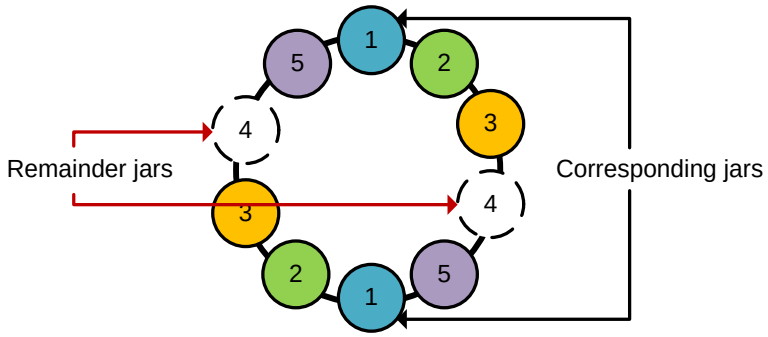


Figure 4.7: A demonstration of the combined jars when rotary splitting

4.3.3.3. Oxygen Reactivity Tests

An aliquot of 80 g tailings was turned into a slurry by adding 300 mL calcium water into a 400 mL beaker. The magnetic stirrer was switched on to prevent settling of the slurry, and to promote homogenisation. The oxygen feed pipe and multiprobe were placed in the sample, and the beaker was sealed with parafilm. See Figure 4.8 for an illustration.

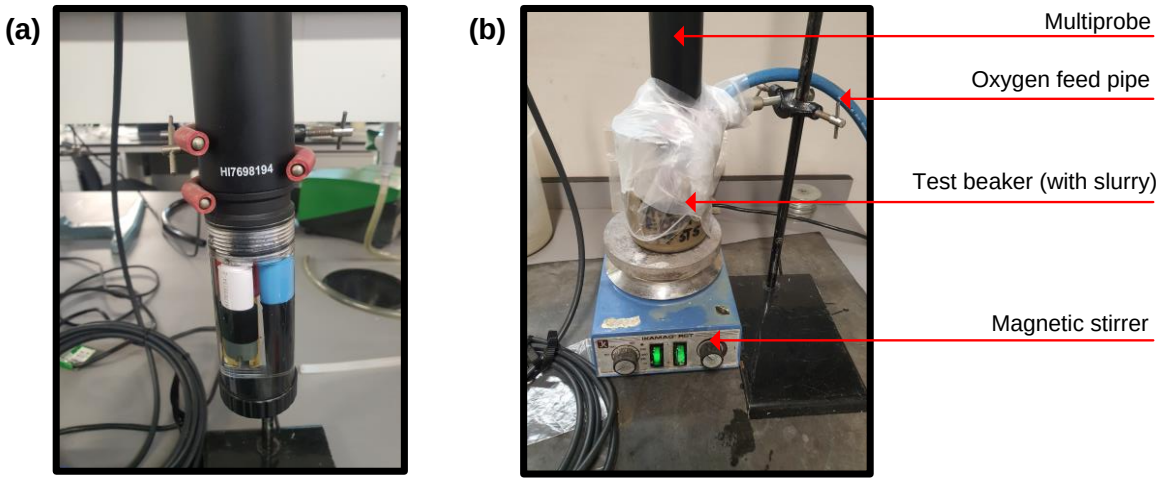


Figure 4.8: The setup for the oxygen reactivity tests; (a) the HI98194 multiprobe; (b) the multiprobe when immersed in an airtight beaker along with the oxygen feed pipe

Initial measurements for pH, Eh and dissolved oxygen (DO) of the pulp were taken every second, until they stabilised, at which point, the oxygen tank feeding the oxygen into the test beaker was switched on. The oxygen was sparged into the beaker at 3 L/min, for 3 minutes. The multiprobe continued to take measurements of the rise of oxygen in the pulp (at one-second intervals).

At the 3-minute mark, the oxygen was switched off, and this time, the multiprobe measured the decay of oxygen in the pulp. This was also done at one-second intervals, but for 20 minutes. The procedure is summarised by Figure 4.9.

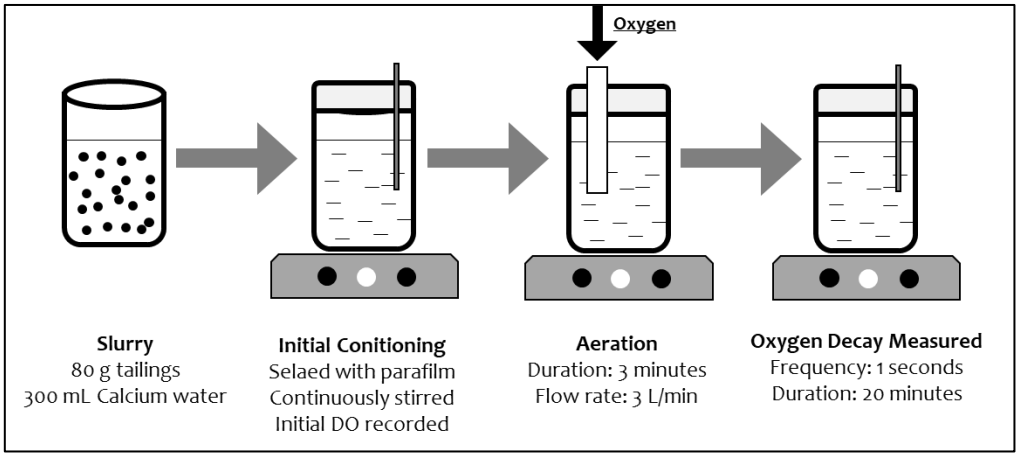


Figure 4.9: The oxygen reactivity test steps

The desirable pH of the test is between 8.5 and 9.5 (Becker, 2009; Sibiya, 2022) ; there was no need for modification as the natural pH of the slurry was within this range.

The oxygen consumption rate constant ($\mathbf{k_La}$) was then calculated using Equation 4.3 (where $\mathbf{DO_0}$ is the **DO** concentration at time $\mathbf{t = 0}$) (Becker et al., 2010; Owusu et al., 2013).

$$DO = DO_0 e^{-K_L a \cdot t} \qquad 4.3.$$

4.4. Froth Flotation Experiments

Different operations use different reagents suites (combinations of collectors, activators, frothers and depressants) to recover the relevant PGEs and PGMs (Wiese et al., 2004). However, the *individual* reagents tend to be common.

For example, the most widely used collectors are thiols, either sodium isobutyl xanthate (SIBX) or sodium isopropyl xanthate (SIPX). The most popular frothers include polyglycol ethers. The most commonly used depressants are guar gum and carboxymethyl cellulose (CMC). And sometimes, activators such as copper sulphate are used to activate the copper-bearing value minerals; although, it is theorised that this practice also leads to the activation of gangue minerals (Wiese et al., 2006; Wiese and Harris, 2012).

4.4.1. Reagent Suite Selection

This study's aim is simply to test the floatability of tailings, and not the various combinations of various reagents. As such, the more readily available of these reagents were used in the trial design.

A collector and frother were obvious inclusions. Additionally, a large percentage of the tailings is comprised of gangue minerals (See Section 5.1.). A reasonable assumption to make is that a depressant must be included in the trial. Based primarily on availability, the chosen reagent suite was thus as follows: SIBX as the collector, CMC as the depressant, and DOW200 as the frother.

The frother was kept constant (at 50 g/t); and the primary tests were conducted to elucidate the ability of SIBX to recover whatever value remained in the tailings; as well as the efficiency of CMC in depressing the overwhelming fraction of gangue minerals. Thus, and finally, a factorial design with two variables (SIBX and CMC), set at two different levels (minimum and maximum) could be constructed. This is illustrated by Figure 4.10.

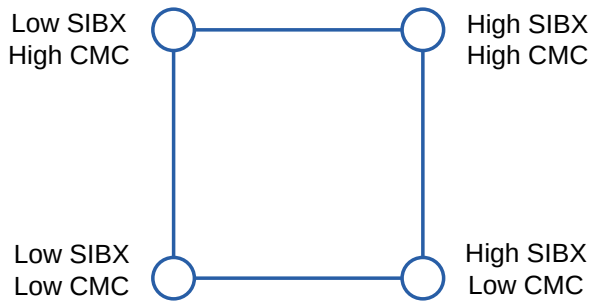


Figure 4.10: The two-variable, two-level factorial used in the batch flotation trial. The generic factorial skeleton was adapted from Mäkelä (2017)

The actual dosages corresponding to Figure 4.10 are presented in Table 4.1.

Table 4.1: The trial reagent dosages for the batch flotation tests

Reagent	Minimum Level	Maximum Level	Units
SIBX	125	200	g/t
CMC	175	300	g/t

4.5. Reagent Preparation and Storage

The SIBX and CMC, both in powder form, were supplied by Senmin. The frother (in liquid form) was supplied by Betachem. Their properties are summarised in Table 4.2.

Table 4.2: The chemical properties of the reagents used in the batch flotation tests

Reagent	Chemical Formula	Molecular Weight (g/mol)	Purity (%)
SIBX	$(CH_3)_2CHCH_2OCS_2Na$	172	97
CMC (SENDEP 30F)	$[C_6H_7O(OH)_3{-}x(OCH_2COOH)_x]_n$	221231	72
DOW200	$CH_3(C_3H_6O)_3OH$	206	100

None of the reagents were corrected for active content when added to the flotation cell.

4.5.1. Collector Preparation

SIBX decomposes quickly (Hadler et al., 2005). It was prepared daily, immediately prior to the experiments. The 1% (w/v) collector solutions were prepared as follows: 1 g powder of SIBX was dissolved in 100 mL distilled water and sealed (Corin et al., 2011). Residual xanthate solutions were discarded as outlined by the material safety data sheet and CMR laboratory rules.

4.5.2. Depressant Preparation

The CMC solution was also prepared at a concentration of 1% (w/v). 1 g of powder was added to 100 mL of distilled water; and since CMC is not as readily soluble in water, the solution was placed on a magnetic stirrer for at least 3 hours, until the solution was fully hydrated (Wiese, 2009).

4.5.3. Frother Preparation

DOW200 was dosed as supplied. After use, it was stored at room temperature.

4.6. Batch Flotation Tests

A 1 kg tailings sample was emptied into a 3-litre Barker flotation cell (pictured in Figure 4.11). Tap water was then added to achieve 35% solids. The cell's speed drive was set to 1200 rpm, and the slurry was allowed to homogenise for 5 minutes.

A feed sample was taken from the cell. The first dosage combination to be tested was the lol-low setting, i.e. 125 g/t SIBX and 175 g/t CMC. The depressant was added first, and allowed to

condition for 2 minutes. The collector was added next, and also conditioned for 2 minutes. The frother was added last, and conditioned for 1 minute. Then the air valve was opened and the air flow rate maintained at 7 L/min for all tests.

Figure 4.11: The Barker flotation cell

Four concentrates were collected at 2, 6, 12 and 20 minutes of flotation, during which the froth was scraped into a collecting pan every 15 seconds. The froth height (of 2 cm) and water level were kept constant by adding tap water (Wiese et al., 2005).

At the end of flotation, a tails samples was taken and the air was switched off. The speed drive was stopped and the cell was emptied into a tailings bucket for filtration. Figure 4.12 summarises the experimental sequence that was followed.

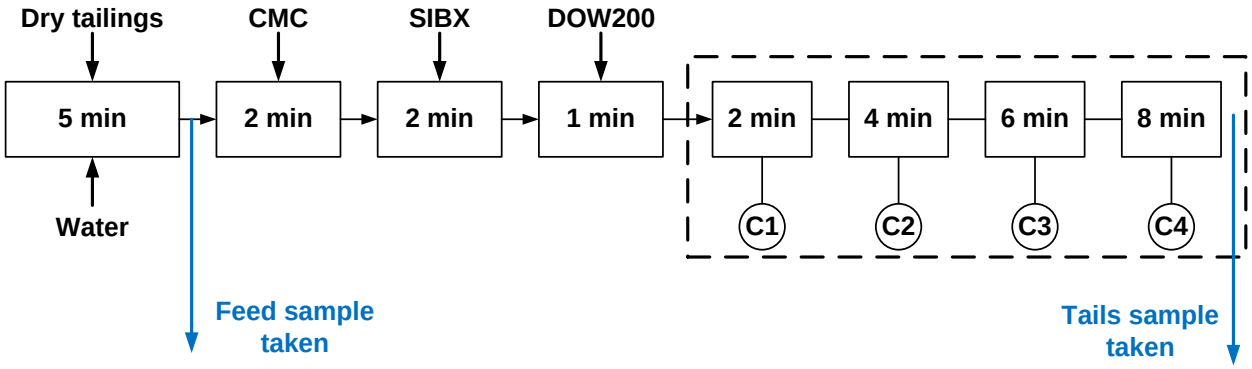


Figure 4.12: A summary of the experimental sequence, with depressant included

The flotation feed, concentrates and tailings were filtered, dried and weighed. They were then sent for XRF analysis to determine the amount of copper and nickel contained in each.

The filtration process was, overall, arduous. It was observed that the floated materials were very fine, easily clogging the filter paper and prolonging the process such that it took far longer to filter one concentrate than it did to float all four. This suggested a physical/handling issue in the case of a plant scale pilot. As such, settling tests were conducted to quantify this drawback.

4.7. Settling Rate Tests

The particle settling rate tests were conducted by drawing 10 mL of a slurry from the cell at the beginning of the flotation process. The sample was transferred to a vial compatible with the Hannah turbidity meter (HI98703-01), shaken thoroughly, and placed in the metre. Ideally, from this point the turbidity readings can be taken at predetermined intervals (every 30, 60, 90, seconds, etc.). However, for MER, UG2R and UG2D, even after an hour of letting the vial contents settle, the meter was still unable to read the sample turbidity. The sample was simply too fine, and still too cloudy to allow the laser mechanism of the equipment to penetrate the vial contents.

Therefore, the time it took for the metre to be able to make a reading was also recorded. As soon as the first measurement was made, the stopwatch was started, and readings were taken every 30 seconds, for an hour. The settling rates were then determined as the slopes of the obtained graphs. This is because the settling rate can be expressed as the change in turbidity over time (Equation 4.4.) (Arjmand et al., 2019; Ma et al., 2019).

$$\text{Settling rate} = \frac{\text{turbidity (NTU)}}{\text{time}} \qquad 4.4.$$

4.8. Revised Batch Flotation Tests

Another thing revealed by the flotation tests was that in the presence of a depressant, very little of the tailings floated, and in fact, even less of the target minerals were recovered, failing to achieve even a fraction of the target of 30% copper recovery.

As such, the design factorial was modified to exclude the dosage of a depressant, and in effect, make this a collector variation study. The revised reagent dosages are summarised in Table 4.3.

Table 4.3: The conditions taken forward after CMC was excluded from the study

Reagent	Minimum Level	Maximum Level	Units
SIBX	125	200	g/t

The experimental sequence was also modified to account for the CMC exclusion. A summary is presented in Figure 4.13. Everything else was kept the same.

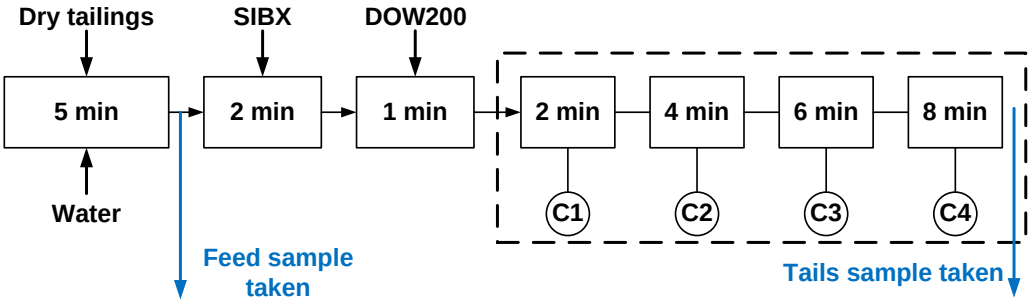


Figure 4.13: A summary of the experimental sequence, without depressant

4.9. Collector Adsorption Kinetics

Tests were conducted to elucidate the effect of CMC presence on SIBX activity. This was done by determining the amount of collector still remaining in solution at certain intervals in the flotation process. However, as concentrates are scraped from the cell, and the slurry level is maintained by adding water throughout the process, this would naturally dilute the collector concentration, and not at a level that could be actively controlled between different tests. The collector activity tests, i.e. SIBX adsorption tests, had to be done separately from the flotation tests.

4.9.1. SIBX Adsorption Tests

A 1 kg tailings sample was split into 100 g aliquots. Each aliquot was placed in a 400 mL beaker, and 290 mL tap water was added (to replicate the 35% solids slurry in the flotation cell). This slurry was placed on a magnetic stirrer and continuously stirred for 2 minutes to achieve homogeneity.

A corresponding concentration of SIBX was added to the slurry and conditioned for 2 minutes. As a reminder, for the initial set of tests, 125 g/t SIBX was added to the flotation cell; on a solution basis, this corresponds to 43.1 ppm. Therefore, 43.1 ppm was also added to the 400 mL beaker.

To replicate the duration of the flotation process, a slurry sample was drawn from the beaker (using a 20 mL syringe) at 2, 6, 12 and 20 minutes. As soon as each sample was drawn, it was filtered through a Millipore filtration funnel fitted with a 0.22 µm filter paper. The filtrate was then analysed for residual SIBX. In this way, the amount adsorbed onto the tailings could be determined using Equation 4.5, in which case, the dosed SIBX is known, and the remaining SIBX can be measured. These tests were conducted both in the presence and absence of CMC.

$$\text{SIBX adsorbed by tailings} = \text{Dosed SIBX} - \text{SIBX remaining in solution} \qquad 4.5.$$

4.9.2. The Calibration of SIBX Adsorption

SIBX has an absorbance peak at 301 nm (Hadler et al., 2005); the residual SIBX of each supernatant (the filtrates obtained in Section 4.9.1.) was therefore measured using a UV/Vis spectrophotometer (Figure 4.14).

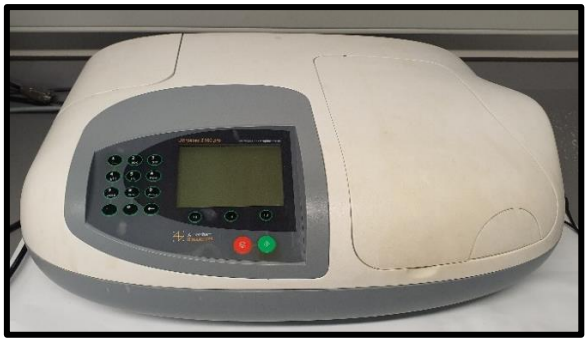


Figure 4.14: The UV/Vis spectrophotometer

From the absorbance, the SIBX concentration was calculated using Beer-Lambert's Law (Equation 4.6.), which expresses absorbance as directly proportional to concentration (Yates, 2012).

$$A = \varepsilon l c \qquad 4.6.$$

In Equation 4.6., **A** is the dimensionless absorbance of a solution; **c** is the concentration of a compound in solution, measured in mol/L; **ℓ** is the path length of the cuvette in which the sample is contained when analysed by UV/Vis spectrometry, measured in centimetres, and **ε** is the molar absorptivity, measured in L/mol.cm. The path length of a cuvette is constant, and is often 1 cm. Additionally, molar absorptivity, or the amount of light absorbed per unit concentration, is constant for a given substance; hence, the **εℓ** term becomes constant.

Since the Beer-Lambert Law is in the linear form **y = mx, εℓ** can be expressed as the slope of a graph plotting concentration against absorbance (Yates, 2012).

To obtain the graph plotting concentration against absorbance, standard solutions of known SIBX concentrations were prepared, and their absorbances determined. Figure 4.15 shows the absorbance curves of different concentrations of SIBX in distilled water.

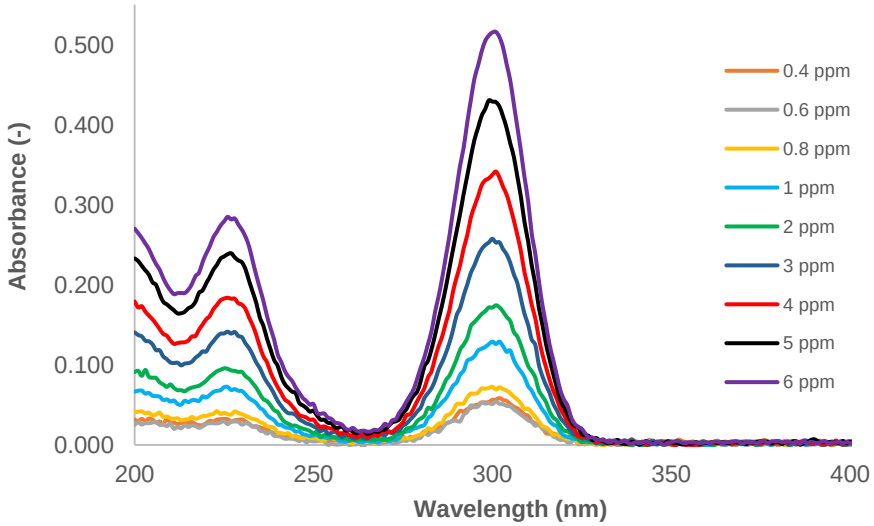


Figure 4.15: The absorbance of SIBX at different concentrations

From Figure 4.15, a calibration curve was drawn for a concentration range of the same order of magnitude. For example, two calibration curves were plotted, with one curve lying in the concentration range 0.2 to 1 ppm SIBX in solution, and the second curve in the concentration range 2 to 6 ppm. Figure 4.16 shows calibration curve for 2 to 6 ppm SIBX solution.

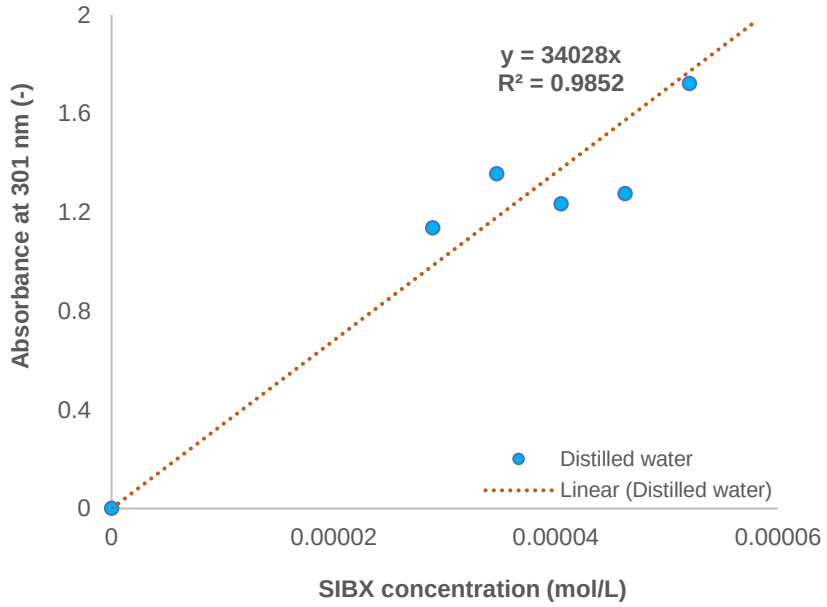


Figure 4.16: A calibration curves for the SIBX concentration range of 2 to 6 ppm

The obtained supernatants had unknown concentrations of SIBX; by rearranging Equation 4.6., and using the respective slope values obtained from the calibration curves, their concentrations were determined using Equation 4.7. and Equation 4.8.

$$c = \frac{A}{\varepsilon l} \qquad 4.7.$$

$$c = \frac{A}{\text{slope of calibration curve}} \qquad 4.8.$$

Equation 4.5. could finally be applied, i.e., as the initial SIBX concentration was known, and the amount of non-adsorbed collector could be determined, the amount of SIBX adsorbed onto the mineral particles was indirectly determined as the balance between these two values (Hadler et al., 2005; Raju and Forsling, 1991).

4.9.3. Normalising the Adsorption Tests

When measuring the residual SIBX concentrations, it was observed that regardless of how much collector was dosed, the absorbance readings were the same. From an experimental perspective, this suggested one of (at least) two possible scenarios. Either the same amount of SIBX was consumed regardless of initial dosage, or, more worryingly, beyond a certain experimental threshold, the spectrophotometer did not measure the absorbances accurately.

Additionally, the Beer-Lambert Law tends to break down at very high concentrations, and in fact, the linearity tends to break down above absorbance values of 1 (-) (Clark, 2023). For context, the near-identical readings that caused concern in this study were all beyond the value of 2 (-).

As a result, the adsorption kinetics tests were simulated such that they did not correspond to the collector concentrations used in the batch flotation tests. For example, an initial concentration of 43.1 ppm (125 g/t SIBX) would be ideal for the adsorption tests, as it would directly match the amount dosed in the batch flotation tests. However, the tailings consumed too little of this dosage throughout the test duration, and as such, the concentration remaining in solution at the end was too high for the Beer-Lambert Law to apply accurately.

A lower SIBX concentration was therefore used for the adsorption kinetic tests. In effect, the study simply tested whether the presence of a depressant affected the overall adsorption of the collector. Two SIBX concentrations (10 ppm and 25 ppm) were tested, thus expanding the study's scope to examining whether the initial concentration had any effect on the kinetics.

4.10. Desliming of the Tailings Bulk

As floating untreated tailings proved to have practical limitations, a secondary set of flotation tests was conducted. In this case, each tailings was deslimed i.e. a fraction of the fine particles were removed prior to flotation. This was achieved by wet screening pre-determined tailings aliquots.

The study acknowledges that in the wider minerals beneficiation context, desliming removes fine and light materials which could potentially precipitate at the surface of valuable minerals and interfere with factors such as froth stability. As the removal of fine particles in this study did not take into consideration such parameters as specific gravity, in this context, desliming is used simply to mean the removal of sub-25 μm particles, and the word "desliming" is used for convenience.

4.10.1. Wet Screening of the Tailings

The size deportment of the tailings (and therefore the fraction to be removed) was determined by wet screening. The CMR Best Practices for Wet Screening (Gierdien, 2022) suggests that the split sample be 200 g for the 200 mm screen shaker. As a first step, two screen sizes were selected: 25 μm and 53 μm. An empty 20 L bucker was placed under the vibrating ring, and the required screen size was fastened in the ring.

The 200 g sample was made into a slurry, poured onto the screen, and the vibrating machine was switched on. A pipe was used to gently spray water onto the sample, hence facilitating the passage of the fine particles through the sieve.

The shaker can only handle one screen at a time. The lowest screen in the series (always the 25 µm) was used first. The sample was screened until the water passing through the sieve was clear, suggesting that all -25 µm particles were washed out. The -25 µm material (in the bucket) were kept there, and the +25 µm materials (on the sieve) were transferred to the largest sieve in the series (the 53 µm in this case) and wet screened again.

The sample retained on the 53 µm sieve was washed from the sieve, filtered, dried and weighed. The -53 µm sample was transferred to the 25 µm sieve, and the screening process repeated. Any sub-25 µm sample was added to the fines buckets and the entire sample was filtered, dried and weighed. The setup is as shown in Figure 4.17.

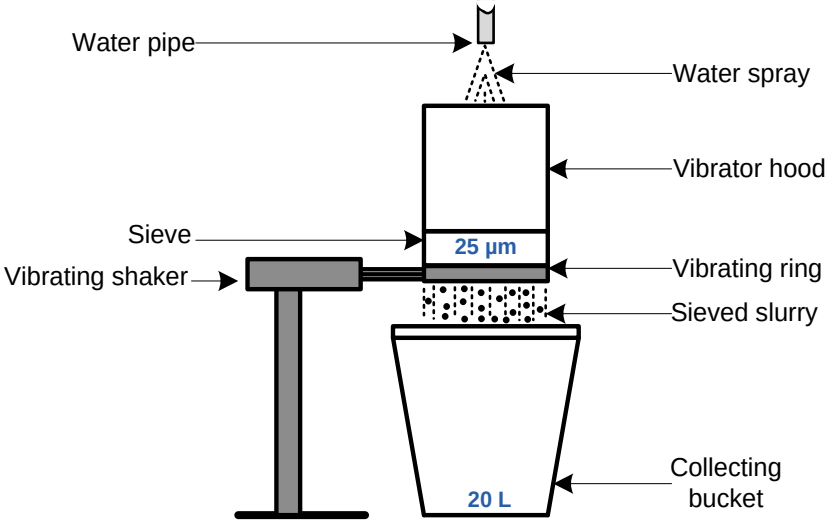


Figure 4.17: The wet screening setup

4.10.2. The Size Deportment of the Tailings

An analysis of the screened samples showed that approximately 20% of the MER particles are smaller than 25 µm. This was also the case for the UG2 tailings (Figure 4.18).

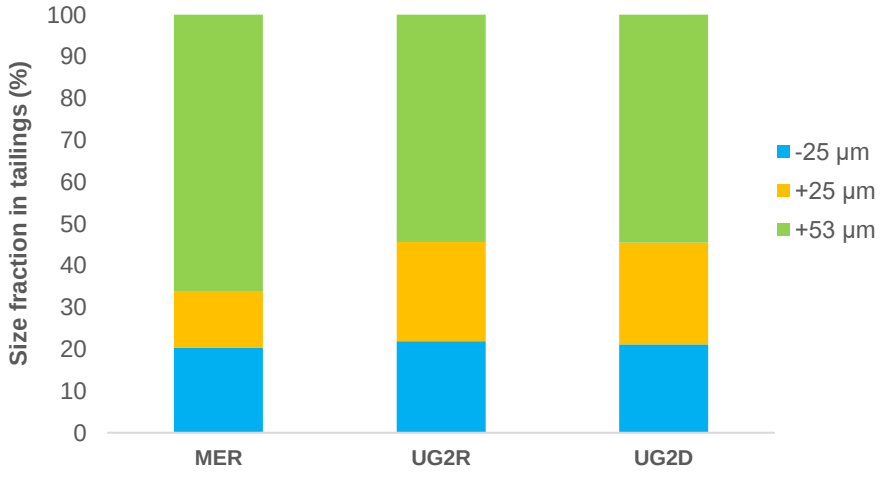


Figure 4.18: The size deportment of the tailings bulks

In desliming the bulks, it was most practical to get rid of the -25 µm particles for various reasons. They are as follows: based on Figure 4.18, for every 1 kg sample, 800 g of the sample is above 25 µm. The easiest thing to do would be, simply, to float this mass. However, floating 800 g would corrupt the ~35% solids density ideal for the Barker cell. Additionally, the wet screening apparatus can only hold one sieve at a time, and the sieve performs optimally when sieving 200 g. That means in order to obtain 1 kg, more than six screening tests would need to be carried out.

This necessitated the use of a smaller flotation cell. Such a cell is available at the CMR; it floats ~165 g of ore to achieve the ideal pulp density. This was practical since the deportment in Figure 4.18 shows that for every 200 g aliquot, ~160 g of the sample is above 25 µm. Therefore, by sieving any 200 g aliquot with a 25 µm sieve, ~160 g of sample could be made available for flotation.

4.11. Extended Tailings Characterisation

As the desliming process outlined in Section 4.10. essentially altered any aliquot's composition, it was necessary to expand the characterisation to include this change. Figure 4.19 is an expansion of the pseudo-matrix that aims to measure particle alteration against characterisation.

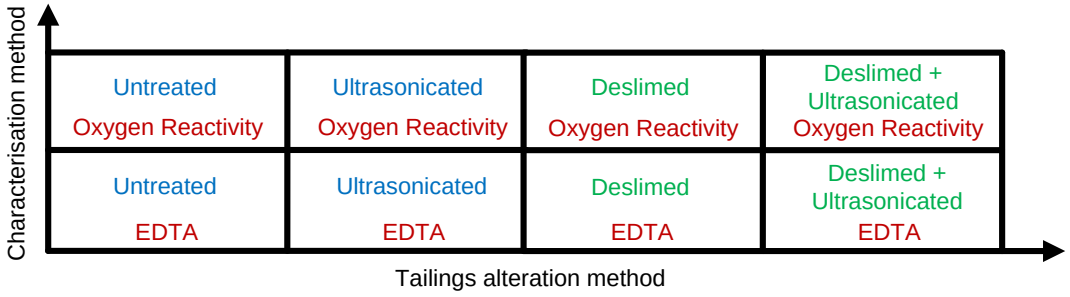


Figure 4.19: The extended variables for the characterisation for the tailings

4.12. Experimental Design: Extended Batch Flotation Tests

The final experimental design for the flotation of the tailings (Figure 4.20) was therefore as follows:

1. Four states were floated (untreated; sonicated; deslimed and deslimed-sonicated).
2. One collector was tested at two dosages (125 and 200 g/t).

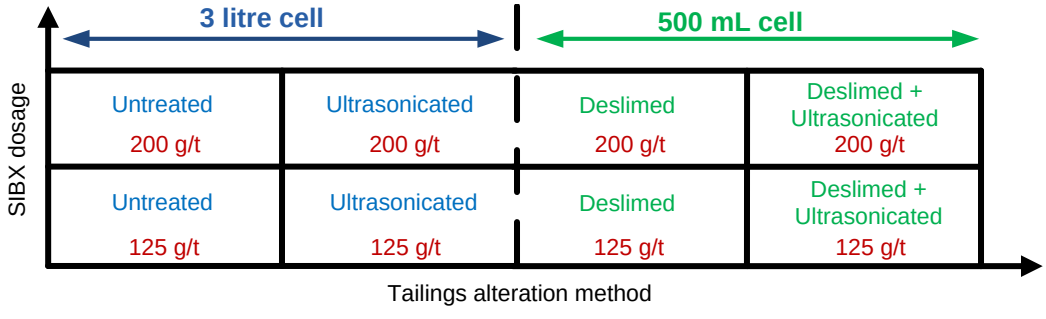


Figure 4.20: The finalised batch flotation plan for the tailings

4.12.1. Flotation Conditions of the Baby Cell

A sample of 160 g was washed from the 25 µm sieve into a 500-mL Chamic Baby flotation cell (pictured in Figure 4.21). Tap water was then added to achieve 35% solids. The cell's speed drive was set to 200 rpm, and the slurry was allowed to homogenise for 5 minutes. A feed sample was taken from the cell, then the collector was added and conditioned for 2 minutes. The frother was added after that, and conditioned for 1 minute. The air valve was opened and the air flow rate maintained at 4 L/min for all tests.

Figure 4.21: The Chamic Baby flotation cell

Every other test condition and parameter was kept the same as for the 3-litre Barker cell.

4.13. Ultrasonication of the Tailings

Where necessary, and as outlined in the preceding sections, ultrasonication tests were performed as a precondition for certain batch flotation and characterisation tests. Depending on which tests the slurry was conditioned for, one of two Labotec Sonic Cleaner baths was used (see Figure 4.22). The differences in the parameters are as summarised in Table 4.4.

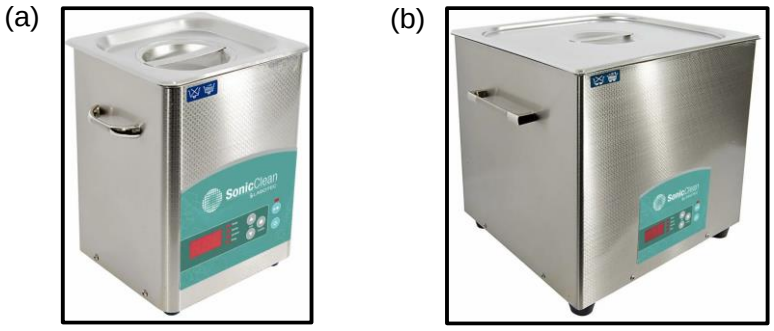


Figure 4.22: The ultrasonic baths; (a) the bath used for the characterisation study and 500 mL flotation, (b) the bath used for the 3-litre flotation study, adapted from Labotec (2023). (The baths are not to scale in the illustration)

Table 4.4: A summary of the ultrasonication parameters

Study	Instrument	Bath volume	Frequency	Power
Characterisation	DESC 2.5 L	300 mL	20 kHz	50 W
Batch flotation	DESC 25 L	10 L	40 kHz	500 W

A slurry was made by emptying a tailings sample of relevant mass (depending on whether the sample was being prepared for characterisation or batch flotation; see Table 4.5 for a summary) into a beaker, and adding water. The beaker was placed in the bath, and sonicated for 20 minutes.

Table 4.5: The parameters relevant to the ultrasonication tests

Experiment	Tailings size	Water added	Beaker size	Ultrasonication unit
EDTA extraction	10 g	50 mL	100 mL	DESC 2.5 L
Oxygen reactivity	80 g	150 mL	300 mL	DESC 2.5 L
500 mL flotation	160 g	280 mL	400 mL	DESC 2.5 L
3 L flotation	1 kg	800 mL	1000 mL	DESC 25 L

For the batch flotation tests, the sonicated slurry was immediately transferred to the flotation cell, homogenised for 5 minutes, and the previously outlined flotation procedure was started.

For the characterisation tests, the slurry needed to be prepared with a specific solution, i.e. EDTA for EDTA extraction tests, and calcium water for the oxygen reactivity tests. Therefore, after being removed from the sonication bath, each beaker of slurry was filtered, and the filter cake was transferred into another beaker and mixed with the relevant solution of relevant volume.

4.14. Feed, Tails and Concentrate Analysis

The batch flotation performance was measured by analysing the recoveries of the following parameters: the overall ore material, copper, nickel and water. The respective copper and nickel amounts contained in each concentrate, feed and tailings sample were used to indicate the performance of chalcopyrite and pentlandite. This was done with the assumption that the stoichiometry of chalcopyrite is $CuFeS_2$, and that of pentlandite is $(FeNi)_9S_8$ (Corin et al., 2011).

The copper and iron content in each sample was determined using an energy dispersive Thermo-NITON XL3 950 GOLDD+XRF spectrometer (Thermo Scientific, USA) equipped with an Ag Anode X-Ray tube capable of 50 kV and 200 microA. The quantitative data were collected using Thermo Scientific's standard Niton Data Transfer (NDT) PC software system (Sibiya, 2022).

5. A DISCUSSION ON THE TAILINGS CHARACTERISATION

This chapter presents the results of the characterisation experiments performed on the tailings, and discusses them. It is divided into three sections. The first outlines the mineralogy of the tailings, the second deals with EDTA extraction, and the third, with oxygen reactivity.

The study objectives relevant to this chapter are therefore as follows:

- To characterise selected South African PGM tailings.
- To determine the ability of non-extensive methods in characterising low-grade materials.
- To determine if mitigating the tailings' weathered state will change their degree of oxidation.

Throughout this chapter, when the results concerning any tailings sample are designated as 'untreated,' it simply means the tailings/sample was experimented on without the following pre-treatments: ultrasonication and/or desliming.

5.1. The Mineralogical Profile of the Tailings

The most obvious differences between the tailings are demonstrated by their variable bulk mineralogy profiles, presented in Figure 5.1 for the complete list of detected minerals, and Figure 5.2 for the composition of the primary elements. The dominant gangue minerals in MER are plagioclase (42.0%) and orthopyroxene (39.4%). The dominant gangue minerals in UG2R and UG2D are chromite (52.3%), orthopyroxene (22.9%) and plagioclase; (18.7%).

