A STUDY OF CYANIDE-GLYCINE SYNERGISTIC LIXIVIANT AND THE IGOLI PROCESS AS SUITABLE REPLACEMENTS FOR MERCURY AMALGAMATION IN ARTISANAL AND SMALL-SCALE GOLD MINING

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ACKNOWLEDGEMENTS

I thank the Lord Almighty for giving me strength and resilience in this journey when it got tough while also providing fun and memorable moments. Without God none of this would be possible. Glory to God. AMDG.

I would like to thank my main supervisor Doctor Thandazile Moyo for the guidance and trusting me to be part of this project which is dear to her. I cherish the kind and wise words you always had for me when I ran into seemingly impossible problems. Thank you for your encouragement, patience, and trusting me to take ownership of this project. I appreciate the laughs and always checking on me because you understood that there is life outside of research and we called you, our counsellor.

I would like to thank my co-supervisor, Professor Jochen Petersen, a wise and humble man who always had words of encouragement and insightful solutions. Even when you were busy, thank you for always making time for me when I was stuck. Thank you for your everlasting patience, kindness, willingness to help, and the infectious passion for problem solving.

To my lab manager, Doctor Kathija Shaik, to who I am deeply grateful to, and Archippe Ngwey Manzila who provided help and guidance in my research. Thank you for your kindness and willingness to help especially during the early days when I was absolutely confused. I will miss the chemistry chats and the laughs we shared as the lab team. It really made my laboratory life enjoyable.

I would like to express my deepest gratitude to the Julian Baring Scholarship fund led by Justin Baring, the Minerals to Metals initiative (MtM) and the National Research Foundation (NRF) through the Minerals Beneficiation SARChI Chair held by Professor Jochen Petersen for their financial support throughout my research.

I am grateful to the Centre for Minerals Research (CMR) for assisting me in comminution, sizing and splitting of my ore. Kenneth Maseko, Monde Bekaphi, Refilwe Moalosi, Christopher, and Lorraine Nkemba for helping me with the operation of the CMR equipment with the permission of CMR lab manager Shireen Govender. Gary Groenmeyer, thank you for letting me use your lab centrifuge which was central to the success of my experiments. Andrea Molifie, thank you for helping me with the QEMSCAN analysis of my samples.

I would like to acknowledge Sandeeran Govender, Christophe C, Russell Geland, Sibongile Nyimbinya (UCT Analytical Laboratory Services), Kelly Moir (Scientific Services), Metsolutions, and Dorcas Hanyane (Mintek) for their time and effort in analysing my samples.

I would like to sincerely thank the Mintek team and organisation for sharing their data and information on the iGoli process. Also, my deepest gratitude to NUST Chemical Engineering Department for allowing me access to perform tests in their lab.

A heartfelt thank you to Donatello Mzilethi for sourcing the ore samples and organising visits to ASGM sites alongside Dr Thandazile Moyo. A big thank you to the ASGM sites visited who allowed me to conduct my research there.

To all the colleagues and seniors in the Hydromet and MtM research groups, thank you for your very invaluable advice and feedback throughout the course of my research. Special thanks to my laboratory family: Melissa Gugu Gonte, Jordy Dinga, Fernando Ortega Jimènez, Eddy Miiro, and Dr Emmanuel Ajiboye for the fun chats and ranting in the laboratory when things got hectic. Thank you for never hesitating to help me when needed, I know the reactors were heavy.

I would like to thank my family and friends for their love and support. To my father Paul who taught me to be courageous, my mother Chresentiana who instilled in me the value of hard work, my brothers Sean, Hugh and Lynden who I love and miss dearly, my sister Monalisa Musa who has always had my back, and my nieces Theresa and Kim who have my heart, having you in my life is such a blessing, thank you for your everlasting love.

Finally, to the love of my life Sandrene and our lovely children Sibongile and Lungile. Thank you for your love and strength. I know it was hard when I was away, thank you for persevering and walking this journey with me. Without you I would not have had the heart to run this race. I dedicate this thesis to you.

ABSTRACT

Artisanal and Small-scale Gold Mining (ASGM) operations are characterized by the use of rudimentary tools and technologies owing to limited access to capital. ASGM is predominantly a poverty-driven exercise practiced as a source of livelihood, typically in rural communities where people lack other employable skills. Globally, ASGM accounts for 20-25% of gold production, while at local scales, this number varies and can be as high as 65% in countries such as Ghana and Zimbabwe.

Mercury is used in ASGM to capture gold from free-milling ores, in a process called mercury amalgamation. This is the go-to technology in most ASGM operations owing to its availability and ease of operation. However, mercury amalgamation has low recoveries in the range of 30-33% of gold from the otherwise rich gold ores typically mined in ASGM. In the amalgamation process, about 70% of the mercury used is lost to the environment with the amalgamation tailings and during the roasting process. Mercury is a toxic heavy metal, and mercury poisoning can lead to neurological and behavioural disorders and has been a major concern globally, leading to the signing of the Minamata Convention treaty. Mercury-free gold concentration and extraction methods such as shaking tables and roasting with borax have been put forward over the years, but their uptake has been very limited. The reasons for this poor uptake have never been systematically studied but it is thought that, among other reasons, it has to do with that some technologies are too complex for the ASGM context. Beyond the mercury-free technologies proposed for the ASGM sector, gold extraction and recovery in the large-scale mining sector has attracted researchers' attention for years, with a plethora of technologies having been proposed and tested. Little effort has been made to establish if any of these technologies could be a good fit for ASGM.

In this study, two mercury-free technologies (cyanide-glycine lixiviant and the iGoli process) were tested to establish their effectiveness in the leaching of gold from ores sourced from two ASGM sites. The ores were characterized using QEMSCAN, XRD and XRF to identify mineral phases, and quartz was found to be the most dominant mineral. Sulphide minerals in both ores host the largest percentage of gold. The cyanide-glycine lixiviant uses a combination of cyanide and glycine to improve gold extraction. The results from this showed that dissolution rate increases with an increase in glycine concentration in non-agitated systems at 3g/l NaCN while the reverse was true in agitated systems at the same cyanide concentration and when it was varied. The percentage of gold extracted in the non-agitated system after 72 hours was 36% at 5 g/l glycine, 21% at 2 g/l glycine and 19% when no glycine was added. In agitated systems at 5g/l cyanide, the highest extraction after 24 hours was 81% at 2 g/l glycine. Increasing glycine concentration led to lower gold extractions with 5 g/l and 10 g/l glycine extracting 74% and 68% respectively. This trend of decreasing extraction with an increase in glycine concentration was observed at different fixed cyanide concentrations i.e., at 1 g/l, 3 g/l and 5 g/l. The iGoli process uses hydrochloric acid and sodium hypochlorite to leach gold. The extractions were very low and reported below the detection limit of the analytical instrument, and thus they cannot be reported with confidence. However, iron was analyzed and showed a 55% extraction of the total iron in the ore. Results from these two technologies were compared to those of mercury amalgamation and benchmarked against the conventional cyanide process.

Beyond the purely technical, a case study of two ASGM sites was done with the objective to observe and understand the day-to-day operations in a typical ASGM site and identify limitations and opportunities for mercury-free technology adoption. Based on insights drawn from the case studies, it was concluded that the cyanide-glycine lixiviant is relatively easy to implement given the current process operation in the ASGM sector which makes use of vat tanks that do not agitate the slurry (lixiviant + ore). However, the observed poor recoveries associated with the technology in non-agitated systems would be a limitation. When more

profits are realized, the ASGM practitioners can upgrade to agitated systems and add hydrogen peroxide as an oxidizing agent to improve extraction.

1 INTRODUCTION

1.1 BACKGROUND

Artisanal and Small-scale Mining (ASM) refers to mining done by individuals, communities or small businesses with limited capital investment and production. They use manual to semi-mechanized techniques (rudimentary) in exploiting ore deposits i.e. mining and processing the ores (Veiga and Fadina, 2020). ASM is still largely informal, and capital thresh-holds which qualify a project to be ASM are difficult to have, therefore, most definitions of ASM are rooted on type of operation, size of operation and equipment used. Artisanal and Small-scale Gold Mining (ASGM) falls under ASM, and as the name suggests, the mineral being targeted is gold. ASGM accounts for 20-25% of the world's annual gold production (Telmer and Stapper, 2012). As already mentioned, ASGM is a subset of ASM. The socio-economic contexts of the two are similar and for the purposes of this thesis, the term/acronym ASGM will be used so as to avoid interchanging between the two and to keep the reader aware of that this thesis has a focus on the artisanal and small-scale mining of gold.

ASM in general is an essential activity in many third world countries as it provides a source of livelihood, particularly in regions where economic alternatives are critically limited (Serfor-Armah *et al.*, 2004). The sector is a source of livelihood for an estimated 15 million people worldwide, most of whom have taken up mining activities in an attempt to escape poverty and generate supplementary incomes (Davies, 2014), (Telmer and Stapper, 2012). ASGM provides indirect jobs for local goldsmiths, carriers, panners or washers, carpenters, steel benders, and masons to earn income (Bansah *et al.*, 2018). ASGM, and broadly speaking ASM, spurs a local community economy of sorts that is backed by its activities. Shops, restaurants, and other small enterprises pop up, that sell goods and services to miners. When products are not smuggled out of the country, informal ASGM contributes to government revenue as their products will ultimately go to the government which makes an income during export (Chipangura, 2019; Hlungwani, Yingi and Chitongo, 2021).

The rapid population growth in third world countries will increase hunger and poverty where food, water, and farmland are already in short supply (B.Westley, 2013; ZIMSTAT, 2022). Coupled with the dwindling youth employment rates (International Labour Organisation, 2022), there is expected to be an increase in ASGM activities as a source of livelihood. Since artisanal and small scale mining is associated with significant environmental degradation and deplorable social conditions, it is reasonable to expect these negative attributes to increase with an increase in the number of people participating in the sector (Mondlane and Shoko, 2003). One of the key challenges of ASGM is that of the safety, health and environmental (SHE) risks associated with mercury pollution. In the processing of gold ores from ASGM, mercury is the technology of choice owing to its accessibility, relative cheapness and ease to operate (Telmer and Stapper, 2012). Beyond the SHE risks, mercury is problematic due to its inefficiency as an extractant, with the technology reported to only extract and recover 30-33% of gold from the otherwise rich gold ores typically mined in ASGM (Veiga *et al.*, 2009)(Telmer and Stapper, 2012). Depletion of these rich gold ores has led miners to process relatively more complex ores, and this is problematic in the ASGM sector which is limited by the one-size-fits-all mercury amalgamation technology. The extractions are expected to be significantly lower since the mineralogy of an ore deposit determines the best extraction process, and, in particular, the performance of all chemical processes involved in gold extraction (Marsden and House, 2009). Therefore, there is a need to understand the characteristics of the ore and how it affects the extraction of gold.

In the amalgamation process, about 70% of the mercury used is lost to the environment with the amalgamation tailings and during the roasting process (Veiga *et al.*, 2009). Mercury is a toxic heavy metal which can find its way into the human body through consumption of fish from contaminated water bodies, consumption of vegetables and other plants growing in mercury-contaminated soils and via inhalation of mercury-vapour (Veiga, 1997; Vieira, 2006; Drace *et al.*, 2012). Mercury poisoning can lead to neurological and behavioural disorders (Veiga, 1997; Vieira, 2006; Drace *et al.*, 2012) and has been a major concern globally, leading to the signing of the Minamata Convention, a treaty aimed at reducing global anthropogenic emissions and releases of mercury and mercury compounds (World Health Organisation, 2016). If amalgamation tailings undergo cyanidation, the residual mercury in the tailings reacts with cyanide forming mercury-cyanide which is more toxic than either mercury or cyanide.

In light of the number of people reliant on ASGM operations and the magnitude of resulting impacts, there is a need to develop and implement appropriate measures and technologies that can mitigate the problems created (Hinton, Veiga and Veiga, 2003). An understanding of ASGM is needed before blanket solutions are pushed forward. Insight on their operations, social and financial structures will be crucial in understanding willingness or lack thereof to move to new technologies, since proposed technologies have had poor uptake. These proposed technologies also must be evaluated on how they map into ASGM.

1.2 PROBLEM STATEMENT

Efficiency in extraction and processing as well as the associated SHE implications of the processing technologies have a significant bearing on the overall contribution of ASGM to local economic development and sustainability (Telmer and Stapper, 2012).

The technology of choice for gold extraction in ASGM is mercury amalgamation which has a low extraction efficiency of 30-33% but is favoured because of availability and ease of operation (Veiga *et al.*, 2009; Telmer and Stapper, 2012). Mercury is a powerful neurotoxin that is harmful to people, but especially to developing foetuses, and young children (Veiga, 1997; Telmer and Stapper, 2012). Once emitted, mercury can travel great distances through the atmosphere, causing global contamination of ecosystems, fish, birds, mammals, and the human food chain. Consumption of mercury contaminated seafood and fresh water species puts billions of people at risk of mercury poisoning, which affects the development and function of the brain and the nervous system (Veiga, 1997; Telmer and Stapper, 2012). Mining communities and those surrounding where mercury is used are the most at risk. ASGM miners typically mine high grade ores, but as these deplete, they move to mining more complex ores. The characteristics of an ore deposit and its mineral assemblages determine the extraction process and the performance of all chemical processes involved in gold extraction (Marsden and House, 2009).

Regardless of the known negative impacts from mercury usage, it remains the technology of choice in the ASGM sector even though there are alternative technologies available. This raises the question as to why the proposed technologies to replace mercury have had little to no uptake. Also, the mineralogy of ores in ASGM is hardly explored in literature despite it being known that this has major bearing on the performance of processing technologies. This study will test and validate two mercury-free technologies and use the insight gained from field studies and ore characterization to comment on the suitability of the technologies for adoption in the ASGM context. The first is the iGoli process which was designed for small-scale miners and has been reported in literature to have good results on enriched gravity tailings (Guest and Mahlatsi, 2003; Mahlatsi and Guest, 2003). The second is the cyanide-glycine process which was designed for large scale industry. Cyanide leaching has produced good results in industry and has been successfully mapped onto ASGM for example in Indonesia with extractions of over 93% being achieved (Veiga *et al.*, 2009). Cyanide-glycine is a variant which is said to produce the same great results with less cyanide being used (Eksteen and Oraby, 2015; Oraby, Eksteen and Tanda, 2017).

1.3 OBJECTIVE OF THE STUDY

The objective of this study is to test and validate 2 mercury-free technologies proposed for uptake by artisanal and small-scale gold miners with ore samples typical for this sector. Furthermore, the study conducts field studies of ASGM sites in an effort to understand the context, identify barriers to mercury-free technology adoption and identify entry points for mercury-free technologies. To achieve this, a comparative study on gold extraction using mercury, cyanide-glycine and the iGoli process were carried out while cyanide leaching of the gold was used as a baseline in this study. The comparative study aims to evaluate the gold extraction efficiency and analyse the control parameters of each process. Also, a mineralogical characterisation of the ore from ASGM sites will be carried out.

1.3.1 SPECIFIC OBJECTIVES

I. To study ASGM ore mineralogy using sophisticated tools such as QEMSCAN and XRD analysis, and a more accessible approach of diagnostic leaching.
II. To understand ASGM operations, social and economic structures (case study).
III. To test and compare gold extraction when using a two-step mercury-amalgamation followed by cyanidation at an ASGM site (section 4.2.1.2)against the iGoli Process and Cyanide-Glycine synergistic lixiviant.
  - To analyse the effect of lixiviant concentration on extraction.
  - To evaluate extraction kinetics and efficiency of each process.
  - To analyse the effect of process variables like lixiviant concentration, pH, and agitation on extraction.
  - To carry out a bench marking test with cyanide.
  - To evaluate if the technologies can translate into ASGM.