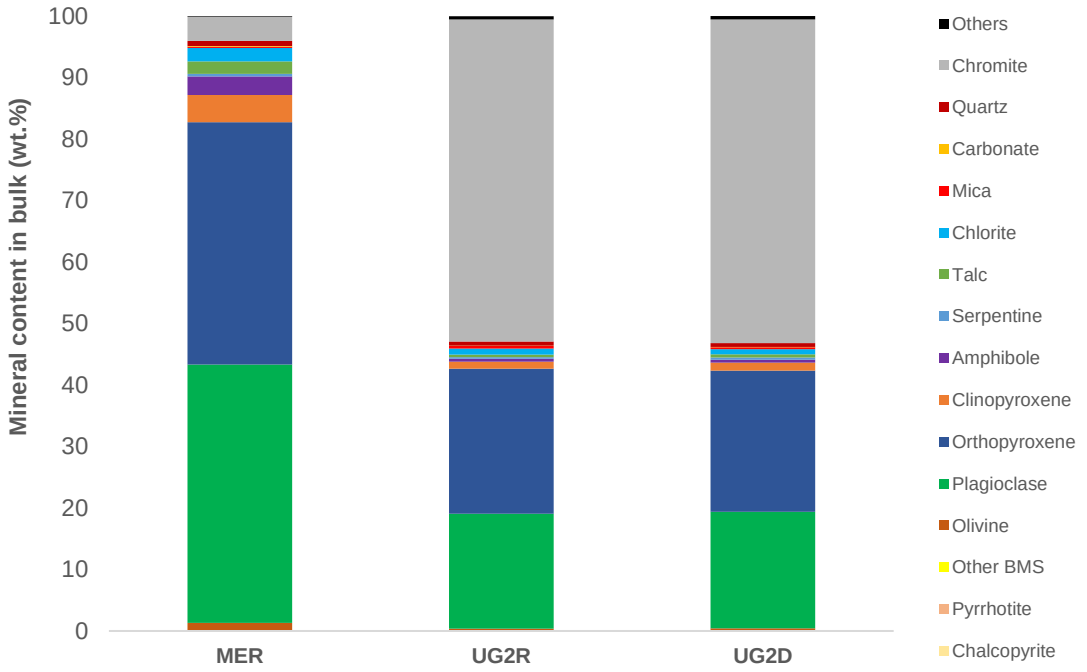


Figure 5.1: The mineral compositions of MER, UG2R and UG2D

The dominant elements for all tailings, as determined by XRD, are Si, Mg, Fe and Al; and for UG2R and UG2D, there are significant fractions of Cr (at roughly 24.4% for both tailings).

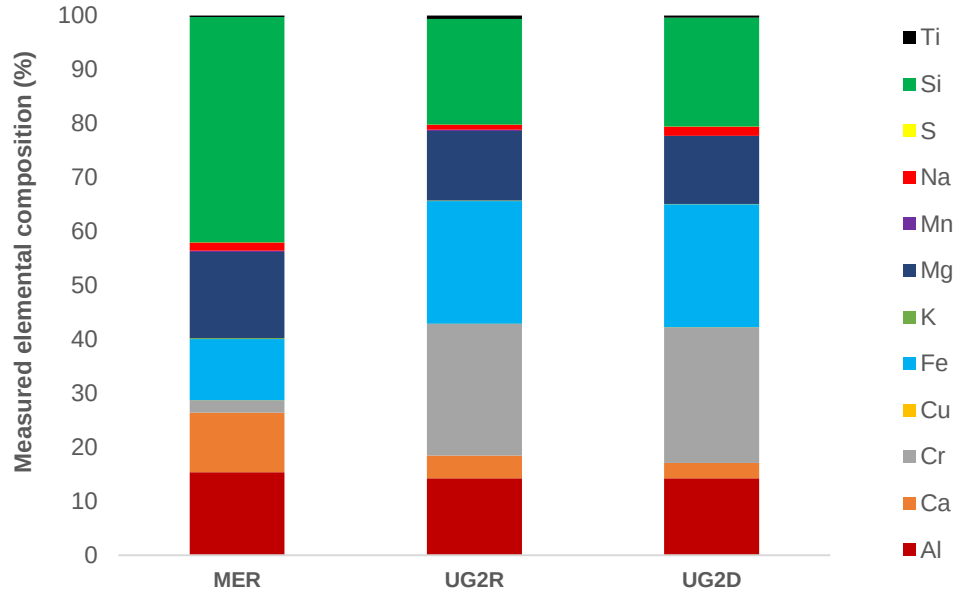


Figure 5.2: The elemental compositions of MER, UG2R and UG2D

UG2R and UG2D have such similar mineral and elemental compositions, that they almost seem identical to each other. However, the base metal sulphide composition reveals that UG2R has a higher overall sulphide fraction than UG2D. The measured values are as presented in Figure 5.3, which shows that MER contains 0.06% sulphides, UG2R contains 0.05%, while UG2D contains 0.02%. Figure 5.3 also shows that MER has a higher chalcopyrite fraction (at 0.03%), while UG2R and UG2D have identical fractions (at 0.02%). The content of other BMSs that were not distinguished are primarily pyrite, with trace amounts of pentlandite (<0.01%; see Appendix C).

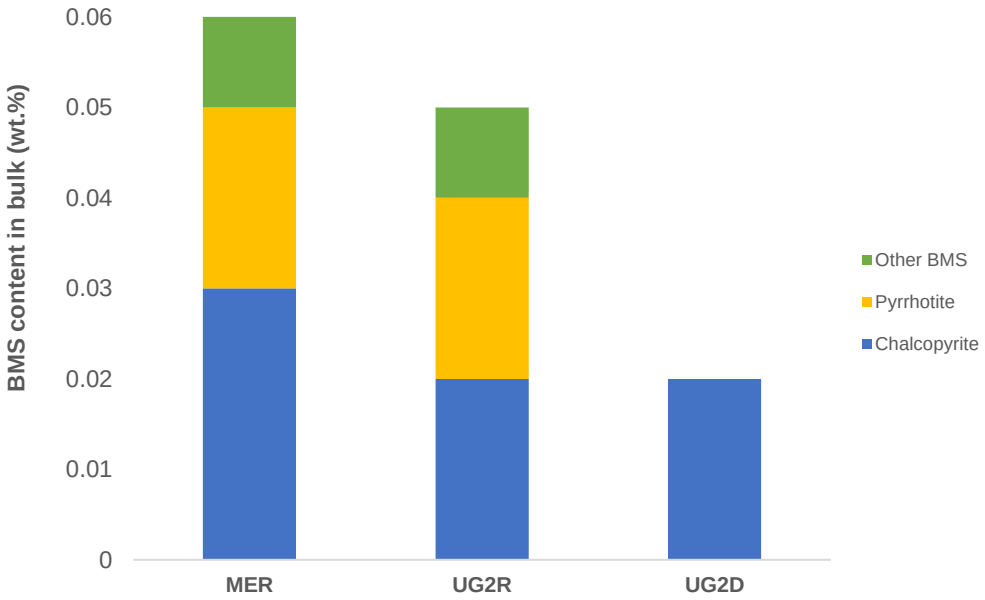


Figure 5.3: The base metal sulphide content in MER, UG2R and UG2D

It is apparent that the desliming done at the plant, in addition to removing a fraction of the silicates, also removes a portion of the sulphides from the raw UG2 tailings, potentially affecting the sample's reactivity, especially where collector action and affinity for oxygen are concerned.

5.1.1. Size-by-Size Mineralogy

To test whether EDTA extraction and oxygen reactivity could detect changes made to the tailings, experiments were conducted in which the tailings were first deslimed; and in which they were deslimed *and* ultrasonicated (Chapter 4). The lab desliming of MER, UG2R and UG2D fundamentally altered the mineral compositions and distributions in the tailings. A sized analysis of the composition (XRD and QEMSCAN) was therefore necessary to determine the new bulk mineralogy; the same procedure as that elaborated in Chapter 4 was followed. The remaining minerals presented themselves in new quantities and ratios that didn't match the original bulk.

Figure 5.4 shows the distribution of the MER, UG2R and UG2D minerals across three size fractions: sub-25, plus-25 and plus-53 µm.

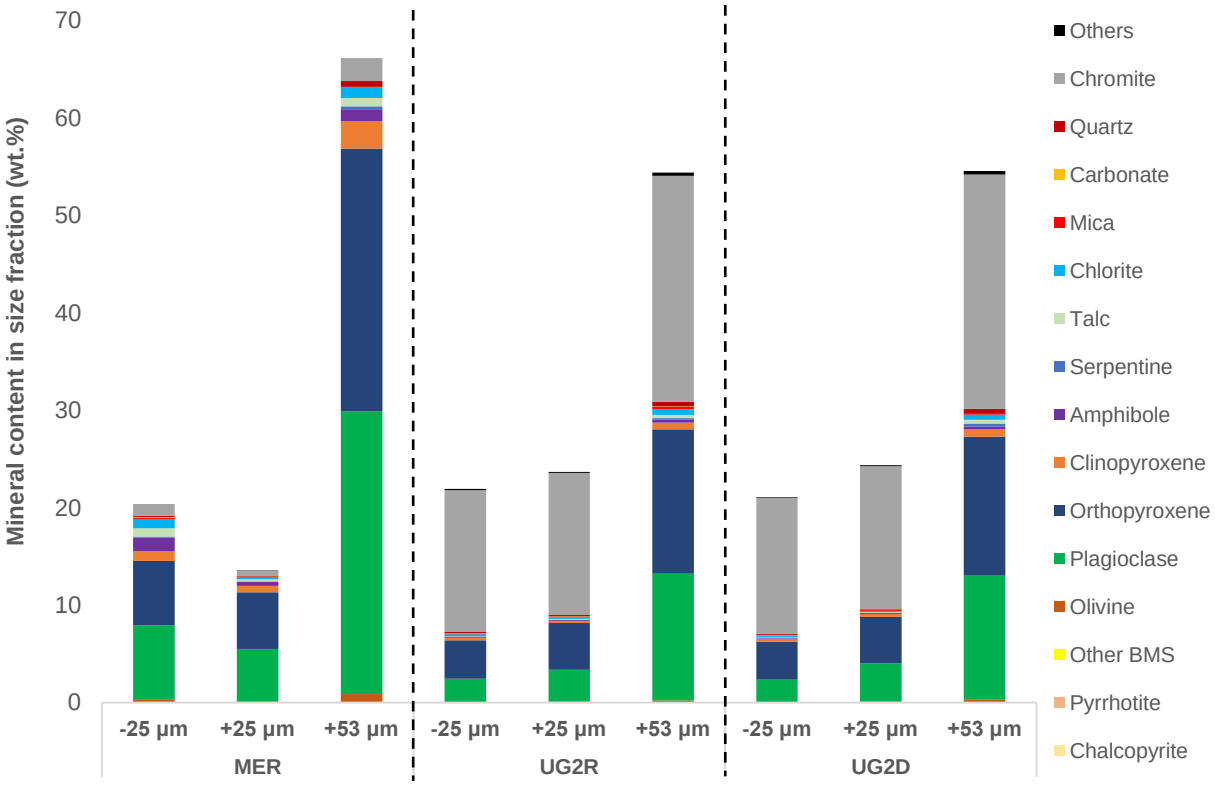


Figure 5.4: The deportment of the MER, UG2R and UG2D minerals on a size basis

The sulphide content of each tailings, more significantly, the chalcopyrite content, was altered by the desliming process. 28.2% of the chalcopyrite in MER is comprised in the sub-25 µm size fraction; for UG2R, the value is 49.2%, and for UG2D, it is 43.1%. Figure 5.5 shows the deportment of chalcopyrite across the three analysed size classes.

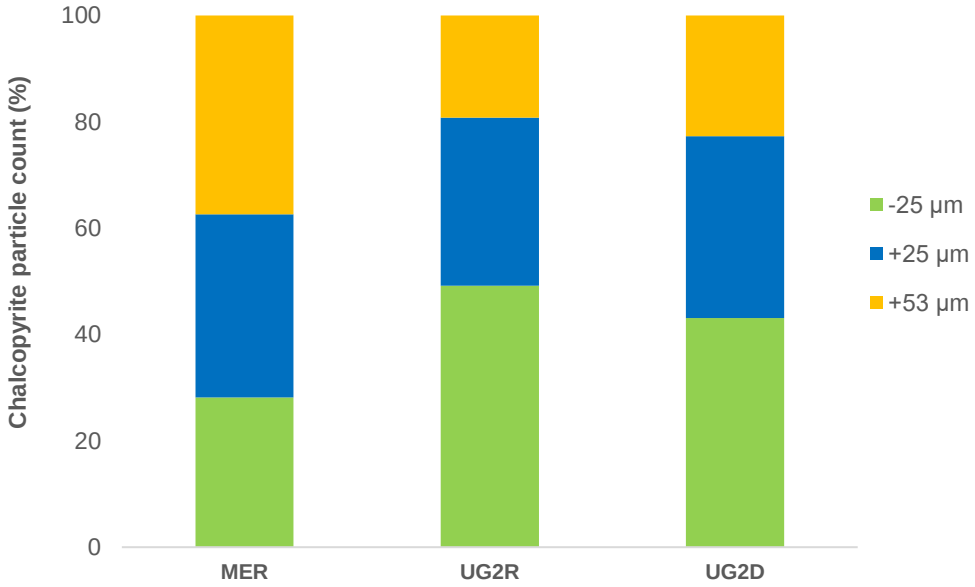


Figure 5.5: The deportment of chalcopyrite in different tailings size fractions

That means in desliming the tailings and discarding the sub-25 µm fraction, 28.2% of the chalcopyrite in MER is also discarded, and in UG2R and UG2D, a respective 49.2% and 43.1% chalcopyrite is discarded. It is thus expected that the EDTA extraction indices and oxygen reactivity parameters of the tailings will be affected by the desliming process. More obviously, it is expected that the copper recovery will decrease as, on a simple mass basis, the untreated tailings contain more chalcopyrite than their deslimed counterparts.

5.1.2. Chalcopyrite Liberation

The liberated fraction of chalcopyrite in each size class was also determined, and the results are summarised in Figure 5.6. The liberation legend is summarised in Table 5.1.

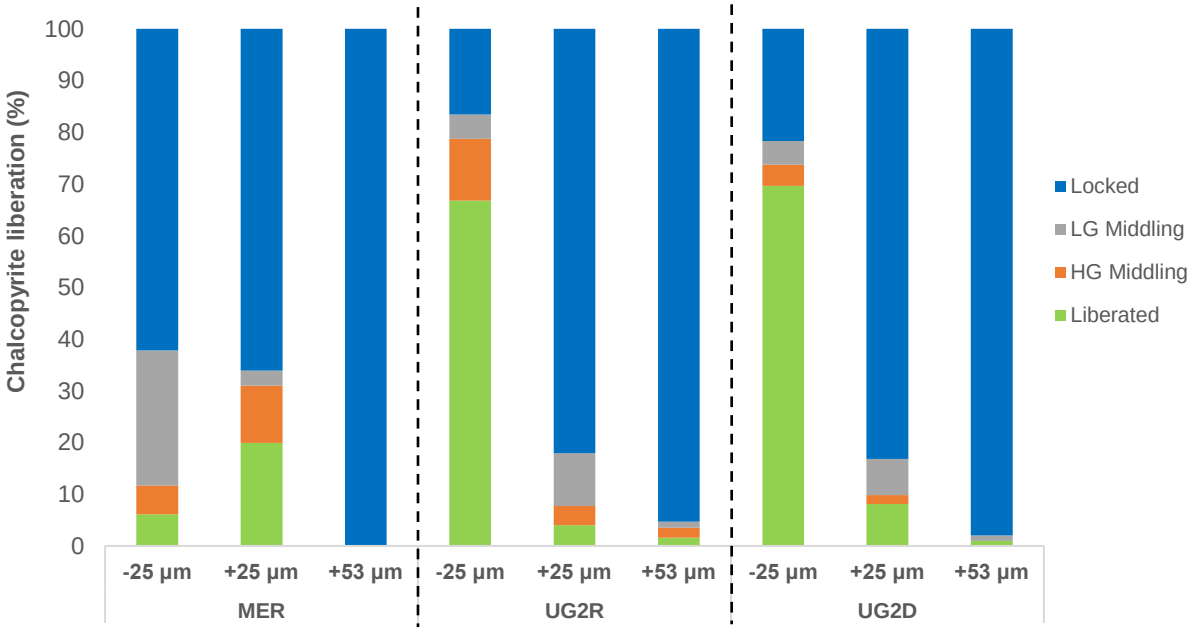


Figure 5.6: The liberation profile of chalcopyrite in MER, UG2R and UG2D (on a size fraction basis)

Table 5.1: The liberation ranges as presented in Figure 5.6

Designation	Liberation Range
Liberated	>90%
HG Middling	60 – 90%
LG Middling	30 – 60%
Locked	<30%

For all tailings, the chalcopyrite in the UG2 tailings was similarly liberated, and better liberated than MER-chalcopyrite. Moreover, the sub-25 µm fraction has the highest degree of liberation while the +53 µm particles are the least liberated. In fact, there is no chalcopyrite liberation in MER for the +53 µm class. This further indicates that in desliming the tailings, not only was the total chalcopyrite content in each tailings decreased, but the liberated fraction was also decreased. If the chosen characterisation methods (EDTA extraction and oxygen reactivity) can measure changes in surface properties, the changes in mineralogy can be expected to produce distinct results. The same can be expected of the flotation behaviour. The UG2 tailings showed another difference, in that UG2R has better chalcopyrite liberation in all analysed size classes, but most notably, in the +53 µm class, possibly owing to UG2D being previously deslimed on the plant too.

5.1.3. Chalcopyrite Liberation and Associations

Given that the tailings contained such significant quantities of gangue minerals, and low fractions of chalcopyrite, the association of the chalcopyrite with these minerals was also determined and are demonstrated in Figure 5.7 for the untreated MER, UG2R and UG2D samples.

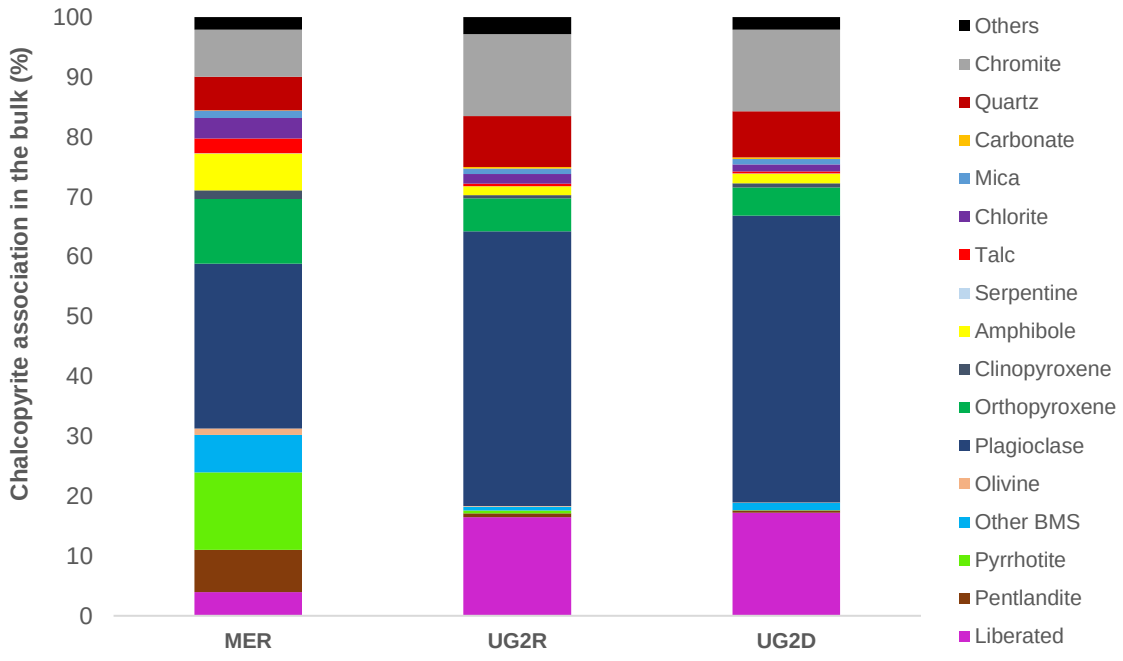


Figure 5.7: The association of chalcopyrite with the minerals in MER, UG2R and UG2D, as well as its liberation

In MER, chalcopyrite is most closely associated with the gangue minerals plagioclase and orthopyroxene, and also with the base metal sulphides present. In UG2R and UG2D, it is most closely associated with plagioclase, chromite and quartz, or it is liberated.

The MER size-based associations for chalcopyrite are illustrated in Figure 5.8; for UG2R, they are illustrated in Figure 5.9, and for UG2D, in Figure 5.10. The majority of the MER sulphides are comprised in the sub-25 µm size fraction, and chalcopyrite's association with these minerals is stronger there. However, its liberation is strongest in the plus-25 µm fraction.

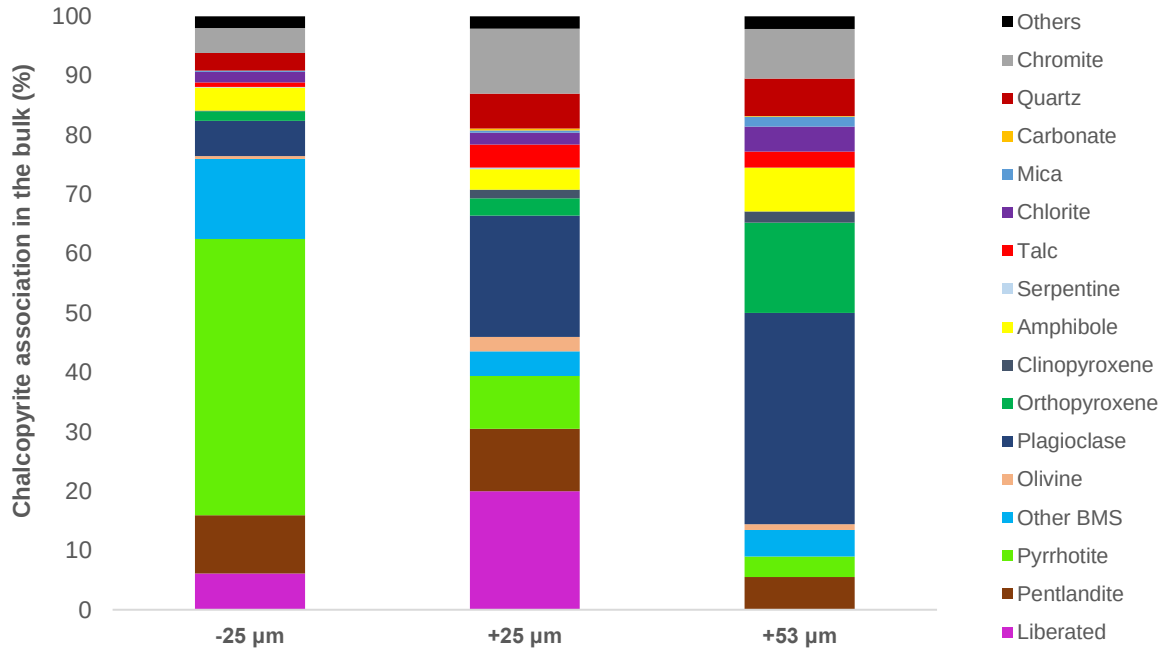


Figure 5.8: The association of chalcopyrite with the minerals in MER, as well as its liberation

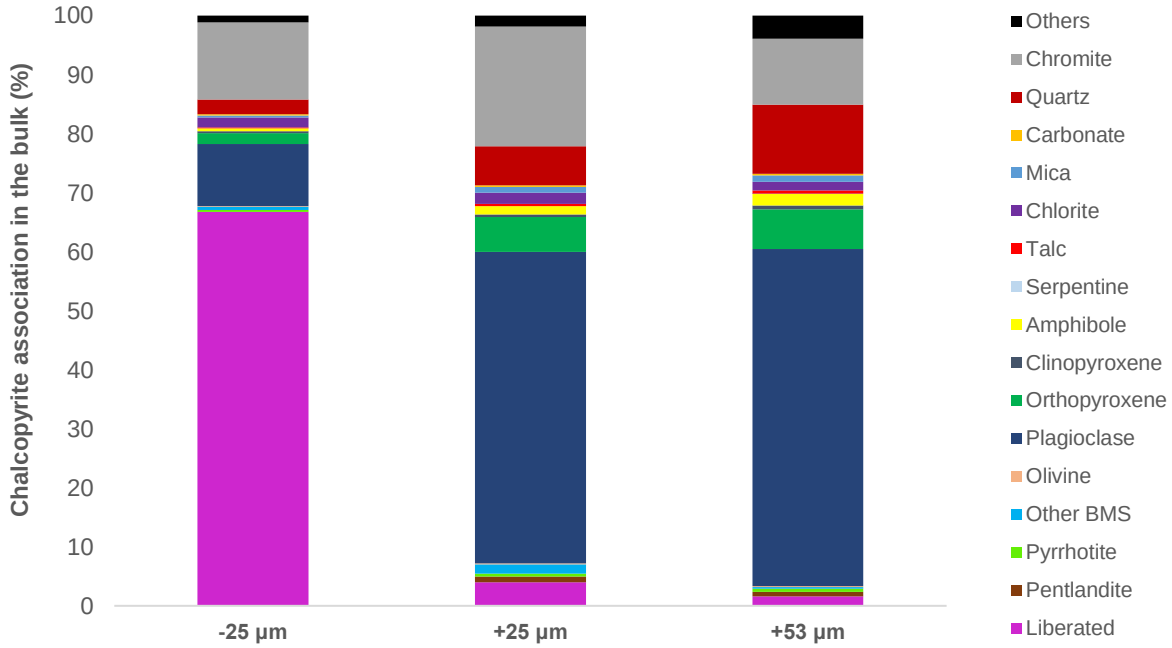


Figure 5.9: The association of chalcopyrite with the minerals in UG2R, as well as its liberation

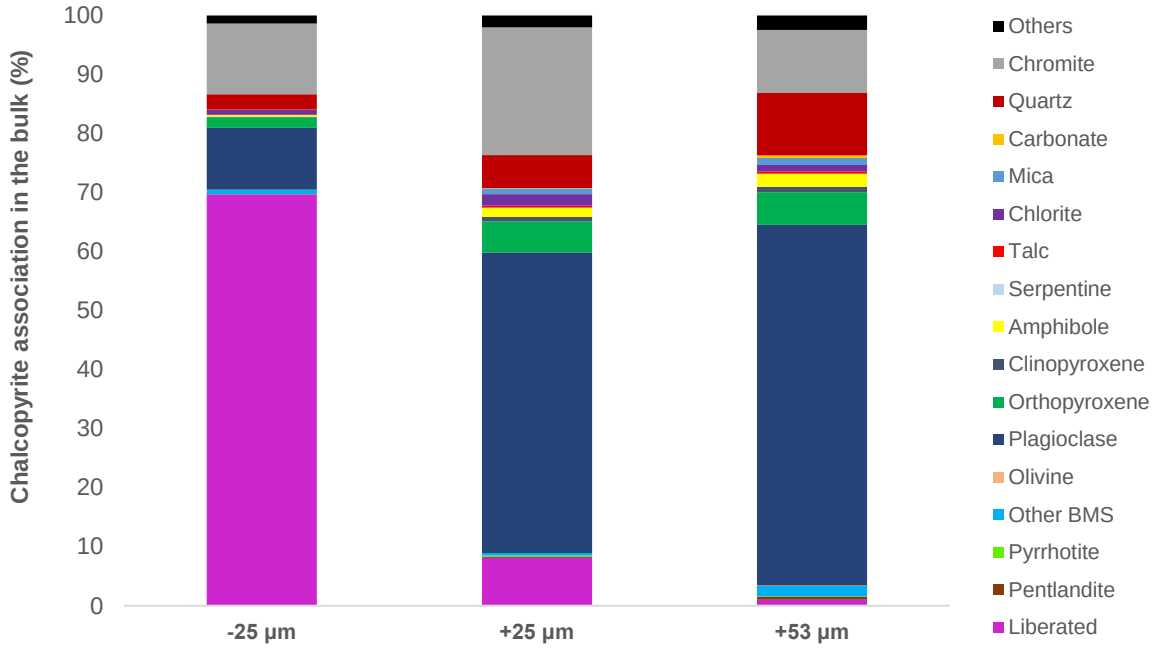


Figure 5.10: The association of chalcopyrite with the minerals in UG2D, as well as its liberation

Contrary to MER, the UG2 tailings have the highest chalcopyrite liberation in the -25 µm fraction. Moreover, the association of chalcopyrite with other base metal sulphides is weak in both UG2 tailings, which should be expected since neither bulk contained significant quantities to begin with.

Also worth noting is that the MER tailings showed the strongest association between chalcopyrite and pentlandite, at 10.6%, followed by UG2R at 9.78%, and UG2D at 5.52%. It can perhaps be posited that overall, MER had the highest pentlandite quantity. The chalcopyrite-BMS associations for the full tailings are summarised in Figure 5.11.

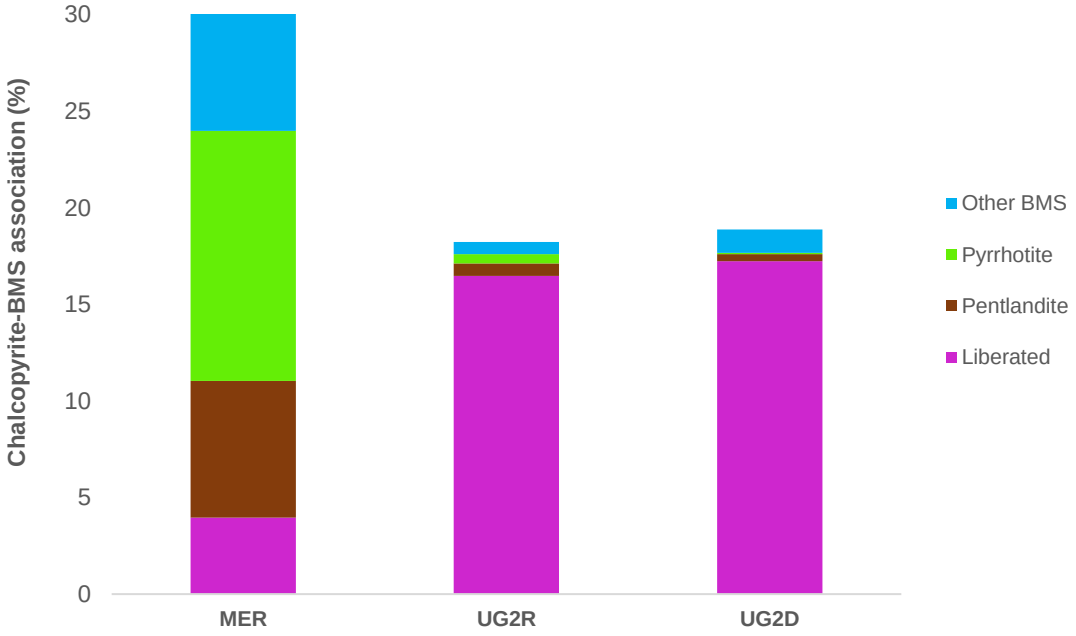


Figure 5.11: The association of chalcopyrite with base metal sulphides in MER, UG2R and UG2D

5.2. EDTA Extraction

This study is concerned with testing whether the surfaces of weathered, low-grade materials can be analysed. More specifically, it is concerned with determining whether the surfaces of different tailings are oxidised to different degrees, and whether this can be quantified. Secondly, are the respective surfaces still active enough such that, even after artificial alteration, their oxidation can be mitigated, and can the degree of the mitigation be detected? The surfaces of concern are the copper-bearing and nickel-bearing sulphides, chalcopyrite and pentlandite, respectively.

Ideally, three EDTA extraction products would have been measured: iron, copper and nickel. However, the nickel quantities in some of the tested supernatants were simply too low to be detected through ICP atomic emission spectroscopy. Only the copper and iron extraction indices will be reported and analysed.

The untreated tailings were the baseline, then they were artificially altered to test whether the measured copper and iron extraction products would change with the alteration. The artificial modifications were mechanical. The first was ultrasonication. The second was a desliming of the tailings, where only +25 μm particles were experimented on. The final cleaning method, was a combination of first desliming the tailings, and subsequently sonicating them. A revised summary of the parameters is provided in Table 5.2.

Table 5.2: The experimental parameters for EDTA extraction indices

INPUTS		OUTPUTS
Tailings	**Surface Conditions**	**EDTA Extraction Products**
• MER • UG2R • UG2D	• Untreated • Ultrasonicated • +25 μm particles only • Ultrasonicated +25 μm particles only	• Copper • Iron

Figure 5.12 compares the EDTA-extraction products of the copper-bearing species, obtained when the tailings were untreated, and when they were ultrasonicated. The extraction products are expressed in units of mg/g, or more specifically, in mg of the EDTA-extracted metal (copper), per g of copper contained in the entire ore material (or tailings) sample. Figure 5.12 shows that the tailings each had a different copper extraction index, with MER having the lowest, and UG2D having the highest. This was true for the untreated as well as the ultrasonicated set, further suggesting that the method is also able to detect a difference in surface properties when minerals from the same sample are cleaned through ultrasonication.

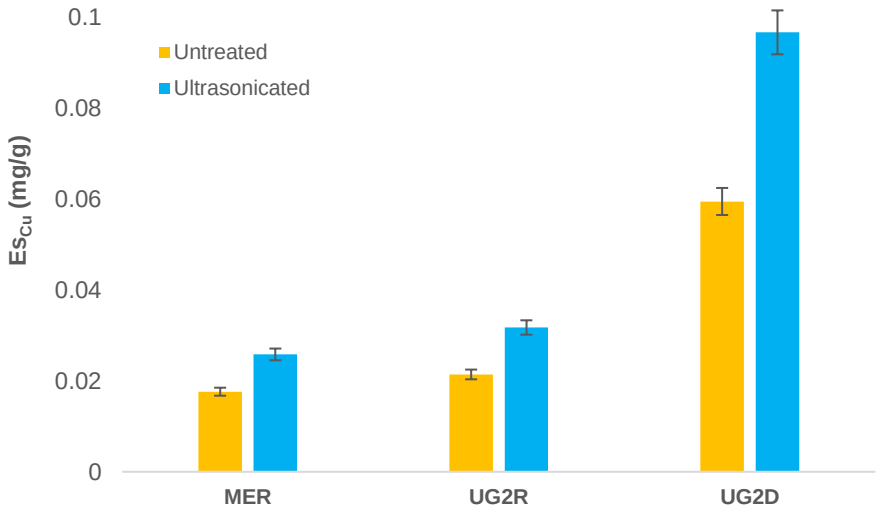


Figure 5.12: EDTA extraction products of the copper-bearing minerals in untreated and ultrasonicated tailings

According to, among others, Bicak (2019), Bicak and Ekmekci (2012) and Rumball and Richmond (1996), higher extraction indices indicate more pronounced oxidation, either in the form of secondary species, or in the presence of oxidised species. This means the copper species in UG2D are more susceptible to EDTA extraction than those in UG2R and MER.

It is also apparent that the susceptibility copper has towards extraction, is independent of the overall amount of the copper fraction in each tailings sample. To be precise, MER contained 0.03 wt.% chalcopyrite, while UG2R and UG2D both contained 0.02 wt.%. However, the fine fraction (sub-25 µm) of chalcopyrite in MER was lower than in UG2R and UG2D (Figure 5.5), and the UG2 tailings were both better liberated than MER (Figure 5.6).

In short, the chalcopyrite particles in UG2R and UG2D likely had higher surface areas owing to their smaller size, and they were more exposed owing to their liberation. It is apparent that these factors contributed to more pronounced oxidation in the UG2 tailings, and thus the higher indices.

The method therefore does not elucidate the quantity of copper, but rather, the amount of secondary and oxidised copper materials. This is even more apparent when considering the fact that the respective sonicated samples contained the same amount of chalcopyrite as their untreated counterparts, and yet they yielded higher indices. And so, the following assertions can be made:

- The copper species and minerals in UG2D have a higher degree of surface oxidation than those in MER and UG2R.
- Sonicating these tailings increases the degree of copper surface oxidation.

To test the method's robustness, the deslimed and deslimed-sonicated indices were plotted against the untreated and sonicated results. As outlined in Section 5.1., the desliming fundamentally altered

the tailings' mineralogy. If it is assumed that all the copper in each sample came from chalcopyrite, that means a respective 28.2%, 49.2% and 43.1% of the copper in MER, UG2R and UG2D is discarded with the sub-25 µm particles. But more importantly, the liberation and association profiles of the remaining chalcopyrite changed. Figure 5.13 compares the copper extraction indices for untreated, sonicated and deslimed tailings.

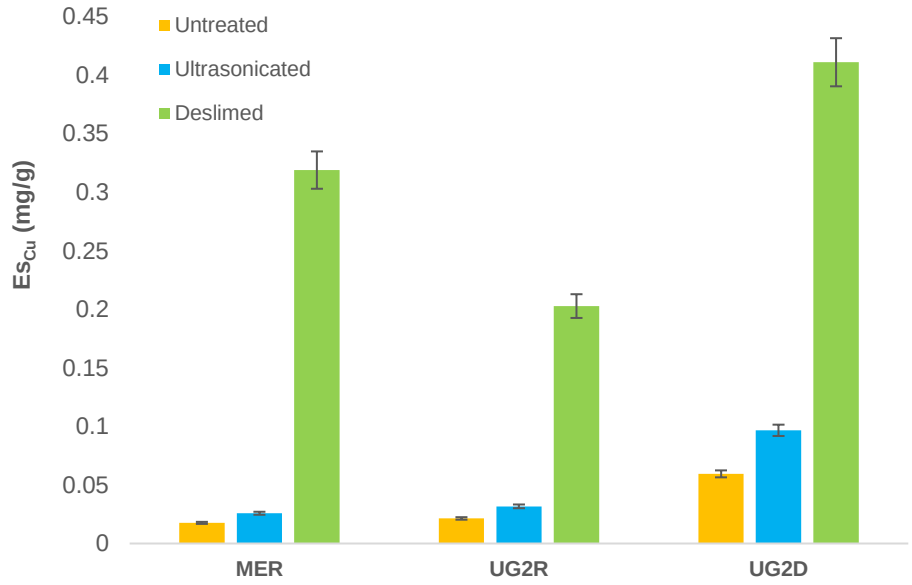


Figure 5.13: EDTA extraction indices for copper; for untreated, ultrasonicated and deslimed tailings

The results once again showed that the method could detect changes in the chalcopyrite surfaces of the different tailings, i.e., MER is different from UG2R, which is different from UG2D. Moreover, when the tailings were deslimed, their copper extraction indices increased across the board. MER showed the biggest change; its deslimed index is 18.1 times bigger than its untreated value. Although UG2R and UG2D had different indices, each of their deslimed values increased by a factor of 9.47 when compared to their untreated counterparts.

The rise in magnitude after desliming is rather significant, showing even more pronounced copper oxidation. It is possible that at this point, the chalcopyrite has become so oxidised, it is behaving like ferric hydroxide, as opposed to cupric hydroxide, as posited by Pugh and Tjus (1987).

When the deslimed tailings were sonicated, variable extraction indices were once again determined (shown in Figure 5.14). This time, UG2R's behaviour deviated from MER and UG2D. Its index alone increased, while UG2D and MER indices decreased. This suggests that either UG2R is an experimental outlier, or that UG2D and MER simply reached some threshold parameter (not yet reached by UG2R), after which, their indices entered a region of decline. Because UG2R hadn't yet reached this point, its index continued the rising trend.

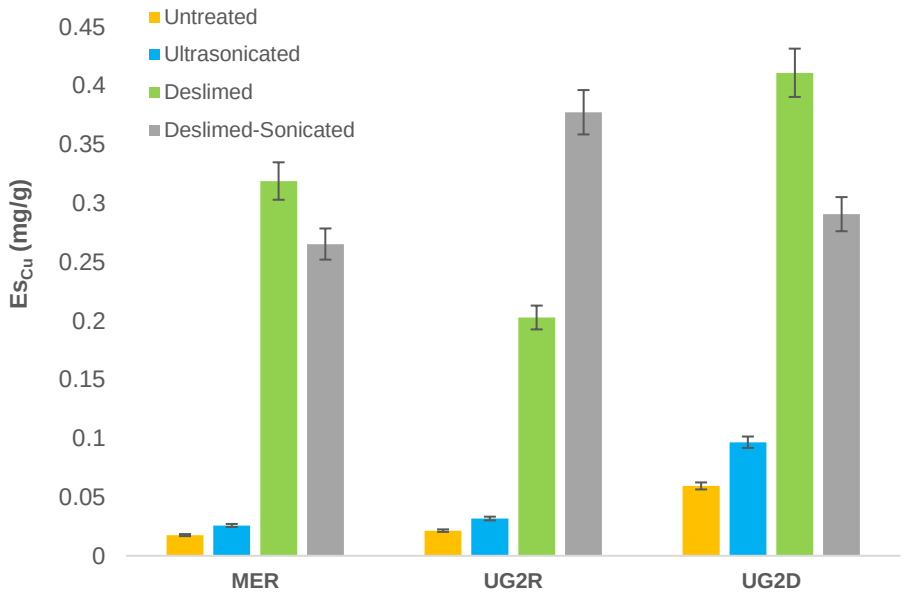


Figure 5.14: EDTA extraction indices for copper; for untreated, sonicated, deslimed and deslimed-sonicated tailings

To further test the method's robustness, the extraction indices of a second metal, i.e. iron, were also determined. They are presented in Figure 5.15 (for all tested tailings).

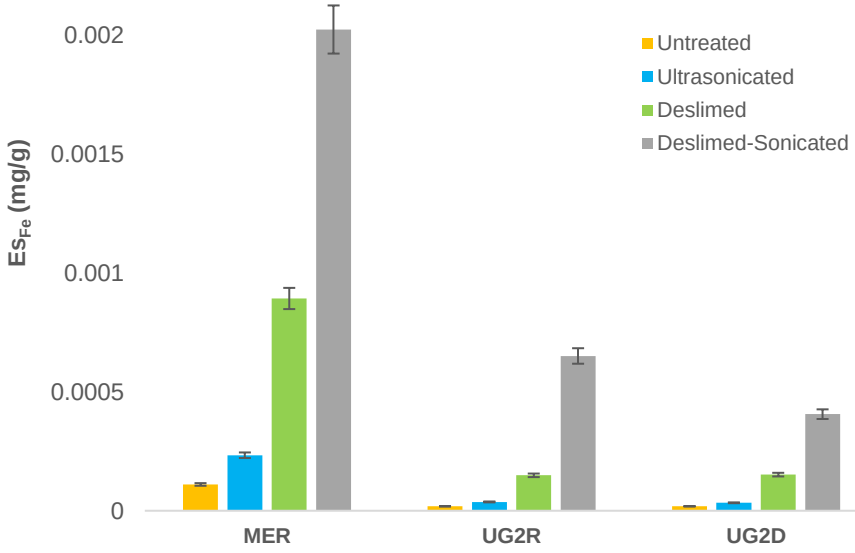


Figure 5.15: EDTA extraction indices for iron, for all tailings

The EDTA extraction method was able to detect differences for the iron species in each tailings. However, while UG2D tended to yield higher indices where copper was concerned, and MER yielded lower values, for iron, the opposite is true. It's also worth noting that the iron scale is much smaller than the copper scale (by a factor of a hundred), perhaps suggesting that the copper species were that much more leachable or reactive than the iron species. A similar trend has been observed by Bicak (2019), where the study showed iron indices of a Cu-Pb-Zn ore to be consistently, significantly lower than copper, lead and zinc. Bicak (2019) attributed the phenomenon to a lower degree of surface oxidation of pyrite particles in the ore.

Pyrite has the distinction of generally having the highest rest potential when compared to other sulphide minerals. Galvanic interaction models predict that as a result, electrons will flow from most sulphides (chalcopyrite, galena, chalcocite, etc.) towards pyrite, further resulting in the anodic oxidation of the sulphide minerals, and hence higher degrees of surface oxidation than pyrite (Ekmekçi and Demirel, 1997; Majima, 1971). Another contributing factor is that the complete dissolution of iron has been noted by studies such as Rumball and Richmond (1996), to require longer durations (up to eight hours). It has become the norm to simply set a standard leachate time for all measured metals, as was done in the current study.

When considering the difference in magnitude of the copper indices, it is apparent that the desliming process had a greater impact on the mineral surfaces than sole ultrasonication. This was quantified using Figure 5.16, which summarises how much the copper and iron indices of each deslimed, sonicated, and deslimed-sonicated tailings changed when compared to the untreated values. As Figure 5.16 compares the change experienced in the surface after being treated, there are no values for the untreated systems, as everything else is expressed relative to them.

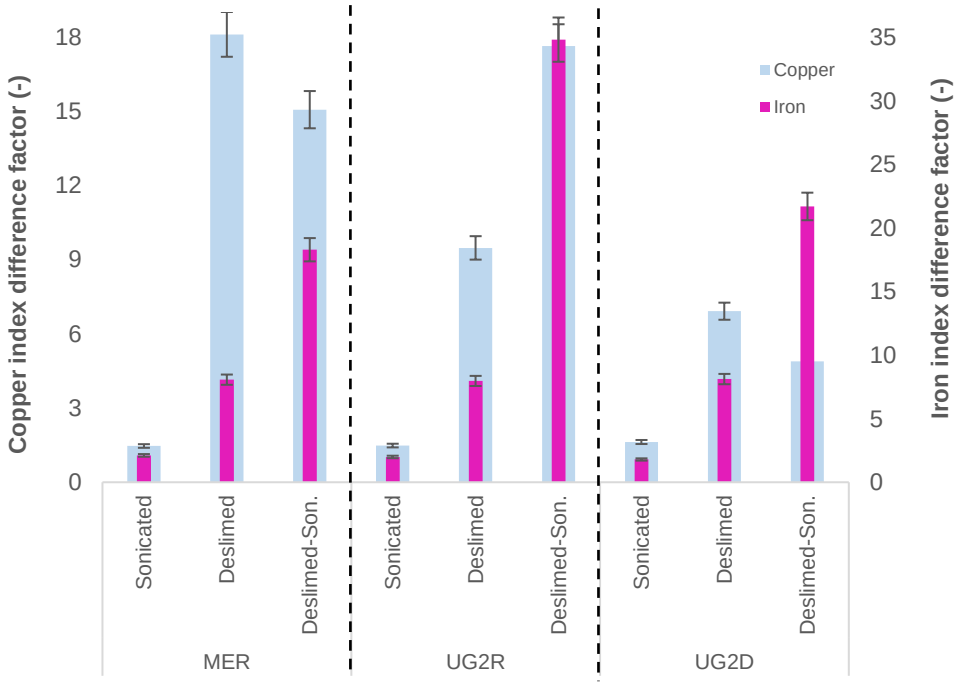


Figure 5.16: The difference in magnitude of the copper and iron extraction indices when the treated tailings are compared to their untreated counterparts

And so, the surface oxidation of the chalcopyrite in the tailings was successfully quantified using the EDTA extraction products of copper at different surface conditions. The study predicts that, as higher extraction indices indicate more pronounced surface oxidation, poorer copper flotation can be expected for tailings with higher copper extraction indices.

5.3. Oxygen Reactivity

The second surface quality to be determined for the tailings, was their reactivity to oxygen. According to, among others, Abraitis et al. (2004), Abraitis and Rimstidt (2003), and Owusu et al. (2013), the demand for dissolved oxygen of an ore material can be used as a measure of that ore's electrochemical reactivity, which in turn influences flotation performance.

The dissolved oxygen profiles of the untreated tailings were measured, and the results are shown in Figure 5.17. The initial rise in each curve shows the region where oxygen was sparged into the beaker. The declining region shows the time after it was switched off; in this region, the declining oxygen concentration demonstrates each tailings sample's affinity for oxygen consumption.

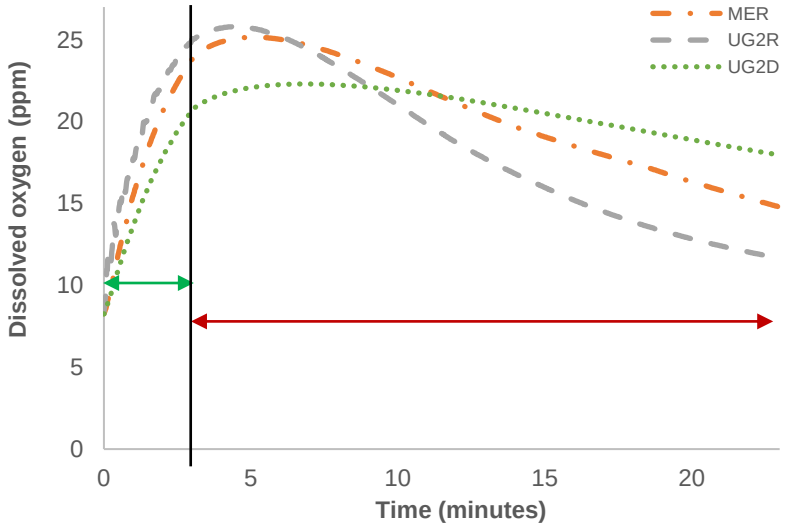


Figure 5.17: The dissolved oxygen profiles of untreated tailings

Figure 5.17 demonstrates the tailings are distinct enough to react with oxygen at different rates and exhibit different behaviours. However, the mathematical relationship (Equation 4.3.) and corresponding graphical representation (Figure 2.6 in Section 2.4.2.) relating dissolved oxygen to the demand rate constant, suggest that the initial dissolved oxygen of the material on which the mathematical model is applied, is 0 ppm. MER, UG2R and UG2D did not have initial DO concentrations of 0 ppm.

$$DO = DO_0 e^{-k_L a \cdot t} \qquad 4.3.$$

Applying the model yielded the oxygen profiles depicted in Figure 5.18, none of which match the experimental reality previously discussed, as each tailings exhibited a quantifiable DO concentration before oxygenation commenced. This deviation suggests one of two things – either an entirely different mathematical relationship must be applied, or Equation 4.3. must be modified. The objective for both cases is simply to account for the fact that even without sparging oxygen

into the systems contextualised here, there exists a certain amount of natural dissolved oxygen that, at the very least, must indicate a (unique) inherent and measurable quality about that tailings.

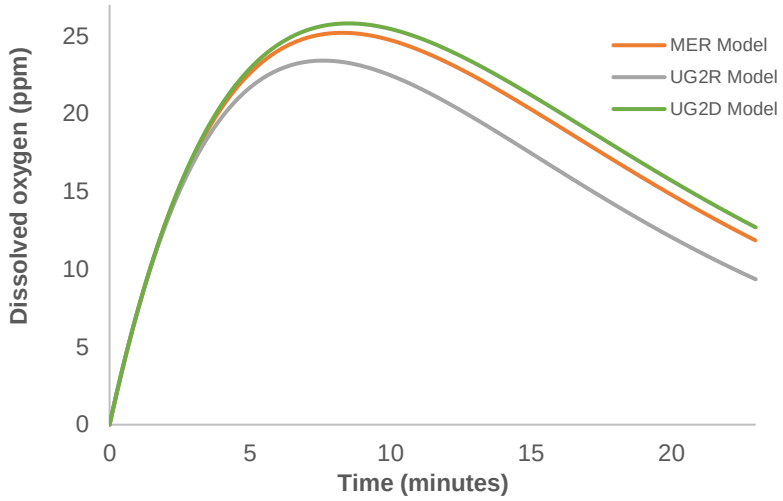


Figure 5.18: The dissolved oxygen profiles of untreated tailings, as predicted by Equation 4.3

5.3.1. Regression Modelling of the Reactivity Data

Regression modelling was thus applied to the raw data. A trial-and-error analysis in which the model was gradually modified, was conducted. The best fit between the data and model was achieved when the latter fit the general Equation 6.1. The R^2 data can be found in Appendix A.

$$y = A + \left(A \cdot x \cdot e^{-B \cdot x}\right) \qquad 6.1.$$

Time, being the independent variable, is easily translatable as **x**, while **B**, being the factor controlled by the exponent, can be translated to $\mathbf{k_La}$. That leaves the unknown constant **A**, which, when considering literature, is related to $\mathbf{DO_0}$. Equation 4.3. can thus be modified into Equation 6.2.

$$DO = A \cdot \left(1 + t \cdot e^{-k_L a \cdot t}\right) \qquad 6.2.$$

The oxygen demand rate constants ($\mathbf{k_La}$) were determined using the predictive model presented by Equation 6.2. For an aerated (or oxygenated) stirred system, such as the oxygen reactivity tests, $\mathbf{k_La}$ is a combination of two factors. These are $\mathbf{k_L}$, which is the mass-transfer coefficient for a gas-liquid system; and **a**, a physical system parameter defined by Equation 6.3. (Welty et al., 2004).

$$a = \frac{A_i}{V} = \frac{\text{area available for interphase mass transfer } (m^2)}{\text{liquid volume } (m^3)} \qquad 6.3.$$

Thus, the study will not only determine the oxygen consumption rate constant $\mathbf{k_La}$, but the unknown constant **A**, too, and attempt to elucidate its meaning. The study will not, however, decouple $\mathbf{k_L}$ from **a**; as the continual collision of the gas bubbles in the system makes it impossible

to measure the interfacial mass transfer area (Welty et al., 2004). For the sake of convenience, the parameter **A** will be referred to as "resting oxygen concentration" henceforth.

5.3.2. The Oxygen Demand Rate Constants

As previously demonstrated by Figure 5.17, untreated MER, UG2R and UG2D displayed different dissolved oxygen profiles. The resting oxygen concentrations, and consumption rate constants were subsequently determined and are compared in Figure 5.19.

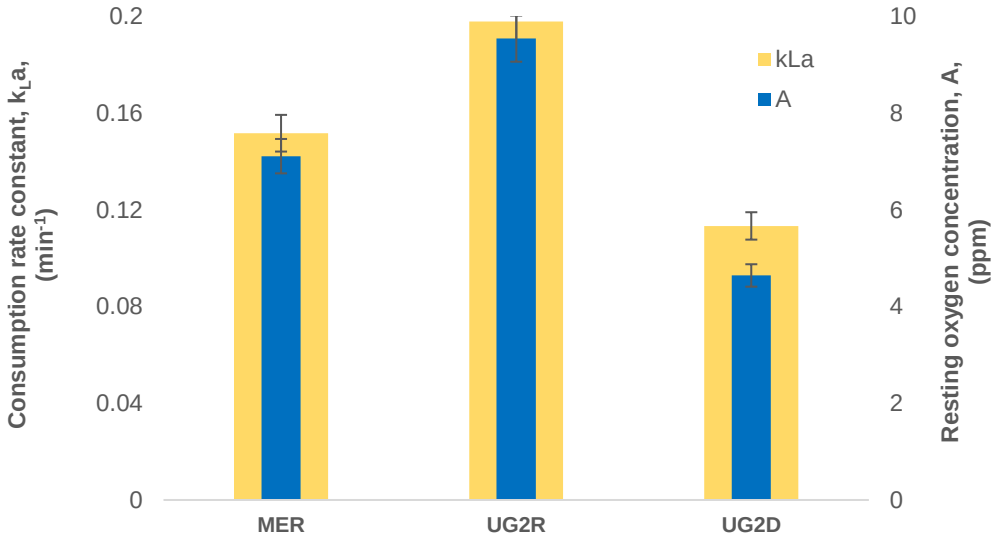


Figure 5.19: The resting oxygen concentrations and consumption rates of all untreated tailings

As shown by the respective **A** values, UG2D had the lowest resting oxygen concentration (4.64 ppm), while UG2R had the highest (9.54 ppm). MER lay between them with 7.11 ppm. After the oxygen feed was switched on, the dissolved oxygen concentrations rose, but the concentration in the UG2D system was continuously lower than that in the MER and UG2R systems (Figure 5.20 to Figure 5.22). Once the oxygen feed was switched off, the dissolved oxygen concentrations for MER and UG2R declined faster than for UG2D, and in fact, UG2D had the lowest consumption rate constant (0.113 min^{-1}). UG2R had the highest rate at 0.198 min^{-1}, and MER once again lay between them with 0.152 min^{-1}. Table 5.3 summarises other oxygen performance indicators relevant to the untreated tailings. These are: the maximum and final DO contents (in ppm) in each system, and the amount of oxygen consumed by each tailings (in ppm, and as a percentage).

Table 5.3: Oxygen content indicators for all untreated tailings

Parameter	MER	UG2R	UG2D
Maximum DO (ppm)	25.2	25.8	22.3
Final DO (ppm)	14.8	11.7	17.9
Consumed O_2 (ppm)	10.4	14.2	4.34
Consumed O_2 (%)	41.3	54.8	19.5

UG2R consumed the highest amount of oxygen, such that at the end of the test duration, 54.8% of the oxygen that was fed during aeration, was consumed by the present minerals. MER consumed 41.3% of the dosed oxygen, while UG2D used only 19.5%. It is important to note that even before the numbers are converted to percentages, UG2R still consumed the highest sheer quantity (14.2 ppm), while UG2D consumed the lowest (4.34 ppm).

According to, among others, Owusu et al. (2013), and Sibiya (2022), this means UG2R is the most reactive of the untreated tailings, and suggests that the processing of UG2R is most likely to result in more reducing environments than the other two tailings. The interaction of oxygen with the ions released to form Cu, Fe, Ni and other oxidation species means the oxygen is used, decreasing its concentration in the pulp, and also decreasing the Eh. As a result, there now exists an oxygen deficit in the pulp, and the demand for oxygen increases in turn (Greet, 2018).

The results suggest that the described phenomenon is more pronounced for UG2R, followed by MER, and lastly, UG2D. The pattern was such that the tailings with the higher resting oxygen concentration consumed the most oxygen, thus yielding a higher consumption rate constant.

It was expected that MER, having the highest sulphide content, would exhibit higher reactivity when compared to the other tailings. And this was, indeed, true, when compared to UG2D. However, UG2R was the most reactive overall. At this point it is important to note the following: between MER and UG2R, the latter had a higher fraction of sub-25 μm chalcopyrite particles, and it also showed one of the highest liberation values for the most ubiquitous sulphide in both bulks (chalcopyrite). Moreover, although MER has more sulphides, UG2R is only 0.01 wt.% lower; suggesting that this, coupled with the chalcopyrite liberation and size distribution, have some combined effect that allows UG2R to be more reactive despite containing less sulphides. But when comparing UG2R to UG2D, it is apparent that between tailings with similar overall mineralogies, chalcopyrite liberation and size distribution, the tailings with more sulphides is more reactive.

As literature has shown the consumption rate constant to be a reliable measure of any ore material's propensity to react with oxygen, given the patterns of the current study thus far, it is apparent that the parameter **A** is closely related to the investigated tailing's oxygen consumption patterns. That is to say, some unique and perhaps quantifiable relationship exists between each tailing's resting oxygen concentration, and its consumption rate constant. To test this supposition, the tailings were then ultrasonicated to see if the observed patterns would hold true. The tailings were also deslimed, and deslimed *and* ultrasonicated. Figure 5.20 compares the oxygen profiles for all MER tests, Figure 5.21 does the same for UG2R tests, and Figure 5.22 for UG2D tests.

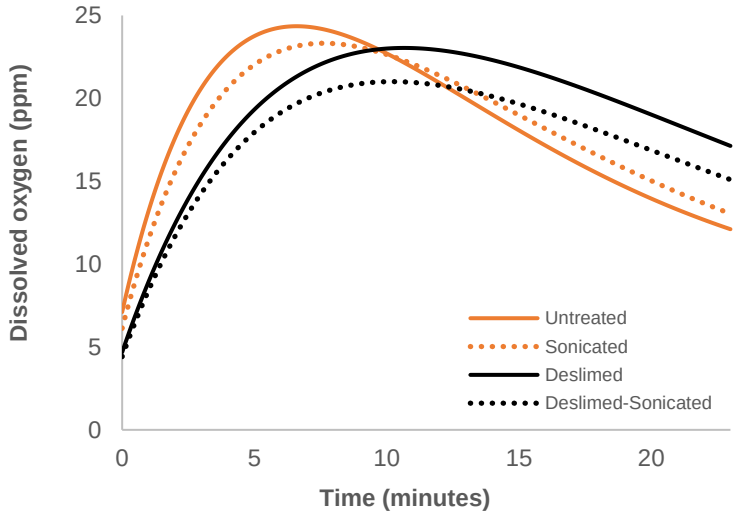


Figure 5.20: The dissolved oxygen profiles of MER tailings for all tested surface conditions

For MER, the oxygen profiles of the tailings (Figure 5.20) were such that the resting oxygen concentration decreased (from 7.11 to 6.13 ppm) when the tailings were sonicated, and decreased further when they were deslimed (to 4.68 ppm). The lowest resting concentration was achieved for the deslimed-sonicated system (4.41 ppm). The consumption rate constants varied in tandem with the resting concentrations. They were as follows: 0.152 min^{-1} for the untreated system, 0.131 min^{-1} for sonicated, 0.0938 min^{-1} for deslimed, and 0.0979 min^{-1} for the deslimed-sonicated system.

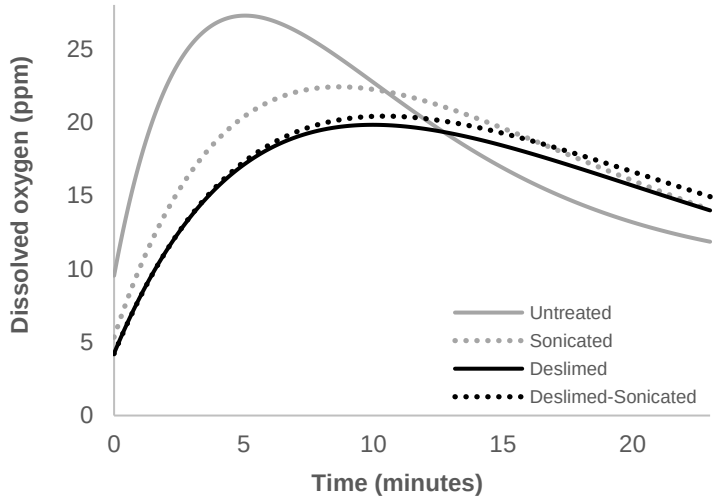


Figure 5.21: The dissolved oxygen profiles of UG2R tailings for all tested surface conditions

A similar pattern was observed for UG2R oxygen profiles (Figure 5.21). The resting oxygen concentration decreased (from 9.54 to 5.34 ppm) when the tailings were sonicated, and decreased further when they were deslimed (to 4.24 ppm). The lowest resting concentration was achieved for the deslimed-sonicated system (4.22 ppm). The consumption rate constants varied in tandem with the resting concentrations. They were as follows: 0.198 min^{-1} for the untreated system, 0.115 min^{-1} for sonicated, 0.100 min^{-1} for deslimed, and 0.0958 min^{-1} for the deslimed-sonicated system.

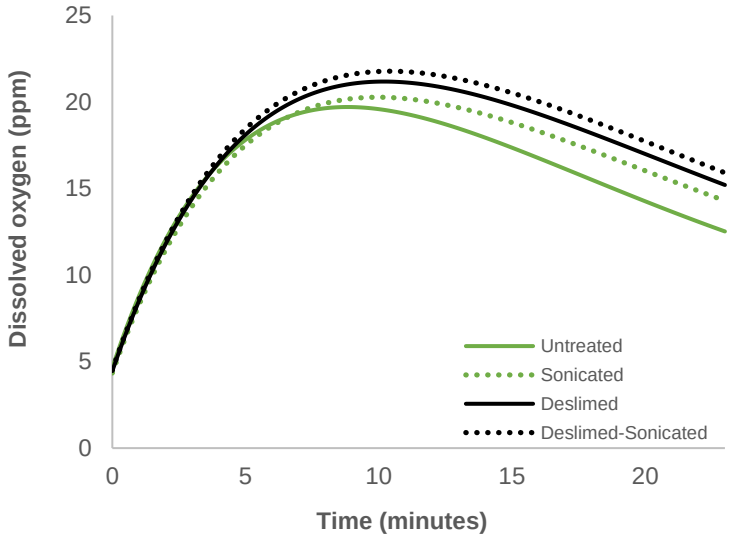


Figure 5.22: The dissolved oxygen profiles of UG2D tailings for all tested surface conditions

UG2D (Figure 5.22) deviated from the established oxygen profile pattern in one key way, the resting oxygen concentrations were nearly identical to each other; all of them were within 0.298 ppm of one another. The maximum achieved **A** was for the untreated system (4.64 ppm), and the minimum was for the sonicated (4.34 ppm). The consumption rate constants were also very close to each other; they were: 0.113 min^{-1} for the untreated system, 0.0981 min^{-1} for sonicated, 0.0959 min^{-1} for deslimed, and 0.0958 min^{-1} for the deslimed-sonicated system. Figure 5.23 compares and summarises the resting oxygen concentrations, and consumption rate data across all tailings.

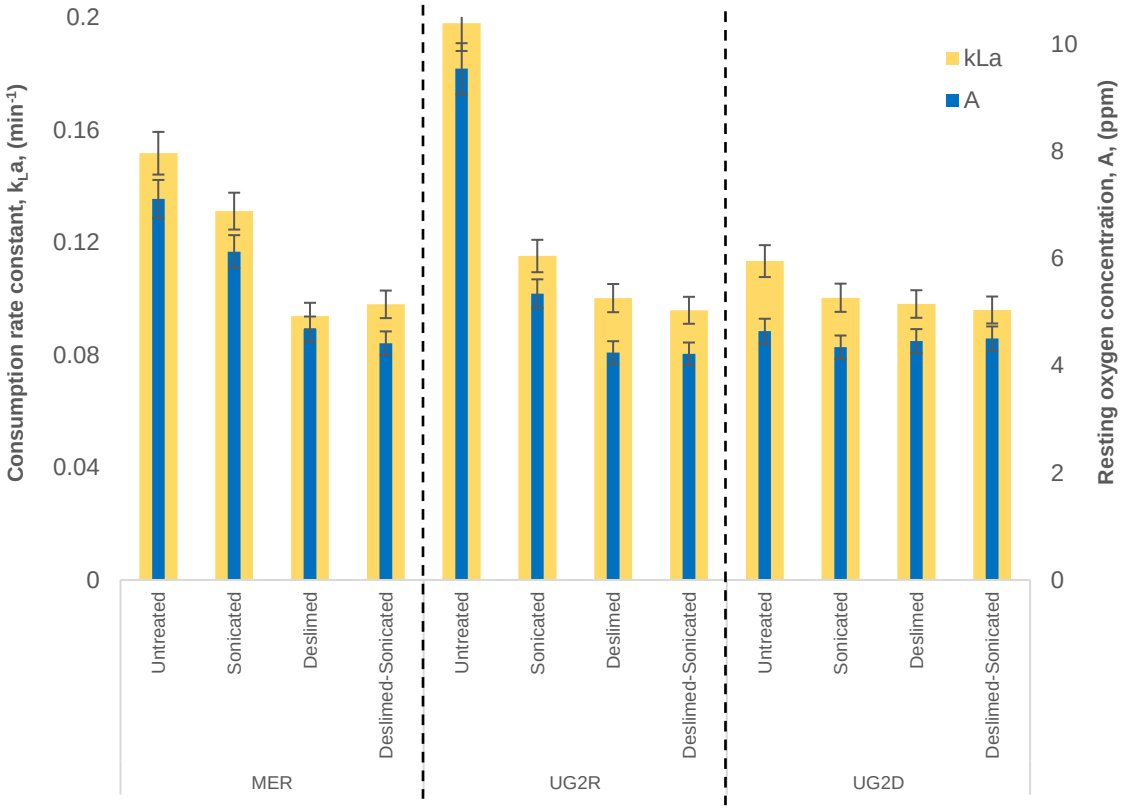


Figure 5.23: The resting oxygen concentrations and consumption rate constants of all tailings

For each tailings, the highest consumption rate constant was achieved for the untreated system; more oxygen was consumed there, showing that more oxygen reacted with the present minerals. When the tailings were sonicated, both the resting concentration and consumption rate decreased, showing that less oxygen reacted with the present minerals. Desliming the tailings decreased these parameters even further, and desliming *and* sonication, decreased them even more.

Every decline in the consumption rate constant means the demand for oxygen in the pulp became less and less, suggesting a decrease in the reactivity of the mineral surfaces. More of the dosed oxygen will be left over, as the active sites on the mineral surfaces have reacted with oxygen and are now occupied (Owusu et al., 2013; Richardson and Walke, 1985). That means the cleaning methods employed in this study induced a surface passivation effect in which the tailings became less reactive to oxygen. For each cleaning method that was used, the effect was likely generated by a phenomenon that is mostly unique to that specific method.

For example, desliming the tailings theoretically discarded all sub-25 μm particles, and in turn, decreased the specific surface area of the ore materials. More than 29% of all the chalcopyrite has also been discarded. In effecting these conditions, the mineralogies have effectively been altered, and if it is robust, the method should be able to detect these changes. In a study investigating the effect of ore liberation on oxygen reactivity, Sibiya (2022) showed that less sulphide mineral liberation results in lower reactivity. In effect, increasing the specific surface area will make more active sites available and therefore result in increased oxygen reactivity. On the other hand, ultrasonicating the tailings releases slime coatings into the pulp, supplying it with an increased fraction of fine particles. While this might be expected to increase the specific surface area of the ore material, and therefore the reactivity of the pulp, it is important to recall that the EDTA extraction results showed that sonicating the systems released more oxidation products into the pulp, effectively lowering its reactivity by flooding it with hydrophilic and oxidised particles.

And so, as the tailings were subjected to these changes and their effects, the mineral surfaces became less active, and their demand for oxygen decreased as a result.

The maximum and final DO contents in each system, and the amount of oxygen consumed by each tailings are summarised by Table 5.4. The data continued to demonstrate that with higher oxygen consumption rate constants, more total oxygen was consumed (both as a quantity and percentage) by each tailings.

Table 5.4: Oxygen content indicators for ultrasonicated, deslimed and sonicated-deslimed tailings

Parameter	MER	UG2R	UG2D
Ultrasonicated Tailings			
Maximum DO (ppm)	24.7	24.3	22.7
Final DO (ppm)	17.2	18.9	20.2
Consumed O_2 (ppm)	7.51	5.42	2.48
Consumed O_2 (%)	30.4	22.3	10.9
Deslimed Tailings			
Maximum DO (ppm)	24.3	22.3	23.6
Final DO (ppm)	23.0	19.8	21.4
Consumed O_2 (ppm)	1.28	2.52	2.21
Consumed O_2 (%)	5.27	11.3	9.35
Deslimed-Ultrasonicated Tailings			
Maximum DO (ppm)	23.1	22.8	23.9
Final DO (ppm)	21.2	20.9	21.9
Consumed O_2 (ppm)	1.99	1.81	2.00
Consumed O_2 (%)	8.59	7.93	8.36

Finally, the resting oxygen concentrations were obtained before medical-grade oxygen was actively sparged into the respective systems. Each concentration was observed for a full minute before active oxygen sparging, and in every case, the value remained constant for the full minute. MER, UG2R and UG2D each yielded a different value; this demonstrates that each tailings has some natural capacity to carry a specific amount of dissolved oxygen. When the tailings were subjected to sonication and desliming, their capacities changed, indicating that the capacity is dependent on mineral properties. For the untreated tailings, the parameter A can therefore be posited to be the natural oxygen concentration each tailings can hold. When deslimed, or cleaned through sonication, each tailings is able to hold less oxygen, since the mineral surfaces and compositions have changed, and the tailings now interact differently with oxygen.

As the natural oxygen concentrations decreased along with the consumption rate constants, it suggests that tailings which are naturally able to hold more oxygen, react more readily with it. The parameters k_La and A can thus be concluded to have a directly proportional relationship with one another. The study therefore predicts that tailings which naturally hold less oxygen and have lower oxygen consumption rate constants will have less active sites and demand less oxygen, and their valuables will float more poorly.

6. A DISCUSSION ON THE TAILINGS' FLOTATION

This chapter presents the results of the batch flotation experiments, and discusses them. The study objectives relevant to this chapter are therefore as follows:

- To use a lab-scale reprocessing method with the aim of gaining understanding of any potential plant-scale performance. **The reprocessing method is batch flotation.**
- To determine if mitigating the tailings' weathered state will change their flotation performance. **The investigated mitigation methods are ultrasonication and desliming.**

Similar to the convention used in Chapter 5, when the results concerning any tailings are designated as 'untreated,' it simply means the tailings sample was floated without first being ultrasonicated or deslimed. For UG2D, it means the tailings were not deslimed further.

For the concentrators from which MER, UG2R and UG2D were collected, a reprocessing venture would be deemed economically viable if 30% of the copper present in the tailings was recovered (personal communication). The flotation performance was analysed with copper recovery as the primary positive indicator. Nickel behaviour was also tracked in case of supporting elucidations, and also because pentlandite is the primary PGE-carrier for Merensky and UG2 fresh ores (Vermaak, 2005). Pentlandite's performance, while not central to this study, is still worth analysing.

As outlined in Chapter 4, two sets of flotation tests were carried out. The first set was conventional (in that it followed standard flotation procedures typically used at the CMR (Corin et al., 2011; Wiese et al., 2005)). The second set concerned only a certain size fraction of the tailings, i.e., only particles larger than 25 µm were floated. The former set is analysed in Section 6.1., and the latter, in Section 6.2. The chapter's full scope is as summarised by Figure 6.1.

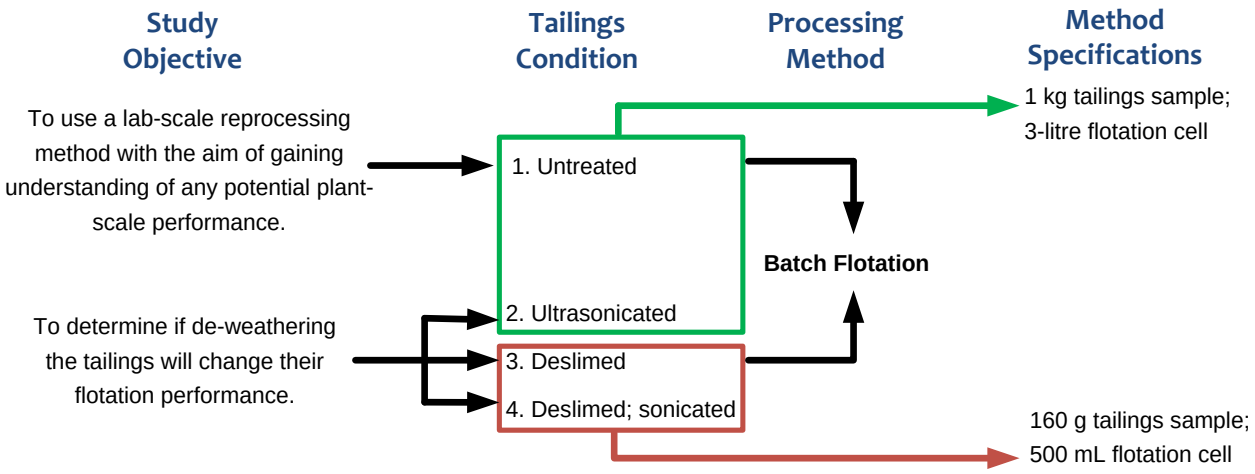


Figure 6.1: The scope of Chapter 6

6.1. Batch Flotation of the Full Tailings

In this section (6.1.), the batch flotation of the full tailings will be analysed. A summary of the scope is shown in Figure 6.2.

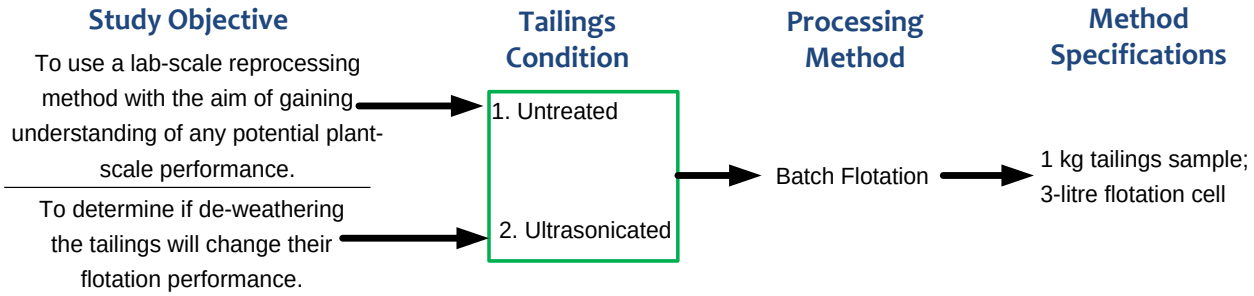


Figure 6.2: The scope of Section 6.1.

6.1.1. Establishing a Baseline for the Tailings' Flotation

The first step in processing the tailings, was simply to test that they could, in fact, be processed at all. For instance, the UG2 reef is known for its high chrome content, little of which has floating ability (Nel et al., 2004). It was expected that the UG2 tailings, also containing a significant chrome concentration (Figure 5.1), and having the added disadvantage of being previously beneficiated, would also have limited floating ability. A flotation baseline for the tailings had to be established; and from this, the rest of the flotation tests could be planned.

And so, all untreated tailings were first floated in 125 g/t SIBX and 175 g/t CMC. The underlying assumption made for the addition of a depressant, was that the overwhelming amount of gangue minerals must surely be actively depressed in order to enhance the selectivity of the process. However, this proved to be a flawed assumption. Figure 6.3 compares the cumulative recovery of solids when the tailings were floated both in the presence and absence of CMC. The collector type and dosage in both cases was the same (125 g/t SIBX).