1.3.2 KEY QUESTIONS

I. What is the nature of the ore and which minerals are associated with gold?
II. What is the current processing approach, social dynamics, and economic models in ASGM?
III. Which technology/operation has the best extraction?
  - How do the proposed technologies compare to the ASGM extraction efficiency?
  - How do process variables like agitation, pH, and solvent concentration affect leaching rate and extraction?
  - How do these technologies compare vs cyanide leaching?
IV. Is there potential for the adoption of new technologies considering the insights from fieldwork?

2 LITERATURE REVIEW

2.1 ASGM

ASGM practitioners are predominantly nomadic, settling in mining camps surrounded by rich mineral deposits (Mondlane and Shoko, 2003). When these deposits are spent or an area with higher recoveries is reported they move to the next area. ASGM has a general lack of capital and resources which means most of their operations are rudimentary to semi-mechanized (Mondlane and Shoko, 2003; Veiga and Fadina, 2020). In ASGM, miners use rudimentary equipment like shovels, hoists, and jack hammers for mining. The processing stage involves hammering the ore down to feed size for hammer mills and sometimes stamp mills because these are the most affordable. Mercury is the choice of extractant because of relative affordability, availability, its relatively fast and easy to use (Veiga and Fadina, 2020). ASGM has been shown to economically empower the poor and unemployed who take up this activity. Local economies develop as community members become buyers and sellers of commodities (Mondlane and Shoko, 2003). This benefits the previously impoverished communities.

70 – 80% of all artisanal and small scale mining operations are informal and illegal, because they do not possess the requisite licences and permits required by law to operate (Morgane et al, 2018). There is a cost to acquire licences to mine and operate at each site. With most artisanal miners being nomadic, this would entail that they need to purchase the requisite mining and operating licences for every new site they move to which is expensive and impractical. Therefore, that’s why the majority in this sector are unlicenced, making their operations illegal and informal since they do not operate under the state structure. Informality leaves the sector open to corruption, embezzlement, criminality, loss of revenue, and they cannot be afforded the benefits of legal protection (Morgane et al, 2018; Zimbabwe Economic Policy Analysis and Research Unit, 2018). Rampant informality is unsustainable and if allowed to persist, it leads to a variety of damaging socioeconomic, health and environmental impacts and development challenges that lead to community impoverishment instead of financial empowerment (Hilson, Hilson and Pardie, 2007). Since ASGM is largely poverty driven, there is always a need to make the most money in the shortest amount of time. This coupled with a lack of resources has led to wastage and lack of reclamation in their operations (Mondlane and Shoko, 2003; Veiga and Fadina, 2020). Environmental problems like mercury contamination and land degradation are left in the wake of ASGM (Veiga, 1997). The lack of understanding of ore mineralogy leads to losses in income because they use one processing technology on all gold ores they mine. A lot of social ills have been synonymous with ASGM. It is reported to have led to increased instances of prostitution, alcohol abuse, conflicts, spread of diseases, and child labor (Mondlane and Shoko, 2003; Tschakert and Singha, 2007; Banchirigah, 2008).

The poor working and living conditions, wasteful mining, inefficient processing and environmental degradation can be lessened by financial, regulatory, institutional, and technical support (Mondlane and Shoko, 2003). Figure 2.1 summarizes the challenges faced by ASGM.

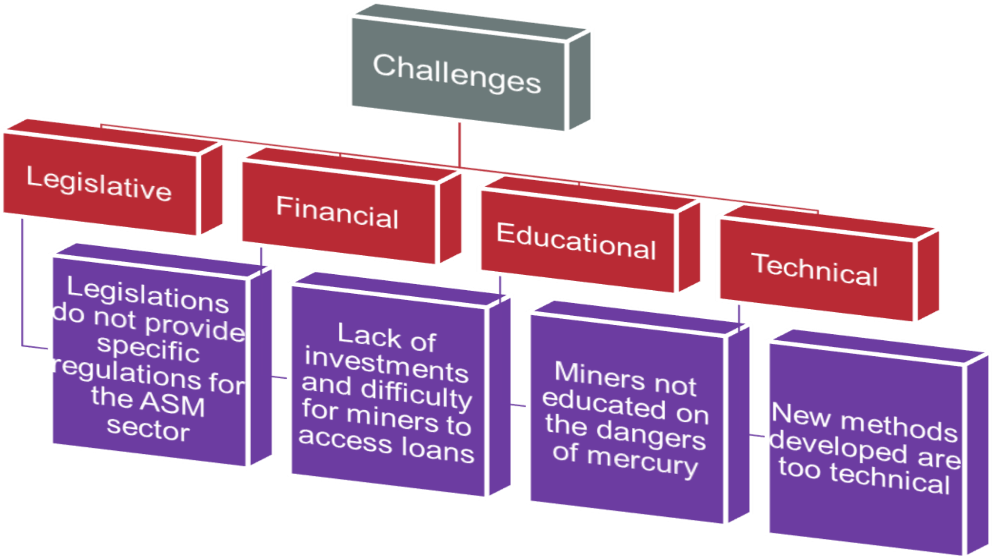

Figure 2.1: Problems that affect ASGM [Adapted from (Mondlane and Shoko, 2003; Veiga, Angeloci-Santos and Meech, 2014; Veiga and Fadina, 2020)*]*

ASGM is an important development opportunity which can contribute directly to poverty alleviation and regional development (Telmer and Stapper, 2012). Although social ills and environmental decay are common in this sector, there is an opportunity to transform mineral wealth gained from ASGM into lasting local development. This study will focus mainly on the technical aspect looking into mercury-free technologies.

2.2 ASGM OPERATION

Mining is predominantly carried out with picks and shovels. Shafts are sunk and the ore is hauled out using metal buckets which are hoisted to the surface as shown in Figure 2.2. The run-off mine ore is ferried to crushing sites were comminution takes place with use of primary crushers then milling.

Figure 2.2: Hauling ore from a mine shaft (authors own)

Mercury amalgamation is the preferred method of gold extraction used by artisanal and small scale gold miners because mercury is effective, simple (amalgamation can be carried out by one person, unlike more technically sophisticated processes) and a very inexpensive reagent to extract gold (1kg of Hg costs the same as 1g of Au) when it is used correctly (Veiga, 1997). The mercury-gold amalgam formed contains 40% – 50% mercury and the ratio of mercury used to gold recovered ranges from 4:1 to a very high 50:1 for ores which contain silver (Grayson, 2007; Telmer and Stapper, 2012).

There are two main methods employed by ASMG practitioners in using mercury to extract gold. The first is whole ore amalgamation where mercury is brought into contact with 100% of the ore (Telmer and Stapper, 2012). Mercury is lined on the plate of the sluice box and milled ore is washed over it or mercury is added to the mill during grinding. Gold particles stick to the mercury and are scrapped off as mercury-gold amalgam (Telmer and Stapper, 2012). Whole ore amalgamation loses approximately 70% of the mercury used (Veiga *et al.*, 2009). The first is due to flouring of mercury when it is directly added to ball mills during milling and the second is by mercury flowing away with the tailings when it is lined on sluices (Veiga *et al.*, 2009). The second approach is to amalgamate gravity concentrates which are produced from the pre-treatment of ore by gravity methods before mercury amalgamation is employed. The gravity methods typically employed in ASGM are panning, sluicing, use of Gemini tables and centrifuges (Davies, 2014). These are better methods compared to the first because the total amount of mercury lost is significantly less since less ore is being treated. However, there are still mercury losses with the tailings, during roasting and refining. The gangue portion is separated from the gold-mercury amalgam by panning, forming an amalgamation tailing. Panning is carried out in water-boxes or in pools excavated in the ground (Veiga, 1997; Veiga, Angeloci-Santos and Meech, 2014). Figure 2.3 shows a mercury-gold amalgam.

Figure 2.3: Amalgam (authors own)

Mercury extracts more than 90% of gold from gravity concentrates. The excess mercury from the amalgamation process is recovered by squeezing the material through a piece of cloth. The mercury contained in the gold-mercury amalgam is mostly burnt off in open pans. Roasting in pans contributes to approximately 30% of mercury losses. The process produces a gold sponge (shown in Figure 2.4)containing about 20 g of mercury per kg of gold (Grayson, 2007). It should be noted that some in the ASGM sector have adopted the use of retorts where mercury is recycled (Babut *et al.*, 2003; Bosse Jønsson, Charles and Kalvig, 2013). Mercury-gold amalgams are heated in a closed system to evaporate the mercury which is then condensed by passing the mercury vapor through a water-cooled jacket.

Figure 2.4: Sponge Gold (authors own)

2.3 GOLD MINERALOGY AND HOW IT AFFECTS EXTRACTION

Gold occurrences can be found in all rock types of geological ages i.e., Precambrian, Palaeozoic, Mesozoic, and Cenozoic. The characteristics of an ore deposit and its mineral assemblages determine the mining method, extraction process, and in particular, the performance of all chemical processes involved in gold extraction (Marsden and House, 2009).

Therefore, a full understanding of the mineralogy of an ore deposit is required to design or operate a gold extraction process at optimum efficiency.

The gold mineralogy in each ore deposit is unique, due to the variations in the following:

- Mineralogical mode of the occurrence of gold
- Gold grain size distribution
- Host and gangue mineral type
- Host and gangue mineral grain size distribution
- Mineral associations
- Mineral alterations
- Variations of the above within a deposit or with time (Marsden and House, 2009).

This section will discuss gold mineralisation. The focus will be on the minerals it is associated with and how they affect gold extraction. A probable extraction process will be included.

2.3.1 COMMON GOLD MINERAL ASSOCIATIONS

Of the gold-bearing minerals, the most common and important are those composed of Gold and Silver where gold is greater than 50% (Afenya, 2000). However, it should be noted that in some deposits the Ag content is greater than Au.

Gold fineness is used to describe purity of gold $\left[Fineness = \frac{wt\%\ Au*1000}{wt\%\ Au+wt\%\ Ag}\right]$ (Afenya, 2000; Marsden and House, 2009). Fineness is a system of denoting the purity of a metal by parts per thousand of pure metal by mass in the alloy. For example, an alloy containing 85% gold is denoted as "850". This measure is important because silver tends to report with gold in extraction processes. Fineness as a measure of gold purity becomes decreasingly valid with an increase in concentration of other impurities such as Cu and Fe.

The next most common gold compounds are tellurides, with sylvanite $[(Au, Ag)_2Te_4]$, calaverite $[AuTe_2]$ and petzite $[Ag_3AuTe_2]$ being the most common gold bearing tellurides. They are often associated with free gold and sulphides (Marsden and House, 2009).

Gold less commonly occurs with bismuth in the mineral maldonite $[Au_2Bi]$ and even less with copper in intermetallic compounds auricupride $[AuCu_3]$ and tetra-auricupride $[AuCu]$.

The following deductions were made by Afenya (2000), on gold-bearing minerals:

1. The predominant gold bearing minerals are Au-Ag alloys with trace amounts of copper.
2. The second predominant group of elements is the platinum group of metals which form intermetallic compounds with gold.
3. Thirdly its elements in group IV A to VI A of the periodic table that form intermetallic compounds and other complexes with gold. These elements are Pb, Se, Bi, S, Sb, Te, and Tl.
4. Gold in a solid solution with arsenopyrites

Therefore, in designing a process for extracting gold it is important to consider the elements in association with gold in the ore as some do take part in the extraction reactions and therefore appear as impurities in the final product if not considered.

Host minerals of gold can be divided into two, the rock-forming minerals and ore minerals.

2.3.1.1 ROCK FORMING MINERALS

The common rock-forming minerals acting as host minerals for native gold are quartz, carbonates (calcite, ankerite, manganocalcite, dolomite), chlorite, sericite, graphite, carbonaceous matter, and tourmaline (Afenya, 2000). Other minerals include apatite, amphiboles, feldspar, mica etc which have been found to also host trace amounts of native gold (Afenya, 2000). Gold may also occur in association with gypsum, fluorite, alunite, pyroxene, serpentinite, and wollastonite.

Gold occurs in all 3 rock types i.e., igneous, sedimentary, and metamorphic rocks. Gold appears in all forms of igneous rocks from ultramafics to felsics and in extension therefore any minerals constituting these rocks. In sedimentary rocks it is usually associated with quartz, mica, zircon, and iron oxides, while in metamorphic rocks it is associated with chlorite, talc, sericite, and mica (Afenya, 2000).

2.3.1.2 ORE MINERALS

Ore minerals tend to host a substantial amount of gold in gold deposits. However, they are significantly less when compared to the rock-forming minerals (Afenya, 2000). The most common ore mineral hosts of gold are pyrite, arsenopyrite, pyrrhotite and copper sulphide (Marsden and House, 2009). Gold may associate with these minerals physically as grains in ore, chemically bonded with elements in the minerals, or solid solution (Afenya, 2000).

Some of the gold may also occur as alloys with some elements in the mineral, in fractures, along cleavages and at mineral grain boundaries. Fine gold encapsulated in ore minerals and/or present in solid solutions presents the greatest problems in liberation and extraction (Afenya, 2000). Encapsulated gold will remain unreacted in cyanide leaching especially when locked in non-porous sulphide grains.

2.3.2 REFRACTORINESS

Cyanidation has so far been the most efficient process for extracting gold from ore and it is widely applied. Gold extractions of above 90% are usually expected and are commonly achieved in industrial operations (Marsden and House, 2009).

Refractoriness is defined by gold recovery when applying direct leaching with cyanide. Non-refractory gold ores are those that respond readily to direct cyanidation producing gold recoveries of more than 95% (Vaughan, 2004). Refractory gold ores produce gold recoveries of less than 90% on direct cyanidation. However, there are 4 levels of refractoriness i.e., non-refractory (>95% recovery), mildly refractory (80-95% recovery), moderately refractory (50-80% recovery), and highly refractory (0-50% recovery) (Vaughan, 2004). Refractoriness is due to one or a combination of the following:

I. Chemical bonding of gold with other elements in the ore to form gold compounds.
II. Solid solution of gold in pyrite and arsenopyrite.
III. Fine to sub-microscopic gold encapsulated within non-porous sulphide minerals, silicates, silica, and oxides which are unreactive to cyanide.
IV. Ores containing preg-robbing carbonaceous material and/or clay as well as cyanide and oxygen consuming minerals such as , chalcocite, covellite, arsenic, and antimony sulphides (Afenya, 2000).
V. Gold particles that are too coarse to dissolve in the available leaching time (Marsden and House, 2009).

2.3.3 EXTRACTION PROCESS FOR DIFFERENT MINERAL ASSOCIATIONS

2.3.3.1 GOLD - QUARTZ - CARBONATES, WITH MINOR BASE METAL SULPHIDES

In this first mineralisation, gold occurs mainly with quartz and to a lesser extent with carbonates. So, this falls under rock-forming minerals of gold, and most are brittle with well-defined cleavages. Therefore, gold can be easily liberated during comminution, making extraction with cyanide easier (Marsden and House, 2009). Mineralisation of this type is responsible for non-refractory ores that may be treated as follows:

comminution ± gravity separation + cyanidation + elution + Zn dust precipitation/electrowinning

(Afenya, 2000).

2.3.3.2 GOLD - QUARTZ ± CARBONATES - PYRITE- ARSENOPYRITE, WITH MINOR Cu, Zn, Pb SULPHIDES

In this second mineralisation we have gold occurring with quartz, pyrite, arsenopyrite and pyrrhotite. If the gold is not locked within the sulphide minerals, recoveries over 90% can be realised making the ore non-refractory. Consequently, gold that is locked within pyrite and arsenopyrite renders that ore refractory (Afenya, 2000). If the gold is on fractured pyrite the liberation is easier than from arsenopyrite. If the gold occurs in solid solution with pyrite and arsenopyrite then liberation would be impossible even with fine grinding (Afenya, 2000; Marsden and House, 2009). Therefore, to recover gold from this mineralisation would require a process that will breakdown the sulphides first. Some ores will also contain preg-robbing carbonaceous materials (carbon containing compounds). Carbonaceous material adsorbs gold from the pregnant leach solution (Vaughan, 2004). Therefore, the hinderances to a good extraction are pyrite, arsenopyrite, pyrrhotite and carbonaceous materials in the ore.

Bacterial oxidation, pressure oxidation, and several other techniques have been developed and used both to increase gold recoveries from the ores and to meet new environmental standards (Vaughan, 2004). Below are one or a combination of the following treatment options:

I. *comminution + gravity concentration + flotation + roasting + cyanidation with CIP (carbon in pulp)*
Roasting is employed to burn off SO_2 and As_2O_3 gas in the pyrites. Due to environmental regulations, it is mandatory to scrub the flue gases produced. After roasting the ore goes for CIP leaching which involves leaching with cyanide first then stripping gold from the lixiviant using activated carbon in another vessel (Afenya, 2000).

II. *comminution ± gravity concentration + flotation + bio-oxidation + cyanidation with carbon-in-leach (CIL)*
Bio-oxidation is used if the greater proportion of the sulphide gold is locked within pyrrhotite and arsenopyrite. This is because pyrrhotite and arsenopyrite have fast bio-oxidation rates. However, carbonaceous material is relatively inert to bio-oxidation. It is therefore imperative to use CIL, where carbon is added to the leach vessel so that leaching and adsorption take place in the same tanks, during cyanide leaching (Afenya, 2000; Vaughan, 2004; Marsden and House, 2009).

III. *comminution ± gravity concentration + flotation + pressure oxidation + cyanidation with CIL/CIP*
Pressure oxidation is employed if most of the gold is locked within crystallised pyrite. This is a more rigorous process, but it's used since pyrite has a slow bio-oxidation rate. Then after this it is leached with cyanide in CIP. However, if preg-robbing carbonaceous material is present, CIL is used. This is because pressure oxidation cannot sufficiently deactivate carbonaceous material (Afenya, 2000).

2.3.3.3 GOLD- QUARTZ- CARBONATES- ARSENOPYRITE- PYRRHOTITEPYRITE, WITH MINOR BASE METAIS

The third mineralisation is associated with banded iron formation (BIF) containing hematite, Ca-Mg-Fe carbonates, quartz sandwiching the platy silicate minerals, and the sulphide minerals i.e., arsenopyrite, pyrrhotite, and pyrite which carry the gold (Afenya, 2000). On comminution, the gold and iron sulphides associated with the carbonates and the platy silicates (micas, sericite) are readily liberated. The gold locked within the hematite and magnetite isn't readily liberated. This leads to a differential grinding problem. Therefore, the ore goes through flotation since it has sulphides after which it is roasted to drive them off and then CIP. Another option would be pressure leaching of the concentrate from the flotation process followed by CIP/ CIL.

comminution + gravity concentration + flotation + roasting/pressure leaching + cyanidation with CIP/CIL (Afenya, 2000)

2.3.3.4 GOLD-TELLURIUM-SILVER

For gold ores which are silver rich the overall cyanide consumptions are higher than those obtained for leaching of gold ores with low silver content because the silver is leached with the gold (Marsden and House, 2009). So, you will have a silver rich and gold rich leachate. However, gold adsorbs more preferentially on carbon than silver. So, the silver can then be precipitated using zinc after (Marsden and House, 2009).

comminution ± gravity separation + CIL + elution + Zn dust precipitation/electrowinning

A majority of telluride ores respond well to flotation to produce a tellurium-rich concentrate, with only a few being able to respond well to direct cyanidation after comminution (Marsden and House, 2009). The concentrate from flotation must be oxidized to liberate the contained gold before leaching. Chlorination and roasting have been used for this purpose commercially with chlorination being most suitable for ores with low sulphide content while roasting is best for high sulphide ores (Marsden and House, 2009).

comminution ± gravity concentration + flotation + roasting/chlorination + cyanidation

2.4 SOCIAL, ECONOMIC, HEALTH AND ENVIRONMENTAL EFFECTS OF ASGM

ASGM has become synonymous with environmental decay because of land degradation, contamination due to mercury usage, pollution, and harming biodiversity (Veiga, 1997; Serfor-Armah *et al.*, 2004; Kitula, 2006; Hilson, Hilson and Pardie, 2007). These environmental problems coupled with the danger these mining activities cause to workers and the surrounding communities is attributed to the lack of knowledge, poor technology, limited capital, lack of law enforcement, and inadequate environmental legislation (Bansah *et al.*, 2018). This was also noted by Mondlane and Shoko (2003), who carried out a study on the socio-economic and environmental impacts of artisanal and small-scale mining in Nampula Mozambique. Although lack of law enforcement and inadequate environmental legislation are reported to contribute to the ills of artisanal and small scale mining, stringent legislation and over policing can lead to violent altercations between miners, mining firms, and the government (Andrew, 2003; Aubynn, 2009).

It is important to also speak to the positive socio-economic impacts of ASGM because it promotes local commerce and national income, provided the trade of the mined gold goes through formal channels (Shen and James, 2006; Fisher *et al.*, 2009; Hilson, 2016; Bansah *et al.*, 2018). The number of people dependant on ASGM is expected to grow due to a growing population in third-world countries and increasing formal unemployment rates.

2.4.1 ECONOMIC

Informal ASGM provides employment to poor people, mostly in the rural areas. Most of the people involved in ASGM lack alternative employable skills so this is a welcome source for livelihood (Bansah *et al.*, 2018). As noted by Banchirigah (2008), rural community people displaced by large-scale mining companies resort to informal ASGM for income to support themselves and their families. Informal ASGM provides indirect jobs for local goldsmiths, ore carriers, panners or washers, carpenters, steel benders, and masons to earn an income (Bansah *et al.*, 2018). ASGM contributes to the growth of the local economy as shops also pop up that sell goods to miners. Informal ASGM also contributes to government revenue as their products will ultimately go to the government which makes an income during export. Revenue collection from ASGM may be poor owing to the illegal trade and exportation/smuggling of the gold (Mondlane and Shoko, 2003).

Most miners seldom operate legally and thus, have limited access to formal markets when selling the gold bullion they produce. This results in them selling in parallel markets were prices are below market value resulting in less gains for the effort made to get the gold (Mondlane and Shoko, 2003). The price is usually 70% of the market value (Telmer and Stapper, 2012). According to Mondlane and Shoko (2003), this could be solved by a facilitating role by the government in terms of buying gold without questions asked and with help and monitoring given on the technical side to make sure they operate sustainably. The downside of a no questions asked policy might be that the government becomes powerless to police reclamation and safe operations at ASGM sites. The hope would be that by setting up a buying site, the government might potentially tackle illegalities like smuggling. When the miners are selling at a fair price thereby making more for their effort, they may also think sustainability and future because of more financial security as they can send their kids to school and afford health care etc.

Even though ASGM is largely poverty driven, there is evidence of wealthy individuals, professionals, semi-skilled personnel, and university graduates entering the fold (Hilson and Potter, 2005). University graduates and semi-skilled personnel usually engage in ASGM because of high unemployment rates (Hilson and Potter, 2005)(Banchirigah, 2008). The wealthy individuals and professionals do not directly engage in the mining but act as sponsors, investing in the operations (Hilson and Potter, 2005). Gold dealers and processing centers are also involved in the sponsoring. They offer resources needed by miners for daily operations like food, fuel, mercury, and money lending facilities. This type of relationship is more beneficial to the sponsor in that they are first in line for the product at relatively discounted prices and/ get the amalgamation tailings as miners are indebted to them (Hilson and Potter, 2005). There is a need to understand the business model of ASGM operations because these players will influence decision making which is not limited to technology of choice.

2.4.2 SOCIAL

Most ASGM practitioners are nomadic moving to sites which are producing higher gold recoveries, and they normally stay in mining camps (Mondlane and Shoko, 2003). Many informal workers see mining as a way of life that existed long before large-scale mining operations(LSM) (Tschakert and Singha, 2007). This is because even though they do not possess licenses and permits required by law, they have a "social licence" to operate from the local community due to social and cultural norms that have developed over many decades (Morgane et al, 2018). Informal ASGM leads to direct and indirect jobs. This growth point leads to development of a community which in turn entices the government and other organizations to build schools and hospitals in those areas. Parents can send their children to school. Also, female participation has increased in ASGM which is positive (Mondlane and Shoko, 2003).

On the other hand, ASGM is reported to have led to increased instances of prostitution, alcohol abuse, conflicts, and spread of diseases such as HIV/AIDS especially in the mining camp style of living (Tschakert and Singha, 2007; Banchirigah, 2008). Children are also reported to be taking part in these ASGM operations helping their parents owing to the high labor demands and that profits are directly linked to how much ore is mined and processed (Mondlane and Shoko, 2003). This involvement of children in ASGM constitutes child labor and leads to poor academic performance and truancy (Mondlane and Shoko, 2003). ASGM has also been linked to conflict between informal ASGM workers and the local community (Hilson and McQuilken, 2014). This due to fights over resources like land and water. Sometimes these conflicts result in violent confrontations leading to fatalities and injuries (Hilson and McQuilken, 2014). Violent disputes between artisanal miners, mining firms, and the government over land disputes, legislation, and policing have also broke out (Andrew, 2003; Aubynn, 2009). Due to improper practice in ASGM, death and injuries have been caused when shafts cave in. These are usually not reported due to fear of authorities acting (Mondlane and Shoko, 2003; Hilson and McQuilken, 2014). While this has not been directly linked to technical challenges in ASGM, it is important to mention it in order to provide a clear picture of the ASGM landscape especially in informal practices.

2.4.3 ENVIRONMENTAL

Land degradation, water pollution, mercury contamination, air pollution, and loss of flora and fauna have been identified as major environmental issues of ASGM (Hilson, Hilson and Pardie, 2007). The miners begin by clearing the land. This entails cutting down trees. Water streams are diverted to where the miners will be working. This water is meant for their mining and gold processing operations. A lot of erosion takes place as trenches are dug. Landscapes of abandoned overburden, open shafts, and vast areas of barren land due to clearing are common features at these sites (Mondlane and Shoko, 2003). Miners move-on quickly without making effort to rehabilitate the land they would have been working on. Furthermore, these abandoned shafts are hazardous and deadly fall traps for villagers and livestock.

Water sources are contaminated heavily by ASGM operations due to seepage of chemicals, dredging, and panning activities. Babut *et al* (2003) conducted a study in Dumasi, Ghana, to determine the environmental impacts of mercury prior to the introduction of (mercury) retorts. The study showed that there was a steep increase in water treatment costs because of upstream ASGM activity. The ASGM activities had caused an increase in suspended solids, heavy metals, mercury, and oil and grease contamination. By diverting streams, they deprive downstream communities of that source of water which communities may have been dependent on.

Mercury used for gold amalgamation may end up in water sources contaminating aquatic life. Other research papers have shown that 60% of mercury used is lost to the atmosphere while 30% is lost to water bodies with the tailings (Mondlane and Shoko, 2003). Although few studies have been done on heavy metal levels in fish obtained from informal ASGM affected waters, a study conducted by Babut *et al* (2003), found elevated mercury levels in fish samples obtained from informal ASGM affected streams in the Western Region of Ghana. This usually finds its way back to humans especially the communities in those areas who have fish as a staple (Veiga, 1997; Vieira, 2006; Drace *et al.*, 2012)

2.4.4 HEALTH

Common health related diseases that cause havoc in ASGM communities are malaria, diarrhoea, venereal diseases, and TB.

Abandoned unreclaimed shafts are a bane to miners, the community, and livestock. They are an accident waiting to happen because people and animals can fall in causing harm and death (Mondlane and Shoko, 2003). They accumulate water and become breeding grounds for disease spreading mosquitoes. Malaria runs rampant in a majority of ASGM sites and is the biggest cause of death (Mondlane and Shoko, 2003).

Malaria is closely followed by diarrhea which is caused by unsanitary conditions at these mining camps (Mondlane and Shoko, 2003). This is exacerbated by unsafe drinking water and the absence of ablution facilities. The mixing of people from different places because of the nomadic nature of this activity coupled with the fact that miners are there without their families encourages sexual relations with prostitutes. STD's and HIV/AIDS are therefore the third most prevalent disease in ASGM communities (Mondlane and Shoko., (2003).

Also, mercury poisoning which affects the renal and nervous system, leading to death in adults and fetuses is quite notable in ASGM communities (Veiga, 1997; Telmer and Stapper, 2012). This problem is on the rise because of the growth of the industry and the fact that ASGM has the largest mercury demand and is the largest source of mercury pollution (Telmer and Stapper, 2012).

All these are made worse by the lack of health facilities in most ASGM communities because of remoteness. Where the communities have been large enough and health facilities built, they seem to crumble as soon as the gold deposits are spent, and miners move on to the next prospective site (Mondlane and Shoko, 2003).

2.5 MERCURY PROBLEM

It is important to note that all the mercury used in amalgamation is eventually all lost to the environment. Mercury lost to the environment contaminates the soil, vegetation, and water bodies. Part of the mercury lost is transformed by biochemical processes into methylmercury which is rapidly taken up by aquatic species. When ingested by humans and fish eating species regularly it will lead to a bioaccumulation of methyl-mercury in the system causing problems in the renal and nervous systems which persist and ultimately lead to death (Veiga, 1997; Vieira, 2006; Drace *et al.*, 2012). Inhalation of mercury, usually from amalgam roasting, affects metabolism in the nervous system and the effects are more immediate (Veiga, 1997). The health effects of mercury vapour emissions in ASGM practitioners and communities in gold mining towns is much more evident, immediate, and dramatic than the effects of methylmercury by fish ingestion in mining communities. The main cause of environmental problems related to mercury releases is due to whole ore amalgamation, whereas the main health problem is caused by inhalation of metallic mercury vapours when amalgams are thermally decomposed in an open pan (Veiga *et al.*, 2014).

ASGM accounts for 25% of the world's annual gold production and is the single largest source of human-made mercury emissions in the world. Given that 37% of total mercury emissions are attributed to ASGM processes (Stoffersen *et al.*, 2018) and mercury release from ASGM is estimated to be about 1400 tons/year with virtually all of the mercury used being released into the environment (Telmer and Stapper, 2012), there is an urgent need to address mercury use in ASGM. Globally, sub-Saharan Africa is responsible for 16% of the mercury emissions and it is established that the major contributor to those emissions is ASGM, therefore there is a need reduce, substitute or eliminate mercury use in that sector(Eksteen and Oraby, 2015).

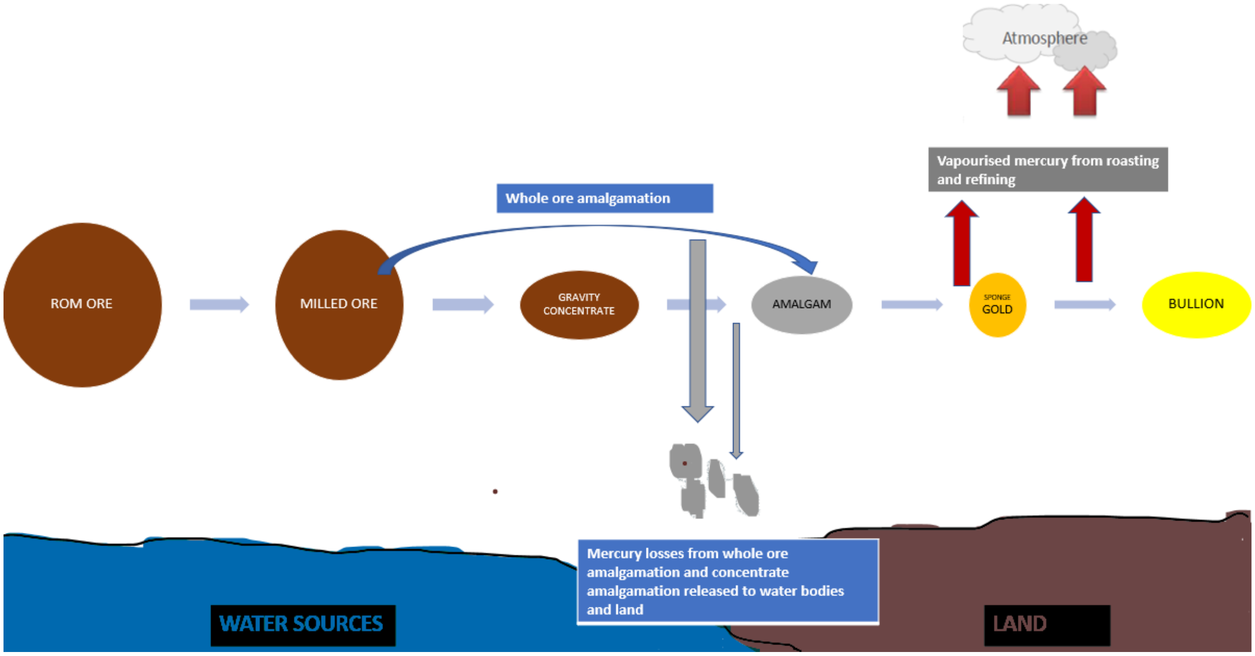

Figure 2.5: Mercury losses during processing (authors own)

Figure 2.5 shows the whole process which is largely carried out by ASGM practitioners and the mercury losses at each stage are shown. As can be seen from the figure, all the mercury added to capture gold is eventually all lost:

I. to the environment with the tailings during amalgamation (whole ore amalgamation or amalgamation of concentrate) and
II. to the atmosphere during amalgam roasting and during refining.