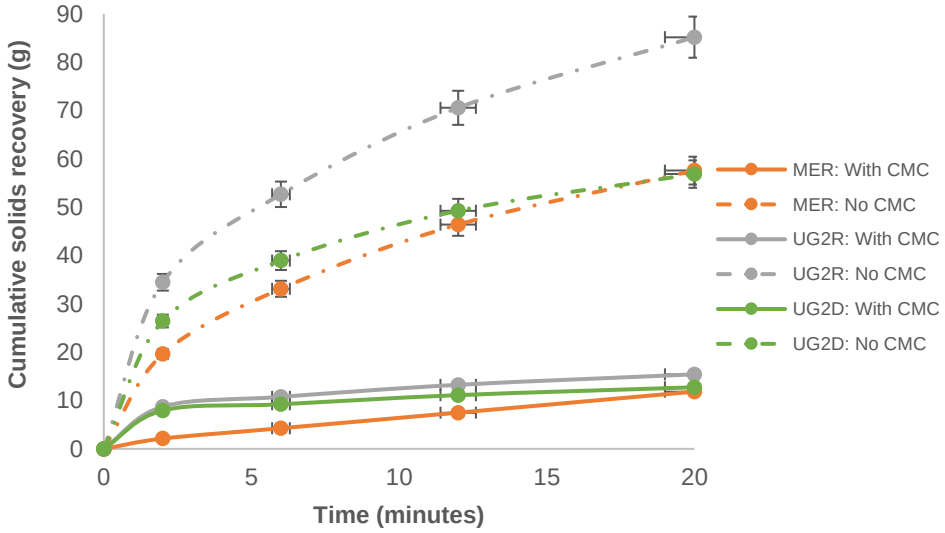


Figure 6.3: The recovery of solids against flotation time, for all untreated tailings, floated with and without CMC

As demonstrated by Figure 6.3, when the tailings were floated with CMC, only 12 g of the MER and UG2D masses were recovered, while the best performing tailings, UG2R, yielded a recovery of 15 g (which translates to 1.5% solids recovery). When the tailings were floated without the depressant, but with every other parameter being kept constant, the recovery improved across the board, with UG2R showing the best improvement (from 1.5% solids recovery, to 8.5%).

The value minerals of interest, chalcopyrite and pentlandite, demonstrated similar recovery patterns. Copper was used as the indicator for chalcopyrite, and nickel was used for pentlandite. The XRF analysis of the recovered concentrates showed that in the presence of CMC, very little copper and nickel were recovered, while in the absence of CMC, the recoveries of both metals improved. This is demonstrated by Figure 6.4 (for copper) and Figure 6.5 (for nickel). In fact, as much as 25% copper was recovered when the UG2R tailings were floated without CMC, while only 3.9% recovery was achieved when the same tailings were floated with CMC.

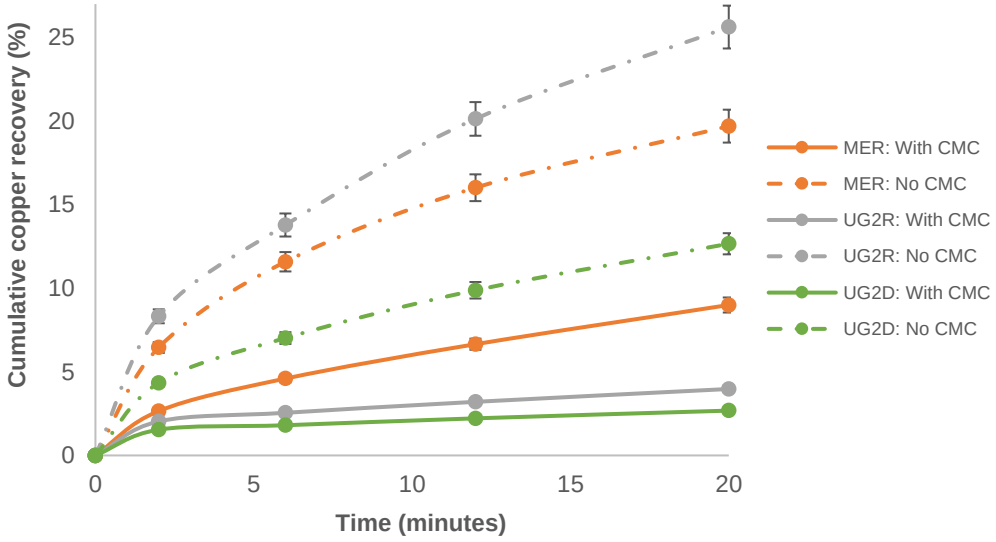


Figure 6.4: Copper time-recovery curves for all untreated tailings when floated with and without depressant

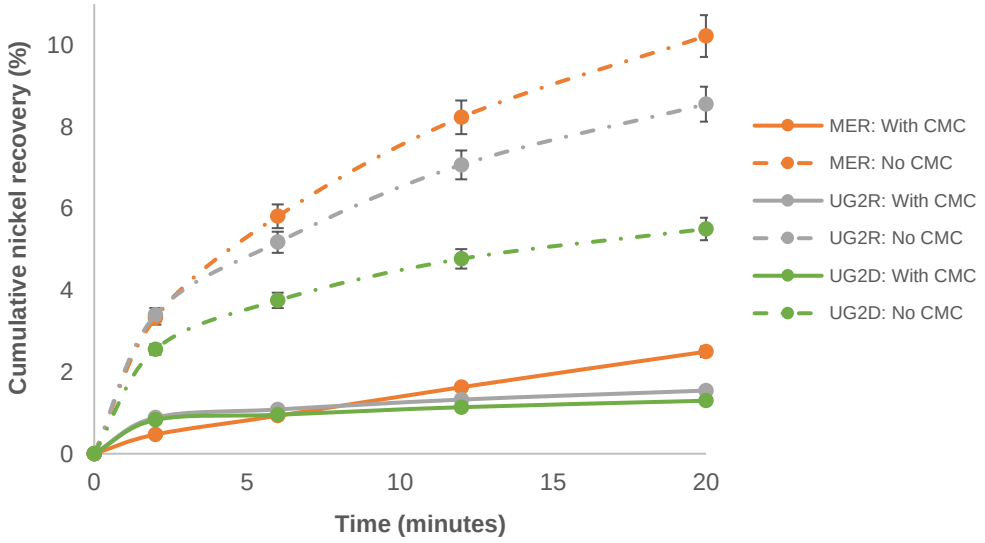


Figure 6.5: Nickel time-recovery curves for all untreated tailings when floated with and without depressant

Figure 6.4 and 6.5 also demonstrate that the copper recoveries of all the tailings are markedly higher than their nickel counterparts. This was an expected result since pentlandite is a naturally slower-floating mineral than chalcopyrite (Gray et al., 2006). The percentage of chalcopyrite association to pentlandite is presented in Table 6.1.

Table 6.1: The association of chalcopyrite to pentlandite in the bulk MER, UG2R and UG2D

Tailings	MER	UG2R	UG2D
Chalcopyrite association to pentlandite (%)	7.07	0.649	0.362

Also noteworthy is the fact that under CMC flotation, the MER tailings yielded the highest copper and nickel recoveries, but when the CMC was omitted, UG2R yielded higher copper recoveries. This is likely the result of various colliding factors. Firstly, of the investigated tailings, MER contained the highest chalcopyrite as well as total sulphide fraction (Figure 5.3); the association of chalcopyrite with the present sulphide minerals was also strongest in MER (Figure 5.11). On the other hand, while it was better liberated (Figure 5.6), the chalcopyrite in UG2R and UG2D was more strongly associated with the gangue minerals quartz, plagioclase and chromite. The results suggest that when these gangue minerals were depressed, so too was the chalcopyrite, at least to a greater degree than the MER-chalcopyrite and the mineral associations existing for that bulk.

Secondly, one of the core advantages with processing sulphides via froth floating is that they are weakly polar. They typically interact poorly with water (Wills and Napier-Munn, 2006; Wrobel, 1970). In this study's context, it means the naturally hydrophobic fraction of MER (0.06 wt.% sulphides) was higher than that of UG2R (0.05 wt.% sulphides) and UG2D (0.02 wt.% sulphides). It is perhaps expected that as it contained a higher naturally floatable fraction than its UG2 counterparts, MER might yield higher recoveries than UG2R and UG2D. Moreover, UG2D is then expected to perform poorer than UG2D.

Thirdly, MER's chalcopyrite was predominantly locked, while UG2R and UG2D's chalcopyrite was better liberated (Figure 6.6 shows the liberation profiles for the untreated tailings). It must therefore be considered that when CMC was not added to the respective systems, and when the previously discussed gangue minerals were not actively depressed, the more liberated chalcopyrite now had a better chance of exhibiting its natural floatability, and of interacting with the dosed collector, with all three phenomena contributing to improved copper recoveries. While this effect was not enough for UG2D to overtake MER, it worked rather well for UG2R for the possible reason that UG2R had sufficient overall sulphide content, and marginally higher chalcopyrite liberation than UG2D.

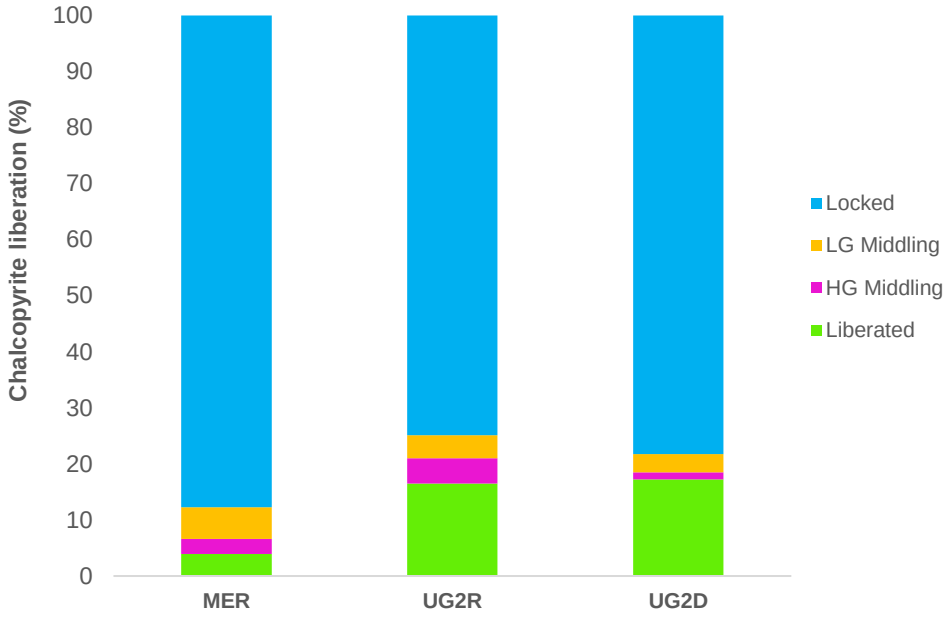


Figure 6.6: The liberation of chalcopyrite in the MER, UG2R and UG2D bulks

Another possible contributing factor is as follows: since the depressant was added to the flotation process first, it coated the target gangue minerals, including those that locked the valuables, rather efficiently, such that when the collector was added, there was little of the tailings surfaces to be affected by the collector, and therefore little opportunity for the collector to perform optimally. If that is true, it would mean flotation batches with CMC added to them would consume less SIBX than those without. This can easily be tested by checking the SIBX consumption of each test.

Figure 6.7 does exactly that; it shows the adsorption profile of SIBX when contacted with the untreated tailings, both in the presence and absence of CMC. The initial concentration of SIBX for all results depicted in Figure 6.7 was 10 ppm.

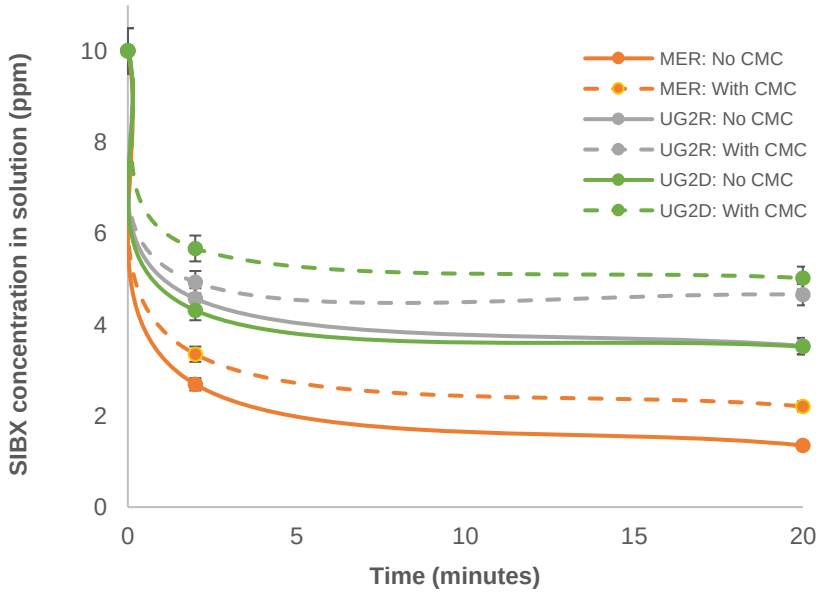


Figure 6.7: Residual concentrations of SIBX for all untreated tailings, both with and without CMC added in the test

In this context, the amount of collector adsorbed by the tailings was measured as that abstracted from solution; and the total adsorbed amount was measured as that abstracted at the end of the flotation period (Hadler et al., 2005; Finkelstein and Lovell, 1972). Thus, in Figure 6.7, at the 20-minute mark, if a test has a higher SIBX concentration remaining in solution when compared to the others, it means in that particular test, less SIBX was adsorbed by the tailings.

Figure 6.7 shows that indeed, for each tailings, the presence of CMC hindered the adsorption of SIBX onto the mineral particles, therefore lending credence to the supposition that the collector and depressant are in some form of adsorption competition. It is theorised by, among others, Fuerstenau and Chander (1986) and Leja and Schulman (1954), that species dissolved in solution influence collector adsorption. In this case, it has been shown that in the presence of CMC, the performance, or rather, the adsorption of SIBX onto the PGM tailings became limited, and as a further result, the target value minerals floated more poorly.

Figure 6.8 shows solids recovery as a function of water recovery for all untreated tailings, both with and without the addition of CMC.

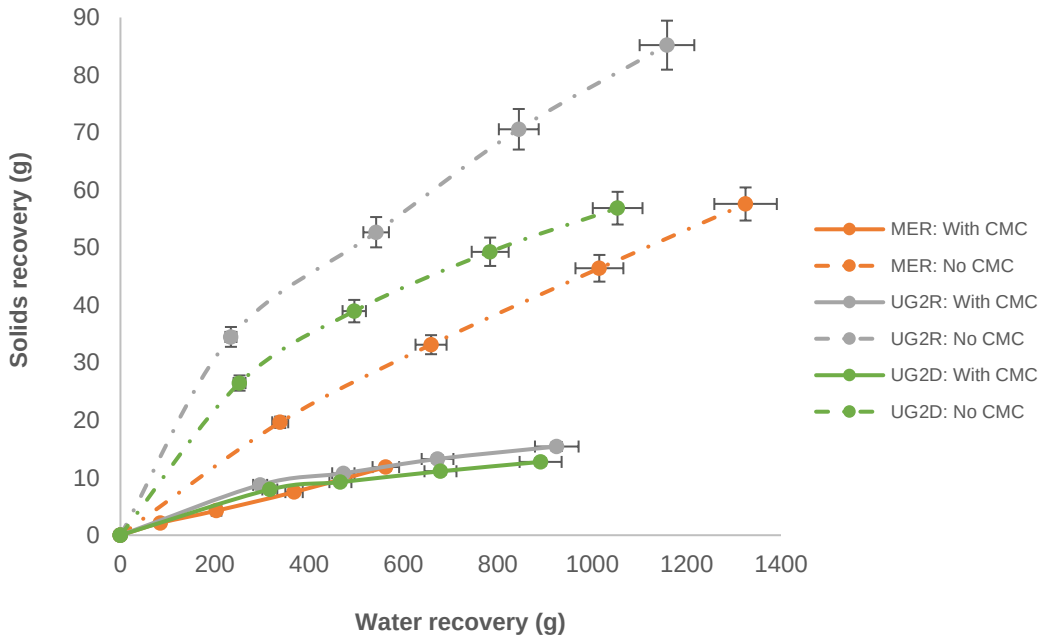


Figure 6.8: Solids vs. water recovery for all untreated tailings when floated with and without CMC

Water recovery can be used as an indicator of froth stability, with higher water recoveries generally indicating more stable froths (Manono et al., 2013; Tao et al., 2000). Moreover, entrainment is a function of water recovery (Kawatra, 2009). Figure 6.8 demonstrates that in every case, when there was no CMC in the system, both the recovery of solids and water increased. In the most extreme cases, the recovery of UG2R solids increased by a factor of 5.7 (from to 15 to 85 g), and the water recovery associated with MER flotation doubled (from 672 to 1325 g).

This suggests that in the absence of CMC, the higher recoveries of solids had to be expected for two reasons. The first is more obvious, as it simply informs that the recovery of gangue materials was not actively discouraged by the presence of a depressant. The second is more complicated, as it suggests that not only were the naturally floatable gangue minerals curbed, but entrainment was reduced as well. The mechanism by which depressants attach to minerals is complex and little understood (Steenberg and Harris, 1984). However, it can be posited from these results, that to some degree, the addition of CMC in the flotation of these tailings curbs entrainment too. This is because it cannot be conclusively stated that all the gangue materials that reported to the concentrate in the presence of CMC, did so by entrainment. Nor can it be concluded that in the absence of CMC, all the gangue materials that reported to the concentrate, did so by true flotation.

Figure 6.9 shows the copper recovery-grade curves for all the untreated tailings, and Figure 6.10 shows the same for nickel.

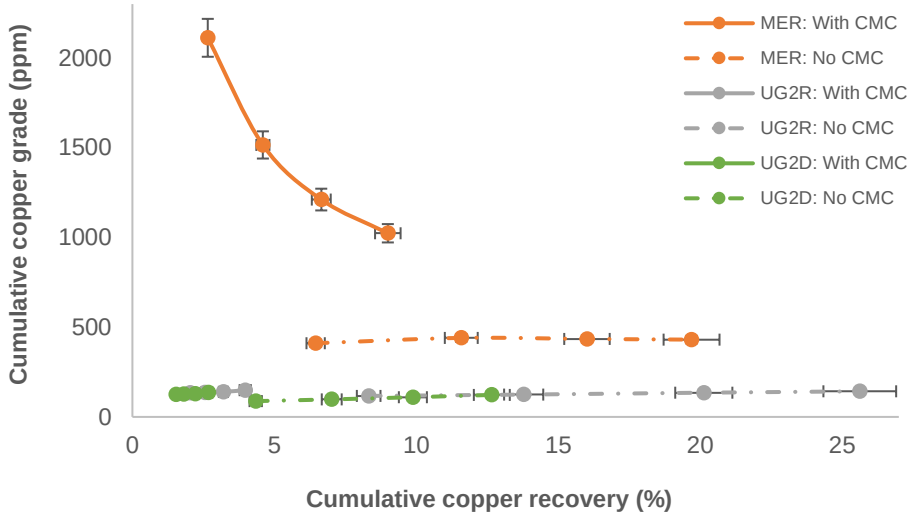


Figure 6.9: Copper recovery-grade curves for all untreated tailings when floated with and without CMC

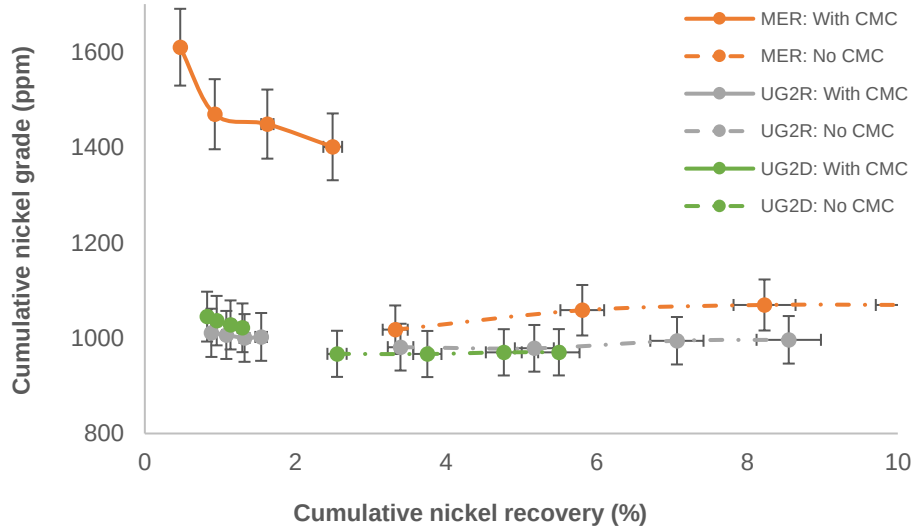


Figure 6.10: Nickel recovery-grade curves for all untreated tailings when floated with and without CMC

The first thing to note is that the grades were extremely low, necessitating the use of 'ppm' as the unit of measurement on the axis, instead of the more conventional '%'. Secondly, the curves clustered together in a way that made it difficult to decipher meaningful patterns. As such, the final values are better depicted in bar-form, presented in Figure 6.11 (for copper) and Figure 6.12 (for nickel). The convention of using bar graphs to depict grades was extended to the rest of the thesis to allow for better discussion. Corresponding recovery-grade curves can be found in Appendix B.

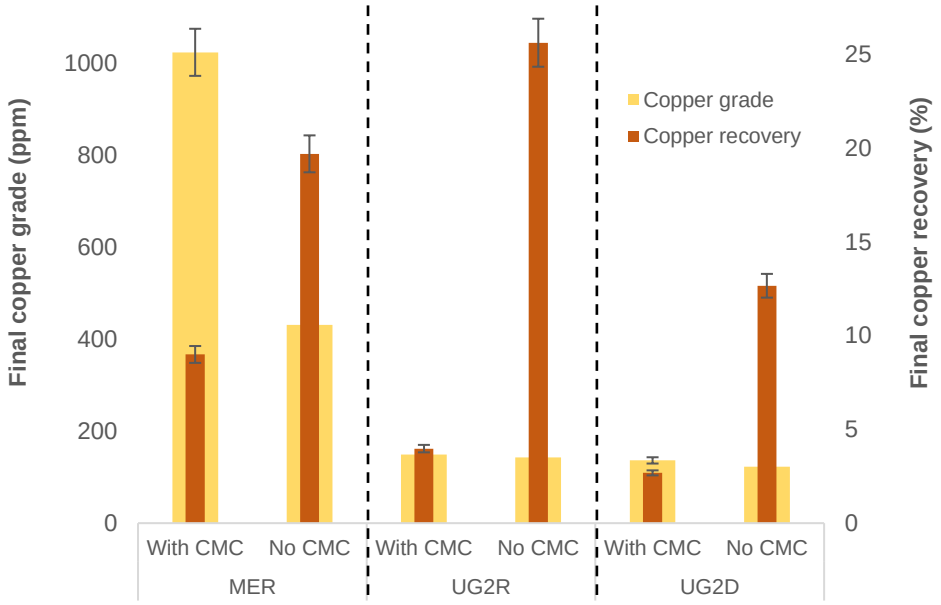


Figure 6.11: Final copper recovery and grade for all untreated tailings when floated with and without CMC

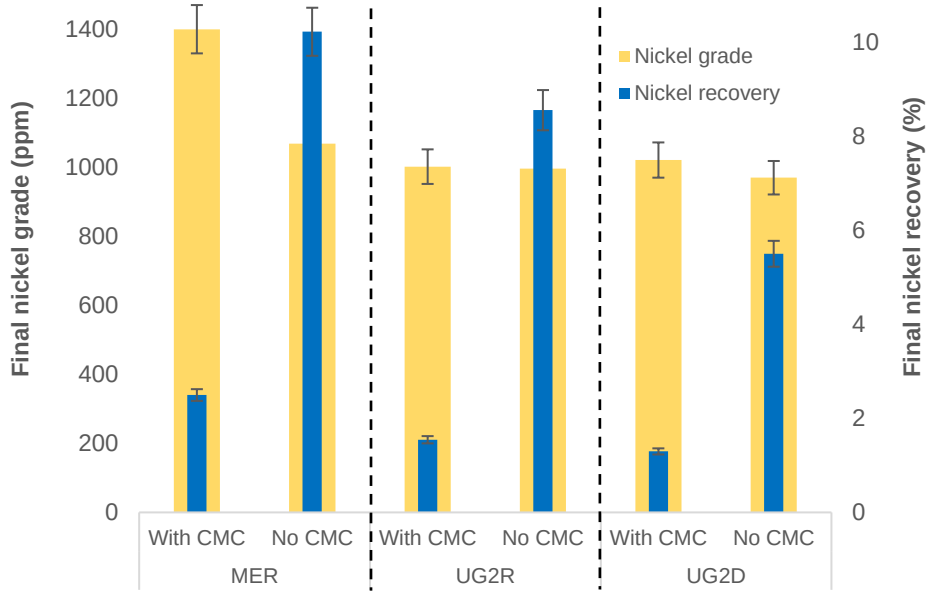


Figure 6.12: Final nickel recovery and grade for all untreated tailings when floated with and without CMC

Figure 6.11 and 6.12 demonstrate that while the absence of CMC improved the recoveries of copper and nickel for all tailings, this did not, however, significantly affect the grades for either of the UG2 tailings. It was only in the case of MER that the absence of CMC reduced the concentrate

grades for both copper and nickel, suggesting that the depressant improved the selectivity of the flotation process. Given that all experimental conditions and parameters were kept the same, it is apparent that the different mineralogy profiles of the tailings significantly affected their respective flotation behaviours.

A study by Wiese (2009) investigated the effect of increasing the depressant (guar) dosage on the recovery of naturally floatable gangue (NFG), in the flotation of a Merensky ore. The study showed that at 500 g/t guar, the NFG was completely depressed. This allowed Wiese (2009) to develop an entrainment factor from a linear relationship between the recovered solids per unit water.

The tests without CMC (in the present study) consistently showed higher water and solids yields than those observed for CMC-dosed tests. The large differences in the recovered quantities (Figure 6.8) further suggest that without a depressant, the flotation process was far less selective, and that gangue materials associated with UG2R are more floatable. See Figure 6.13 for a comparison of the most dominant gangue minerals in the samples. MER had the highest concentration of pyroxenes and plagioclase, while the UG2 tailings had higher chromite fractions.

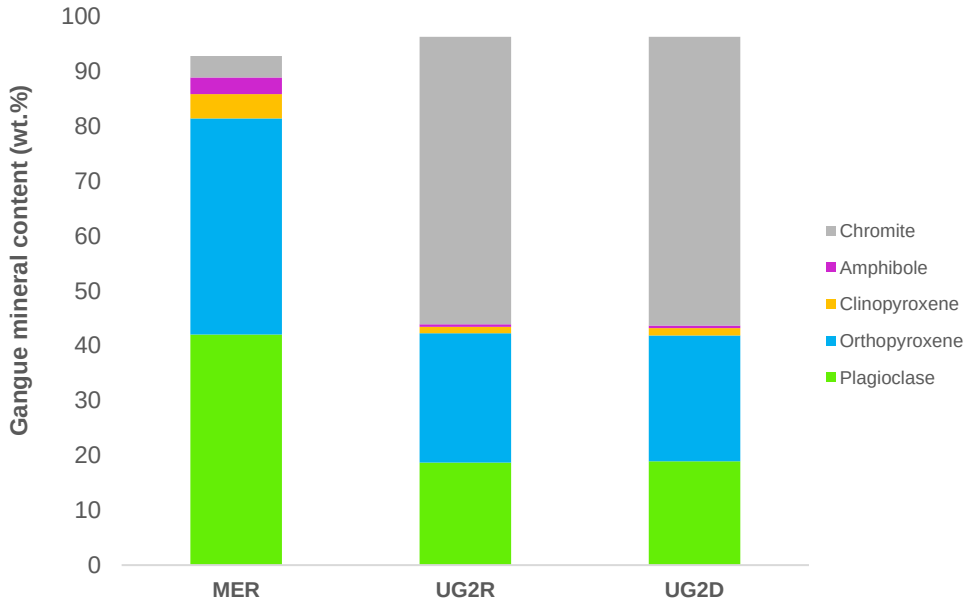


Figure 6.13: A comparison of the concentrations of the dominant gangue minerals

Chromite is well known to have little floating ability, and its ubiquity in the UG2 tailings should indicate little floating ability for the bulks as well (Nel et al., 2004). However, the association of chalcopyrite with the present gangue minerals is stronger in the UG2 tailings. The study therefore makes the following proposal: if the chalcopyrite-gangue composites in UG2R and UG2D were, indeed, more depressed by CMC, it must be true that in the absence of CMC, the composites will immediately have a better chance of recovery. This suggests the composites behave in a complex manner that somewhat adopts the characteristics of the more favoured part of the composite.

For example, CMC was effective in depressing the gangue-fraction, thus overall copper recovery was reduced. But in the absence of CMC, the collector was the only specialised reagent added, and the chalcopyrite fractions of the composites were better-favoured by pulp conditions, causing them to behave more like chalcopyrite, and yielding better copper recoveries. And so, improved chalcopyrite flotation inadvertently improved the associated gangue recoveries.

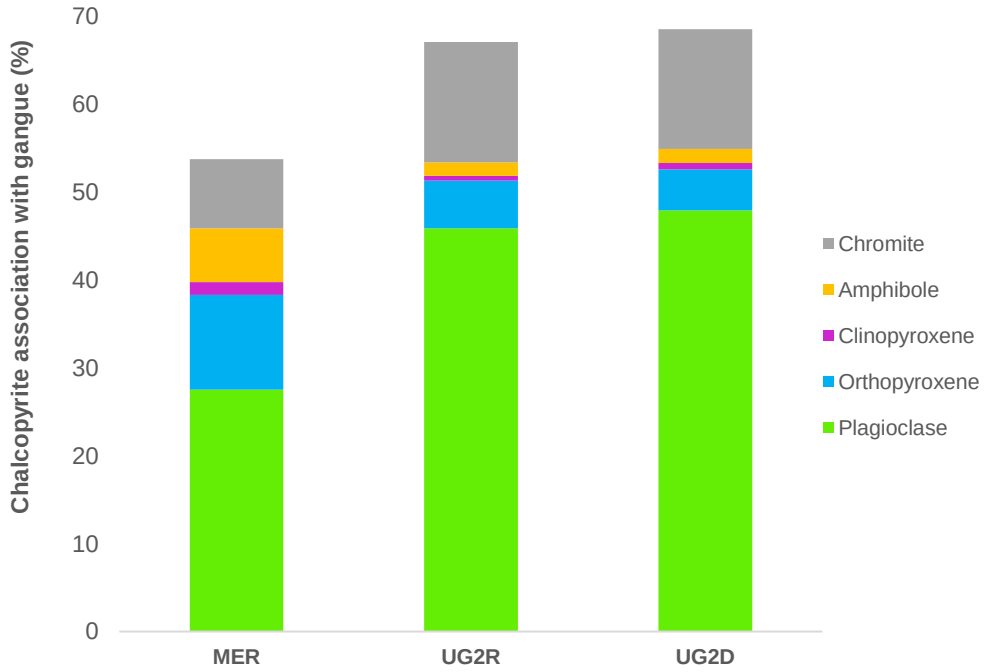


Figure 6.14: A comparison chalcopyrite association with the dominant gangue minerals in MER, UG2R and UG2D

This part of the study thus answered the question: ***what happens when these tailings are floated with a depressant?***

The answer was that the target value minerals are recovered poorly, and in terms of the UG2 tailings, there is no desirable trade-off in terms of improving the concentrate grades. Even with MER, where the grades are improved, it makes little practical sense, and perhaps economic sense too, to pursue recovery rates well below 20% for a mineral as famously floatable as chalcopyrite. Moreover, without CMC, UG2R came rather close to meeting the target 30% copper recovery.

The flotation baseline can therefore be summarised as follows: no depressant would be added in the flotation process, and only the effect of the collector would be investigated.

6.1.2. The Effect of Collector Dosage on the Tailings' Flotation

Now that it was shown the tailings could float, the next step was to investigate whether the flotation performance could be enhanced in any way. As one of the two investigated reagents, the depressant, was discarded, the most obvious adjustment that could be made, was to investigate the variation of the remaining reagent – the collector.

A fundamental tenet of froth flotation is that the separation efficiency is reliant on the degree of hydrophobicity achieved by the target particles. In turn, the hydrophobicity is reliant on the collector adsorption (Fuerstenau, 1984).

In an attempt to optimise adsorption and therefore particle hydrophobicity, a higher collector dosage was now used. And so, all untreated tailings were floated in 200 g/t SIBX and no CMC. All other experimental parameters were kept the same as before.

Figure 6.15 compares the cumulative solids recovered when the tailings were floated in 125 g/t SIBX ("Low SIBX" in the figure legend) and 200 g/t SIBX ("High SIBX" in the figure legend). (The 125 g/t SIBX results were taken from the last section – Section 6.1.1.).

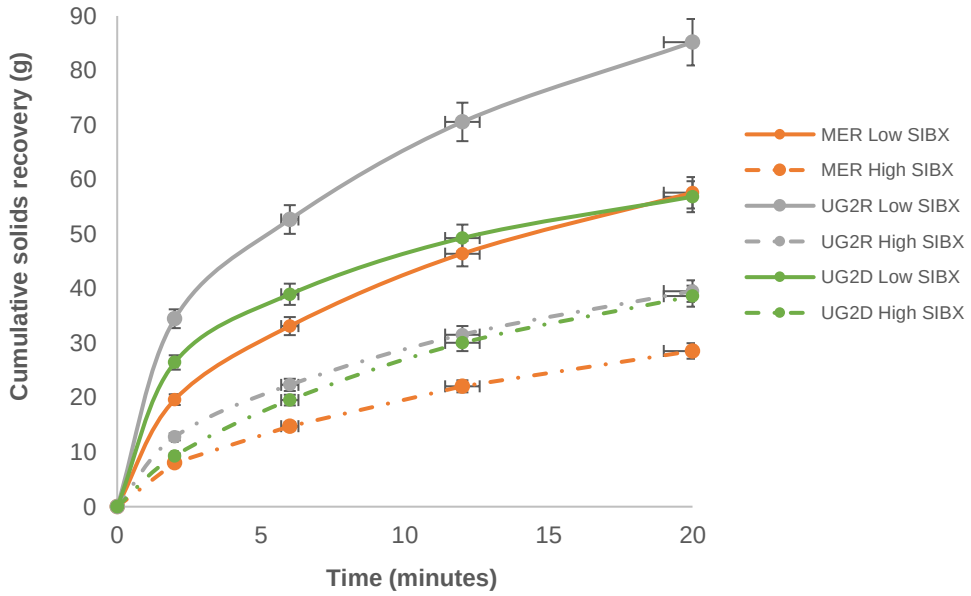


Figure 6.15: The recovery of solids against flotation time, for all untreated tailings, floated in 125 and 200 g/t SIBX

As can be seen in Figure 6.15, increasing the SIBX dosage resulted in less solids being recovered for all tailings. In the most extreme case (UG2R), the amount of recovered solids was more than halved (from 85 to 38 g) when the SIBX was increased.

In addition, the corresponding water recoveries also decreased when the amount of dosed collector was increased. This is shown in Figure 6.16, which compares the cumulative solids recovery for each tailings as a function of cumulative water recovery.

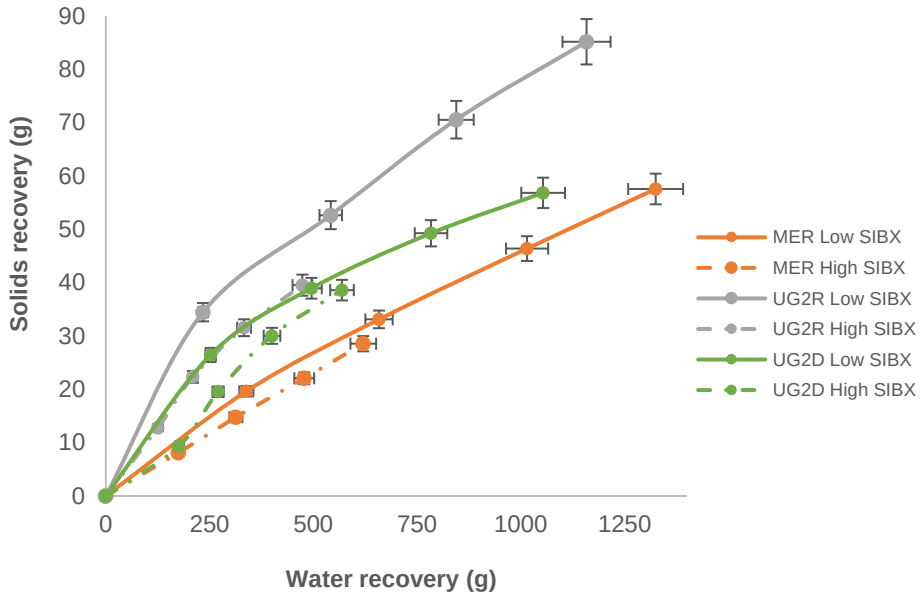


Figure 6.16: Solids vs. water recovery for all untreated tailings when floated in 125 and 200 g/t SIBX

It is apparent that the SIBX affected the overall mass of materials recovered to the concentrate. However, and as shown by Figure 6.17, the corresponding copper recoveries were higher when the collector dosage was increased. It is worth noting that the UG2 tailings were, once again, the most improved in this regard. For UG2R, the copper recovery went from 25 to 34%; for UG2D, it went from 12 to 22%; and for MER, it went from 19 to 23%.

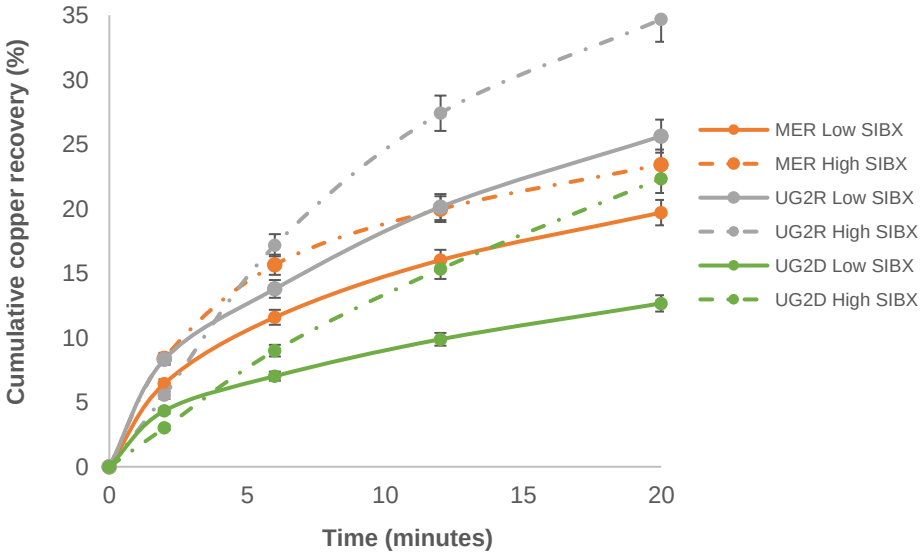


Figure 6.17: Copper time-recovery curves for all untreated tailings when floated in 125 and 200 g/t SIBX

But on the other hand, and as shown by Figure 6.18, for each tailings, higher nickel recoveries were achieved at 125 g/t SIBX. MER had higher yields; although the nickel recovery dropped from 10 to 7.4%. UG2R showed the worst deterioration, with its nickel recovery dropping from 8.6 to 4.4%. So, while chalcopyrite and pentlandite continued to behave differently, UG2R continued to be the most sensitive to the investigated parameters.

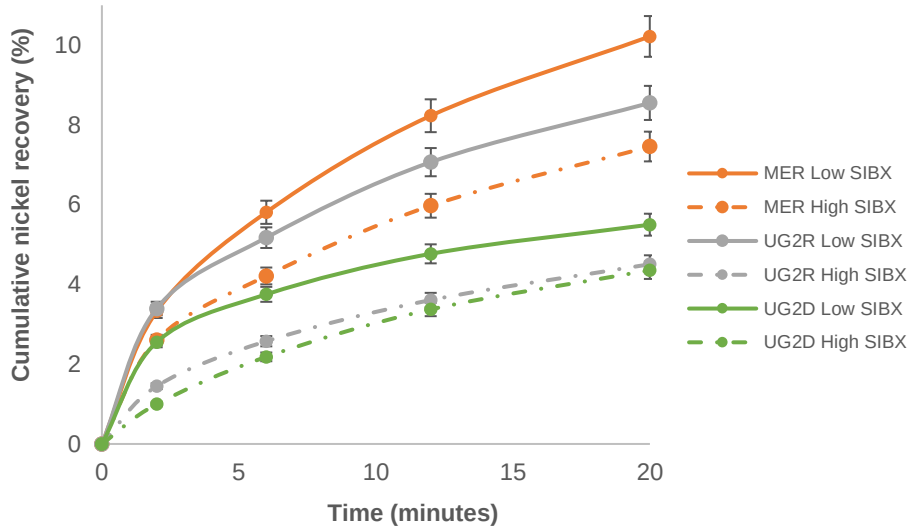


Figure 6.18: Nickel time-recovery curves for all untreated tailings when floated in 125 and 200 g/t SIBX

When investigating the effect of CMC, it was observed that the tests that consumed more SIBX yielded higher mass pulls (total water and solids) to the concentrate. However, when there was no CMC, and SIBX was the only species primed for interaction at the mineral-water interface, lower mass pulls were yielded for the higher collector dosage.

Studies such as Hadler et al. (2005) and Wang (2016) propose that lower collector adsorption densities result in lower particle hydrophobicities, and as a result, the particles recovered to the froth phase do not affect the froth stability. However, as collector adsorption increases, and particle hydrophobicity increases, froth stability reaches a maximum. Beyond this maximum, further particle hydrophobicity leads to films in the froth phase being ruptured, which leads to increased drainage of water and gangue minerals from the froth. Thus, the stability of the froth phase has a direct impact on the concentrate grades.

At this point two supposition can be made. Firstly, increasing the collector dosage from 125 to 200 g/t resulted in higher adsorption densities, and hence, increased particle hydrophobicity. Secondly, the increased particle hydrophobicity resulted in ruptured films, which subsequently led to reduced water and solids recoveries. And if that is the case, a third supposition can be drawn – at 200 g/t SIBX, the concentrate grades must have improved.

The first supposition can usually, easily be determined with the adsorption profiles of the two dosages. However, as outlined in Chapter 4, the tailings in this study abstracted too little SIBX. As a result, the spectrophotometer could not accurately measure the residual concentrations. To remedy this, two SIBX concentrations that were low enough to allow for accurate measurement, were investigated. These were 10 and 25 ppm. As a reminder, these values did not match the actual flotation concentrations of 43.1 ppm (125 g/t) and 69 ppm (200 g/t); however, the objective here

was simply to test whether different initial concentrations were abstracted at different rates, and to different levels of consumption. Figure 6.19 shows the adsorption profiles of 10 and 25 ppm of SIBX when contacted with all untreated tailings for 20 minutes.

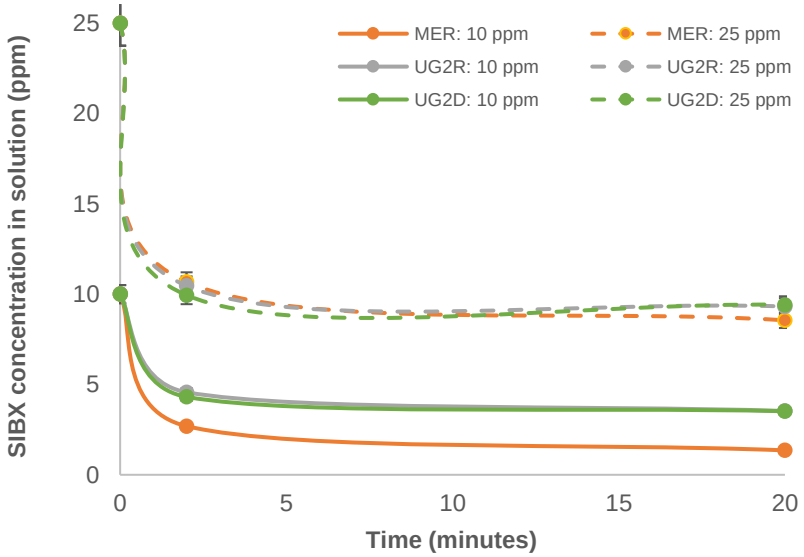


Figure 6.19: Residual concentrations of SIBX for all untreated tailings, for different initial collector concentrations

On a basic level, Figure 6.19 shows that at 25 ppm, more collector was leftover in solution at the end of the test duration, while at 10 ppm, less SIBX was leftover. It can be easy to interpret this to mean that more collector was adsorbed for the 10-ppm profile. But when considering the total amounts that were actually abstracted, it becomes clear that greater amounts were adsorbed for the 25-ppm profile. This is shown in Figure 6.20.

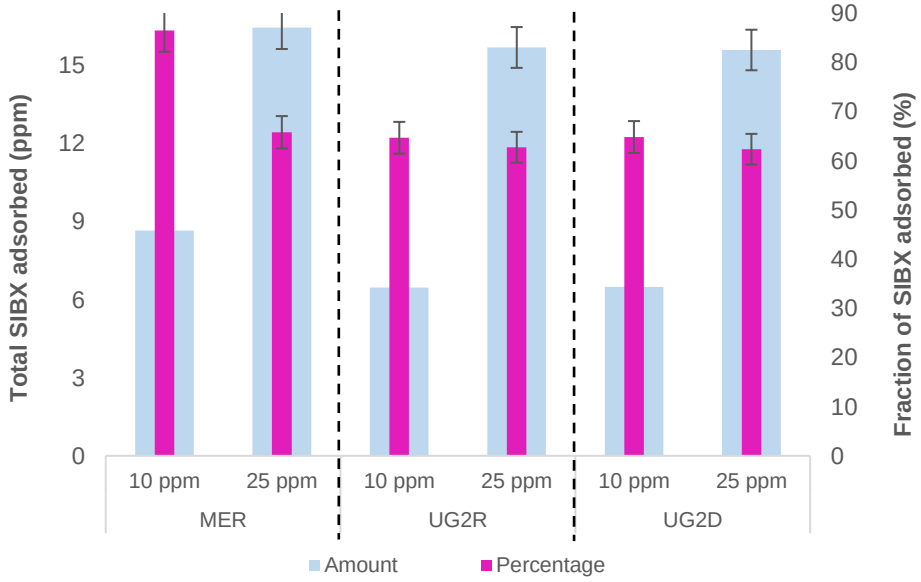


Figure 6.20: The SIBX adsorbed expressed as a total amount, and as a percentage of the initial concentration

For both dosages, and for all tailings except MER-10 ppm, roughly the same percentage (62-65%) of SIBX was abstracted from solution. But on the whole, as more SIBX was made available in

solution, more of it was adsorbed. For example, for the least collector-abstracting tailings, UG2D, when 10 ppm SIBX was dosed, 6.48 ppm was adsorbed; but when 25 ppm SIBX was dosed, 15.6 ppm was adsorbed. This trend was true for the other tailings, i.e., simply making more collector available in solution resulted in more collector being adsorbed by the tailings. A similar finding was made in a study where Hadler et al. (2005) investigated the effects of frother and collector distribution on flotation performance of an unspecified South African PGM ore.

In the present study, as less collector was adsorbed when the SIBX dosage was lower, it is likely that at 125 g/t SIBX, the target value minerals were less hydrophobic. At 200 g/t, they were likely more hydrophobic, affecting the froth stability and hence the total solids and water recoveries. The final grades (Figure 6.21 for copper and Figure 6.22 for nickel) show that indeed, the concentrate grades for both minerals were improved under 200 g/t SIBX flotation.

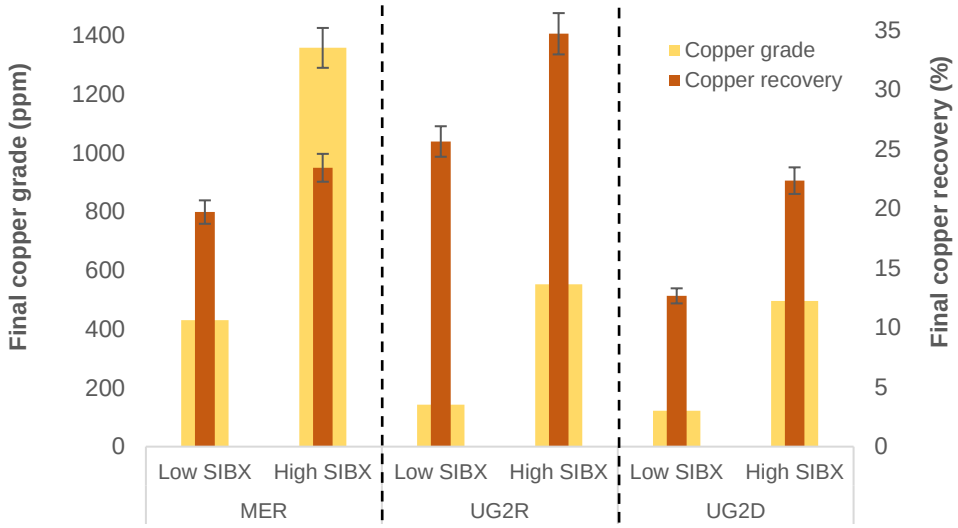


Figure 6.21: Final copper recovery and grade for all untreated tailings when floated in 125 and 200 g/t SIBX

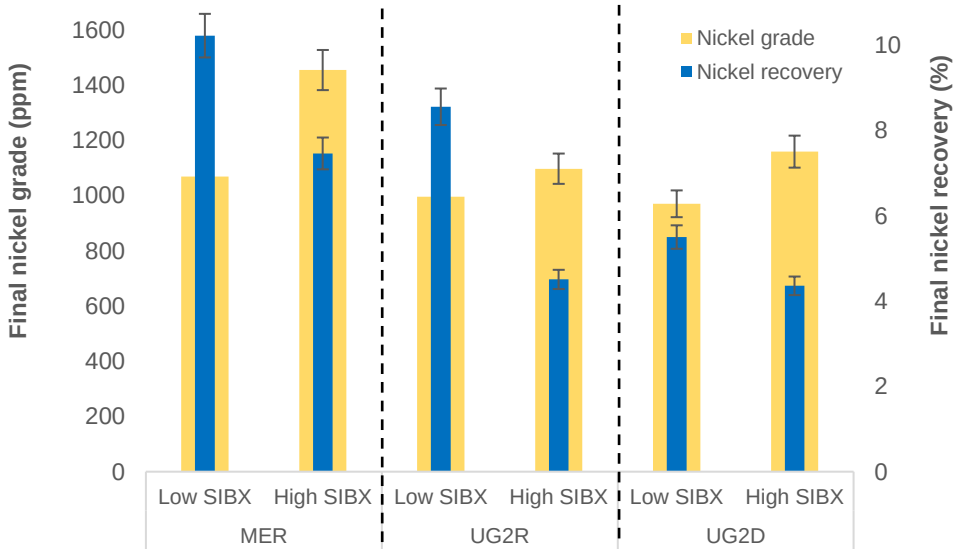


Figure 6.22: Final nickel recovery and grade for all untreated tailings when floated in 125 and 200 g/t SIBX

In terms of the copper grades, MER showed the best improvement when the collector dosage was increased, with its nickel grade rising from 430 to 1400 ppm. UG2R and UG2D showed very similar trends, both their copper grades hovering around 140 ppm under the lower collector dosage, and rising to ~550 ppm when the SIBX was increased.

In terms of nickel grades, MER once again showed the best improvement when the collector dosage was increased, its nickel grade rising from 1069 to 1455 ppm. The UG2 tailings once again performed similarly, both rising from ~970 to 1100 ppm.

The patterns shown here, where both copper and nickel indicators increased in tandem, were unique to this part of the study. In simply tampering with the collector dosage, and perhaps tampering with the mineral hydrophobicity in a predictable way that could not be confused with the effects of other reagents, the grades improved across the board. The only thing that was compromised is the recovery of nickel; at the higher dosage, it, alone, decreased.

This part of the study thus answered the question: ***what happens when these tailings are floated at different collector dosages?*** The answer is that MER and UG2D come closer to the 30% copper recovery objective, while UG2R exceeds it.

The flotation basis can therefore be amended as follows: no depressant would be added in the flotation process, and only the effect of the collector would be further investigated. To achieve higher copper recoveries, and higher copper and nickel grades, the higher collector dosage of 200 g/t SIBX will be taken forward. This is better than the alternative of proceeding with the lower dosage of 125 g/t SIBX, as in that case, only the trade-off of higher nickel recoveries is achieved, with everything else being compromised.

6.1.3. The Effect of Cleaning the Tailings Particle Surfaces

Up to this point, all flotation tests were performed on untreated tailings. Now that it was shown tailings flotation was possible, and that it could be improved, the next step was to investigate whether pre-treating the tailings would enhance the flotation performance in any way.

And so, all the tailings were first ultrasonicated for 20 minutes before being floated in 200 g/t SIBX. All other experimental parameters were kept the same as before.

Figure 6.23 compares the cumulative solids recovered when the untreated tailings were floated in 200 g/t SIBX ("Untreated" in the figure legend), and when they were first sonicated prior to being floated with 200 g/t SIBX ("Sonicated" in the figure legend). (The untreated results were obtained from the last section – Section 6.1.2.).

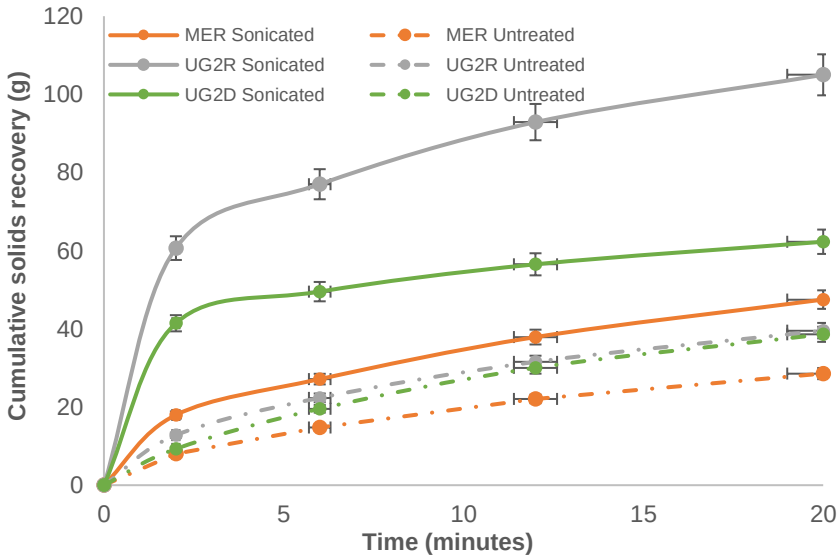


Figure 6.23: The recovery of solids against flotation time, for all untreated and ultrasonicated tailings, when floated in 200 g/t SIBX

For each tailings, the solids recovery was higher under sonication. Thus, there was improvement in the floatability of the ore materials as a whole. UG2R once again had the highest recovery improvement, going from 38.6 g without sonication, to 105 g when sonicated. MER had the lowest recovery improvement, only going from 28.6 g when not sonicated, to 47.5 g when sonicated.

Studies such as Aldrich and Feng (1999), Celik (1989), and Djendova and Mehandjiski (1992), have shown that sonicating ore materials prior to, or during batch flotation, can increase the recovery of the valuables by removing fine and oxidised materials from the mineral surfaces. The acoustic waves produced by a mechanical aid such as sonication increase the solute (or collector) mass transfer rate and therefore improve the adsorption efficiency. The dispersion of the collector in solution, as well as the other relevant chemicals, can be improved in this way (Reddy et al., 2010; Roosta et al., 2014). Additionally, for oxidised and slime-coated ore materials, not all metallic ions

on the surface function as active sites; when a collector is added, these surfaces fail to interact with it optimally (Fang et al., 2018). Removing the slime coatings and oxidation products should make more active sites available for the collector (Newell et al., 2006). Figure 6.23 therefore suggests the following: sonicating the tailings cleaned the mineral surfaces, improved collector efficiency, and as a result, more solids floated and were recovered to the concentrate.

On the other hand, it is possible that as the slime coatings in the form of fine particles were shaken loose, they became available for entrainment. And as finer particles (-38 µm) are more susceptible to entrainment (Ata et al., 2004; Wills and Napier-Munn, 2006), it stands to reason that as their fraction in the pulp phase increased, so did the likelihood of their being entrained and recovered, thus increasing the total solids recovery. But then again, it might be the case that both natural flotation and entrainment increased. To detangle these positions, other indicators were analysed. Figure 6.24 compares the cumulative solids recoveries as a function of water recovery.

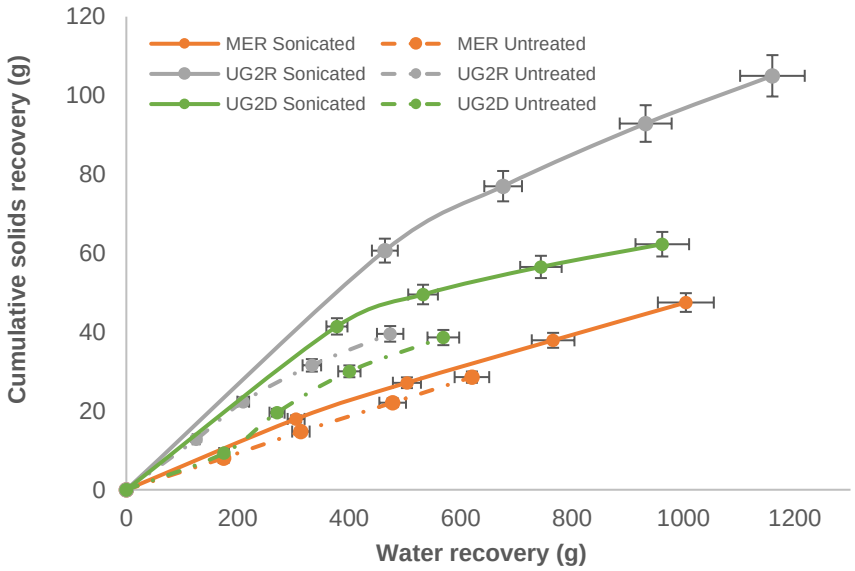


Figure 6.24: Solids vs. water recovery for all untreated and sonicated tailings, floated in 200 g/t SIBX

In line with the solids, the water recoveries also increased when the tailings were sonicated. UG2R saw the highest increase, going from 474 to 1160 g water recovery. MER saw the lowest increase; going from 620 to 1004 g water recovery. Based on the material recoveries, it can be posited that loose fines stabilised the froth further.

If it is assumed that the solids increased purely, and solely as a result of the mechanical cleaning and the resultant improved mineral-collector interaction, it must also be the case that the froth phase likely contained more hydrophobic particles, and perhaps, that the films ruptured and drained water and gangue materials back to the pulp phase. Two things would happen as a direct result. Firstly, the valuable minerals stood a better chance of being recovered since they now had

more active sites; as demonstrated in Section 6.1.2., chalcopyrite stood a better chance. Secondly, the mineral grades stood a chance of improving since the gangue materials would be drained back to the pulp phase. However, as can be seen in Figure 6.25 and Figure 6.26, this was not exactly the case. Figure 6.25 compares the copper recoveries between untreated and sonicated tailings, and Figure 6.26 does the same for nickel.

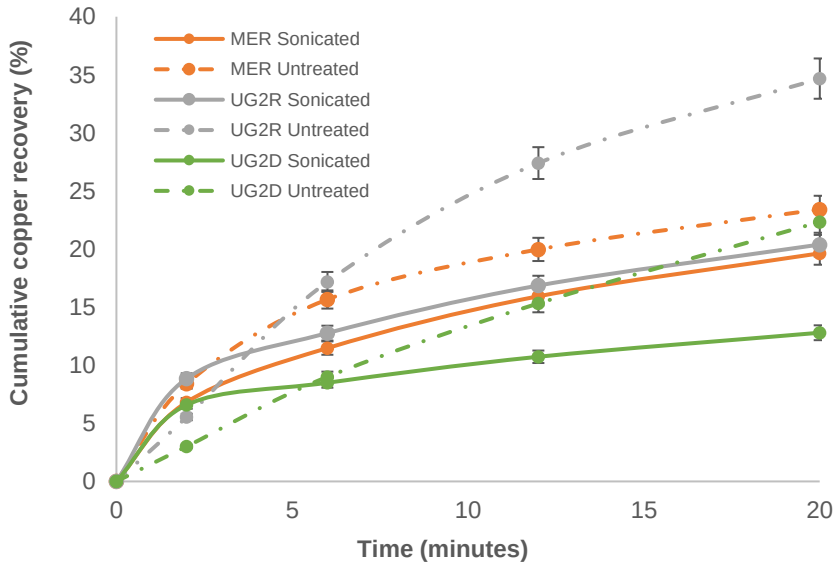


Figure 6.25: Copper time-recovery curves for untreated and ultrasonicated tailings when floated in 200 g/t SIBX

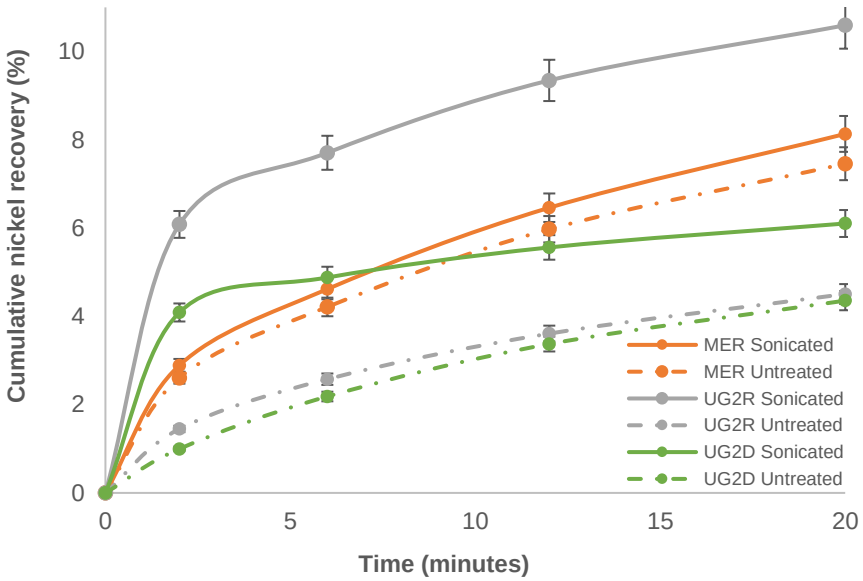


Figure 6.26: Nickel time-recovery curves for untreated and ultrasonicated tailings when floated in 200 g/t SIBX

Copper recoveries decreased when the tailings were sonicated. The copper associated with UG2R was the most sensitive to sonication, decreasing from 34.6 to 20.4% recovery. MER-copper was the least sensitive, showing a slight drop from 23.4 to 20.4% recovery. This shows that cleaning the surfaces (or loosening the species present in these tailings) with sonication did not improve

the floatability, and perhaps the hydrophobicity, of chalcopyrite. Contrary to this, the nickel recoveries increased, showing that for pentlandite, cleaning the surfaces with sonication likely improved the natural floatability of the particles.

Although the valuable minerals behaved differently, and somewhat unexpectedly, when it came to overall mutability, UG2R showed the biggest change, MER showed the smallest, and UG2D lay in the middle. The nickel recovery in sonicated UG2R increased from 4.36 to 10.6%; but in MER, it only increased from 7.46 to 8.13%.

The final copper and nickel grades are shown in Figure 6.27 and Figure 6.28, respectively. The value minerals behaved similarly here, both copper and nickel grades decreased. MER showed the biggest dip for copper (from 1358 to 557 ppm) and nickel (from 1455 to 1069 ppm). UG2D showed the smallest dip for copper (from 496 to 127 ppm) and nickel (from 1159 to 965 ppm).

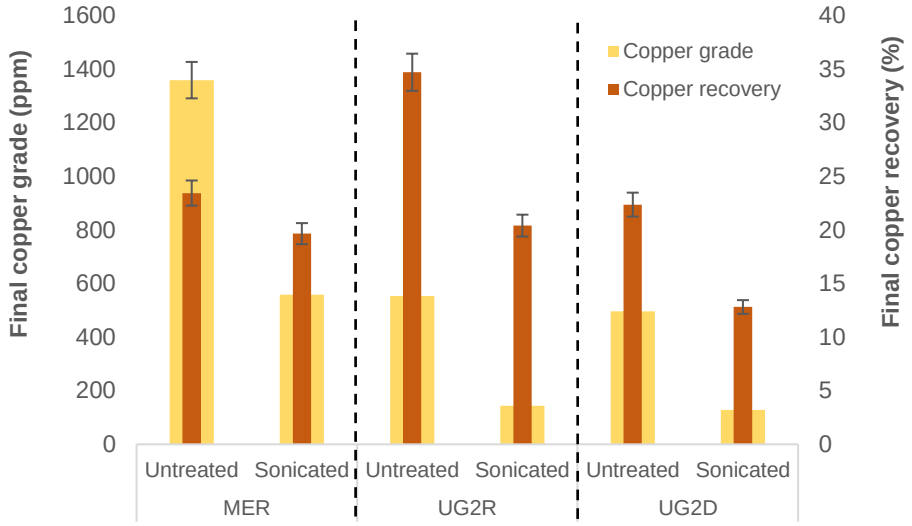


Figure 6.27: Final copper recovery and grade for all untreated and sonicated tailings when floated in 200 g/t SIBX

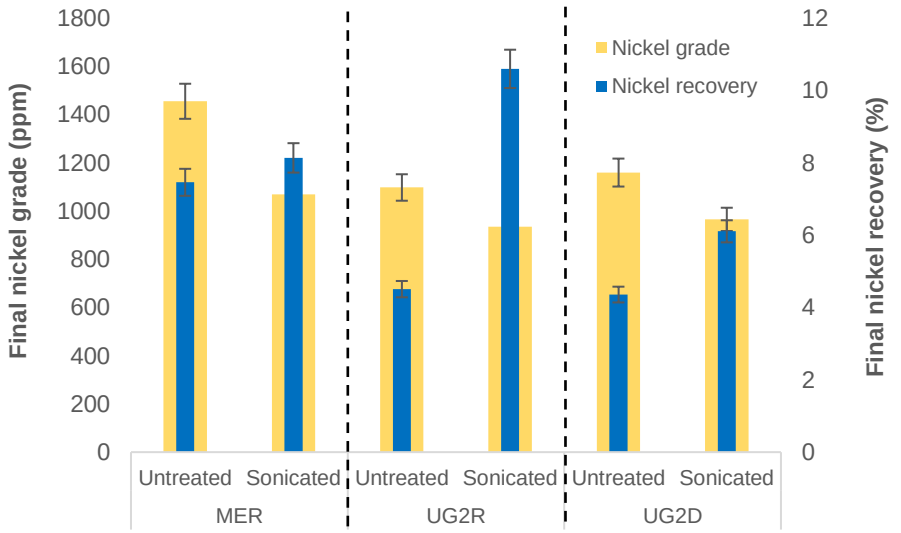


Figure 6.28: Final nickel recovery and grade for all untreated and sonicated tailings when floated in 200 g/t SIBX

Another indicator that was analysed, was the collector effect and/or behaviour, as SIBX was shown in the two previous sections to be effective in influencing the tailings' performance. Figure 6.29 shows the SIBX adsorption profiles for when the tailings were untreated, and when they were sonicated. The initial concentration in this case was 25 ppm.

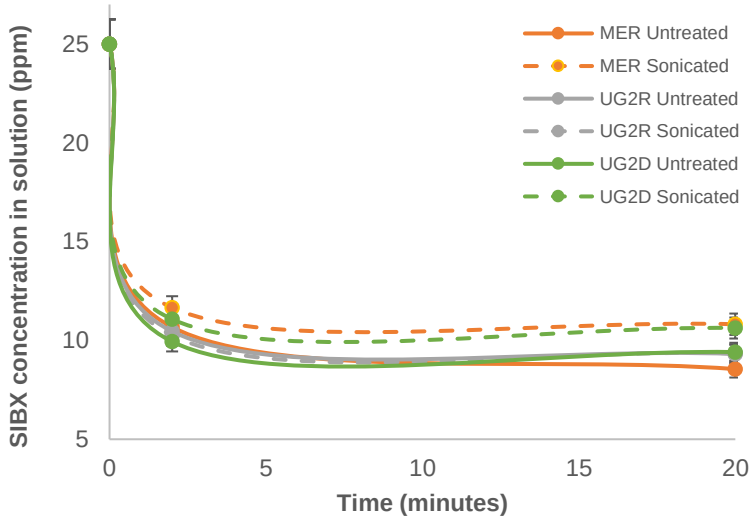


Figure 6.29: Residual concentrations of SIBX for untreated and sonicated tailings

As can be seen in Figure 6.29, there was very little difference in the adsorption profiles. The same amount of SIBX remained in solution at the end of all tests. This suggests that with or without ultrasonication, each tailings likely achieved the same mineral-collector interaction, further suggesting that collector-induced hydrophobicity was likely not improved by sonication. And if the floatability was not improved by increased hydrophobicity, it lends more credence to the position of increased entrainment.

A possible explanation to the different behaviours of chalcopyrite and pentlandite is as follows: chalcopyrite is naturally faster-floating and more active than pentlandite; when the tailings were untreated, chalcopyrite therefore had an advantage over pentlandite as it relied on its own natural floatability as well as better interaction with the collector. However, when the mineral surfaces were cleaned and more active sites became available on the pentlandite, the SIBX that was available for abstraction was likely more evenly distributed between the two minerals, adsorbing less selectively, providing the slower-floating mineral with increased collector-induced floatability.

In true flotation complexity, all of these factors – entrainment and particle hydrophobicity – likely affected each other as explained, producing the presented results. This part of the study thus answered the question: ***what happens to the flotation of the tailings when their surfaces are mechanically cleaned using ultrasonication?*** The answer is that more solids will be recovered, compromising mineral grades. Copper recovery will also suffer, but nickel recovery will increase.

6.2. Batch Flotation of the Deslimed Tailings

This section will analyse the batch flotation of deslimed tailings. In the context of this study, desliming means a certain size fraction was removed from the bulk and discarded. In this case, particles smaller than 25 µm were screened out, and only particles larger than 25 µm were floated. A summary of the scope is shown in Figure 6.30.

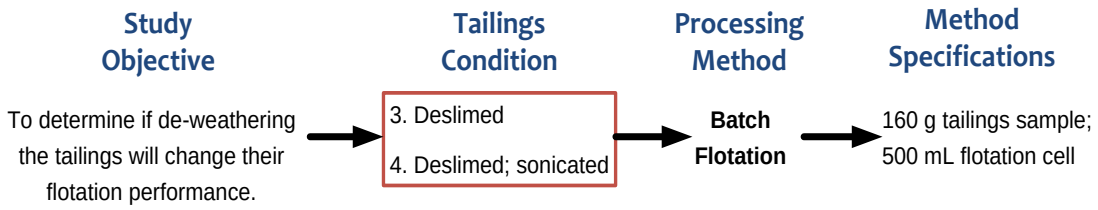


Figure 6.30: The scope of Section 6.2.

6.2.1. Technical Motivation for Desliming

As the effect of cleaning the mineral surfaces through ultrasonication was shown to have a detrimental effect on the chalcopyrite recovery, in particular, it was worth investigating another method. Section 6.1.2. showed that an increase in collector adsorption favours key performance markers, and it was the only trial thus far to yield positive results. The study therefore considered exploiting this finding further.

Crawford and Ralston (1988) have shown that at the same surface coverage of hydrophobic species, intermediate size particles float faster than fine particles. Moreover, a study by Phiri et al. (2019) has shown that desliming an ore (Kansanshi mixed copper) material by simply sieving out the finer fraction can improve the flotation of chalcopyrite. Desliming the tailings in this study therefore stood a chance of hitting two birds with one stone. Firstly, the fine fraction would be decreased, theoretically providing the +25 µm particles with a better chance of interacting with the collector more optimally. Secondly, the tailings would be easier to handle in sub-processes such as filtration/dewatering. It was also assumed that since the +25 µm sample would still fulfil the recommended lower limit of -10 µm, sufficient flotation of the tailings could still be achieved.

The obvious drawback with desliming, was the potential destabilisation of the froth, as finer particles, currently absent from the samples, tend to do (Bruckard et al., 2011; 2011; Lovell 1982). The second disadvantage became apparent when a mineralogical analysis of three size fractions of all the tailings showed that a significant portion of the chalcopyrite was contained in the -25 µm size fraction (28.2% for MER, 49.2% for UG2R, and 43.1% for UG2D). The objective here, was therefore to test whether the remaining chalcopyrite could be optimally recovered by exploiting the discussed aspects. This section therefore deals solely with the flotation of deslimed tailings.

6.2.2. Practical Motivation for Desliming

Particle settling tests were conducted to measure whether there was a practical advantage to desliming. The slurries were so murky, and the fine particles took so long to settle, that the turbidity metre was not immediately able to make measurements. See Figure 6.31 for examples of the MER experiments photographed at a time the turbidity metre was unable to make the measurements, and after it was able to do so.

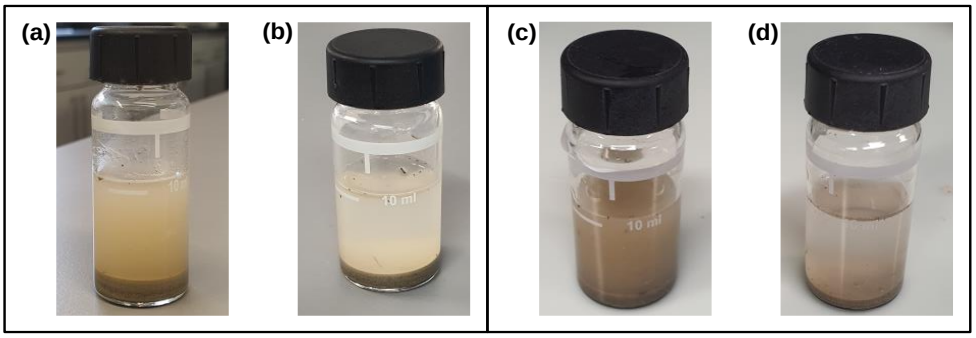


Figure 6.31: The particle settling tests for the MER tailings; (a) untreated MER before turbidity test, (b) untreated MER after test, (c) deslimed MER before test, (d) deslimed MER after test

Figure 6.32 compares the time it took for the metre to be able to make measurements, for all untreated tailings, and for deslimed tailings.

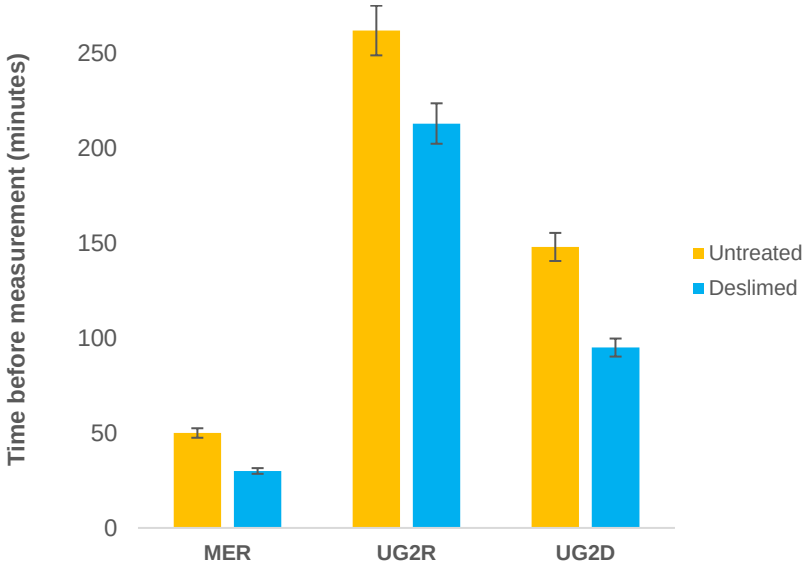


Figure 6.32: The time elapsed before the turbidity metre could take measurements of each tailings' turbidity

Figure 6.33 compares the turbidity measurements of the tailings, and shows that MER's turbidity decreased faster than that of UG2R and UG2D. It also shows that the turbidity of all deslimed samples decreased faster than that of their untreated counterparts. 1000 NTU is the highest measurement the metre can read, and was therefore the first turbidity reading for all tailings and tested conditions.

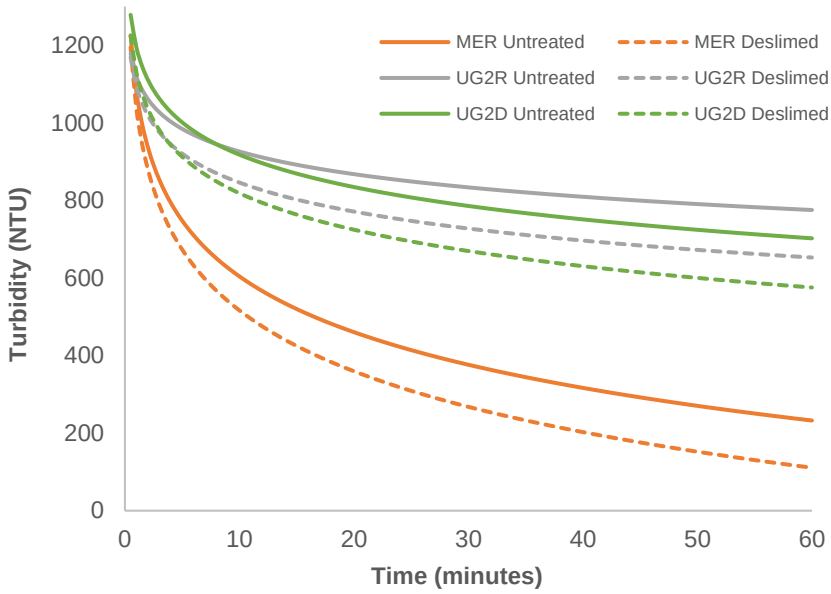


Figure 6.33: The turbidity of the tailings against time

The graphs in Figure 6.33 are governed by Equation 6.1; from this, the settling rate of each tailings was determined as the slope of each graph (Coulson et al., 1999).

$$y = -A \cdot \ln(x) + B \qquad 6.1$$

The obtained setting rates are presented in Figure 6.34.