These negative impacts from mercury use led to the Minamata Convention, a treaty aimed at reducing global anthropogenic emissions and releases of mercury and mercury compounds.

2.6 ALTERNATIVE TECHNOLOGIES

Several solutions to the mercury problem have been researched and proposed. This section will look at alternative technologies.

2.6.1 SLUICE BOXES

Sluices are a widely used in the ASGM sector due to their low operating costs. They separate gold from gangue by virtue of a marked difference in density, achieving a very high concentration ratio in the range of 10 000:1 to as high as 500 000:1 (Vieira, 2006). Sluices are lined with a cloth/mat at the bottom and the slurry (milled ore plus water) is fed from the top and allowed to flow on the sluice as shown in Figure 2.6. Gold particles due to their higher density resist motion and are trapped on the cloth while the tailings flow through and out. Hand sorting and screening is used to upgrade the concentrate followed by panning of the fines. After obtaining the upgraded gravity concentrate, mercury amalgamation can be performed or an alternative technique such as direct smelting to form ingots. Sluice boxes are relatively cheap and are easy to operate, making them an attractive alternative to mercury use (Davies, 2014). None the less, sluices do not perform very well over a large range in sizing. Gold deposits in the sands and gravels of streams (placer ores) which are usually processed as is without comminution would require the sluice to be tuned frequently for the differing size particles (Vieira, 2006). The parameters to be adjusted are the slope, feed rates (water and solids), type of matting, number of clean-ups, number of stages in sluicing, and reduction of feed top size.

A note-worthy variation of the sluice box is the Cleangold sluice which was invented by David Plath. It is constructed from aluminum and is comprised of polymeric magnetic sheets to trap magnetite, a mineral commonly found in gold deposits (sands) near streams. The gold concentrate is trapped below the magnetite layer which is then be scraped into a pan and then magnets are then used to remove the magnetic material (magnetite). The sluices cost US$75 each and yield a high concentration ratio. Using a magnet, the magnetite is removed and a high grade of gold concentrate is obtained (Davies, 2014). The obvious downside is that the method only works well with placer gold ores which have magnetic gangue (Grayson, 2007). The concentrate will require further enrichment to have a saleable product.

Figure 2.6: Clean gold sluice (Vieira, 2006)

2.6.2 SHAKING TABLES

These are very common and employ the use of a one direction shaking motion and variable speed to separate gold from gangue by virtue of the different densities (Grayson, 2007).

An interesting variation of the shaking table is a Gemini Table shown in Figure 2.7. The tabletop is constructed from fiberglass and is supported by a steel frame. It has a longitudinal adjustable tilt and just one-direction shaking movement with variable speed. It produces a rich concentrate without employing mercury especially when the table is fed with pre-concentrate. Recovery efficiencies are excellent down to approximately 325 mesh size (Vieira, 2006). A constant supply of clean water is a big requirement. In areas with a scarce supply of clean water, this technology becomes ineffective. In addition, the price range of a Gemini table is in the proximity of US$8000 (R120,000), which is quite pricy for an average ASMG practitioner and impoverished communities (Davies, 2014). These technologies usually require a next step like borax smelting or amalgamation to recover gold from the product.

Figure 2.7: Gemini Table (Vieira, 2006)

2.6.3 MAGNETS

Magnets can be used to separate gangue from gold provided the gangue is magnetic. The gold ore is milled and goes through a gravity separation process to produce a gravity concentrate. The concentrate is panned, and magnets are then used to separate magnetic gangue from the gold. The process is repeated several times, and the final product is estimated to contain 89–93% pure gold which is not processed further and sold as is (Drace *et al.*, 2012). The panning and removal of magnetic gangue is shown in Figure 2.8. The process is economic, but the drawback is that it can only be applied to gold which occurs with magnetic gangue.

Figure 2.8: Gold Separation using Magnets (Drace *et al.*, 2012)

(A) Ore from the connecting pipe and centrifuge is collected and panned. (B) Sediment containing gold and iron. (C) A speaker magnet is used to remove iron and magnetic species. (D) After separation, mostly gold remains.

2.6.4 CENTRIFUGES

The treatment of gold has experienced an advance in research with the introduction of centrifugal concentrators in the gold mining industry. Centrifugal concentrators include the Knelson, Falcon and Knudsen centrifuges. The Knelson is more popular, while various replicas of the Knudsen concentrator are also being developed with one in use at Clean Tech Mine in Mozambique (Drace *et al.*, 2012). These centrifuges enhance separation between gold and gangue by increasing the gravitational force (Vieira, 2006).

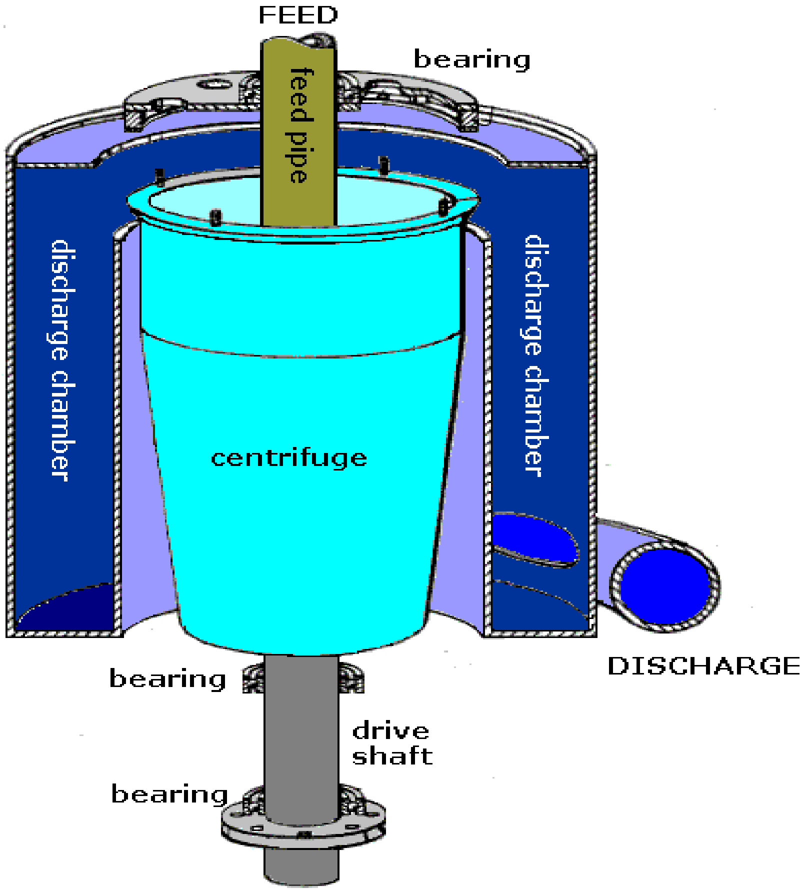

Figure 2.9: Knelson Concentrator (Grayson, 2007)

The Knelson concentrator shown in Figure 2.9 is made up of a ribbed rotating cone, into which a pulp of 20 to 40% solids by mass is fed (Grayson, 2007). The gold concentrate is accumulated in the ribs of the rotating cone. Compaction is prevented by injecting water in a counter flow manner. A fluidized bed is created, which allows gold particles to penetrate the concentrate layer. The penetration rate is increased by the rotation of the vessel. The volume between the ribs is constant, therefore the concentrate volume collected after operating time will be constant (Vieira, 2006).

Centrifuges are however very expensive and require the availability of clean water and skilled labor for them to be operated effectively (Davies, 2014).

2.6.5 BORAX

Sodium tetraborate $(Na_2B_4O_7 10H_2O)$ or 'borax' reduces the melting point of all minerals, allowing gold to be melted out of the concentrate (Davies, 2014). Borax smelting extracts and recovers gold from a rich concentrate which has gone through panning and sluicing. Borax is mixed with the rich concentrate at a ratio of 3:1 and heated as shown in Figure 2.10. Gold will then settle at the bottom of the pan/container and is easily tapped.

Figure 2.10: Borax Process, Smelting concentrate to recover gold (Grayson, 2007)

Stoffersen *et al.*, (2018) conducted a comparative study on gold recovery between borax and mercury at 2 ASGM sites in Cabo Delgado, Mozambique. The results from the first site showed that borax yielded 78% more gold than mercury, however the sluicing technique used on the borax process was better and more efficient compared the one used on the mercury-amalgamation process. The second trial yielded the same recovery from both methods. A limitation of the study was that the comparison was only carried out twice and the upstream concentration processes were different which skews results. Researchers who have studied the acceptance of borax as an alternative to mercury in ASGM have concluded that showing that borax can yield more gold than mercury at lower costs would be enough to induce a change among miners (Davies, 2014).

A glaring disadvantage that borax has over mercury is that it is more sophisticated taking more time and would require more patience and training (Davies, 2014). For borax smelting to be effective, the concentration process must achieve high gold grades of above 30,000ppm of gold (Appel and Jøsson, 2010; Appel and Na-Oy, 2012). Figure 2.11 shows the hypothetical relationship between mass of concentrate, gold grade, and gold recovery. A continual increase in the concentrate grade results in lower and lower gold recovery. Enrichment to 30,000ppm gold concentrate grade is too high and it compromises gold recovery to an unacceptable level (Veiga, Angeloci-Santos and Meech, 2014). Also, the borax method is inefficient with high sulphide ores (Appel and Na-Oy, 2012)(Appel and Na-Oy, 2013).

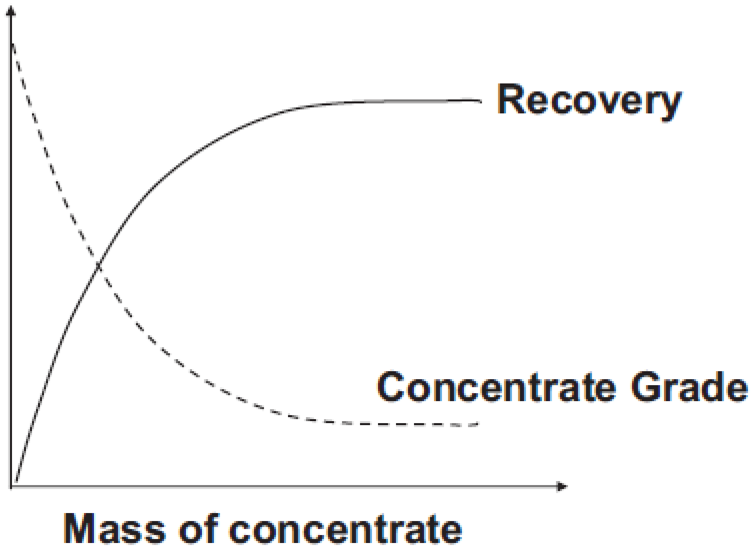

Figure 2.11: Hypothetical relationship between mass of concentrate, gold grade and gold recovery (Adapted from (Veiga, Angeloci-Santos and Meech, 2014)*)*

2.6.6 THIOSULPHATE LEACHING

Thiosulphate leaching is capable of leaching gold from difficult refractory hard rock ores (Grayson, 2007).

The thiosulphate leaching method uses a solution of sodium thiosulphate ($Na_2S_2O_35H_2O$)in the presence of ammonia to make an alkaline leachate at 10-10.5 pH and copper an oxidizing agent to dissolve fine gold as a strong complex $[Au(S_2O_3)_2]^{3-}$ as shown in equation 1 (Grayson, 2007).

Equation 1: Thiosulphate leaching

$$4Au + O_2 + 2H_20 + 8S_2O_3^{2-} \xrightarrow{NH_3} 4Au(S_2O_3)_2^{3-} + 4OH^-$$

Thiosulphate leaching is less toxic and environmentally safer than mercury or cyanide but the reagents are unavailable in locations were ASGM is dominant (Veiga, Angeloci-Santos and Meech, 2014). The strict balance of reagents requires a skilled individual (Veiga, Angeloci-Santos and Meech, 2014) (Veiga *et al.*, 2014). Thiosulphate leaching achieved lower extractions when directly compared with cyanide leaching (Manzila, Petersen and Moyo, 2021). The reagents used in this process like ammonia are volatile and would require constant topping up given vat tanks which are open which ASGM operators use. Also, ammonia gives off a strong pungent smell.

2.6.7 THIOUREA LEACHING

Thiourea was billed in the early years as a replacement to cyanide leaching because it was reported to leach gold four to five times faster which also made it a viable option to leach whole ores inclusive of large gold particles from placer gold, but as yet, few if any industrial operations have proved to be a commercial success (Grayson, 2007). A study by Tanriverdi, Mordoğan and Ipekoğlu, (2005) found that dissolution rates using thiourea were faster than cyanidation and thiosulphate leaching but relatively high consumptions of thiourea makes this process too expensive.

The thiourea $[CS(NH_2)_2]$ leaching method makes use of a weak solution of thiourea and Fe^{3+} as an oxidising agent to dissolve gold into solution as shown in equation 2 and subsequently precipitate it out (Grayson, 2007).

Equation 2: Thiourea leaching

$$2Au + 4CS(NH_2)_2 + 2Fe^{3+} = 2Au(CS(NH_2)_2)^{2+} + 2Fe^{2+}$$

Thiourea has been reported to be toxic and cause cancer in humans and animals (Grayson, 2007), while other studies say it's less toxic and more environmentally friendly than mercury and cyanide (Veiga, Angeloci-Santos and Meech, 2014). Thiourea is not easily accessible in remote areas and requires a lot of technical chemistry knowledge to be able to control the process which requires strict control of parameters such as pH and Eh which are complicated for unskilled miners (Veiga, Angeloci-Santos and Meech, 2014) (Veiga *et al.*, 2014).

2.6.8 CHLORINE LEACHING

Chlorine leaching was applied extensively early in the 19th century but was replaced in the last decade of the century by cyanidation because of effectiveness and safety concerns (Grayson, 2007). Chlorination procedures were conducted in wooden tanks by pumping chlorine gas through the ore inside a covered vat for 12–18 hours (Veiga *et al.*, 2014). Wooden tanks were used instead of steel tanks because chlorine gas is a powerful oxidant and aggressively corroded steel tanks (Grayson, 2007; Airgas, 2021). The dissolution mechanism is shown in equation 3.

Equation 3: Chlorine gas leaching

$$2Au + 3Cl_2 + 2Cl^- = 2[AuCl_4^-]$$

The biggest disadvantage of this technology is that it's a health hazard. Chlorine gas is poisonous and if there is a leak in the system it could be deadly for workers/people in the vicinity. Its high corrosivity would require use of specialized equipment and closed tanks which would be too expensive for regular artisanal miners.