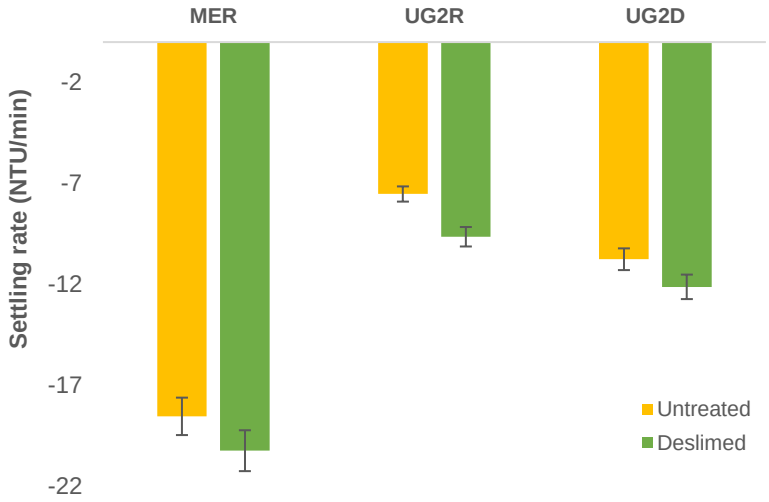


Figure 6.34: The settling rates of the untreated and the deslimed tailings

Figure 6.34 confirm that MER has a higher settling rate than UG2R and UG2D. The figure also confirms desliming the tailings improved their settling rates. To put these rates into context, when investigating the impact that residual reagents in recycled process waters have on the flotation of a Merensky ore, Khan (2023) showed that the fresh ore's settling rates range between -203 and -139 NTU/min, depending on pulp reagent conditions. By comparison, the fastest settling tailings in the present study was deslimed-MER at a mere -20.3 NTU/min.

The deslimed MER particles thus settle at a rate that is at least 6.85 times slower than when a fresh Merensky ore is treated with various combinations of flocculants and coagulants. It can thus be expected that when processing these tailings, the dewatering process will prove challenging, hence the need to attempt mitigating the processing issue by desliming.

6.2.3. Batch Flotation Results

Section 6.1.3. showed that ultrasonicating the tailings does not significantly alter SIBX adsorption; further, that ultrasonication hinders the performance of chalcopyrite and improves pentlandite recovery. It was worth investigating whether ultrasonicating deslimed tailings would induce similar behaviour. Thus, a set of tests in which the deslimed tailings were ultrasonicated, was conducted.

Figure 6.35 compares the overall solids recovered (as a function of time) when the tailings were deslimed ("Deslimed" in the figure legend), and when they were deslimed *and* ultrasonicated ("Sonicated" in the figure legend). The collector dosage in all cases was 200 g/t SIBX.

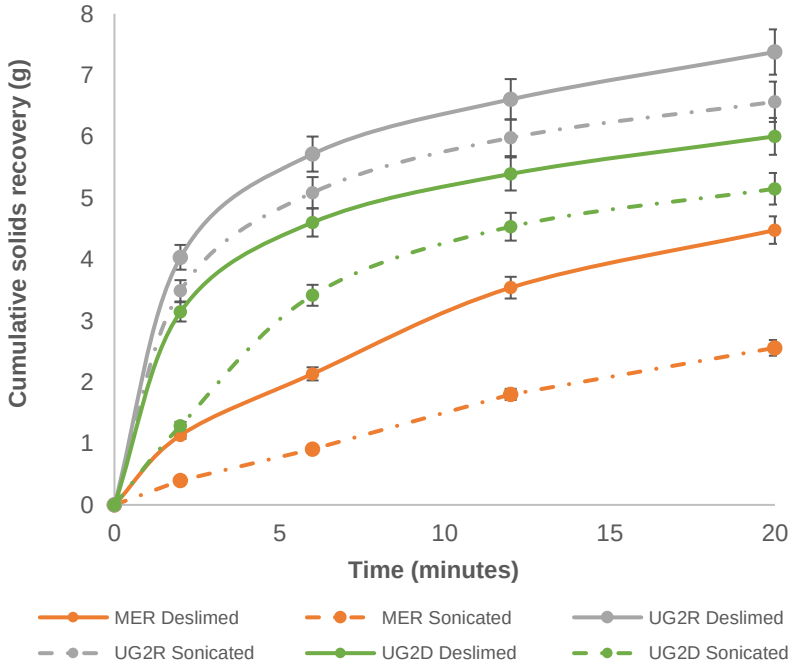


Figure 6.35: The recovery of solids against time, for all deslimed and deslimed-sonicated tailings, under 200 g/t SIBX

For all three tailings, ultrasonication impeded the amount of recovered solids. UG2R had the highest recovery, although it should be noted, this was only 7.34 g when simply deslimed, and 6.57 g when deslimed and sonicated. MER showed the lowest recoveries. A similar pattern was seen for the water recoveries (see Figure 6.36).

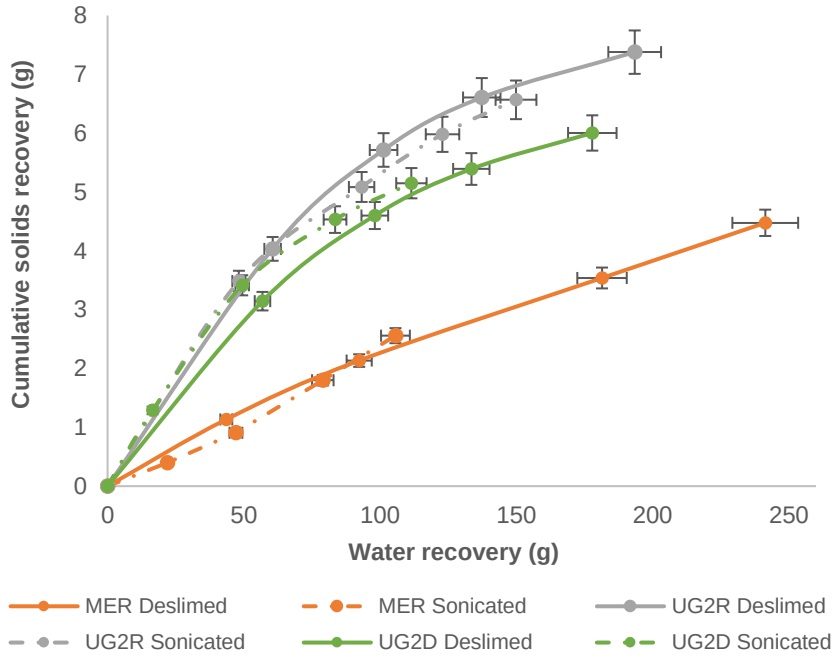


Figure 6.36: Solids vs. water recovery for all deslimed and deslimed-sonicated tailings, floated in 200 g/t SIBX

Figure 6.37 compares the copper recoveries, while Figure 6.38 compares the nickel recoveries. For copper, with the exception of MER, ultrasonication improved the recovery. This was the first instance where, for the same condition, one tailings showed an opposite behaviour to the other two. In all preceding cases, when the surfaces were similarly treated, for example, when they were all floated with CMC, all of them yielded lower copper recoveries. In this current case, however, MER was also the most sensitive to sonication, its copper recovery dropping from 15.9% to 9.54%. Both UG2 tailings saw (slight) recovery copper recovery rises of roughly 2.08%.

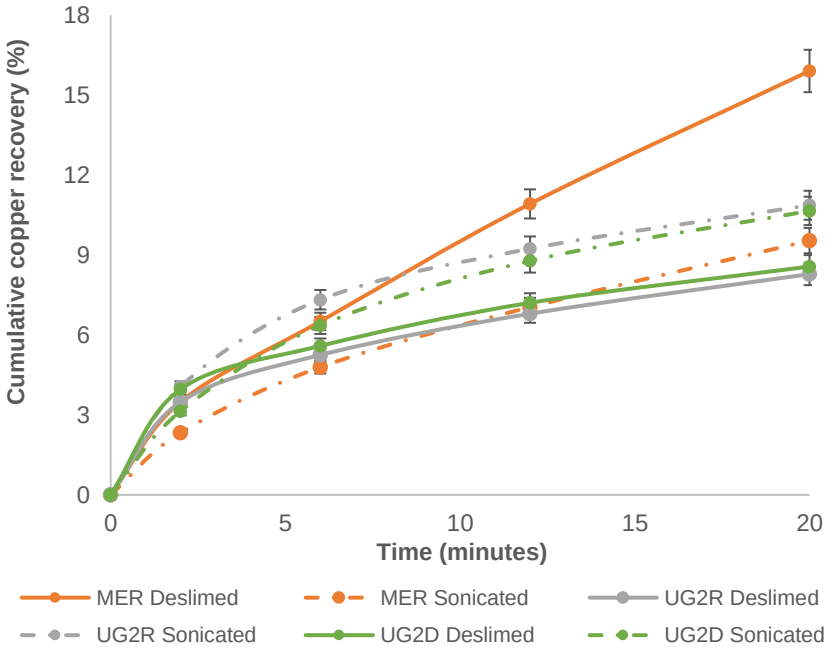


Figure 6.37: Copper time-recovery curves for deslimed and deslimed-sonicated tailings when floated in 200 g/t SIBX

For nickel, ultrasonication reduced recovery for all tailings. This was a return-to-form of overall behaviour, in that each surface condition induced a similar performance across all tailings, decreasing the nickel recovery when the deslimed tailings were sonicated. UG2R and MER were the joint best performers, with a deslimed recovery of 5.38%. However, MER was the most sensitive to change; the nickel recovery dropped to 4.56% when the tailings were sonicated.

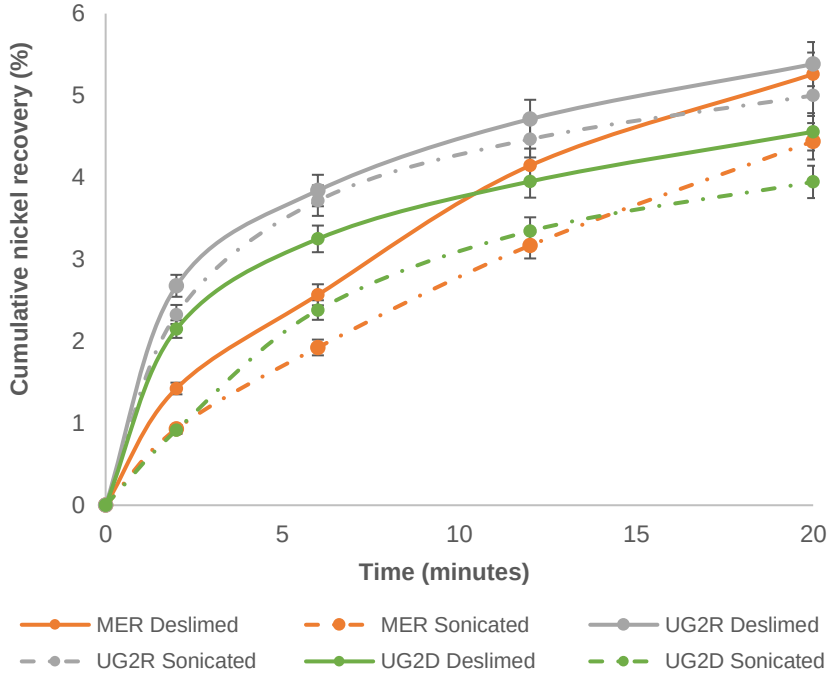


Figure 6.38: Nickel time-recovery curves for deslimed and deslimed-sonicated tailings when floated in 200 g/t SIBX

Figure 6.39 compares the final copper grades for all deslimed and deslimed-sonicated tailings, and Figure 6.40 does the same for nickel.

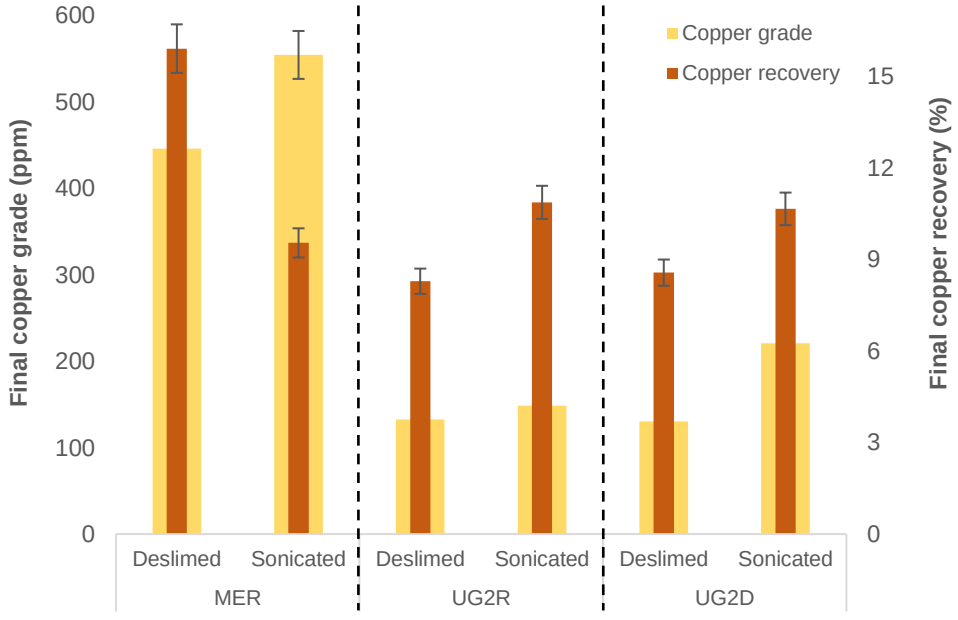


Figure 6.39: Final copper recovery and grade for deslimed and deslimed-sonicated tailings floated in 200 g/t SIBX

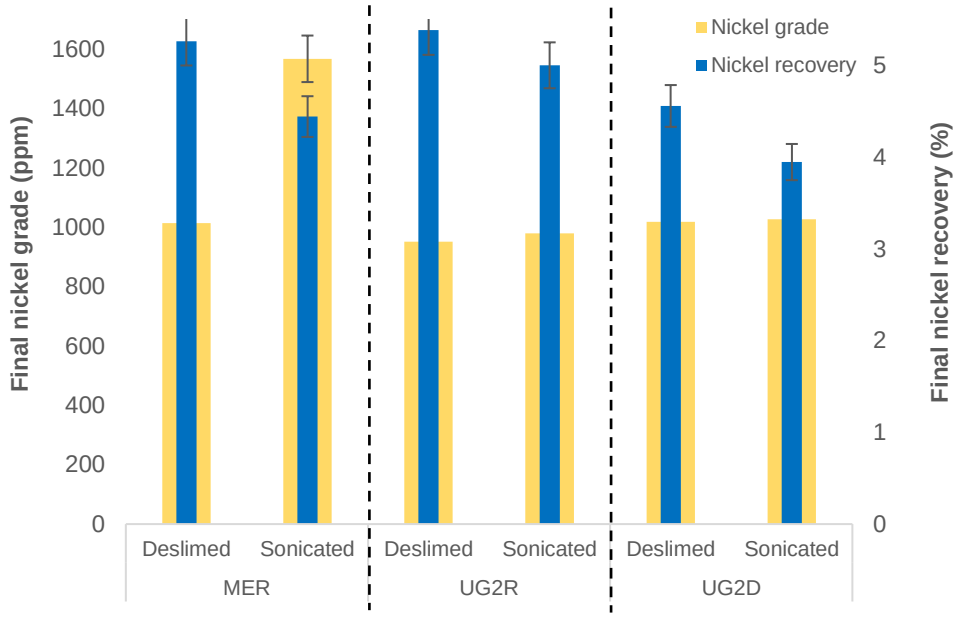


Figure 6.40: Final nickel recovery and grade for deslimed and deslimed-sonicated tailings floated in 200 g/t SIBX

Both copper and nickel grades improved when the deslimed tailings were sonicated; and for both metals, the increase was more pronounced in MER (446 to 554 ppm for copper, and 1014 to 1516 ppm for nickel). The improved grades were expected since the total solids recoveries were lower for the deslimed-sonicated tests. Moreover, it was expected that in reducing the fraction of fine particles, the overall surface area for each bulk would decrease accordingly. This is because the large specific surface area of fine particles increases the adsorption capacity of reagents on a mass basis. While more of any reagent might be adsorbed in the presence of fine particles, a significant ratio of it may not be available for the flotation of larger particles; leading to decreased value mineral recoveries (Chander, 1978; Phiri et al., 2019). Figure 6.41 compares the adsorption profiles of SIBX for deslimed and deslimed-sonicated tailings (for an initial concentration of 25 ppm).

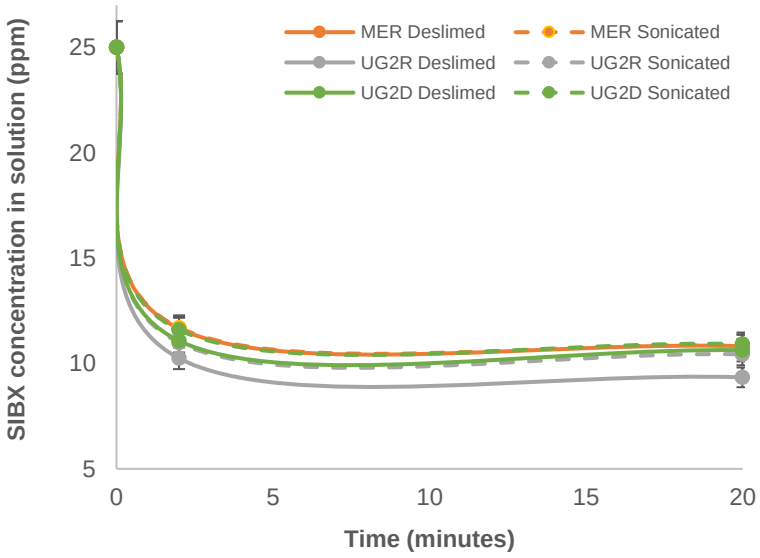


Figure 6.41: Residual concentrations of SIBX for deslimed and deslimed-sonicated tailings

There was no significant difference in the adsorption profiles, meaning similar amounts of SIBX were adsorbed whether or not the deslimed tailings were sonicated. Similar to the untreated tailings, it is possible that ultrasonicating the deslimed tailings shook loose slimes still coating the mineral surfaces, reversing some of the effects gained from the desliming. The gains made in recovery and grade were only marginal, possibly owing to the fact that as shown by the sized mineralogical profiles (Figure 5.6, Figure 5.8, Figure 5.9 and Figure 5.10), a large fraction of the sulphides as well as the better liberated particles were absent from the deslimed systems. Thus, any advantages resulting from more collector being made available for the larger specific surface area of the coarser particles, was mitigated by the particles' reduced sulphide and liberated content.

A comparison was then made between the adsorption profiles of the deslimed tailings, and that of the untreated tailings, simply to assess whether removing the finer size fraction produced the desired effect – that of making more collector available for the coarser fractions. The results are shown in Figure 6.42 (for an initial SIBX concentration of 25 ppm).

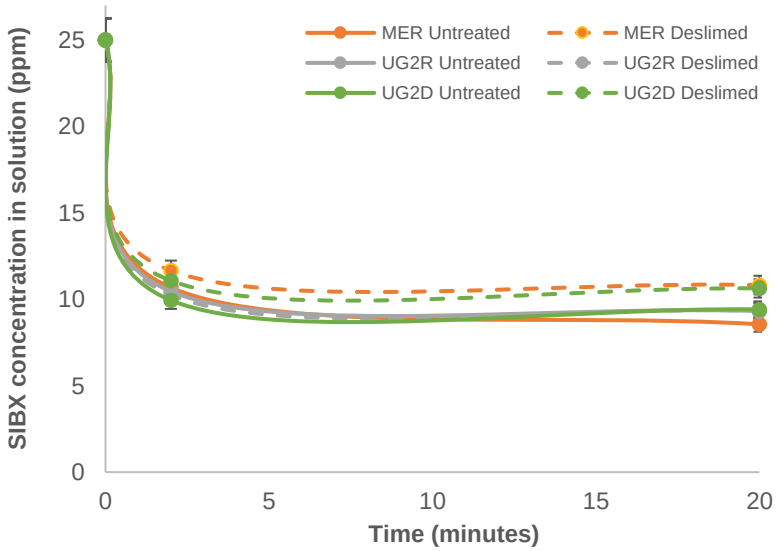


Figure 6.42: Residual concentrations of SIBX for untreated and deslimed tailings

There was no significant difference in the adsorption profiles, meaning similar amounts of SIBX were adsorbed whether or not the tailings were deslimed, perhaps indicating that the larger particles now interacted with the collector more efficiently. However, this did not produce any measurable gains since, as already discussed, desliming the tailings significantly reduced their recoverable value.

The only true advantage of desliming then becomes the easier physical processing of the tailings. This part of the study therefore answered the question: ***what happens when the tailings are deslimed to fit the available processing parameters?*** The answer is that for the investigated discarded size fraction, the floatability of the tailings becomes reduced, as a significant fraction of the recoverable value is comprised in the discarded value.

7. A CONSOLIDATED DISCUSSION OF THE STUDY

Chapter 5 demonstrated that MER, UG2R and UG2D are distinct enough for the EDTA extraction, and oxygen reactivity methods to measure unique oxidation indices and oxygen consumption factors; moreover, that the present minerals can be altered by ultrasonication, desliming, and a combination of the two. The changes induced by these alteration methods produced surfaces that were also amenable to the EDTA extraction and oxygen reactivity methods.

Chapter 6 demonstrated that the tailings were floatable; moreover, that changes made to the mineral surfaces affected the efficiency of the process to separate pentlandite and chalcopyrite from the present gangue minerals. The chapter further demonstrated that reagent variation, or more specifically, SIBX and CMC quantities, affected the flotation of valuable minerals.

This chapter aims to assess whether the parameters determined in Chapter 5 behaved in patterns that favour or hinder ideal flotation (Chapter 6), i.e. whether the extraction indices and oxygen consumption rate constants correlated to flotation. The objective relevant to this chapter is thus:

- To determine whether the qualitative characterisation of any tailings bulk can be used to predict its flotation performance, or explain it.

7.1. The Relationship between EDTA Indices and Flotation

The EDTA extraction results showed that the copper and iron species in the tailings were oxidised to different levels. UG2D had the highest copper indices, while MER had the lowest. In short, and according to the results, UG2D comprises higher secondary copper species, and more oxidised copper minerals than MER and UG2R.

Several studies have shown that flotation depends on the differences in the surface properties of the present minerals, and that surface oxidation influences flotation efficiency. Minor oxidation forms hydrophobic sulphur species that are produced on the mineral surfaces, and therefore positively influences the flotation of all principal sulphides. However, excessive oxidation produces hydrophilic ferric hydroxides, and therefore impedes flotation (Becker et al., 2010; Kelebek, 1993). Hence, it can be predicted that for the same experimental conditions such as reagent dosage, air flowrate, pulp density, impeller speed, etc., UG2D will show the poorest copper performance, while MER or UG2R will show the best. Figure 7.1 summarises the copper extraction indices, and compares the relevant final copper recoveries for the untreated and sonicated tailings. Figure 7.2 does the same for the deslimed systems. The reagent scheme for the tests was 50 g/t DOW200, 200 g/t SIBX, and no CMC.

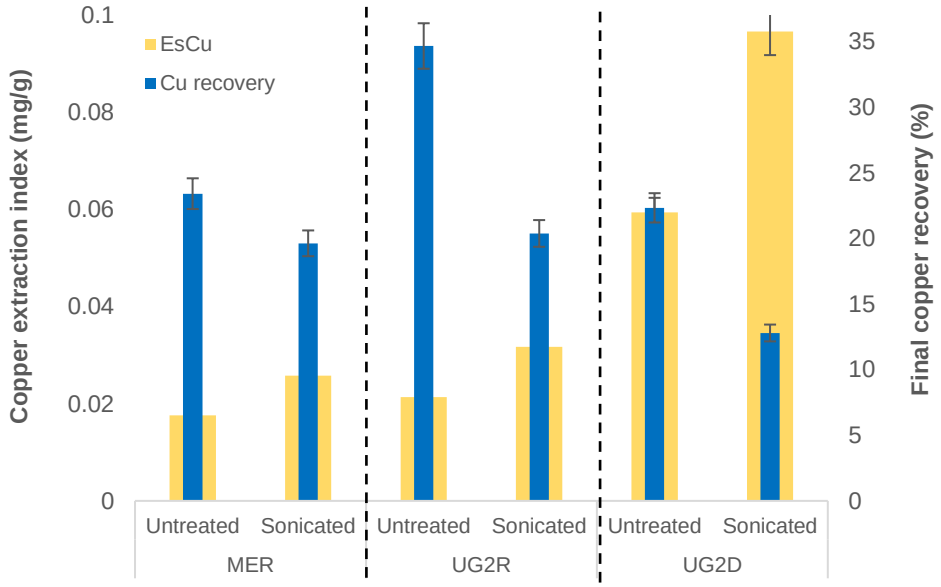


Figure 7.1: Copper EDTA extraction indices, and final copper recoveries for untreated and sonicated tailings

Figure 7.1 shows that indeed, a rise in the EDTA-extracted copper was complemented by a drop in copper recovery for all tailings, with UG2D having the poorest recovery performance under every investigated condition. The highest copper recovery in the study was produced by the untreated UG2R bulk; which also produced one of the lowest copper indices.

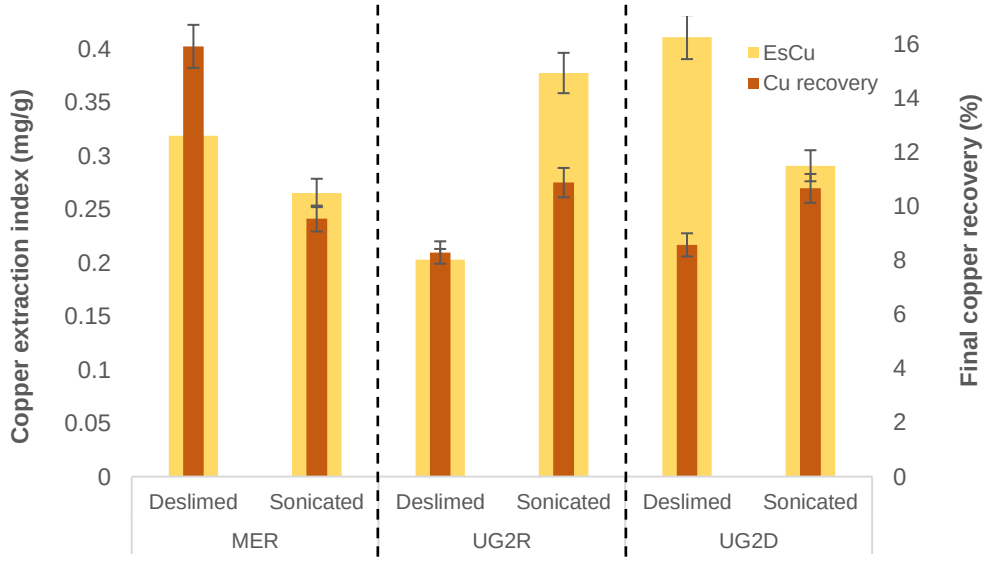


Figure 7.2: Copper EDTA extraction indices, and final copper recoveries for deslimed and deslimed-sonicated tailings

When the tailings were deslimed, as shown by Figure 7.2, the UG2D copper indices remained higher than their MER counterparts, and the copper recoveries were higher in MER-flotation. However, contrary to the study's expectation, for the MER and UG2R deslimed tailings, a decrease in the copper extraction index was complemented by a drop in copper recovery.

The key difference between Figure 7.1 and Figure 7.2, is that the former represents the untreated and sonicated tailings, while the latter represents only the +25 µm fraction. The seemingly

contradictory trend of results is, therefore, likely due to two phenomena. Among these phenomena is the following: in the absence of some of the slime coatings removed with the sub-25 µm particles, ultrasonication was able to be more effective in preparing the surfaces for flotation in the deslimed systems. The coarser particles then interacted with the collector more optimally, improving copper flotation. Secondly, the extraction indices were primed to increase since, as was seen with the untreated systems (Figure 7.1), ultrasonication of the tailings produces this result.

On the surface it seems that the results presented in Figure 7.2 are contradictory when, in fact, they elucidate a complex combination of parameters, giving motivation to treat the batch flotation systems of the full and deslimed tailings as fundamentally different from each other. Moreover, the stepwise flotation of the untreated bulk (Section 6.1.) demonstrated that while the copper extraction index informs on the degree of oxidation of the copper species, it does not mean the oxidation cannot be mitigated. For example, untreated MER has a copper extraction of 0.0176 mg/g, and when these tailings were floated with 125 g/t SIBX and 175 g/t CMC, they yielded a copper recovery of 8.99%. When the same tailings were floated without CMC and with 125 g/t SIBX, the copper recovery increased to 19.7%. When the SIBX dosage was increased to 200 g/t, the copper recovery reached 23.4%. UG2R and UG2D exhibited similar trajectories (see Figure 7.3). In short, for same the copper extraction index, a change in the reagent dosages was able to mitigate, within given limits, the poor flotation predicted by the oxidation index.

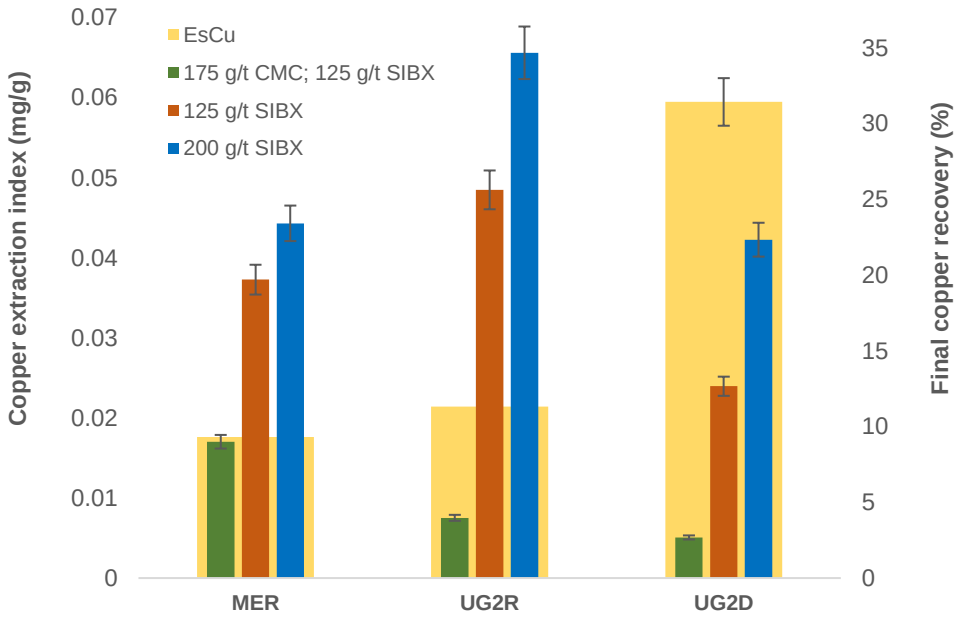


Figure 7.3: A comparison of the final copper recoveries for untreated tailings floated under different reagent schemes

The study previously predicted that, as higher extraction indices indicate more pronounced surface oxidation, poorer flotation (in terms of value mineral recoveries, or more specifically, copper-bearing minerals) can be expected for tailings with higher copper extraction indices.

The observations show the following: for MER, UG2R and UG2D, the correlation between EDTA extraction and the copper flotation performance, is limited within either of the investigated systems – full and deslimed. Within the investigated parameters, for the full tailings system, higher extraction indices indicated poorer copper recovery. In the deslimed system, the opposite was true. In both cases, the system parameters can be adjusted to improve the copper recovery, thus overcoming the poor natural flotation performance indicated by the copper extraction index.

7.2. The Relationship between Oxygen Reactivity and Flotation

Several studies have shown that dissolved oxygen has a significant effect on the pulp potential of a slurry, and on the rate of xanthate adsorption. The oxidation of sulphide surfaces depends on, among other factors, the electrochemical activity of the sulphide minerals and the amount of available oxygen. An increase in the concentration of dissolved oxygen leads to an increase in pulp potential and improved xanthate adsorption (Kuopanportti et al., 1997; Woods, 1971).

Since the investigated tailings yielded different oxygen consumption rate constants, it must be the case that they demonstrated different electrochemical reactivities and influenced different SIBX adsorption profiles. The reliability of this statement was tested by assessing the oxygen reactivity results against pulp potential values and SIBX adsorption profiles.

Table 7.1 summarises the oxygen consumption rate constants against slurry pulp potentials, SIBX consumption in a 10 and 25 ppm dosage system, and material recoveries, all for untreated and ultrasonicated tailings. Measurements relevant to the pulp potentials were made at the same time, by the same probe that measured the oxygen concentrations. The obtained oxidation-reduction potential values were then converted to Eh by adding 200 mV (YSI Environmental, 2001). The initial Eh of slurries has been shown to have a significant influence on the batch flotation of the present sulphide minerals (Graham and Heathcote, 1982; Johnson et al., 1982).

Of the untreated tailings, UG2D was the least reactive to oxygen; its consumption rate constant was the lowest (and it naturally held less dissolved oxygen). MER had the second lowest constant, and UG2R had the highest. UG2D's pulp potential values were, indeed, the highest, and its SIBX consumption and copper recovery were the lowest. UG2R also yielded the highest pulp potential value as well as copper recovery. Nickel, on the other hand, was better recovered in MER; and the values observed for the UG2 tailings were both lower, and nearly identical to each other.

When the tailings were ultrasonicated, the oxygen consumption rate constants decreased for all tailings, their Eh values increased, and their copper recoveries dropped, conforming to study expectations. The nickel recoveries, however, were higher for the sonicated tailings.

Table 7.1: The electrochemical, SIBX adsorption and copper recovery data for untreated and sonicated tailings

Parameter	MER	UG2R	UG2D
Untreated Tailings			
k_La (min^{-1})	0.152	0.198	0.113
Eh (mV)	402	432	429
Total adsorbed SIBX (ppm); 10 ppm initial dosage	8.65	6.47	6.48
Total adsorbed SIBX (ppm); 25 ppm initial dosage	16.4	15.7	15.6
Total recovered solids (g)	28.6	39.5	38.6
Total recovered water (g)	620	474	569
Final copper recovery (%)	23.4	34.7	22.3
Final copper grade (ppm)	1360	553	496
Final nickel recovery (%)	7.46	4.51	4.36
Final nickel grade (ppm)	1450	1100	1160
Ultrasonicated Tailings			
k_La (min^{-1})	0.131	0.115	0.100
Eh (mV)	422	435	444
Total adsorbed SIBX (ppm); 10 ppm initial dosage	8.50	6.46	5.81
Total adsorbed SIBX (ppm); 25 ppm initial dosage	16.9	13.7	12.4
Total recovered solids (g)	47.5	105	62.3
Total recovered water (g)	1000	1160	962
Final copper recovery (%)	19.6	20.4	12.8
Final copper grade (ppm)	557	144	129
Final nickel recovery (%)	8.13	10.6	6.10
Final nickel grade (ppm)	1070	934	965

The different trends observed for copper and nickel are likely a result of various factors. When investigating the effects of pulp conditions on the flotation of a Cu-Pb Black Mountain ore, Ross and Van Deventer (1985) showed that increasing the dissolved oxygen in the pulp, leads to a reduced maximum recovery of galena, but has the opposite effect on chalcopyrite. That means changes in the pulp chemistry can have a different effect on the different target minerals.

In a study investigating the effect of recycled waters on the flotation of a Cu-Co oxide ore, Shengo et al. (2016) found that the accumulation of ionic species dissolved in solution had a detrimental effect on malachite, and a positive effect on heterogenite. In fact, several studies (Bulut and Yenial, (2016), Manenzhe (2018), and Ruan et al. (2018) among them) have shown that dissolved species can influence the target minerals of a polymetallic ore differently. In a study aimed at selectively floating pentlandite from a nickel ore, Senior et al. (1995) posited that the presence and nature of certain gangue minerals can also influence the flotation of target sulphides. For example,

pentlandite floated poorly in the presence of talc, but more positively in its absence. The flotation rate of chalcopyrite also decreased when more talc was added to a talc-chalcopyrite system, showing that the floatability of one mineral can reduce that of another.

Ross and Van Deventer (1985) posit that the increased sulphide mineral recoveries observed at higher concentrations of dissolved oxygen, possibly occur because "*the increased adsorption of molecular oxygen promotes dehydration of the sulphide minerals, which renders them more hydrophobic*." The study went on to show that copper-lead selectivity can be optimised by operating at compatible combinations of dissolved oxygen, pH and collector combinations (isopropyl ethylthionocarbamate combined with SIBX). In short, mineralogical and electrochemical qualities also affect different sulphides in a different way (Owusu et al., 2013; Van Deventer et al., 1993; Ross and Van Deventer, 1985).

In the present study, nickel recovery was favoured by less reducing pulps, while copper fared better in more reducing pulps. Both grades decreased in the less reducing pulp, i.e., when sonicated, and the total water and solids recoveries increased. Overall, more solids were recovered for the UG2 tailings. This is exemplified by Figure 7.4, which shows the non-cumulative solids per unit water recovered in the first concentrate (C1). Figure 7.5 does the same for the fourth concentrate (C4).

As previously discussed, Wiese (2009) has determined an entrainment factor from a linear relationship between the solids recovered per unit water, in which case, higher solids recoveries per unit water indicate increased entrainment. As both UG2 tailings consistently recovered more solids, yet sections 6.1.1 and 6.1.2 showed that untreated MER adsorbs more SIBX (possibly achieving higher hydrophobicity), it suggests that the respective gangue compositions influenced entrainment, and that entrainment was likely a bigger factor in the flotation of UG2R and UG2D.

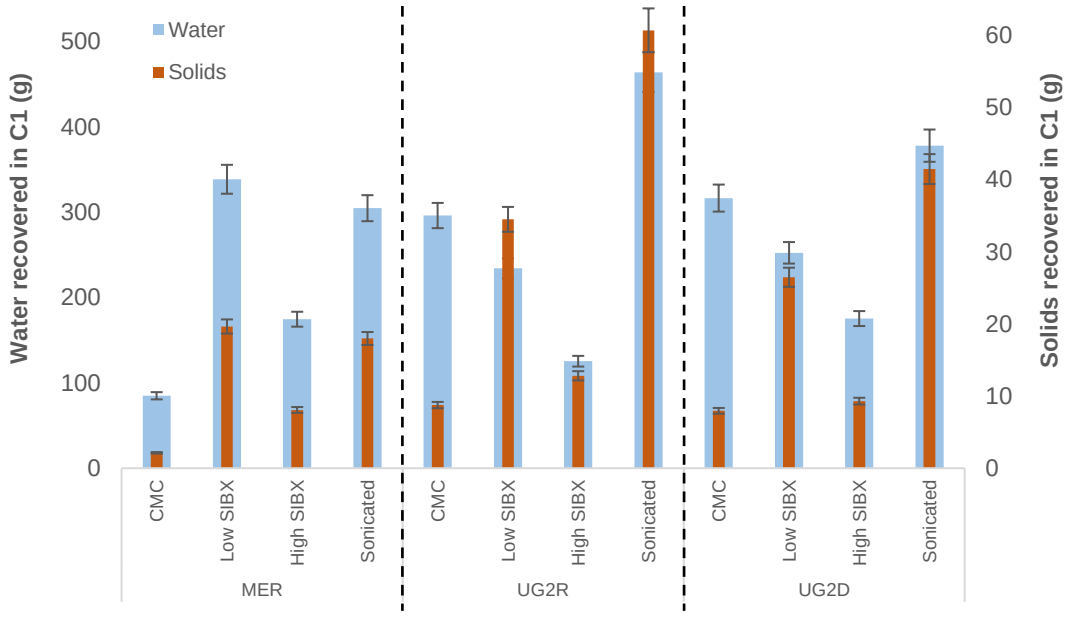


Figure 7.4: A comparison of the non-cumulative recovered solids per unit water in C1, for full tailings

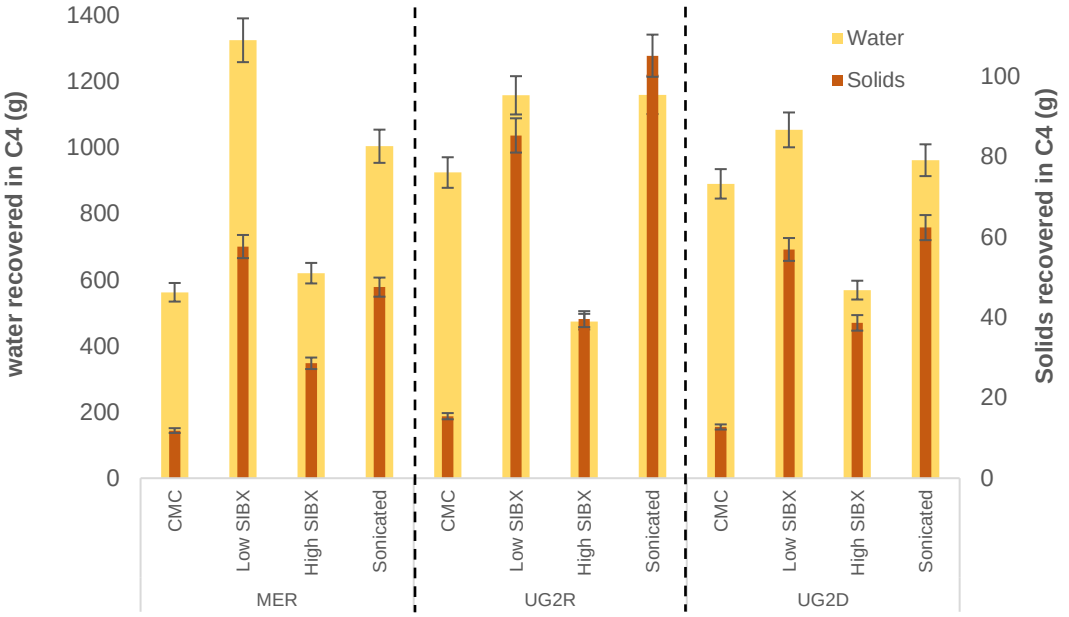


Figure 7.5: A comparison of the non-cumulative recovered solids per unit water in C4, for full tailings

An obvious drawback of UG2R and UG2D pulling more masses, as shown in Table 7.1, is that they consistently showed lower grades than MER.

The parameters concerning the deslimed systems (sub-25 µm) are shown in Table 7.2, which summarises the oxygen consumption rate constants against slurry pulp potentials, SIBX consumption in a 10 and 25 ppm dosage system, and material recoveries. The pattern was such that the deslimed tailings had lower oxygen consumption rate constants than their full (-25 µm included) counterparts, indicating an overall reduction in mineral surface activity. This difference was expected since, as shown in Figure 7.6, the sulphide fraction in each tailings was drastically reduced by the desliming process.

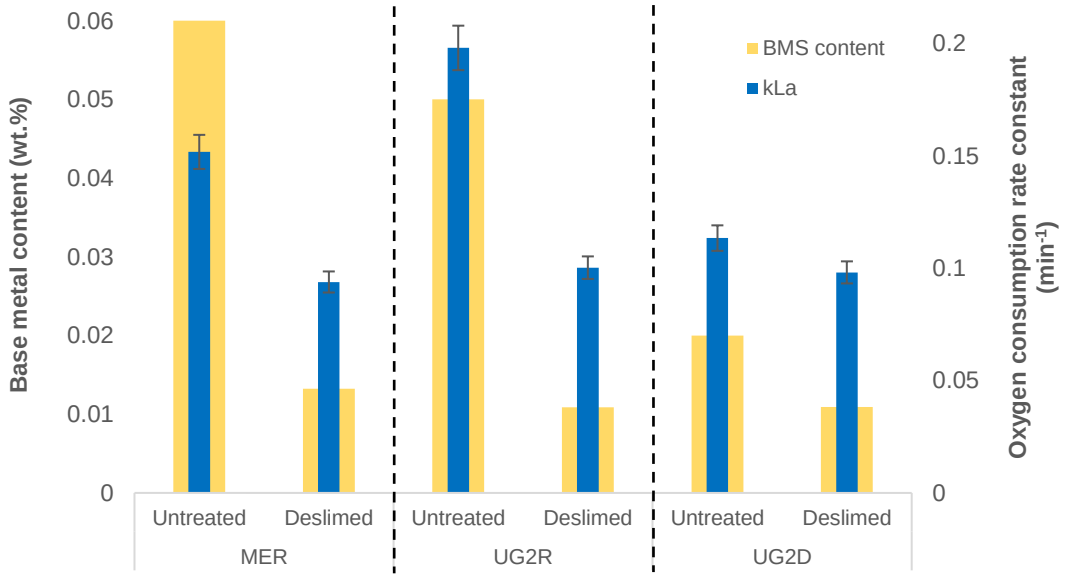


Figure 7.6: A comparison of the oxygen consumption rate constants for the untreated and deslimed tailings

The electrochemical nature of sulphide minerals is such that when they are in contact with one another, there will be electrochemical interaction in the form of electrons being transferred from the less cathodic mineral to a more cathodic one (Kirjavainen, 2002; Rao, 2004). It stands to reason that when some of the sulphides are removed, the galvanic interactions will be affected, and the electrochemical quality of the ore will change, as was the case with the present study, in which case, the pulp potentials increased along with decreasing sulphide fractions of the tailings.

Table 7.2: The electrochemical, SIBX adsorption and copper recovery data for deslimed and deslimed-sonicated tailings

Parameter	MER	UG2R	UG2D
Deslimed Tailings			
k_La (min^{-1})	0.0938	0.100	0.0981
Eh (mV)	447	482	480
Total adsorbed SIBX (ppm); 10 ppm initial dosage	6.69	5.27	7.48
Total adsorbed SIBX (ppm); 25 ppm initial dosage	14.2	15.7	14.4
Total recovered solids (g)	27.9	46.1	37.5
Total recovered water (g)	241	193	178
Final copper recovery (%)	15.9	8.29	8.57
Final copper grade (ppm)	446	133	131
Final nickel recovery (%)	5.26	5.38	4.56
Final nickel grade (ppm)	1010	951	1020
Deslimed-Sonicated Tailings			
k_La (min^{-1})	0.0979	0.0958	0.0959
Eh (mV)	461	476	465
Total adsorbed SIBX (ppm); 10 ppm initial dosage	5.24	5.09	5.52
Total adsorbed SIBX (ppm); 25 ppm initial dosage	14.2	14.6	14.1
Total recovered solids (g)	15.9	41.0	32.2
Total recovered water (g)	106	149	112
Final copper recovery (%)	9.54	10.9	10.7
Final copper grade (ppm)	554	148	221
Final nickel recovery (%)	4.44	5.00	3.95
Final nickel grade (ppm)	1570	979	1030

When the deslimed tailings were sonicated, the UG2R and UG2D oxygen consumption rate constants each showed a marginal decrease, and their Eh values also marginally decreased. MER's consumption rate constant alone, marginally increased, and so did its Eh. Nickel, solids, and water recoveries were all lower in the sonicated set; and perhaps as a consequence of the lower total solids, copper and nickel grades were higher in the sonicated set. Copper behaved uniquely in that for MER, sonication hindered its recovery, but in UG2R and UG2D, sonication favoured it.

Among the key differences between MER and the UG2 tailings, is that the chalcopyrite in MER was completely locked in the +53 µm fraction, while UG2R and UG2D showed varying degrees of liberation across all analysed size classes (Figure 5.6). It is possible that a phenomenon similar to that discussed in Section 6.1.3. took effect, and sonication allowed the SIBX to be more evenly distributed between the available minerals, perhaps adsorbing less selectively. In that case, MER-chalcopyrite, which was less liberated, might be less favoured by this occurrence as its floatability might have been boosted by its sheer fraction, which was lower in UG2R and UG2D (Figure 5.5).

UG2R and UG2D continued to yield higher solids per unit water masses, as exemplified by Figure 7.7, which shows the non-cumulative values for C4, for deslimed and deslimed-sonicated tailings. As a result, the copper and nickel grades were consistently higher in MER.

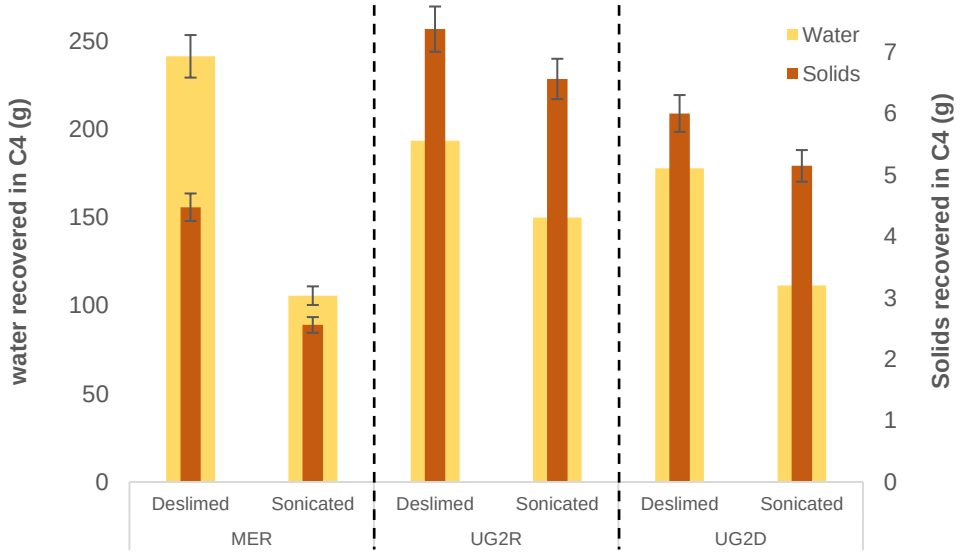


Figure 7.7: A comparison of the non-cumulative recovered solids per unit water in C4, for deslimed tailings

As a whole, desliming the tailings reduced the valuable fraction and drastically impeded flotation performance. It is, however, worth noting that the deslimed tailings floated, and that sonication showed the potential to improve copper performance in UG2R and UG2D, suggesting that under favourable conditions, sonication might be a viable option for these tailings. If a balance is struck between removing the absolutely deleterious slime materials, and retaining the larger fraction of the valuables, the desliming process might not be quite as detrimental as was the case in this study.

The study previously predicted that tailings which naturally hold less oxygen and have lower oxygen consumption rate constants will have less active sites and demand less oxygen, and their valuables will float more poorly. The observations show that for MER, UG2R and UG2D, better reactivity with oxygen can be used as an indicator of a tailings bulk's propensity for a reducing environment that will favour copper floatation.

7.3. The Correlation between EDTA Indices and Oxygen Reactivity

Lastly, the study aimed to assess whether the EDTA extraction indices and oxygen reactivity parameters correlated with one another. Table 7.3 summarises the resting oxygen concentrations for untreated and sonicated tailings, and Figure 7.8 summarises the corresponding k_La values when plotted with copper extraction indices.

Table 7.3: The resting oxygen concentrations for untreated and sonicated MER, UG2R and UG2D

Tailings	MER	UG2R	UG2D
A-Untreated (ppm)	7.11	9.54	4.64
A-Ultrasonicated (ppm)	6.13	5.34	4.34

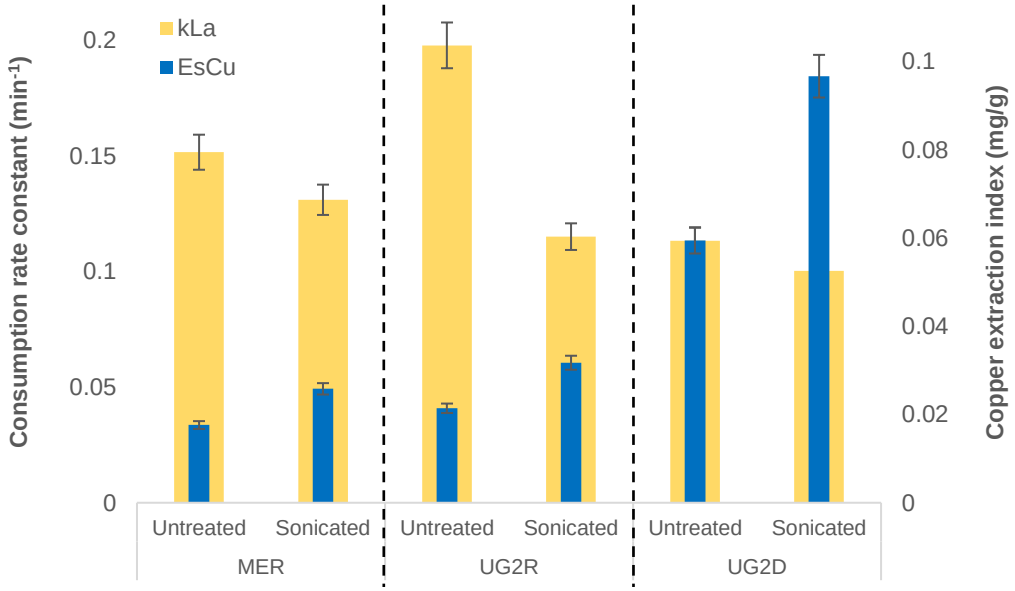


Figure 7.8: The k_La, A, and copper oxidation indices of untreated and sonicated MER, UG2R and UG2D

The observed pattern is such that, high copper extraction indices occur in cases where the tailings have a greater capacity to hold more dissolved oxygen, as indicated by their high A values, and react more readily with it, as indicated by their high k_La values. It infers a relationship in which, the (amount of) EDTA-extractable copper indicates the readiness of the copper species in that tailings to interact with oxygen. When the copper species are less oxidised, as indicated by their low extraction indices, the surfaces are more active and demand more oxygen, raising its capacity in the pulp and thus raising k_La and A. But as the surfaces become more oxidised, as indicated by their high extraction indices, they become more passive and demand less oxygen, lowering its capacity in the pulp and thus lowering k_La and A. And when the copper surfaces are more active, they interact more optimally with the dissolved species, the collector among them, perhaps attaching more optimally to the rising bubbles too; and as a result, the copper is better recovered. For the untreated tailings, UG2D-copper was the most oxidised, the least reactive to oxygen, and

poorly recovered via flotation. MER- and UG2R-copper were less oxidised, more reactive to oxygen, and better recovered. For the sonicated tailings, this trend continued, but the copper in each tailings was now more oxidised, less reactive to oxygen, and less recoverable via flotation.

Table 7.4 summarises the resting oxygen concentrations for deslimed and deslimed-sonicated tailings, and Figure 7.9 depicts the corresponding k_La values plotted with copper extraction indices.

Table 7.4: The resting oxygen concentrations for deslimed and deslimed-sonicated MER, UG2R and UG2D

Tailings	MER	UG2R	UG2D
A-Deslimed (ppm)	4.68	4.24	4.46
A-Deslimed-sonicated (ppm)	4.42	4.22	4.50

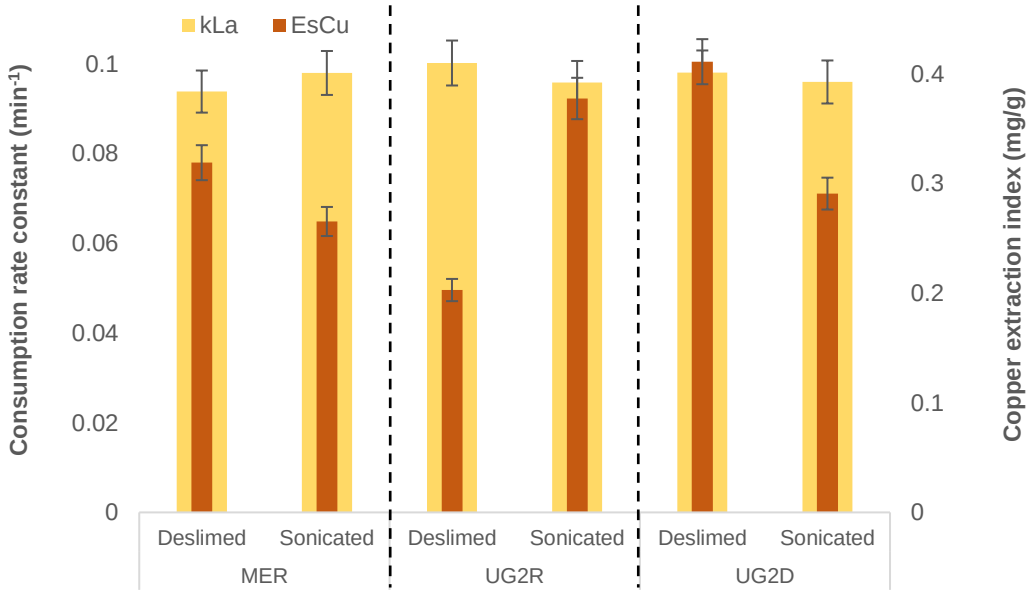


Figure 7.9: The k_La, A and copper oxidation indices of deslimed and deslimed-sonicated MER, UG2R and UG2D

The observed pattern was the same as that seen for the full tailings. The copper extraction indices continued to have an inversely proportional relationship with k_La and A. Sonication, once again, decreased reactivity to oxygen. However, in MER and UG2D, sonication also decreased the amount of EDTA-extractable copper. Higher copper recoveries were seen at higher extraction indices for MER and UG2R, but in UG2D, the opposite is true. Oxidation, therefore, in this case, did not influence typical electrochemical and flotation behaviour.

The relationship between copper oxidation, k_La and A, and copper recovery, is therefore easier to assert for the full tailings, perhaps because the set concerns a complete representation of MER, UG2R and UG2D, and the surface properties influence tailings behaviour in more typical ways. In which case, increased oxidation induces passivation in the present minerals, and also induces a lower capacity to naturally hold dissolved oxygen; and as a result, impedes copper recovery.

8. CONCLUSIONS

The primary objective of this study was to investigate whether selected South African PGM tailings can be qualitatively characterised by using non-extensive, in-situ methods. The study aimed to elucidate whether the characterisation could be used to predict the reprocessing behaviour of the tailings. Flotation was chosen as the reprocessing method to be investigated. Hence, the study further aimed to evaluate the feasibility of floating the selected tailings.

The relationship between the key performance indicators could then be constructed by extending, and focusing the objectives, all of which essentially ask five key questions. It was in answering these questions, that the veracity of the proposed hypotheses could be assessed.

1. **Can the selected tailings be qualitatively characterised using in-situ methods?**

The study showed that MER, UG2R and UG2D could be characterised using EDTA extraction and oxygen reactivity. The data yielded by each method was consistent with the mineralogical profiles of the tailings. MER, which contained the highest fraction of sulphides, and chalcopyrite in particular, reacted well with oxygen, producing high oxygen consumption rate constants and resting concentrations. But UG2R, which contained better-liberated chalcopyrite, and a sulphide fraction only slightly less than MER, produced higher constants, suggesting that the overall reactivity is influenced by a combination of these two aspects. UG2D, which had a similar mineralogy profile to UG2D, but differed in sulphide fraction, was less reactive than both MER and UG2D, therefore showing that indeed, sulphide fraction plays an important role.

In addition to the oxygen consumption rate constants, k_La, the study showed that the respective slurry of each tailings has a resting dissolved oxygen concentration that is unique to it, and follows a relationship of direct proportionality to the k_La relevant for that tailings. That is to say, slurries that naturally contained lower concentrations of dissolved oxygen, reacted slower with it, and those that contained higher natural concentration of oxygen, reacted faster with it.

The EDTA extraction indices supported these observations, yielding the highest copper extraction indices in UG2D, followed by UG2R, with MER yielding the lowest index. In this case, higher indices indicate a higher degree of copper oxidation, and lower indices indicate less oxidation.

2. **If the tailings are altered, can the characterisation methods detect the change?**

The copper extraction indices of MER, UG2R and UG2D increased when the mineral surfaces and distributions were artificially altered through sonication and desliming, indicating increased oxidation and a passivation of the active sites on the mineral surfaces. And indeed, the oxygen

reactivity results showed that sonication and desliming made the tailings less reactive to oxygen, yielding lower consumption rate constants. The capacity of the slurries to hold oxygen was also decreased, as indicated by lower resting dissolved oxygen concentrations.

3. Can froth flotation be used to recover the copper present in the tailings?

MER, UG2R and UG2D floated to various degrees of efficiency, depending on both chemical and physical variations exerted on them. Firstly, they all reacted negatively to being floated with 175 g/t of CMC. Once CMC was removed from the reagent scheme and only the frother and collector remained, their flotation performance improved. When the collector was increased to a higher dosage (200 g/t), UG2R had the distinction of yielding a copper recovery of 34.7%, indicating an economic viability to process this particular tailings under the investigated conditions. While MER and UG2D fell short of meeting the 30% copper recovery objective across all investigated conditions, their flotation showed a capacity for improvement, and therefore a need to be investigated further, under different experimental conditions.

4. Can the characterisation methods predict the flotation behaviour of the tailings?

UG2D, which consistently showed the highest copper extraction indices, and the lowest oxygen consumption rate constants, also consistently showed lower copper recoveries. UG2R, which consistently yielded the highest oxygen consumption rate constants, and middling copper extraction indices (relative to the other tailings), consistently showed high copper recoveries. As the tailings were artificially altered, the copper extraction indices increased, the rate constants decreased, and this was complemented by decreased copper recoveries.

Like the others, MER performed well when the extraction indices were low and the k_La and A values were high; but overall, MER yielded higher copper grades as a function of recovering less total solids than UG2R and UG2D. Although, a relationship that strictly correlates the EDTA extraction indices to the copper grades cannot be conclusively asserted. Nor could a conclusive relationship between k_La and copper grade be put forward for any of the tailings.

5. If the tailings are altered, can their copper still be recovered via froth flotation?

Ultrasonication resulted in the decreased recovery of copper for all tailings. As a result of deliming removing significant portions of the valuables (in the form of chalcopyrite) from the samples, and removing the better-liberated valuables, desliming, as a whole, yielded worse results than ultrasonication. However, sonicating the deslimed tailings improved copper recovery in UG2R and UG2D. MER-copper performance worsened with each new alteration method.

In addition to copper, the performance of nickel was also tracked under all investigated conditions. A sixth key question became necessary:

6. **Are there any other elucidations that emerged from the study?**

The degree of nickel (and therefore pentlandite) oxidation could not be conclusively commented on since, as noted in Chapter 5, the EDTA-extractable quantities were too low in some of the samples to be analysed, and the emerging patterns were therefore incomplete. But when it came to flotation, nickel, overall, performed contrary to copper, often thriving in environments that hindered copper flotation, and floating poorly in those that favoured copper flotation.

The nickel recoveries were also far lower than their copper counterparts, which was expected since pentlandite is slower-floating. The best nickel recovery (10.6%) was yielded when UG2R was sonicated, showing once again, the reprocessing potential of this particular tailings. The second-highest nickel recovery (8.13%) was yielded when MER was sonicated, showing that sonication favoured pentlandite. Even UG2D, which consistently showed the lowest yields under the respective conditions, showed its best nickel recovery (6.10%) when sonicated. And so, under the investigated conditions, UG2R yielded the best recoveries for both copper and nickel.

8.1. An Assessment of the Hypotheses

The hypotheses proposed in Chapter 3 are thus:

- EDTA, a compound that can form complexes with the oxidation products of sulphide minerals, will, in extracting these oxidation products, determine the extent and source (in the form Cu, and Ni ions) of oxidation. Tailings with more pronounced oxidation will have higher EDTA-extractive indices than those with lower oxidation; this is because tailings with more pronounced oxidation are coated with more products of weathering.
- The electrochemical reactivity of differing tailings can be used to determine the extent of oxidation of those tailings. This can be measured by the oxygen consumption constants of the tailings, in which case, when compared to less oxidised tailings, tailings with more pronounced oxidation will consume lower amounts of dissolved oxygen, resulting in lower consumption constants (as fresher surfaces will consume more oxygen); the heightened oxygen consumption will induce more reducing pulps and therefore lower the relevant pulp potential values.

The first hypothesis was thus proven to be correct where copper is concerned. With regards to nickel, the EDTA extraction products were too low for some of the tailings samples and as such, could not be definitively and reliably analysed.

The second hypothesis was also proven to be correct, in which case, the investigated alteration methods induced a passivation effect on the tailings, causing them to be less reactive to oxygen.

8.2. Implications of the Study

As a leading producer of the world's platinum, the BIC holds the unique distinction of also possessing an over-abundance of PGM tailings. Their processing has not taken priority for various reasons. Tailings are low grade, gangue-laden, weathered, and the value still present in them remains largely unquantified and uncharacterised.

This study showed that the in-situ methods, EDTA extraction and oxygen reactivity, can qualitatively characterise the electrochemical qualities of MER, UG2R and UG2D. The EDTA extraction method reliably determined the degree of weathering as the tailings were subjected to different surface conditions, while the oxygen reactivity method profiled the surface readiness to interact with dissolved species. The results were consistent with the relevant tailings mineralogies. The study further showed the tailings can be processed via froth flotation, and that for a UG2R sample with a copper index of 0.0214 mg/g and an oxygen consumption rate constant of 0.198 min^{-1}, an SIBX dosage of 200 g/t is enough to yield a copper recovery of 34.7%.

9. RECOMMENDATIONS

This study aimed to elucidate whether the selected tailings could be characterised, and whether they could be floated. As such, the scope, although focused, was too expansive to consider every experimental scenario, and it would be impractical to execute such an endeavour. And so, while the study makes valuable contribution to understanding the characteristics and behaviour of PGM (Merensky and UG2) tailings, additional areas of concern that expanded beyond the defined scope, but should be better elucidated, were identified, and are outlined henceforth.

1. **Altering the physical state of the tailings without discarding a given size fraction:**

The mineralogy profiles showed that the greater fraction of the chalcopyrite is locked. This was especially true for the coarser size class. It is worth investigating whether liberating this fraction through fine grinding would improve/optimise copper recovery.

2. **Chemical surface alteration methods:**

Only mechanical alteration methods were investigated in this study, and neither of them improved copper recovery for the full tailings. The effect of using other alteration options, such as chemical surface cleaning methods, should be investigated. A key factor to consider, is not only which chemical remedy to use, but its dosage as well as point of addition in the overall process.

3. **The use of flocculants to make physical processing easier:**

As previously discussed, the grater fraction of the chalcopyrite was comprised in the finer size fraction. However, when the entire bulks were floated, processing issues arose, such as prolonged filtration periods and difficulty scraping the recovered concentrates from the filter paper they were dried on. If a future study processes the tailings as they are, or if fine grinding is employed to liberate the locked fraction, it is recommended that the use of flocculants, and the resultant agglomeration of the fine particles be investigated. It might also be worth investigating, in addition, the point at which the flocculants are added to the tailings.

4. **A wider reagent matrix:**

The reagent scheme was shown to be crucial in affecting the copper recovery. It is recommended that the effect of more reagents, for example, activators, slime depressants and sulphidisers be investigated. Their combinations, concentrations, and types (such as SIPX or PAX vs. SIBX), might produce an optimal point at which more copper is recovered from MER, UG2R and UG2D.

5. **Finding an optimal desliming size fraction:**

Ultrasonication improved the copper recovery of deslimed UG2R and UG2D, showing that sonication might be a viable option when the mineral surfaces are made sufficiently amenable to it. There might exist an optimal cut size, so to speak, where desliming that fraction does not significantly rid the bulk of the majority of its valuable minerals, and sonication, or another subsequent method, might yield positive results. For this study, the discarded fraction was dictated by the size of the available batch flotation cell; hence, only one "cut size" was investigated.

6. **The development of a technique for treating only the fine fraction:**

The distribution (and possible dissemination) of chalcopyrite in the fine size fraction strongly suggests that the processing of fine and ultrafine samples might very well be unavoidable. If fine grinding is employed, or if no optimal desliming cut size is found, the processing of ultrafine tailings will become more necessary.

The technique might be a combination of processes that exploit various fundamental concepts of beneficiation. For example, say, desliming the fine fraction, grinding the coarser particles to liberate the locked chalcopyrite, and floating the newly-milled sample. Or, any other combination of processes that are practical, measurable and repeatable.

REFERENCES

African Oxygen Limited (Afrox). (2008). *South Africa Patent No. 2008/09676*.

Abraitis, P., Pattrick, R., & Vaughan, D. (2004). Variations in the compositional, textural and electrical properties of natural pyrite: a review. *International Journal of Mineral Processing*, 41-59.

Aldrich, C., & Feng, D. (1999). Effect of ultrasonic preconditioning of pulp on the flotation of sulphide ores. *Minerals Engineering*, 701-707.

Aldrich, C., & Feng, D. (1999). Effect of ultrasonic preconditioning of pulp on the flotation of sulphide ores. *Minerals Engineering*, 701-707.

Anglo Platinum. (2009). *Annual Sustainability Report, Years 2002 to 2009*. Johannesburg: Anglo Platinum Ltd.

Arjmand, R., Massinaei, M., & Behnamfard, A. (2019). Improving Flocculation and Dewatering Performance of Iron Tailings Thickeners. *Journal of Water Process Engineering*.

Ata, S., Ahmed, N., & Jameson, G. J. (2004). The Effect of Hydrophobicity on the Drainage of Gangue Minerals in Flotation Froths. *Minerals Engineering*, 897-901.

Baker, M., Pietrobon, M., Ralston, J., & Smart, R. S. (1991). *Iron Sulphide Interactions and their Influence on Sulphide Mineral Flotation.* AMIRA Project P260 Final, Report, vol. 4.

Baumann, E. W., & Wallace, R. M. (1969). Cupric-Selective Electrode with Copper(II)-EDTA for Endpoint Detection in Chelometric Titrations of Metal Ions. *Analytical Chemistry*, 2072-2074.

Becker, M. (2009). *The Mineralogy and Chrystallography of Pyrrhotite from Selected Nickel and PGE Deposits and its Effects on Flotation Performance.* Tshwane: University of Pretoria.

Becker, M. H. (2009). Mineralogical Characterisation of Naturally Floatable Gangue in Merensky Reef Ore Flotation. *International Journal of Mineral Processing*, 246–255.

Becker, M., de Villiers, J., & Bradshaw, D. (2010). The Flotation of Magnetic and Non-Magnetic Pyrrhotite from Selected Nickel Ore Deposits. *Minerals Engineering*, 1045-1052.

Bicak, O. (2019). A Technique to Determine Ore Variability in a Sulphide Ore. *Minerals Engineering*.

Bicak, O., & Ekmekci, Z. (2012). Prediction of Flotation Behavior of Sulphide Ores by Oxidation Index. *Minerals Engineering*, 279-283.

Bosch, D. W. (1987). Retreatment of Residues and Waste Rock. In G. G. Stanley, *The Extractive Metallurgy of Gold in South Africa* (pp. 707-743). Johannesburg: South African Institute of Mining and Metallurgy.

Bradshaw, D. J. (1997). *Synergistic Effects between Thiol Collectors Used in the Flotation of Pyrite.* Cape Town: The University of Cape Town.

Bradshaw, D. J., Harris, P. J., & O'Connor, C. T. (1998). Synergistic Interactions Between Reagents in Sulphide Flotation. *Journal of The South African Institute of Mining and Metallurgy*, 187-192.

Breytenbach, M. (2016, October 14). *Gold Tailings Retreatment: An Attractive Proposition in Current Environment.* Retrieved from Mining Weekly: https://www.miningweekly.com/article/gold-tailings-retreatment-an-attractive-proposition-in-current-environment-2016-10-14/rep_id:3650

Bruckard, W. J., Sparrow, G. J., & & Woodcock, J. T. (2011). A Review of the Effects of the Grinding Environment on the Flotation of Copper Sulphides. *International Journal of Minerals Processing*, 1-13.

Buckley, A., & Woods, R. (1984). An X-Ray Photoelectron Spectroscopic Study of the Oxidation of Chalcopyrite. *Aust. J. Chem*, 2403-2413.

Bulatovic, S. M. (2007). *Handbook of Flotation Reagents.* Elsevier Science & Technology Books.

Bulut, G., & Yenial, U. (2016). Effect of Major Ions on Recycled Water on Sulphide Minerals Flotation. *Minerals and Metallurgical Processing*, 137-143.

Bunyak, D. (2000). To Float or Sink: A Brief History of Flotation Milling. *The Mining History Journal*, 35-44.

Burdukova, L. (2007). *Surface properties of New York talc as a function of pH, polymer adsorption and electrolyte concentration.* Cape Town: PhD Thesis, University of Cape Town, Faculty of Engineering and the Built Environment, Chemical Engineering Department.

Buys, S., Rule, C., & Curry, D. (2004). *The Application of Large Scale Stirred Milling to the Retreatment of Merensky Platinum Tailings.* Montreal: CIM.

Cawthorn, R. G., Lee, C. A., Schouwstra, R. P., & Mellowship, P. (2002). Relationship between PGE and PGM in the Bushveld Complex. *The Canadian Mineralogist*, 311-328.

Celik, M. (1989). Effect of Ultrasonic Treatment on the Floatability of Coal and Galena. *Separation Science and Technology*, 1159-1166.

Celik, M. S. (1989). Effect of Ultrasonic Treatment on the Floatability of Coal and Galena. *Separation Science and Technology*, 1159-1166.

Chander, S. (1978). Recent Development in Floatability of very Fine Particles - Review. *Transactions of Indian Institute of Metals*, 21.

Chaplin, M. (2021, June 27). *Carboxymethylcellulose (CMC).* Retrieved from Water Structure and Science: https://water.lsbu.ac.uk/water/carboxymethylcellulose.html

Cho, Y. S., & Laskowski, J. S. (2002). Effect of Flotation Frothers on Bubble Size and Foam Stability. *International Journal of Mineral Processing*, 69-80.

Clark, J. (2023, January 30). *The Beer-Lambert Law*. Retrieved from LibreTexts: https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Electronic_Spectroscopy/Electronic_Spectroscopy_Basics/The_Beer-Lambert_Law

Coelho, A. (2007). *Topas Academic v4.1*. Brisbane: Coelho Software.

Corin, K. C. (2011). The Effect of Ionic Strength of Plant Water on Valuable Mineral and Gangue Recovery in a Platinum Bearing Ore from the Merensky Reef. *Minerals Engineering*, 131-137.

Coulson, J. M., Richardson, J. F., Marker, J. H., & Backhurst, J. R. (1999). *Coulson and Richardson's Chemical Engineering*. Woburn: Butterworth-Heinemann.

Crawford, R., & Ralston, J. (1988). The Influence of Particle Size and Contact Angle in Mineral Flotation. *International Journal of Mineral Processing*, 1-24.

Dean, R. S., & Ambrose, P. M. (1944). *Development and Use of Certain Flotation Reagents*. Washington: United States Government Printing Office.

Deventer, J. S., Ross, V. E., & Dunne, R. C. (1993). The effect of galvanic interaction on the behaviour of the froth phase during the flotation of a complex sulphide ore. *Minerals Engineering*, 1217-1229.

Djendova, S., & Mehandjiski, V. (1992). Study of the effects of acoustic vibration conditioning of collector and frother on flotation of sulphide ores. *International Journal of Mineral Processing*, 205-217.

Djendova, S., & Mehandjiski, V. (1992). Study of the effects of acoustic vibration conditioning of collector and frother on flotation of sulphide ores. *International Journal of Mineral Processing*, 205-217.

Ebben, A., & Carlson, C. (2019). *Tailings Retreatment: The Next Big Revenue Source For The Mining Industry*. Retrieved from FEEECO International: https://feeco.com/tailings-retreatment-the-next-big-revenue-source-for-the-mining-industry/

Eco Partners. (2011). *Strategic Approach to Mine Dumps in South Africa*. Eco Partners Report.

Ekmekçi, Z., & Demirel, H. (1997). Effects of galvanic interaction on collectorless flotation behaviour of chalcopyrite and pyrite. *International Journal of Mineral Processing*, 31-48.

Encyclopaedia Britannica. (2008, January 7). *Flotation: Ore Dressing*. Retrieved from Encyclopaedia Britannica: https://global.britannica.com/technology/flotation-ore-dressing

Engels, J. (2012). *What Are Tailings? - Their Nature and Productio*. Retrieved from Tailings.Info: http://www.tailings.info/basics/tailings.htm

Fairthorne, G., Fornasiero, D., & Ralston, J. (1997). Effect of Oxidation on the Collectorless Flotation of Chalcopyrite. *Int. J. Miner. Process.*, 31-48.

Finch, J. A. (1995). Column Flotation: A Selected Review - Part IV: Novel Flotation Devices. *Minerals Engineering*, 587-602.

Finkelstein, N. P. (1972). Fundamental Studies of the Flotation Process: The Work of the National Institute for Metallurgy. *Journal of the South African Institute of Mining and Metallurgy*, 196-209.

Fuerstenau, D. W. (1982a). Mineral-Water Interfaces and the Electrical Double Layer. In R. P. King, *Principles of Flotation* (pp. 17-30). Johannesburg: South African Institution of Mining and Metallurgy.

Fuerstenau, D. W. (1984). Chemistry of Flotation. In &. J. M. H. Jones, *Principles of Mineral Flotation* (pp. 7-9). The Australasian Institute of Mining and Metallurgy.

Fuerstenau, D. W. (1986). Thermodynamics of Flotation. *Advances in Mineral Processing* (pp. 121-136). Littleton: SME/AIME.

Fuerstenau, M. C. (1982b). Chemistry of Collectors in Solution. In R. P. King, *The Principles of Flotation* (pp. 1-16). Johannesburg: The South African Institute of Mining and Metallurgy.

Fuerstenau, M. C., Kuhn, M. C., & Elgillani, D. A. (1968). The Role of Dixanthogen in Xanthate Flotation of Pyrite. *Transactions: Society of Mining Engineers, AIME*, 148-156.

Fuerstenau, M. C., Miller, J. D., & Kuhn, M. C. (1985). Chemistry of Flotation. *New York: Society of Mining Engineers, AIME*.

Garrels, R. M., & Christ, C. L. (1990). *Solutions, Minerals and Equilibria.* Boston: Jones and Bartlett Publishers.

Ghosh, P. (2012, June 6). Froth Flotation. *Module 6: Lecture 6 - Froth Flotation*. Guwahati, Guwahati, India: NPTEL - Chemical Engineering - Interfacial Engineering.

Gierdien, A. (2022). *Screening Best Practice: CMR Sample Sizing Procedure (Sub 1mm).* Cape Town: The Centre for Minerals Research: University of Cape Town.

Goktepe, F., & Williams, K. P. (1995). Electrochemical Effects in Flotation of a Turkish Complex Sulphide Ore. *Minerals Engineering*, 1035-1048.

Graham, R., & Heathcote, C. R. (1982). The effect of the oxidation state of the pulp on selective flotation of chalcopyrite from Black Mountain Ore. *Proceedings, 12th CMMI Congress* (pp. 867-877). Johannesburg: The South African Institute of Mining and Metallurgy.

Gray, D. C. (2006). *Kevitsa Nickel Copper Mine, Lapland, Finland.* First Quantum Minerals Ltd.