2.6.9 IGOLI PROCESS

MINTEK, a South African research center developed a method to extract gold from enriched gravity concentrates based on chlorine leaching. The iGoli gold extraction system is intended for use by small-scale miners as a substitute for mercury amalgamation as the researchers consider it to be more environmentally friendly (Mahlatsi and Guest, 2003; Grayson, 2007). Hydrochloric acid at 15% is mixed with bleach (sodium hypochlorite at 15%) at a ratio of 1:1 and then mixed with the enriched gravity concentrate into a 30-liter agitated leach tank. The gold is recovered by precipitating it from solution using sodium metabisulphite. After the gold is recovered, calcium chloride, sodium hydroxide, and apatite are added to the effluent to precipitate the other metals in solution to an inert form. Recoveries as high as 98% were achieved with a gold purity of up to 99% (Guest and Mahlatsi, 2003).

Figure 2.12: Mini iGoli plant showing stirred vessels (Adapted from (Mahlatsi and Guest, 2003)*)*

The chemical reactions for the process are shown in equation 4 and 5:

Equation 4: iGoli process leaching reaction.

Leaching

$$Gold(s) + Sodium\ hypochlorite(aq) + Hydrochloric\ acid(aq) = Gold\ chloride(aq) + Sodium\ chloride(s) + Water(l)$$

$$2Au + 8HCl + 4NaClO = 2[AuCl_4^-] + 4NaCl + 4H_2O$$

Equation 5: iGoli process precipitation reaction.

Precipitation

$$Sodium\ metabisulphite(s) + Gold\ chloride(aq) + Water(l) = Gold(s) + Hydrochloric\ acid(aq) + Sodium\ Bisulphate(aq)$$

$$Na_2S_2O_5 + 2[AuCl_4^-] + 3H_2O = 2Au + 6HCl + 2NaHSO_4 + 2Cl^-$$

(Grayson, 2007).

Adopting the iGoli process means the miners must also purchase the processing equipment similar to that shown in Figure 2.12. The critical part is the need to teach them on handling and storage of the lixiviants because they are hazardous. Sodium hypochlorite in particular is unstable in hot conditions and needs to be stored in a cool place (Veiga, Angeloci-Santos and Meech, 2014).

The iGoli process can be a suitable substitute for mercury in ASGM because similar to mercury amalgamation, the miners can recover the gold on their own using the precipitation step. This would quell any issues and accusations of cheating/stealing. The reagents are readily available in most chemical stores and can be bought over the counter. The process itself is not complicated as only 2 reagents are used for dissolving the gold and 1 reagent is used in the next step to recover gold from the solution. The reagents can be neutralized before being disposed which is safe for the environment.

2.6.10 AMINO ACID LEACHING

Gold leaching using low concentration amino acids and hydrogen peroxide solutions was studied by Eksteen and Oraby (2015), as an environmentally friendly alternative. The study made use of varied combinations and concentrations of 3 amino acids (glycine, histidine, and alanine) to find the perfect combination and concentration of lixiviant for in-situ and heap leaching of low concentration gold ores. Hydrogen peroxide was used as an oxidant in the process and increasing the concentration of peroxide used increased the leaching kinetics (Eksteen and Oraby, 2015). The other parameters which were tested for their effect on the system were temperature, copper ions, presence of pyrite and pH.

Oraby and Eksteen (2015), found that the following parameters increased dissolution of gold significantly:

- Heating the leach solution to between 40 and 60 degrees Celsius
- Increasing pH
- Increasing amino acid concentration in particular glycine which furthermore increased the dissolution rate when mixed with histidine in equimolar amounts.
- Increasing concentration of peroxide (Eksteen and Oraby, 2015).

The stoichiometry of gold dissolution in alkaline glycine solutions is shown in equation 6.

Equation 6: Amino acid leaching

$$4Au + 8NH_2CH_2COOH + 4NaOH + O_2 = 4Na[Au(NH_2CH_2)_2] + 6H_2O$$

(Eksteen and Oraby, 2015).

This process can be directly used in ASGM operations which use vat leach tanks. The downside is that the process is very slow taking over 150 hours as compared to the other processes like direct cyanidation and mercury amalgamation.

2.6.11 CYANIDE LEACHING

Cyanide leaching has been used to recover gold since the 1890s but only since the 1960s with the advent of heap leaching has cyanide become the method-of-choice for leaching gold from ores in Large Scale Mining (LSM) (Grayson, 2007). Cyanide leaching extracts gold from ore by dissolving the gold into solution by use of a very weak cyanide solution.

Equation 7: Cyanide leaching

$$4\,Au + 8CN^- + O_2 + 2H_20 \rightarrow 4Au(CN)_2{}^- + 4OH^-$$

Cyanidation is pre-dominantly used where gold is too finely dispersed in ore, that it cannot be recovered using gravitational devices or mercury. Coarse gold, typical of most placer ores, takes too long to leach, a

0.21 mm gold particle takes over 60 hours to dissolve in cyanide (Grayson, 2007). A weak cyanide solution is prepared, usually 0.02-0.05%, and must be kept strongly alkaline (pH 10-11) with use of NaOH and lime to avoid escape of cyanide as HCN gas. Cyanide concentrations used in ASGM are usually higher compared to the ones used in LSM. Cyanide leaching can be done by different methods:

- Vat leaching - cyanide solution percolates down through a vat of gold ore. Commonly used for ground hard rock ore, but also successful in tests on placer gold concentrates.
- Agitated tank leaching - cyanide solution is added to tanks with ore agitated by paddles or blowing in compressed air to keep the material in suspension and mix for better leaching.
- Heap leaching - cyanide solution trickles down through crushed ore stockpiled in a 'heap basin' lined with impermeable material which is inert to cyanide e.g., clay, asphalt, or tarpaulin.
- Mill leaching – cyanide solution is mixed with ore and added to a ball mill, and it is run for two hours and then stopped. The grinding media (balls or rods) are removed then the ball mill runs for a further 6 hours (Veiga *et al.*, 2009).

There were field tests carried out by Veiga *et al.*, (2009) in Ecuador for ASGM practitioners. The objective of the study was to test which method had a better recovery and was more suitable to be tailored for ASGM between agitated and mill leaching. Mill leaching extracted 95% of the gold after its 8-hour operation while the agitated tank extracted 62% after 7 hours and 94% after 32 hours. The mill-leaching process was simple, inexpensive, and well accepted by the local miners as it can be implemented without any additional investment in new equipment since they would use their ball mills for the process and just needed to purchase cyanide, lime, hydroxide, and other consumables. It was reported that local miners were pleased to see more gold in their hands in reasonable short time (24 hours) (Veiga *et al.*, 2009).

The drawbacks to cyanide use are that it is toxic and has dire risks if carelessly handled or is spilled to streams or wells. The cyanide solution must be kept strongly alkaline to prevent the generation of highly toxic hydrogen cyanide gas (Grayson, 2007; Cyanide Code, 2021). However, cyanide complexes naturally decompose to less toxic forms like ammonia and carbon dioxide, unlike mercury which bio-accumulates to chronic levels overtime (Veiga, Angeloci-Santos and Meech, 2014).

2.6.12 CYANIDE-GLYCINE

Gold leaching using alkaline amino acids–hydrogen peroxide solutions at low concentrations was studied by Eksteen and Oraby (2015), as an environmentally friendly alternative. It showed that glycine had good extraction yields but it however took more than 6 days to reach maximum extraction. By mixing cyanide and glycine the efficiency in extraction went up coupled with a 75% decrease in cyanide usage which would normally be used to achieve the same extraction (Oraby, Eksteen and Tanda, 2017). Glycine reduces cyanide usage by complexing with elemental sulphur, iron, copper and other minerals that compete with gold for cyanide (Oraby, Eksteen and Tanda, 2017) (Picazo-Rodríguez *et al.*, 2021). This leaves free cyanide to leach gold. Cyanide-glycine is made more attractive when compared to other technologies which dissolve gold due to its relative non-toxicity.

Given the full view of the socio-economic benefits and the environmental downside of ASGM it is imperative to come up with sustainable solutions. Ore mineralogy is imperative in the choice of extractive technology which needs to be affordable, clean, efficient, and easy to operate. Cyanide and thiosulphate were already investigated by Manzila, Petersen and Moyo (2021), as suitable technologies to replace mercury in ASGM for the typical ore mined in that sector. This study intends to expand this to the cyanide-glycine and iGoli processes.

3 MATERIALS AND METHODS

This section will detail procedures of test works and equipment used in conducting the research.

3.1 ASGM CASE STUDY (MERCURY AMALGAMATION AND SUBSEQUENT CYANIDATION)

Mercury amalgamation and subsequent cyanidation were carried out in the field owing to the substantial quantities of sample required for the test. Two ASGM sites were visited, Kensington, Spring Farm in the Bulawayo province (Site A) and Gwanda in Matabeleland South Province (Site B), both in Zimbabwe. The first site visit was for 2 weeks in May 2021 and the second was for a month from mid-November to December 2021. The ore underwent size reduction by a hammer mill and was then concentrated using a sluice lined with cloth. This is the form of gravity concentration which is most commonly used by the miners in the region, together with panning. After sluicing, the gold ore concentrate was then panned and amalgamated. Samples of the head, concentrate and tailings were taken for fire assay to determine a mass balance and the recovery ratio. Samples after the milling process were also collected to determine particle size distribution. The mining and processing of the ore was carried out by ASGM practitioners as they do normally, shadowed by the author. In addition, the author observed how the stakeholders of ASGM (the miners, claim owners, financers, and plant operators), engaged and interacted with each other to understand the socioeconomic dynamics as it pertains them.

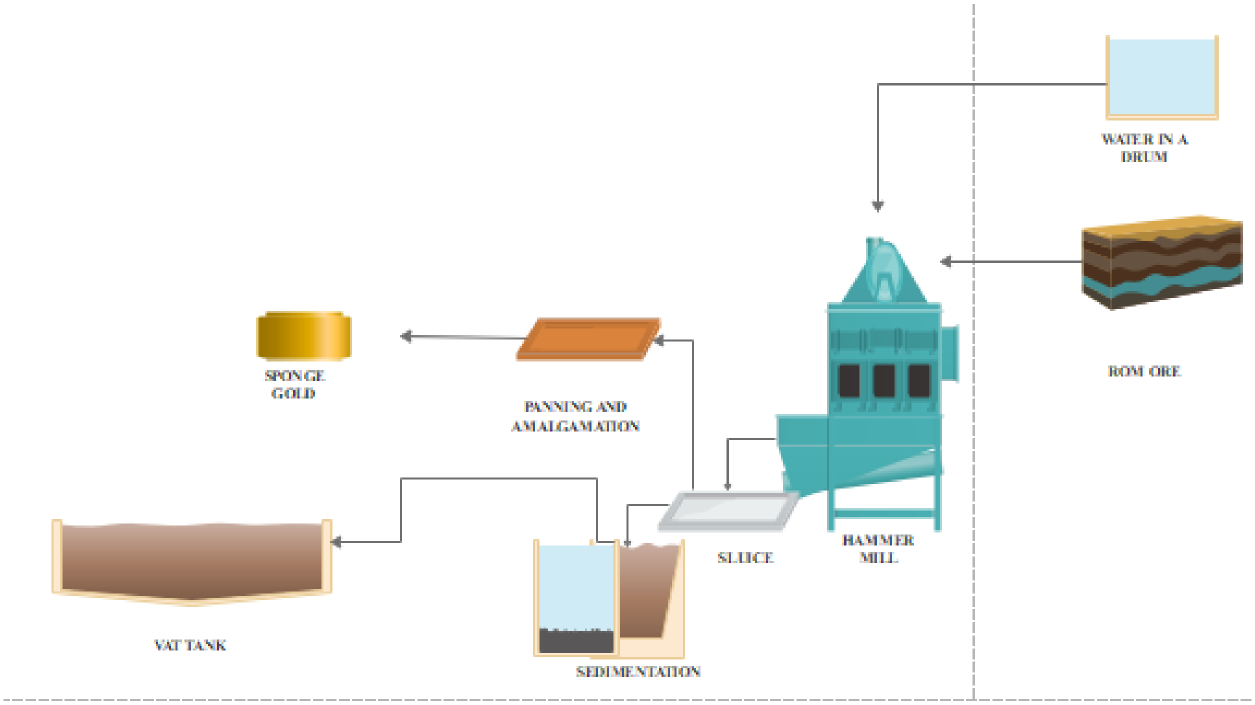

Figure 3.1: ASGM process

Figure 3.1 was the typical process flow at ASGM sites noted from the field trips. Processing involved milling, gravity concentration, mercury amalgamation, then cyanide leaching. The sluice box produces 2 streams, first is the gravity concentrate that goes for panning and amalgamation to produce sponge gold. The second are gravity tailings which undergo sedimentation and are dewatered using a connected pond where the water overflows to. These tailings after being dewatered undergo cyanidation.

3.2 SAMPLE CHARACTERISATION

Two samples were used in the study. Sample A was run-off mine ore from site A with an average gold grade of 11.2 ppm and sample B was run-off mine ore from a mining site which was 25 km away from the site A mining area with an average gold grade of 21 ppm. The samples were crushed, milled then split and sub-sampled for XRD and QEMSCAN analysis. A small portion was pulverized and sent for XRF and fire assay analysis. These tests give a clear picture of the quantity of gold in the ore and the minerals it is associated with which may or may not affect the extraction process.

With this knowledge a diagnostic leach test was performed by alternating a cyanidation step with various acid digestion steps aimed at destroying a particular mineral phase to liberate gold for the following cyanide leach step. The procedure is adapted from Celep, Alp and Deveci (2008). After each step the sample is rinsed with de-ionized water, dried, and weighed so as to maintain a standard pulp density.

Table 3.1 below shows the steps in the diagnostic leach and the expected mineral phases to be destroyed. The leachates from each step will undergo MPAES analysis.

Table 3.1: Diagnostic Leaching procedure

STEP	TREATMENT	CONDITIONS	MINERALS LIKELY DESTROYED/EXTRACTED
1	$\boldsymbol{NaCN}$ (20g/l)	24hrs, Ph 10.5-11, 30% solids, agitated	Gold
2	$\boldsymbol{HCl}$ (33%)	24hrs, 26^0C, 30% solids, agitated	Calcite, Dolomite, Hematite
3	$\boldsymbol{NaCN}$ (20g/l)	24hrs, Ph 10.5-11, 30% solids, agitated	Gold
4	$\boldsymbol{H_2SO_4}$ (48%)	24hrs, 26^0C, 30% solids, agitated	Cu-Zn Sulphides, Labile pyrites
5	$\boldsymbol{NaCN}$ (20g/l)	24hrs, Ph 10.5-11, 30% solids, agitated	Gold
6	$\boldsymbol{HNO_3}$ (33%)	24hrs, 26^0C, 30% solids, agitated	Pyrites, Arsenopyrite
7	$\boldsymbol{NaCN}$ (20g/l)	24hrs, Ph 10.5-11, 30% solids, agitated	Gold
8	Reverse Aqua-Regia	24hrs, 26^0C, 30% solids, agitated	Base metal sulphides, Carbonates, Gold

9	$\boldsymbol{NaCN}$ (20g/l)	24hrs, Ph 10.5-11, 30% solids, agitated	Gold

3.3 APPARATUS

3.3.1 LEACHING EQUIPMENT

All the agitated leaching experiments with the cyanide-glycine process, cyanide baseline tests, and the iGoli process were ran using bottle roller as shown in Figure 3.2.

Figure 3.2: Bottle rollers (authors own)

The roller speed can be varied, and all experiments were run at room temperature. The 2-liter Schott bottles were used as reactors. The caps of the reactors were punctured to allow for natural flow of air for cyanide-based experiments which require oxygen and also for easier addition of reagents and for sampling. For the iGoli process the punctured holes would be closed to prevent escape of HCl(g). Natural flow of air was chosen instead of bubbling oxygen into the slurry as it better mimics the ASGM operation where vat tanks are open to the atmosphere.