Greet, C. (2018). *To Measure is to Know: Plant Audits - Flotation Circuit.* Magotteaux.

Greet, C. J., Small, G. L., Philippe, S., & Grano, S. R. (2004). The Magotteaux Mill: Investigating the Effect of Grinding Media on Pulp Chemistry and Flotation Performance. *Minerals Engineering*, 891-896.

GRID Arendal. (2017). *An Average Day in a Large-Sized Copper Mine*. Retrieved from GRID Arendal: http://www.grida.no/resources/11419

Hadler, K., Aktas, Z., & Cilliers, J. (2005). The Effects of Frother and Collector Distribution on Flotation Performance. *Minerals Engineering*, 171-177.

Harris, P. J. (1982). Frothing Phenomena and Frothers. In R. P. King, *The Principles of Flotation* (pp. 237-250). Johannesburg: The South African Institute of Mining and Metallurgy.

Houot, R., & Duhamet, D. (1990). Importance of oxygenation of pulps in the flotation of sulfide ores. *International Journal of Mineral Processing*, 77-87.

Hudson Intitute of Mieneralogy. (2023). *Mindat.Org*. Retrieved from Bushveld, South Africa: https://www.mindat.org/loc-26589.html

Janse van Rensburg, S. (2016). Guidelines for Retreatment of SA Gold Tailings: MINTEK's Learnings. *Proceedings of the 23rd WasteCon Conference* (pp. 367-376). Johannesburg: Institute of Waste Management of Southern Africa.

Johnson, N., Jowett, A., & Heyes, G. (1982). Oxidationreduction effects in galena flotation: observations on Pb-Zn-Fe sulphides separation. *Transactions of the Institution of Mining and Metallurgy*, C32-C37.

Jones, M. P. (1987). *Applied Mineralogy, A Quantitative Approach*. London: Graham and Trotman.

Kalichini, M. S. (2015). *A Study of the Flotation Charactersitics of a Complex Copper Ore, MSc Thesis*. Cape Town: University of Cape Town.

Kawatra, S. K. (2009). *Flotation Fundamentals*. Retrieved from Mining Engineering Handbook: http://www.chem.mtu.edu/chem_eng/faculty/kawatra/Flotation_Fundamentals.pdf

Kelebek, S. (1993). The Effect of Oxidation on the Flotation Behaviour of Nickel-Copper Ores. *XVIII International Minerals Processing Conference* (pp. 999-1006). Sydney: XVIII International Minerals Processing Congress.

Khan, S. F. (2023). *An investigation into the impact of residual reagents on flotation in response to process water recirculation* . Cape Town: University of Cape Town.

King, R. P. (1984). *Principles of Flotation*. Johannesburg: SAIMM.

Klassen, V. I., & Mokrousov, V. A. (1963). *An Introduction to the Theory of Flotation*. London: Butterworths.

Klimpel, R. D. (1984). *Froth Flotation: The Kinetic Approach*. Johannesburg: Mintek 5.

Knight, R. B., & Haile, J. P. (1984). Sub-Aerial Tailings Deposition. *Panamerican Conference on Soil Mechanics and Foundation Engineering* (pp. 627-639). Vancouver: University of British Columbia.

Koshdast, H., & Sam, A. (2011). Flotation Frothers: Review of Their Classifications, Properties and Preparation. *The Open Mineral Processing Journal*, 25-44.

Kovács, A., Nemcsok, D. S., & Kocsis, T. (2010). Bonding Interactions in EDTA Complexes. *Journal of Molecular Structure: THEOCHEM*, 93-97.

Kuopanportti, H., Suorsa, T., & Pöllänen, E. (1997). Effects of oxygen on kinetics of conditioning in sulphide ore flotation. *Minerals Engineering*, 1193-1205.

Kyllönen, H., Pirkonen, P., Hintikka, V., Parvinen, P., Grönroos, A., & H. S. (2004). Ultrasonically Aided Mineral Processing Technique for Remediation of Soil Contaminated by Heavy Metals. *Ultrasonics Sonochemistry*, 211-216.

Labotec. (2023, April 11). *Ultrasonic Cleaner*. Retrieved from Labotec: https://www.labotec.co.za/product/labotec-ultrasonic-baths/

Lascelles, D., & Finch, J. (2002). Quantifying Accidental Activation. Part I. Cu Ion Production. *Minerals engineering*, 567-571.

Leja, J. &. (1954). Flotation Theory: Molecular Interactions between Frothers and Collectors at Solid-Liquid-Air Interfaces. *Mining Engineering*, 221-228.

Leja, J. (1982). *Surface Chemistry of Froth Flotation, First Edition.* New York: Springer.

Letseli, M., Nheta, W., & Steinmuller, A. (2018). Characterisation and Flotation of a Weathered Platinum Group Metal Ore. *Proceedings of the 4th World Congress on Mechanical, Chemical, and Material Engineering (MCM'18)* (pp. Paper No. MMME 124, pages 1-6). Madrid: MMME.

Lovell, V. M. (1982). Industrial Flotation Reagents. In R. P. King, *Principles of Flotation* (pp. 73-89). Johannesburg: South African Institute of Mining and Metallurgy.

Ma, J., Wang, R., Wang, X., Zhang, H., Zhu, B., Lian, L., & Lou, D. (2019). Drinking Water Treatment by Stepwise Flocculation Using Polysilicate Aluminum Magnesium and Cationic Polyacrylamide. *Journal of Environmental Chemical Engineering*.

Majima, H. (1971). Electrochemistry of Pyrite and its Significance in Sulphide Flotation. *AIME Central Annual Meeting*. New York: 911 Metallurgist.

Mäkelä, M. (2017). Experimental Design and Response Surface Methodology in Energy Applications: A Tutorial Review. *Energy Conversion and Management*, 630-640.

Maksimov, I., Otrozhdennova, A., Borkin, M., Yemelyanov, & Nechay, L. (1993). An Investigation to Increase the Efficiency of Coarse and Fine Particle Flotation in Ore Processing of Non-Ferrous Metals. *Proceedings of the XVII IMPC*, (pp. 665-687). Sidney.

Manenzhe, R. M. (2018). *Investigating the Effect of Water Quality on the Adsorption of a Xanthate Collector in the Flotation of a Sulphide Ore.* Cape Town: University of Cape Town: Engineering and the Built Environment MSc. Thesis.

Manono, M. S. (2013). The Effect of Ionic Strength of Plant Water on Foam Stability: A 2-Phase Flotation Study. *Minerals Engineering*, 42-47.

Mason, T. (2003). High powered ultrasound in physical and chemical processing. *Selected Topics of the New Acoustics*, 95-136.

Michaud, D. (2016, June 8). *Flotation Reagents.* Retrieved from 911 Metallurgist: https://www.911metallurgist.com/blog/flotation-reagents

Michaud, D. (2018, August 21). *911 Metallurgist*. Retrieved from Desliming: https://www.911metallurgist.com/desliming/

Mohamed, S., van der Merwe, E. M., Altermann, W., & Doucet, F. J. (2016). Process Development for Elemental Recovery from PGM Tailings by Thermochemical Treatment: Preliminary Major Element Extraction Studies Using Ammonium Sulphate as Extracting Agent. *Waste Management*, 334-345.

Moimane, T., Huai, Y., & Peng, Y. (2019). Sulphidisation and Flotation of Oxidised Copper Sulphides. *Flotataion '19*. Cape Town.

Mudgil, D., Barak, S., & Khatkar, B. S. (2014). Guar gum: processing, properties and foodapplications - A Review. *J Food Sci Technol*, 409-418.

Nel, E., Theron, J., Martin, C., & Raabe, H. (2004). *PGM Ore Processing at Impala's UG2 Conentrator in Rustenburg, South Africa.* SGS.

NS Energy. (2019, October 04). *Profiling the Top Five Platinum Producing Countries in the World*. Retrieved from NS Energy: https://www.nsenergybusiness.com/features/top-platinum-group-metal-producers/

Oats, W., Ozdemir, O., & Nguyen, A. V. (2010). Effect of mechanical and chemical clay removals by hydrocyclone and dispersants on coal flotation. *Minerals Engineering*, 413-419.

One Mine. (1989). *Controlled Potential Sulphidisation (CPS) Flotation Process.* The Australasian Institute of Mining and Metallurgy.

Osbahr, I., Klemd, R., Oberthür, T., Brätz, H., & Schouwstra, R. (2013). Platinum-group element distribution in base-metal sulfides of the Merensky Reef from the eastern and western Bushveld Complex, South Africa. *Miner Deposita*, 211-232.

Owusu, C., Addai-Mensah, J., Fornasiero, D., & Zanin, M. (2013). Estimating the Electrochemical Reactivity of Pyrite Ores - Their Impact on Pulp Chemistry and Chalcopyrite Flotation Behaviour. *Advanced Powder Technology*, 801-809.

Phiri, T., Tepa, C., & Nyati, R. (2019). Effect of Desliming on Flotation Response of Kansanshi Mixed Copper Ore. *Journal of Minerals and Materials Characterization and Engineering*.

Plaksin, I. N., Glembotski, V. A., & Okolovich, A. M. (1954). Investigations of the Possible Intensification of the Flotation Process Using Combinations of Collectors. In O. Svoboda, *Naachnye Soobshcheniya Institut Gonnogo dela Imeni AA Skochinskogo, Akademiya Nauk SSSR, no. 1 (translated from the Russian language by Dr Olga Svoboda)* (pp. 213-224). Randburg:: Mintek.

Possa, M., & Lima, J. (2000). The effect of viscosity on small-diameter hydrocyclones' performance in desliming process. *Developments in Mineral Processing*, C4-29-C4-35.

Pugh, R. J. (1989). Macromolecular organic depressants in sulphide flotation - A review: 1. Principles, Types and Applications. *International Journal of Mineral Processing*, 101-130.

Pugh, R., & Tjus, K. (1987). Electrokinetic Studies on Cu(II) Hydroxy Coated Zinc Sulfide Particles. *J. Colloid Interface Sci.*, 231-241.

Raju, G. B., & Forsling, W. (1991). Adsorption Mechanism of Diethy Idithiocarbamate on Covellite, Cuprite, Tenorite. *Colloids and Surfaces*, 53-69.

Rao, M. K., & Natarajan, K. A. (1989). Effect of Electrochemical Interactions Among Sulfide Minerals and Grinding Medium on Chalcopyrite Flotation. *Miner. Metall. Process*, 146-151.

Rao, S. R. (2004). *Surface Chemistry of Froth Flotation, Second Edition.* New York: Springer.

Reddy, B., Sivasankar, T., Sivakumar, M., & Moholkar, V. (2010). Physical facets of ultrasonic cavitational synthesis of zinc ferrite particles. *Ultrason. Sonochem*, 416-426.

Richardson, P., & Walke, G. (1985). The flotation of chalcocite, bornite, chalcopyrite and pyrite in an electrochemical-flotation cell. *XV International Minerals Process Congress* (pp. 198–210.). Cannes: GEDIM, St-Etienne. II.

Rimstidt, J. D., & Vaughan, D. J. (2003). Pyrite oxidation: a state-of-the-art assessment of the reaction mechanism. *Geochimica et Cosmochimica Acta*, 873-880.

Robertson, C. (2003). *Development of a methodology to decouple the effects of dispersion and depression in batch flotation.* Cape Town: Masters Thesis, University of Cape Town, Faculty of Engineering and the Built Environment, Chemical Engineering Department.

Roosta, M., Ghaedi, M., Daneshfar, A., Sahraei, R., & Asghari, A. (2014). Optimization of the ultrasonic assisted removal of methylene blue by gold nanoparticles loaded on activated carbon using experimental design methodology. *Ultrason. Sonochem*, 242-252.

Rosner, T. (1999). *The Environmental Impact of Seepage from Gold Mine Tailings Dams Near Johannesburg, South Africa.* Tshwane: University of Pretoria.

Rosner, T., & van Schalkwyk, A. (2000). The Environmental Impact of Gold Mine Tailings Footprints in the Johannesburg Region, South Africa. *Bull Eng Geol Env*, 137-148.

Ross, V. E., & Deventer, J. S. (1985). The interactive effects of the sulphite ion, pH, and dissolved oxygen on the flotation of chalcopyrite and galena from Black Mountain ore. *Journal of the Southern African Institute of Mining and Metallurgy*, 13-21.

Ruan, Y., Zhang, Z., Luo, H., Xiao, C., Zhou, F., & Chi, R. (2018). Effects of Metal Ions on the Flotation of Apatite,Dolomite and Quartz. *MDPI: Minerals*, 1-12.

Rumball, J. A., & Richmond, G. D. (1996). Measurement of Oxidation in a Base Metal Flotation Circuit by Selective Leaching with EDTA . *Int. J. Miner. Process*, 1-20.

Schouwstra, R. P., & Kinloch, E. D. (2000). A Short Geological Review of the Bushveld Complex. *Platinum Metals Rev.*, 33-39.

Schouwstra, R. P., Kinloch, E. D., & Lee, C. A. (2000). A Short Geological Review of the Bushveld Complex. *Plutinum MhLr Review*, 33-39.

Senior, G. D., Trahar, W. J., & Guy, P. J. (1995). The Selective Flotation of Pentlandite from a Nickel Ore. *International Journal of Mineral Processing*, 209-234.

Senior, G., & Trahar, W. (1991). The Influence of Metal Hydroxides and Collector on the Flotation of Chalcopyrite. *Int. J. Miner. Process.*, 321-341.

Senior, G., Trahar, W., & Guy, P. (1995). The selective flotation of pentlandite from a nickel ore. *International Journal of Mineral Processing*, 209-234.

Shengo, L., Gaydardzhiev, S., & Kalenga, N. (2016). Malachite and heterogenite behavior during the locked-cycle recycling of process water in flotation of copper-cobalt oxide ores. *International Journal of Mineral Processing*, 152-162.

Shiwen, F., Wenlu, G., Lin, C., Zhaosheng, Y., Minquan, D., Yan, L., . . . Xiaoqian, M. (2018). Ultrasonic pretreatment effects on the co-pyrolysis of municipal solid waste and paper sludge through orthogonal test. *Bioresource Technology*, 5-11.

Shortridge, P. G. (2002). *The influence of polymeric charge and structure, molecular weight and ionic conditions on depressant ability to reduce the natural floatability of talc.* Cape Town: Masters Thesis, University of Cape Town, Chemical Engineering.

Shortridge, P. G., Harris, P. J., Bradshaw, D. J., & Koopal, L. K. (1999). The effect of chemical composition and molecular weight of polysaccharide depressants on the flotation of talc. *International Journal of Mineral Processing*, 215-224.

Sibiya, A. (2022). *The Use of Simple Analytical Techniques to Assess Surface Oxidation of Sulphide Ores* . Cape Town: University of Cape Town.

Smart, R. S. (1991). Surface Layers in Base Metal Sulphide Flotation. *Minerals Engineering*, 891-909.

Steenberg, E. &. (1984). Adsorption of carboxymethyl cellulose, guar gum and starch onto talc, sulphides, oxides and salt type minerals. *South African Journal of Chemistry*, 85-90.

Stepanov, V., & Stepanov, S. (1998). Energy Use Efficiency of Metallurgical Processes. *Energy Conversion and Management*, 1803-1809.

Subrahmanyam, T. V., & Forssberg, K. S. (1995). Grinding and Flotation Pulp Chemistry of a Low Grade Copper Ore. *Minerals Engineering*, 913-921.

Taggart, A. F., & Hassialis, M. D. (1946). Solubility Product and Bubble Attachment in Flotation. *The American Institute of Mining and Metallurgical Engineers. Inc.*, 1-7.

Tao, D. L.-H. (200). A Parametric Study of Froth Stability and its Effect on Column Flotation of Fine Particles. *International Journal of Mineral Processing*, 25-43.

Tiemann, H., & Betz, K.-H. (1948). Elutriation: Theoretical Considerations and Methodological Improvements. *Marine Ecology Progress Series*, 277-281.

Trahar, W. (1981). A Rational Interpretation of the Role of Particle Size in Flotation. *International Journal of Mineral Processing*, 289-327.

Trahar, W. (1984). The Influence of Pulp Potential in Sulfide Flotation. In M. H. Jones, & J. Woodcock, *Principles of Mineral Flotation, The Wark Symposium* (pp. 117-135). Melbourne: Austral. Inst. Min. Met.

Trujillo, J. Y., Mellado, M. E., Gálvez, E. D., & Cisternas, L. A. (2011). A Method for the Design and Planning Operations of Heap Leaching Circuits. *Computer Aided Chemical Engineering*, 306-310.

United Nations Environment Programme. (2002). *A Threat to Natural Resources.* Retrieved from Waste from Consumption and Production: http://www.grid.unep.ch/waste/html_file/16-17_consumption_threat.html

Vermaak, M. K. (2005). *Literature Review on Platinum Group Metals.* Tshwane: University of Pretoria.

Videla, A., Morales, R., Saint-Jean, T., Gaete, L., Vargas, Y., & Miller, J. (2016). Ultrasound treatment on tailings to enhance copper flotation recovery. *Minerals Engineering*, 89-95.

Vogeli, J., Reid, D. L., Becker, M., Broadhurst, J., & a, F. J. (2011). Investigation of the potential for mineral carbonation of PGM tailings in South Africa. *Minerals Engineering*, 1348-1356.

Von Gruenewaldt, G., & Hatton, C. J. (1987). Platinum Group Metals - A Resource in the Tailings of Chromium Mines in South Africa. *Journal of the South African Institute of Mining and Metallurgy*, 265-268.

Wang, D. (2016). Flotation Reagents: Applied Surface Chemistry on Minerals Flotation and Energy Resources Beneficiation. *Beijing: Metallurgical Industry Press*.

Welty, J., Wicks, C., Wilson, R., & Rorrer, G. (2008). *Fundamentals of Momentum, Heat, and Mass Transfer.* Corvallis: John Wiley & Sons, Inc.

Wiese, J. G. (2009). *Investigating Depressant Behaviour in the Flotation of Selected Merensky Ores.* Cape Town: Masters Thesis, Faculty of Engineering and the Built Environment, University of Cape Town, Chemical Engineering.

Wiese, J. G., Harris, P. J., & Bradshaw, D. J. (2018). The use of very low molecular weight polysaccharides as depressants in PGM flotatin. *Minerals Engineering*, 471-482.

Wiese, J., & Harris, J. (2012). The Effect of Frother Type and Dosage on Flotation Performance in the Presence of High Depressant Concentrations. *Minerals Engineering*, 204-210.

Wiese, J., Becker, M., Bradshaw, D., & Harris, P. (2006). Interpreting the Role of Reagents in the Fotation of Platinum-Bearing Merensky Ores. *International Platinum Conference 'Platinum Surges Ahead* (pp. 175-180). The Southern African Institute of Mining and Metallurgy.

Wiese, J., Harris, P., & Bradshaw, D. (2004). The Influence of the Reagent Suite on the Flotation of Ores from the Merensky Reef. *Minerals Engineering*, 189-198.

Wills, B. A., & Finch, J. A. (2016). Tailings Disposal. In B. A. Wills, & J. A. Finch, *Wills' Mineral Processing Technology* (pp. 439-448). Butterworth-Heinemann.

Wills, B. A., & Napier-Munn, T. (2006). *Mineral Processing Technology: An Introduction to the Practical Aspects of Ore Treatment and Mineral Recovery.* Elsevier Science & Technology Books.

Woods, R. (1971). The oxidation of ethyl xanthate on platinum, gold, copper, and galena electrodes. *The Journal of Physical Chemistry*, 354-362.

Wrobel, S. A. (1970). Economic Flotation of Minerals. *Min. Mag.*, 281.

Yale Environmental. (2015). *Haunting Legacy of South Africa's Gold Mines.* Report by Yale Environmental.

Yang, X., Yang, G., Liu, P., Li, X., Jiang, L., & Zhang, J. (2022). Study on the Desliming Performance of a Novel Hydrocyclone Sand Washer. *MDPI: Separations*, 1-18.

Yates, P. (2012, November 1). *Using the Equation of a Straight Line.* Retrieved from The Royal Society of Chemistry: https://eic.rsc.org/maths/using-the-equation-of-a-straight-line/2000169.article

Yehia, A., Youseff, M., & Boulos, T. (1999). Different Alternatives for Minimizing the Collector Consumption in Phosphate Fatty Acid Flotation. *Mineral Engineering*, 273-278.

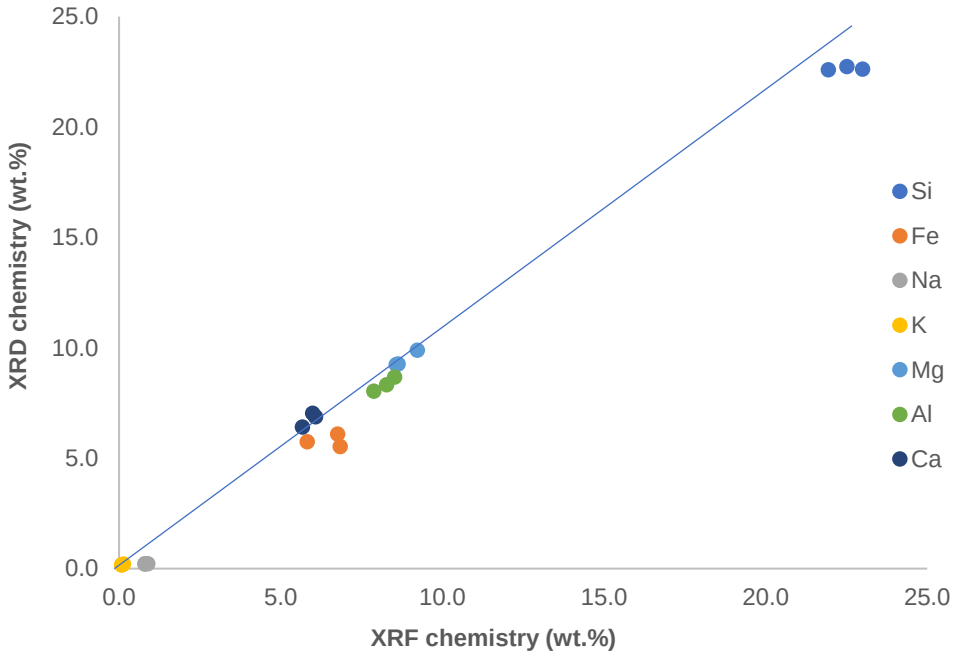
YSI Environmental. (2001). *Measuring ORP : Tips, Cautions and Limitations.* YSI Environmental.

Zhao, Y., Ren, Y., Wang, X., Xiao, P., Tian, E., Wang, X., & Li, J. (2016). An Initial Study of EDTA Complex Based Draw Solutes in Forward Osmosis Process. *Desalination*, 28-36.

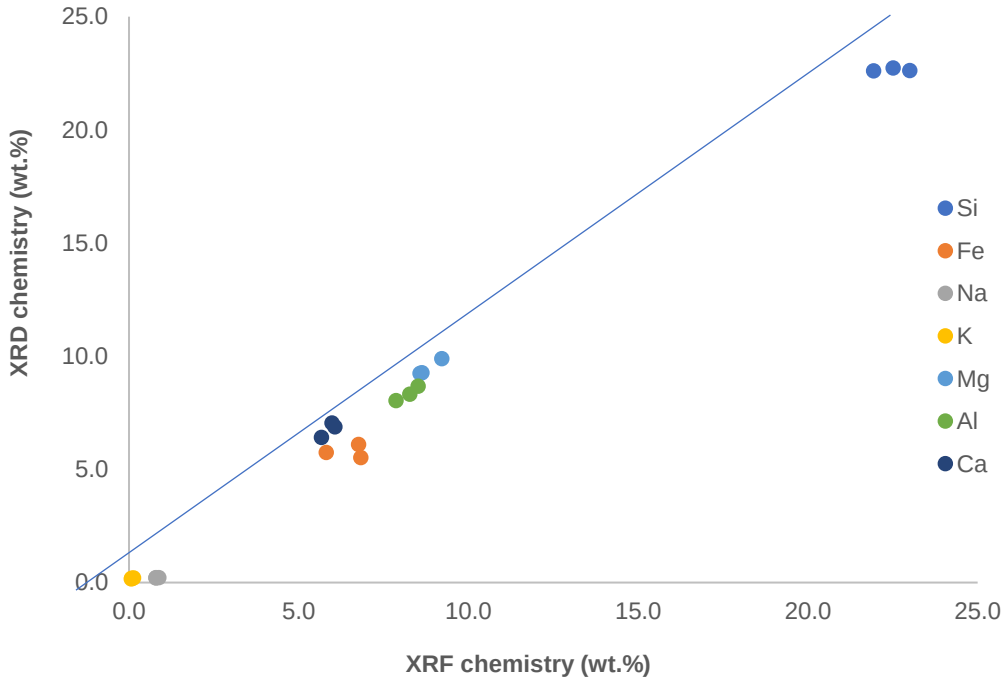
APPENDIX A

A.1. Mineralogy Data

The Validation of XRD against XRF Data for MER:



The Validation of XRD against XRF Data for UG2R and UG2D:



A.2. Oxygen Reactivity Regression Modelling Data

The R^2 values for when the oxygen consumption rate constants (k_La) were determined using the modified model in the study, as expressed by Equation 6.2.

$$DO = A \cdot \left(1 + t \cdot e^{-k_L a \cdot t}\right) \quad 6.2.$$

Tailings	R^2 Value (-)
MER	
Untreated	0.918
Ultrasonicated	0.845
Deslimed	0.539
Deslimed-Sonicated	0.647
UG2R	
Untreated	0.976
Ultrasonicated	0.824
Deslimed	0.734
Deslimed-Sonicated	0.702
UG2D	
Untreated	0.788
Ultrasonicated	0.717
Deslimed	0.702
Deslimed-Sonicated	0.699

The R^2 values for when the oxygen consumption rate constants (k_La) were determined using the current literature model as expressed by Equation 4.3.

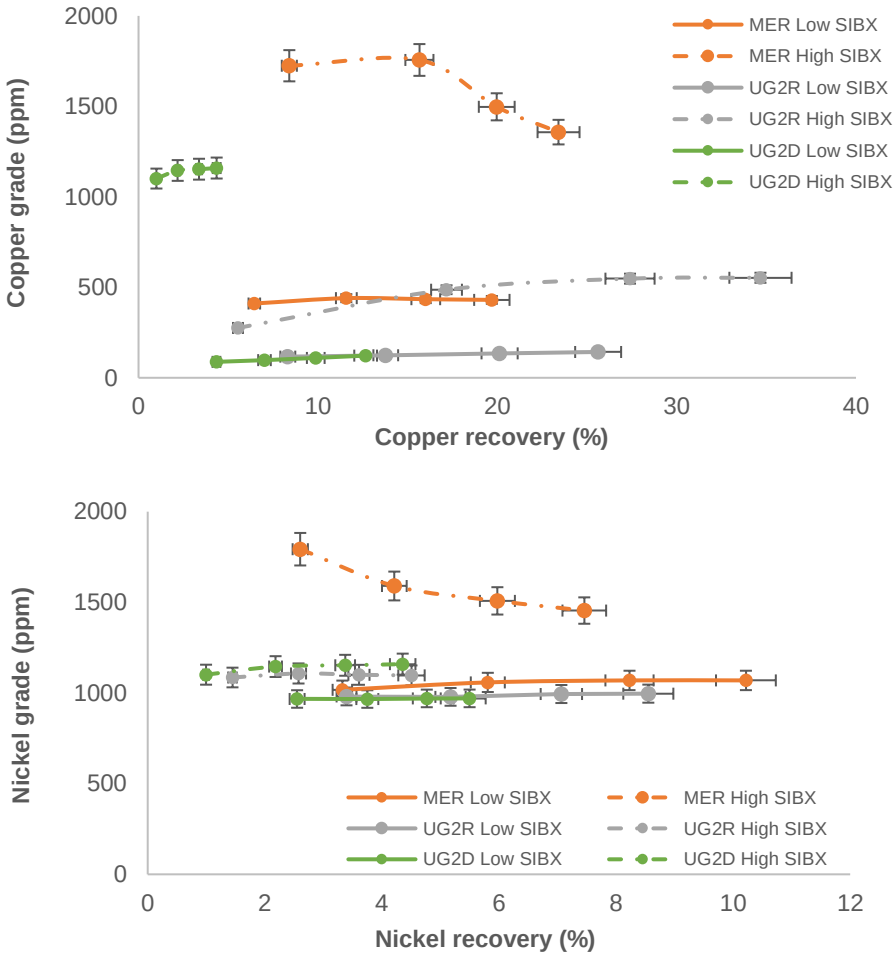
$$DO = DO_0 e^{-k_L a \cdot t} \quad 4.3.$$

Tailings	R^2 Value (-)
MER	
Untreated	-10.1
Ultrasonicated	-15.8
Deslimed	-33.8
Deslimed-Sonicated	-25.9
UG2R	
Untreated	-4.53
Ultrasonicated	-20.3
Deslimed	-23.6
Deslimed-Sonicated	-24.4
UG2D	
Untreated	-20.9
Ultrasonicated	-24.4
Deslimed	-24.7
Deslimed-Sonicated	-24.4

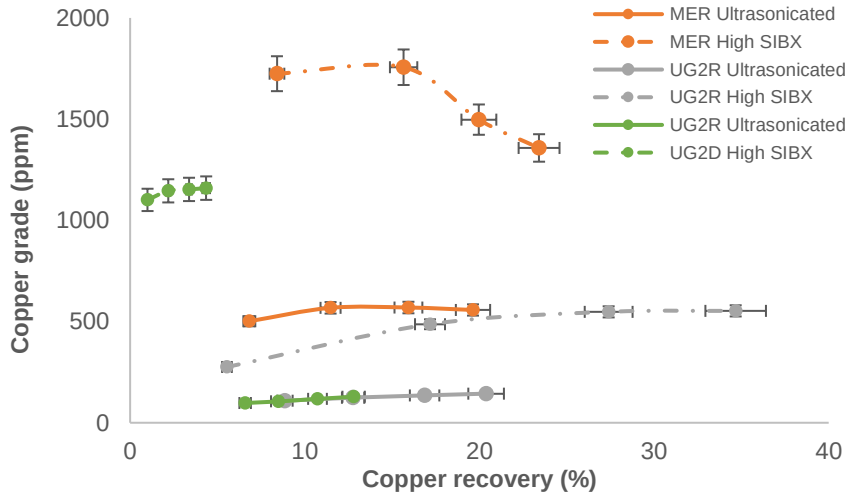
APPENDIX B

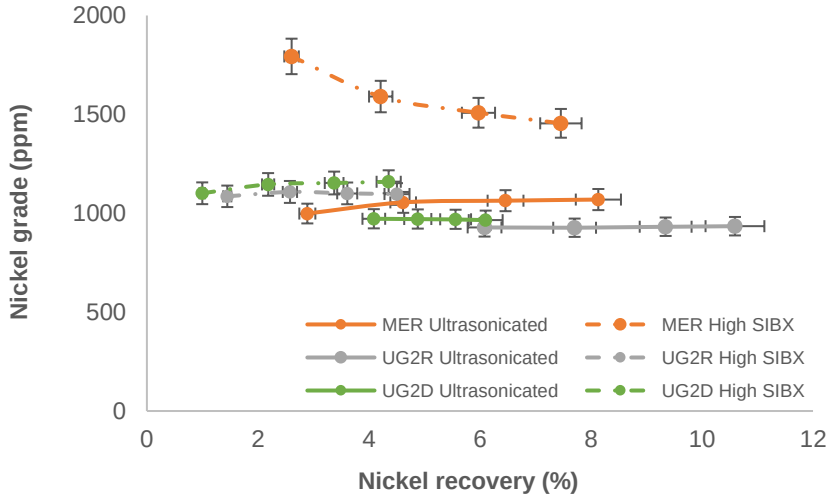
B.1. Flotation Data

The Grade-Recovery Plot for 125 g/t SIBX vs. 200 g/t SIBX:

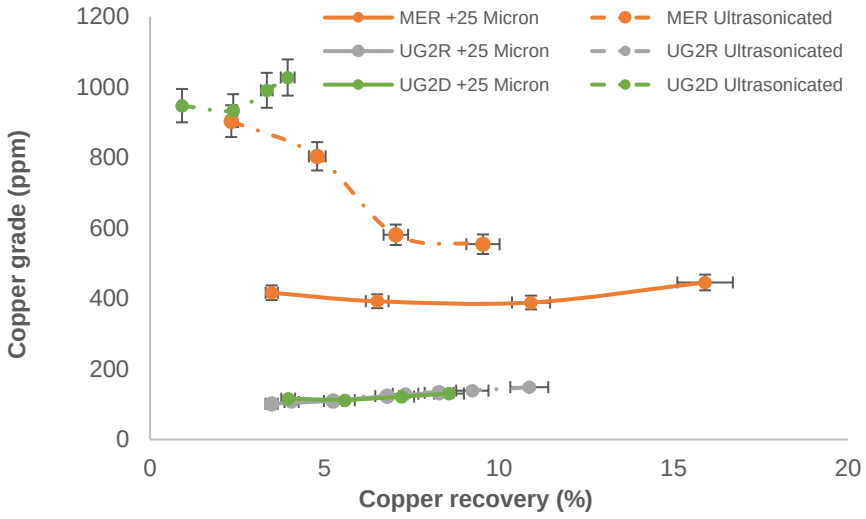


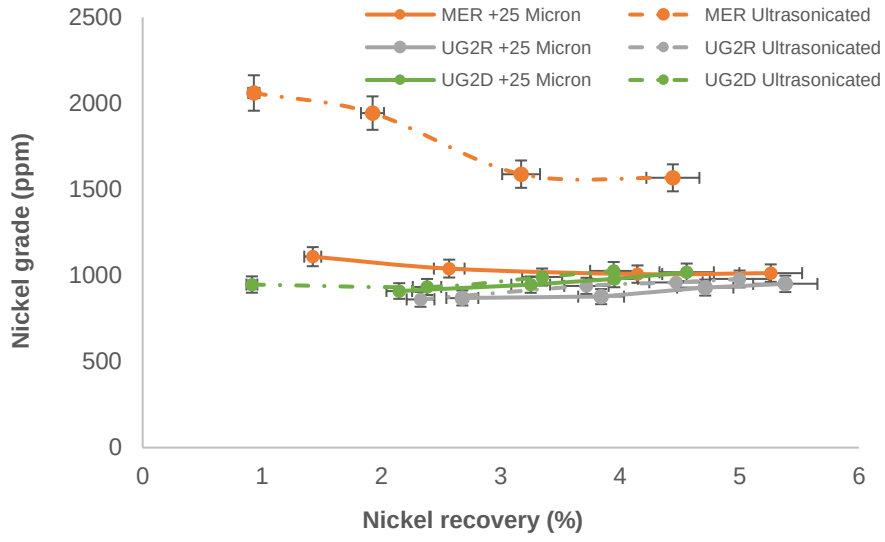
The Grade-Recovery Plot for Untreated vs. Ultrasonicated Tailings at 200 g/t SIBX:





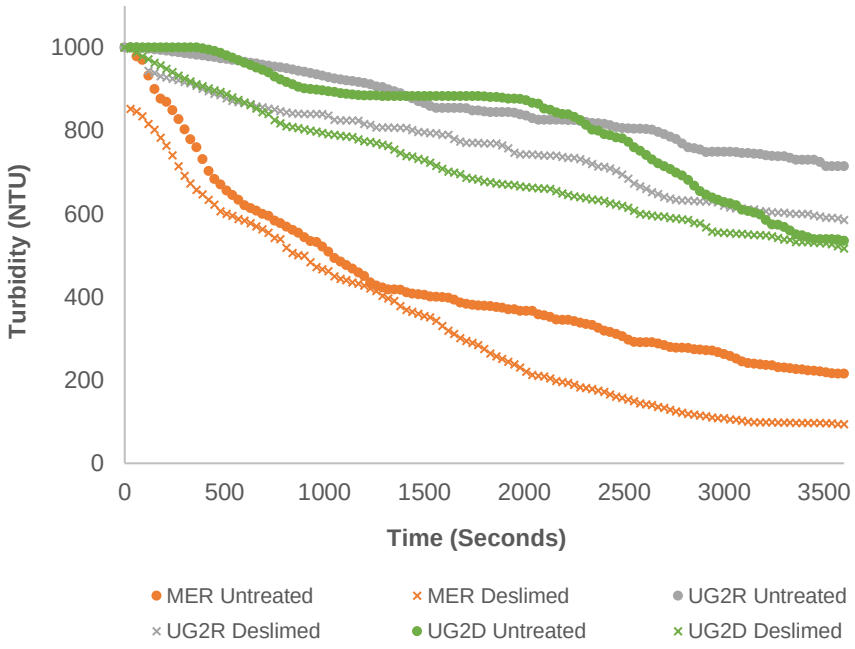
The Grade-Recovery Plot for Deslimed vs. Deslimed-Sonicated Tailings at 200 g/t SIBX:





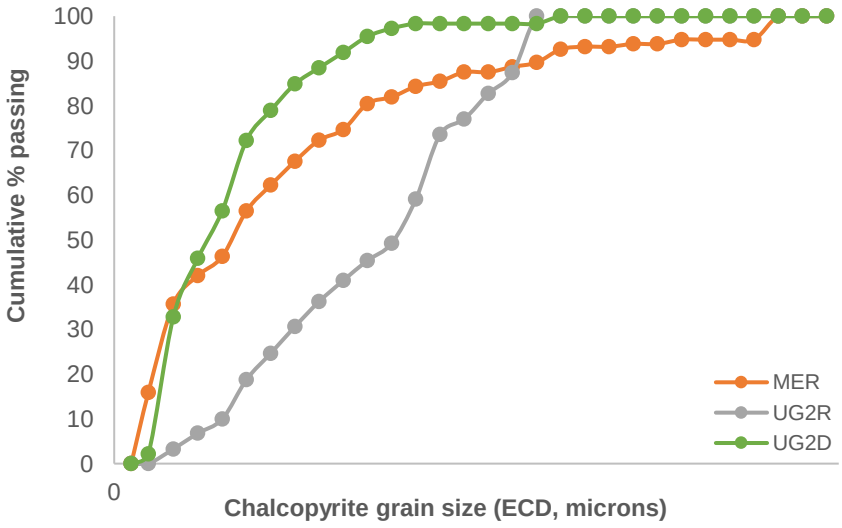
B.2. Particle Settling Data

The raw data for the particle settling rates for all untreated tailings, as well as deslimed tailings:



B.3. Chalcopyrite Grain Size Distribution

The grain size distribution for chalcopyrite is as presented, along with the corresponding modal list grain size:



modal list grain size (µm)	1.41	2.83	4.90	6.93	8.94	11.0	13.0	15.0	17.0	19.0	21.0	23.0	25.0	27.0	29.0
	31.0	33.0	35.0	37.0	39.0	41.0	43.0	45.0	47.0	49.0	51.0	53.0	55.0	57.0	59.0

APPENDIX C

C.1. Online Files

All data pertaining to study has been compiled to, and is available online, as henceforth outlined:

1. The **mineralogy** of the tailings, on a bulk, sized and association basis.
2. **EDTA extraction** measurements and analysis.
3. The **electrochemical data** obtained from the multiprobe.
4. All data and calculations relating to the **batch flotation** of the tailings.
5. All data and calculations relating to the **adsorption of SIBX** (for a 10 and 25-ppm system).
6. The particle **settling data**.