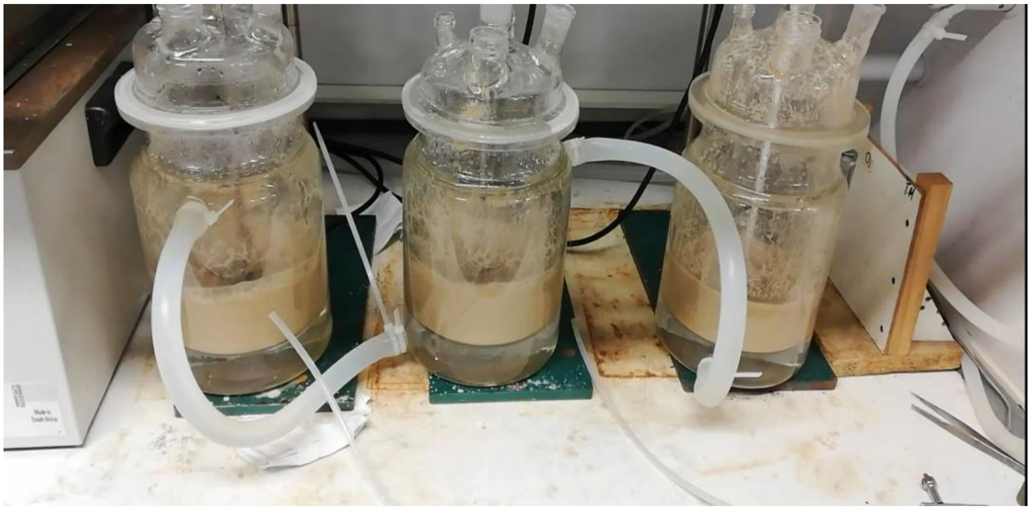

Figure 3.3: Batch stirred tank reactors (BSTR) (authors own)

Acid digestion experiments for diagnostic leaching were carried out in batch stirred tank reactors (BSTR) at room temperature and agitation of 400 rpm. Non-agitated vat experiments were also carried out using BSTRs'. The set up was as shown in Figure 3.3. The open-air vents of the reactors were closed when running acids to reduce fuming while they were left open for non-agitated cyanide-glycine tests.

3.3.2 CLARIFYING EQUIPMENT

During sampling time, the reactors were stopped and the solids in the slurry allowed to settle before a liquid sample was taken. For accurate readings with MPAES, the samples needed to be clarified because solids affect the reading. Therefore, the samples were clarified using a centrifuge which is shown in Figure 3.4, samples before and after clarifying are also shown. The clarified sample is then sent for analysis.

Figure 3.4: a) Centrifuge b) Sample before and after clarification (authors own)

After terminating the experiment, the lixiviants are discarded in the requisite areas and the ore residue is washed filtered and dried as shown in Figure 3.5. The ore residue was then safely discarded or sent for fire assaying so as to complete the mass balance.

Figure 3.5: Filtration Set-up (authors own)

3.3.3 ANALYTICAL EQUIPMENT

The Cynoprobe is Mintek's state of the art on - line cyanide analyzer, which measures both 'free' and weak acid dissociable (WAD) cyanide concentration (Mintek, 2022). Figure 3.6 is a photo of the Mintek lab Cynoprobe.

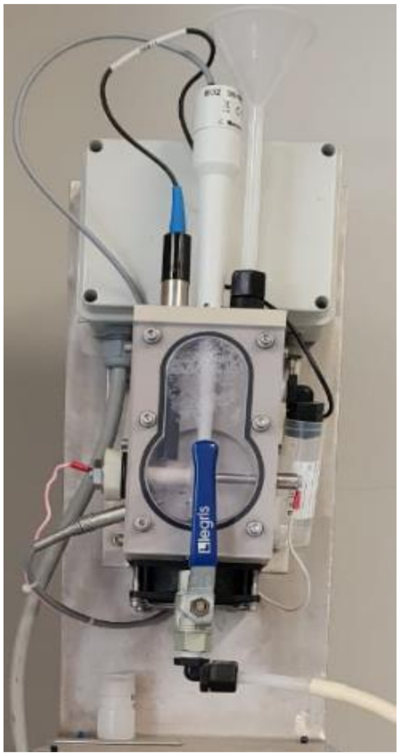

Figure 3.6: Mintek Cynoprobe (authors own)

The Cynoprobe uses an amperometric technique to measure the concentration of $[CN^{-}]$ available to leach gold (Mintek, 2015, 2022). Electric current is produced by the reaction shown in equation 8:

Equation 8: Cynoprobe reaction

$$Ag + 2CN^{-} = Ag(CN)_2^{-} + e^{-}$$

(Mintek, 2022).

The factors that affect this process are:

- Cyanide concentration
- Temperature
- Agitation
- Electrode surface area

To focus on cyanide concentration, all the other parameters were kept constant across all the experiments so that,

$$current = m\,[CN^{-}]$$

Where m is a constant which is calculated during machine calibration.

A 1 g/l cyanide solution was prepared and used to check the Cynoprobe for accuracy and the reading was a concentration of 1,016 g/l. The small discrepancy can be due to human error when measuring the cyanide into solution.

3.4 IGOLI PROCESS

15% HCl and 15% NaOCl were used in the leaching of gold across all the experiments as described in the Mintek iGoli process (Guest and Mahlatsi, 2003; Mahlatsi and Guest, 2003). The iGoli lixiviants dissolve sulphide and iron compounds such as pyrite, preferentially before gold if they are present in the ore (Guest and Mahlatsi, 2003). Therefore, the time taken, and the amount of chemicals used will need to be increased depending on the composition of the ore. The standard iGoli leaching process takes 5 hours. Due to the presence of sulphides and pyrites in the ore (section 4.1.1) the lixiviant to ore ratio was varied and the process run for 24 hours.

The leach was conducted in glass bottle rollers at 400 rpm for 24 hours. 400rpm was chosen because the best extractions were achieved in that range of 300-400 rpm by Manzila, Petersen and Moyo (2021).

3.4.1 PROCEDURE

- 30% HCl which is the standard grade for pool acid is diluted with an equal amount of deionized water in a fume hood to make 15%HCl. Care must be taken to wear gloves and closed shoes in case of any spillages. Acid is added to the water while stirring. **NB: YOU POUR ACID INTO WATER ALWAYS.** Goggles should be worn in case of any splatter.
- 15% NaOCl is used.
- 100 g of ore is measured out and added into the Schott bottle.
- Add 150 ml of 15% HCl to the ore.
- Add 5 ml of NaOCl and start stirring at 400rpm.
- Add 5 ml of NaOCl every minute for the first 10 minutes.
- Add 5 ml of NaOCl every 20 minutes until 5 hours have passed.
- The reactors are left to run until termination on the 24-hour mark.
- A 20 ml sample is extracted at the end of the experiment. No intermediate samples were taken for kinetic tests to maintain the HCl: NaOCl ratio.
- The sample collected is clarified in a centrifuge, and 14 ml of the clarified sample is pipetted out and sent for MPAES analysis. The solid residue and excess lixiviant are returned to the reactor.

The procedure detailed is the designed iGoli process as described by Guest and Mahlatsi (2003), the procedure was repeated with 100 g of ore, 200 ml of 15% HCl and 6.65 ml of 15% NaOCl added at the same intervals. A third cycle was carried out with 100 g of ore, 300 ml of 15% HCl and 10 ml of 15% NaOCl added at the same intervals, the experimental matrix is shown in Table 3.2.

Table 3.2: iGoli lixiviant mixing ratios

EXPERIMENT	HCl (15%)	NaOCl (15%)	SOLID: LIQUID
1	150 ml	130 ml	1: 2.8
2	200 ml	173 ml	1: 3.7

3	300 ml	260 ml	1: 5.6

3.5 CYANIDE-GLYCINE SYNERGISTIC LIXIVIANT

Table 3.3 shows the levels at which cyanide-glycine were mixed and the process ran at. $NaHCO_3$ and Na_2CO_3 were used for pH adjustment. The experiments were run using glass bottle rollers at room temperature and pressure, 400rpm and pH greater than 9.5. 100g of the ore was used for each run. The leach cycle is 24 hours.

3.5.1 PROCEDURE

- Analytical grade reagents were used for this experiment which was run in a cyanide fume hood. Care must be taken to wear gloves and closed shoes in case of any spillages. Goggles should be worn in case of any splatter.
- In a 1-liter volumetric flask which is filled halfway with de-ionized water, add 2g of $NaHCO_3$ and start stirring.
- Add 9.3 g of Na_2CO_3.
- Add 1 g of $NaCN$.
- Add 2 g of Glycine.
- Fill up with de-ionized water to the mark. Make sure all remnants of the reagents are washed into the solution.
- Allow the solution to stir for 10minutes until all reagents are dissolved.
- Measure the pH of the solution. If its below 9.5, discard and prepare a new solution and increase $NaHCO_3$ by 1 gram. If its bordering on 9.5, add 0.5grams of $NaHCO_3$ and stir then measure again. If it's well above 9.5 proceed.
- Add 100g of ore into the Schott bottle.
- Measure out 400 ml of the lixiviant and add into the Schott bottle and shake it well.
- Place the Schott bottle with the slurry on the roller and start rolling at 400 rpm.
- 20 ml samples were taken at 30 minutes, then hourly for the first 3 hours, then on the 6th hour, 9th hour and 24th hour mark.
- The samples collected were clarified by centrifuge and 14 ml of the clarified sample pippeted out into the sample bottle and sent for analysis. The solid residue and excess lixiviant are returned to the reactor.
- The lixiviant sampled was not replaced and the concentration factor was accounted for in the extraction calculations as shown in section 7.2.
- The procedure was repeated with 100 g of ore using 400 ml of lixiviant and same amount of Na_2CO_3 and $NaHCO_3$. What is varied is cyanide and glycine concentrations to measure their effects on gold dissolution.

The procedure for the cyanide baselines is the same as that of the cyanide-glycine, without any addition of glycine. The concentrations of cyanide to be tested are as follows, 1g/l, 3g/l, and 5g/l.

Table 3.3: Cyanide-Glycine lixiviant mixing ratios.

EXPERIMENT	CYANIDE (g/l)	GLYCINE (g/l)
1	1	2
2	1	5
3	1	10
4	3	2
5	3	5
6	3	10
7	5	2
8	5	5
9	5	10

3.6 ANALYTICAL TECHNIQUES

3.6.1 Fire assaying

This is the standard method to determine the analytical amount of gold present in high grade ores. It can be applied to many sample types: soil, chip samples, drill cores, and more. The sample is pulverized and mixed with a fluxing agent in a crucible which is then placed inside a furnace at 850^0C and raised to 1000^0C over a period of thirty to forty minutes, which allows the fusion and melting of the sample and facilitates the separation of the gold from the gangue material (Marsden and House, 2009). A collector material (Ni, Pb) is used to absorb the precious metals which are recovered from the collector via a process called cupellation (Marsden and House, 2009). The cupellation only takes place after the collector has cooled. If Pb is the collector used, it oxidizes and gets absorbed into the cupel leaving behind a bead of precious metal which can then be analyzed using ICP-OES. If Ni is used, the collector is first crushed then dissolved in HCl. The solution is finally filtered, and the precious metals are collected in the filter.

3.6.2 AAS (Atomic Absorption Spectroscopy), MPAES (Microwave Plasma-Atomic Emission Spectrometer) and ICP (Inductively Coupled Plasma spectroscopy) Analysis

These analytical techniques determine the elemental composition of a sample by examining its electromagnetic spectrum, or its mass spectrum (Agilent, 2021). An atom of a specific element is excited using high temperatures and it emits light in a characteristic pattern of wavelengths in the emission spectrum as it returns to the ground state (Agilent, 2021). These are then compared using software against known baselines.

3.6.3 X-Ray Fluorescence

XRF is a method of analyzing chemical composition of all kinds of material (Brouwer, 2010). It detects the fluorescent x-rays radiation emitted from a sample subjected to an x-ray beam (Marsden and House, 2009; Brouwer, 2010). The energies emitted are particular to the subject elements. Detection levels range from about 100 ppm (mg/kg) for lighter elements to about 1 ppm for heavy elements, such as gold (Marsden and House, 2009).

3.6.4 X-Ray Diffraction

X-ray diffraction (XRD) is used to identify the minerals or phases that are present in a sample, based on their crystalline structural properties (Mintek, 2021b). X-rays are directed onto the flat surface of the sample, and the minerals at that surface then diffract the X-ray beam at appropriate angles (Mintek, 2021b). Thus, the sample is scanned over an angular range. The resulting output is a plot of angle vs X-ray intensity obtained from the sample. The mineralogist will then interpret this data with use of software and databases then ascertain minerals or phases present, with an estimate of their abundance.

3.6.5 QEMSCAN

QEMSCAN (quantitative evaluation of minerals by scanning electron microscopy) is a fast chemical data collection system which uses a combination of backscattered electron SEM (scanning electron microscopy) images and EDS (energy dispersive X-ray spectroscopy) analysis to create an image of a sample based on chemical composition (Mintek, 2021a). The images generated are processed to provide mineral abundance, grain size, mode of occurrence and liberation information (Mintek, 2021a).

4 RESULTS AND DISCUSSION

This section will detail and analyze the results of the ore mineralogy, field work, and the lab test works conducted. A summative discussion will be at the end after discussing these three components separately.

4.1 ORE MINERALOGY

Two samples were used in the study, sample A with an average gold grade of 11.2 ppm and sample B with an average gold grade of 21 ppm. Both samples were characterized by QEMSCAN, XRD and diagnostic leaching. The leaching test-works were performed mainly on sample A and sample B was used to confirm the observed trends.

4.1.1 ORE COMPOSITION

XRD and QEMSCAN analysis inform on the composition of the ore and the abundance of mineral phases.

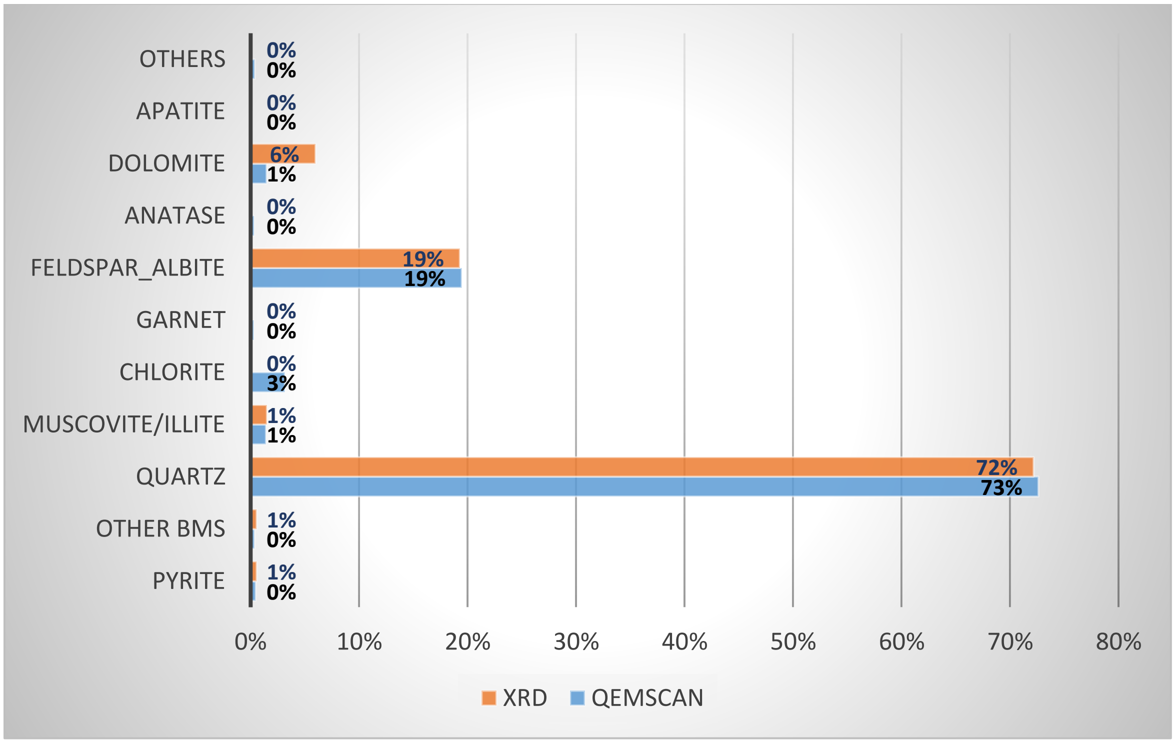

Figure 4.1: Sample A ore composition

Figure 4.1 shows the mineral composition and abundance of sample A from XRD and QEMSCAN analysis. The XRD results indicate that quartz and feldspar are the major minerals in the ore at 72% and 19%, respectively. These results tally with those from the QEMSCAN which show quartz and feldspar being the bulk mineral phases at 73% and 19% respectively. This means that the bulk of the ore is made up of silicate minerals which add up to (quartz, feldspar and illite) 93.7%, with sulphide minerals (BMS and pyrite) totaling just below 1% and carbonates (dolomite) at 1.5%. In terms of ASGM operation it is favorable if quartz makes up a large component because unlike clay it doesn’t become muddy thereby hindering seeping/trickling of the lixiviant through the ore during vat leaching. There is a variance on the dolomite content which was found to be 6% on the XRD but is at 1.5% on the QEMSCAN. This looks to be due to the chlorite, garnet and anatase being picked up on the QEMSCAN but not on the XRD.

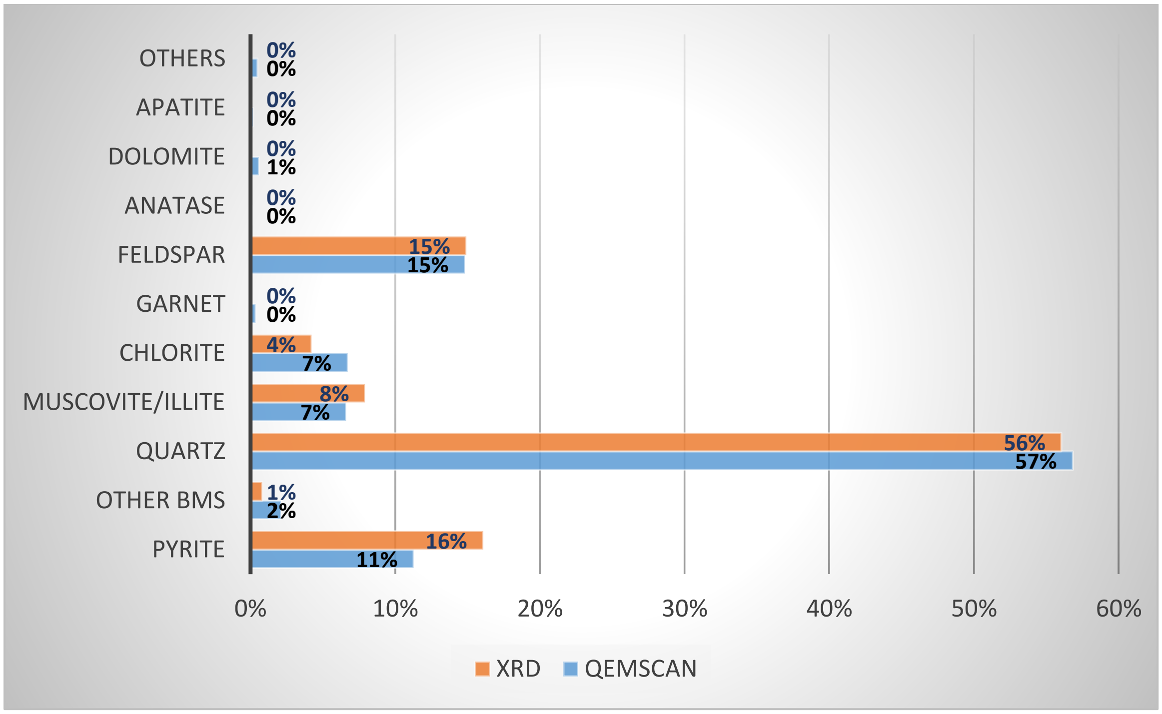

Figure 4.2: Sample B ore composition

Figure 4.2 shows the mineral composition and abundance of sample B from XRD and QEMSCAN analysis. The XRD results approximate those of the QEMSCAN with quartz and feldspar being the major minerals in the ore at just over 56% and 15% respectively. Like sample A (Figure 4.1), the bulk of the ore is made up of silicate minerals at 79%, with sulphides minerals totaling 13%, and chlorites at 7%. There is a significant variance on the QEMSCAN and XRD on chlorite and pyrites. This may be due to a combined total 5% higher readings of BMS, chlorite, garnet, and dolomite on the QEMSCAN which are not being picked up on the XRD and reported as pyrite. This was also the case on sample A (Figure 4.1) when chlorite, garnet and anatase where not picked up on the XRD but were on the QEMSCAN.

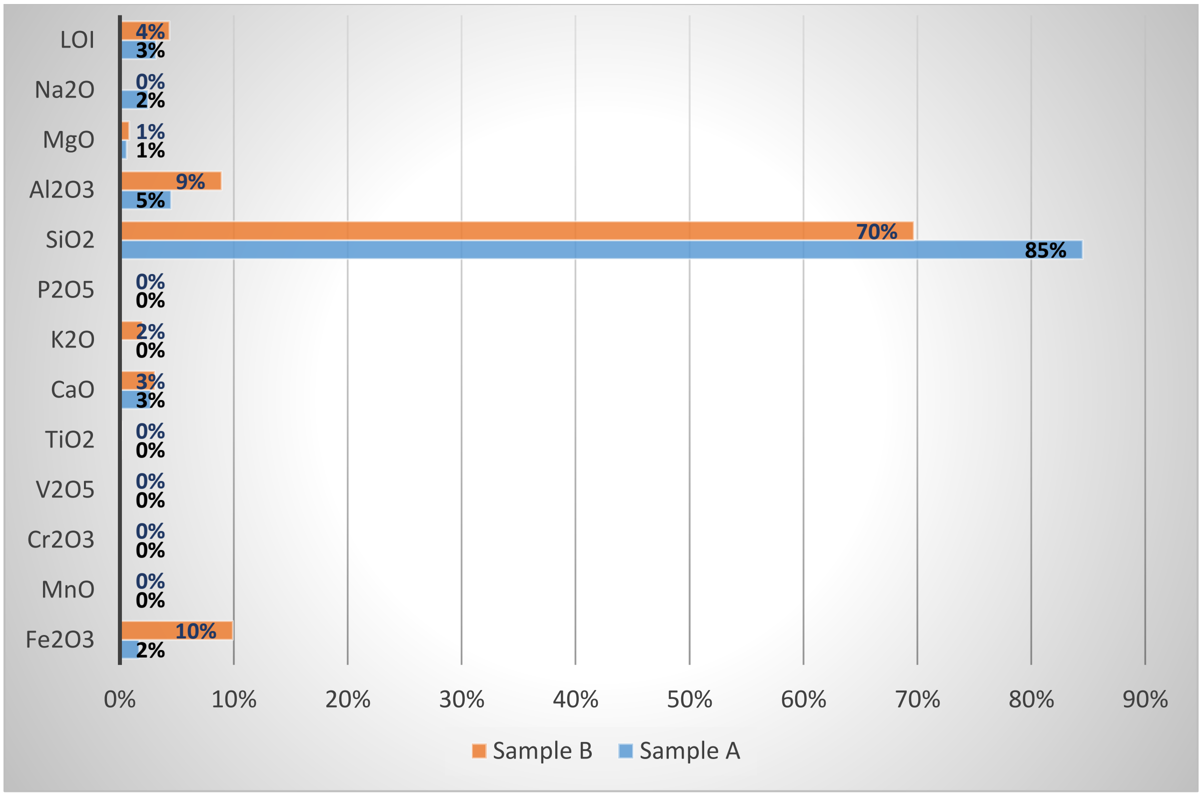

Figure 4.3: XRF composition analysis

Figure 4.3 shows the chemical composition of sample A and B from XRF tests. Loss on ignition (LOI) components are analyzed first to reduce analysis error of XRF results (Inoue *et al.*, 2005). The bulk of the ore is silica minerals which tallies with the QEMSCAN and XRD results for both samples (Figure 4.1 and Figure 4.2). Sample B has an 11% pyrite content from the QEMSCAN, and iron oxide content is at 10% on the XRF which aligns. Aluminum oxide is next largest for sample A in quantity, and this is because of its presence in feldspar. The XRF results are showing all compounds as oxides. However, from the QEMSCAN and XRD results we know some of our minerals are in sulphide phases. From the results both samples did not contain significant carbonaceous compounds which are preg-robbing and copper compounds in a high quantity as they actively compete with gold to dissolve in cyanide.

For ASGM this is good news because presence of carbonaceous material means they need employ CIL, where activated carbon is added to the leach vessel to adsorb the gold from the lixiviant before it is adsorbed by the carbonaceous material in the ore (Afenya, 2000; Marsden and House, 2009). This is difficult to implement in vat tanks used in the ASGM sector because of the high solids loading, recovering the carbons would be an issue if they are placed at the bottom of the tank. If the activated carbon is placed at the top, it will not contact the pregnant lixiviant because gold concentration (in the lixiviant) increases with depth as the lixiviant seeps down the ore. Therefore, they would need to buy or construct the proper agitated vessels for CIL which are not affordable for the regular ASGM practitioner. Presence of copper in the ore leads to high cyanide usage and it also competes to adsorb on the carbons. Solving this problem is difficult, especially for non-technical artisanal miners. The leaching process becomes very expensive because of reagent usage and the gold extractions would be low.

The iron content in the ore is high and significant, which would cause issues in the case of the iGoli process, which preferentially dissolves iron before gold (Mahlatsi and Guest, 2003; Celep, Alp and Deveci, 2008). This means a pretreatment step must be employed for example, pre-treating the ore first with dilute

H_2SO_4 to leach out the iron, or the quantity of lixiviants must be increased so that they leach out all the iron then get to gold dissolution. The process becomes more expensive due to the increased reagent requirement to achieve a good gold extraction.

4.1.2 GOLD LIBERATION AND ASSOCIATION

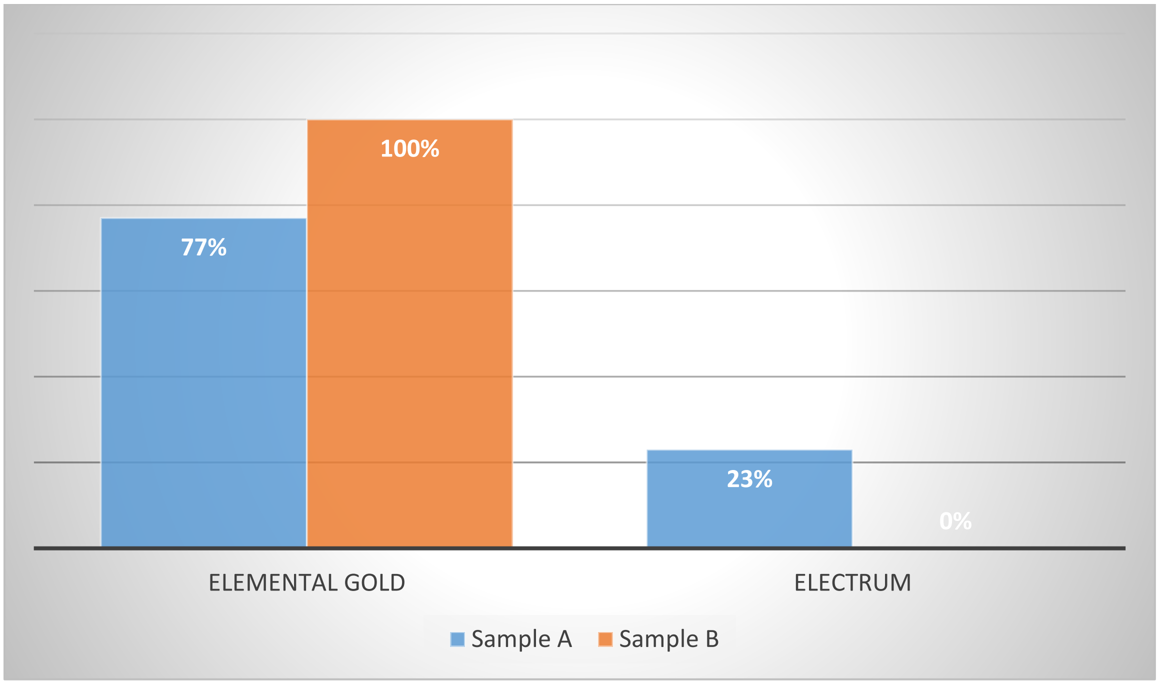

Figure 4.4: Gold Association

Figure 4.4 shows results of the nature of the gold in the samples. All the gold in sample B was found to be in elemental form. For sample A, 77% of the gold was in the form of elemental gold while 23% was in a solid solution with silver (electrum). Silver tends to report with gold during the leaching process. This results in silver competing with the gold to dissolve in the lixiviant resulting in high lixiviant usage (Marsden and House, 2009). This is not a major issue in most operations because gold is deposited preferentially on carbon during adsorption as discussed in (section 2.3.1). In ASGM, the continual recycling of the lixiviant might promote deposition of silver on the carbons overtime and this must be assessed because if silver is eluted with the gold, it reduces purity and the value of the bullion produced. In the mercury-amalgamation process, silver is captured with gold. In the case of electrum, the same happens which reduces the purity of the sponge gold and therefore the price.

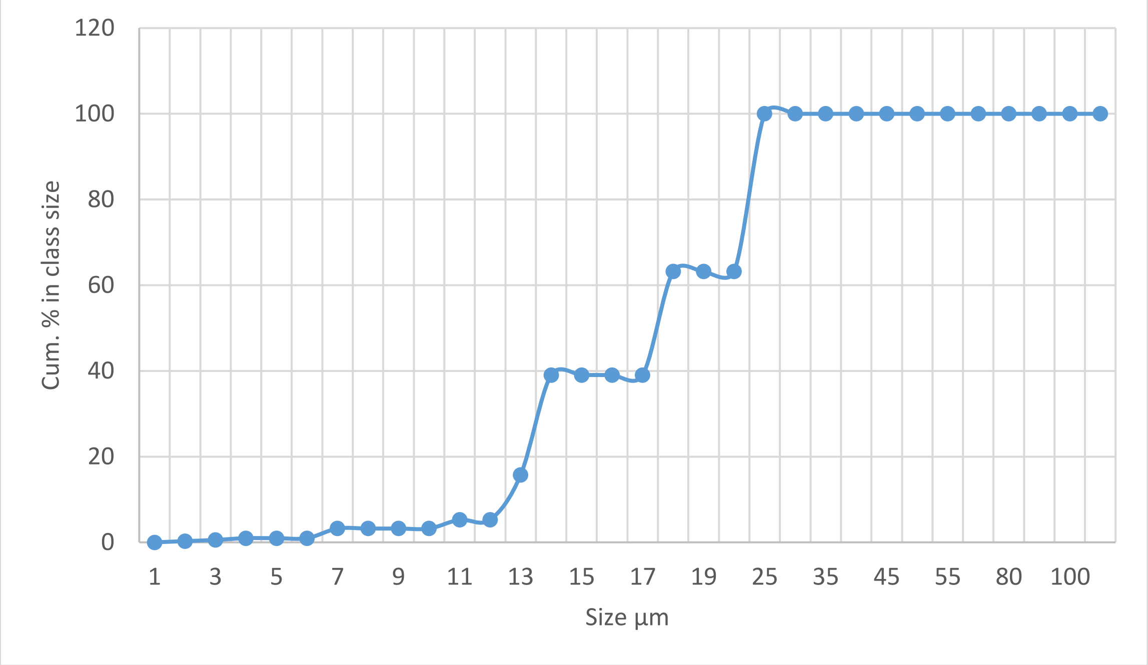

Figure 4.5: Gold grain size distribution Sample A

Figure 4.5 shows the gold grain size distribution in sample A from QEMSCAN. The gold grains are less than 25 microns in size with just over 60% smaller than 20 microns. For a 90% or higher gold liberation, we would need to grind the ore finer to a 12-micron size or less. This would increase extraction using cyanide closer to 100%. This is because a finer grind exposes more of the gold and provides a larger surface area for the lixiviant to contact and dissolve the gold. This effect of sizing on leaching efficiency is well documented by Manzila, Petersen and Moyo (2021).

In the case of mercury amalgamation in ASGM, mercury can only form a mercury-gold amalgam with gold it is in contact with. If the gold is locked inside gangue material regardless of thickness or porosity, a mercury-gold amalgam cannot form. Finer grind sizes would yield higher recoveries from mercury amalgamation because more gold is exposed. However, due to the high cost of machinery like ball and rod mills which can achieve these fine grinds, most miners opt for hammer and stamp mills which are cheaper and more affordable for them. This translates to lower gold recoveries in the mercury amalgamation process because of the low degree of liberation.

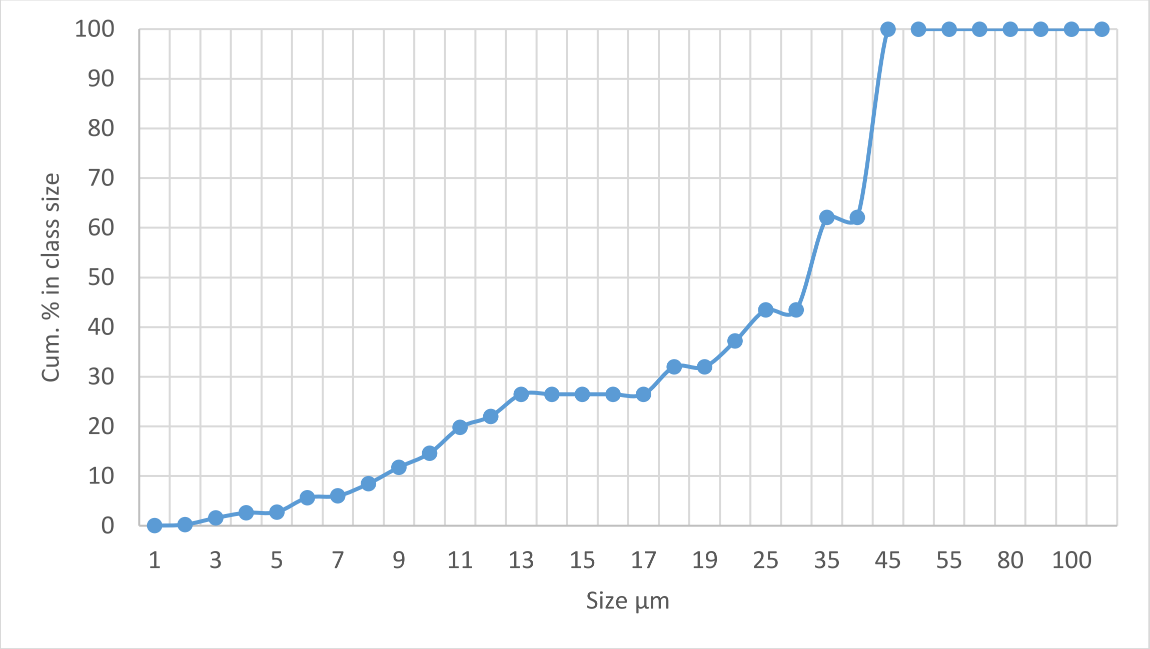

Figure 4.6: Gold grain size distribution Sample B

Figure 4.6 shows results from analyzing gold grain size in sample B. 100% of the gold is less than 45 microns in size with just over 60% smaller than 35 microns. For the gold to be more than 90% liberated, the ore needs to be milled to 8 microns or less. Extractions in the high 90 percentile range can be realized.

Cyanide leaching of gold is a slow process. Large gold grains need a longer residence time to completely dissolve. In a standard leaching operation, incomplete leaching of liberated large gold grains will report as ore refractoriness (Afenya, 2000) (Marsden and House, 2009). Sample B has larger gold grains than sample A. In a leaching operation with all other variables kept the same, sample A will reach optimum extraction in a shorter time than sample B. For mercury amalgamation in ASGM, the larger gold grain sizes of sample B are more ideal. This is because sample A needs to be ground finer than sample B to achieve a similar gold exposure based on the top size of the gold grains (sample A = 25μm; sample B = 45μm).

For the vat leaching in ASGM, if the ore is milled too fine it hinders the seeping of the lixiviant through the ore because it is more compact compared to coarser ore. The slow penetration of lixiviant results in longer leaching cycles from a normal maximum of five days to upwards of seven to ten days. For gravity concentration, i.e., sluice, Knelson concentrator, milling very fine would mean a low size range. This means that separation will be only due to density because the effect of size has been eliminated. This promotes production of a rich gravity concentrate from the gold ore as discussed by Vieira (2006). The concentrate produced will be rich and the subsequent process will recover a higher fraction of the gold.

Figure 4.7 and Figure 4.9 below shows which minerals in the ore are associated (in contact/encapsulating) with gold in sample A and sample B respectively.

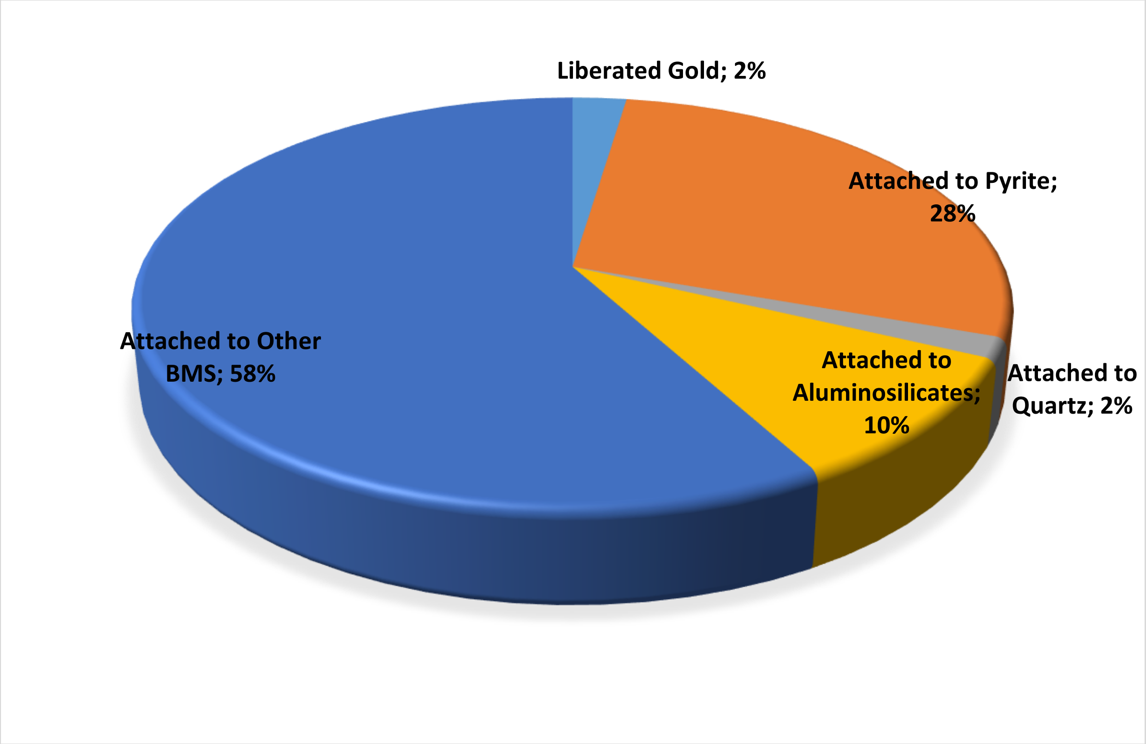

Figure 4.7: Gold association Sample A

Figure 4.7 shows the minerals that host gold in sample A. 86% of the gold in sample A was in association with sulphides, 12% with silicates and only 2% of the gold is liberated. This is interesting given that sulphides make up just about 1% of the ore in terms of composition. It should be noted that sulphides have preg-robbing properties in cyanide deficient solutions (Rees, K.L ; van Deventer, 2000). This means that running at low cyanide concentration which might stoichiometrically leach all the gold is likely to produce lower extractions than expected when side reactions with base metals are also accounted for. The images from the QEMSCAN overleaf in Figure 4.8 show the associations of gold with the different minerals in the ore. From the images, most of the gold is on the outer surface and not locked inside the minerals.

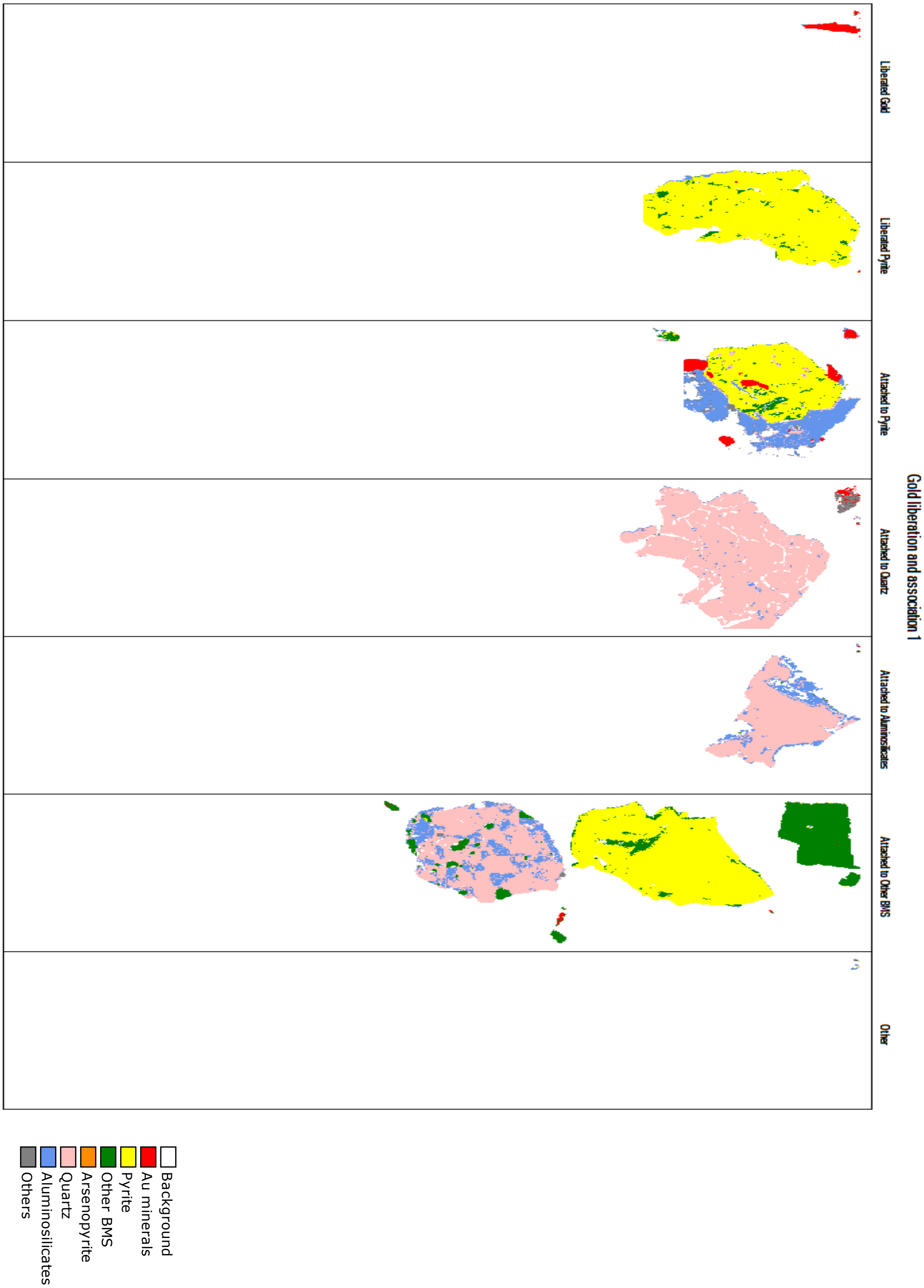

Figure 4.8: Sample A QEMSCAN images.

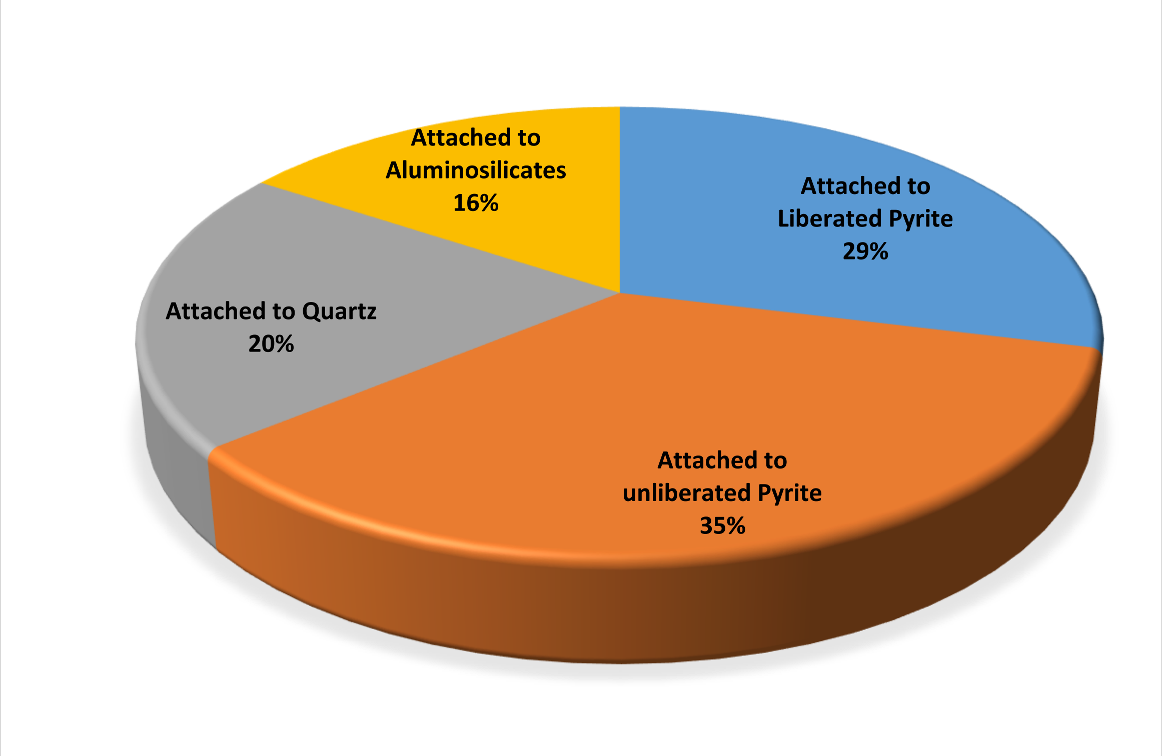

Figure 4.9: Gold association Sample B

In sample B as shown in Figure 4.9, 64% of the gold was hosted by pyrites while the balance 36% was hosted by silicates (aluminosilicates and quartz). The second most abundant mineral in the ore hosts most of the gold while the most abundant mineral hosts the difference. The images from the QEMSCAN in Figure 4.10 overleaf show the associations of gold with the different minerals in the ore. From the images, most of the gold is on the surface of the pyrite and silicates.

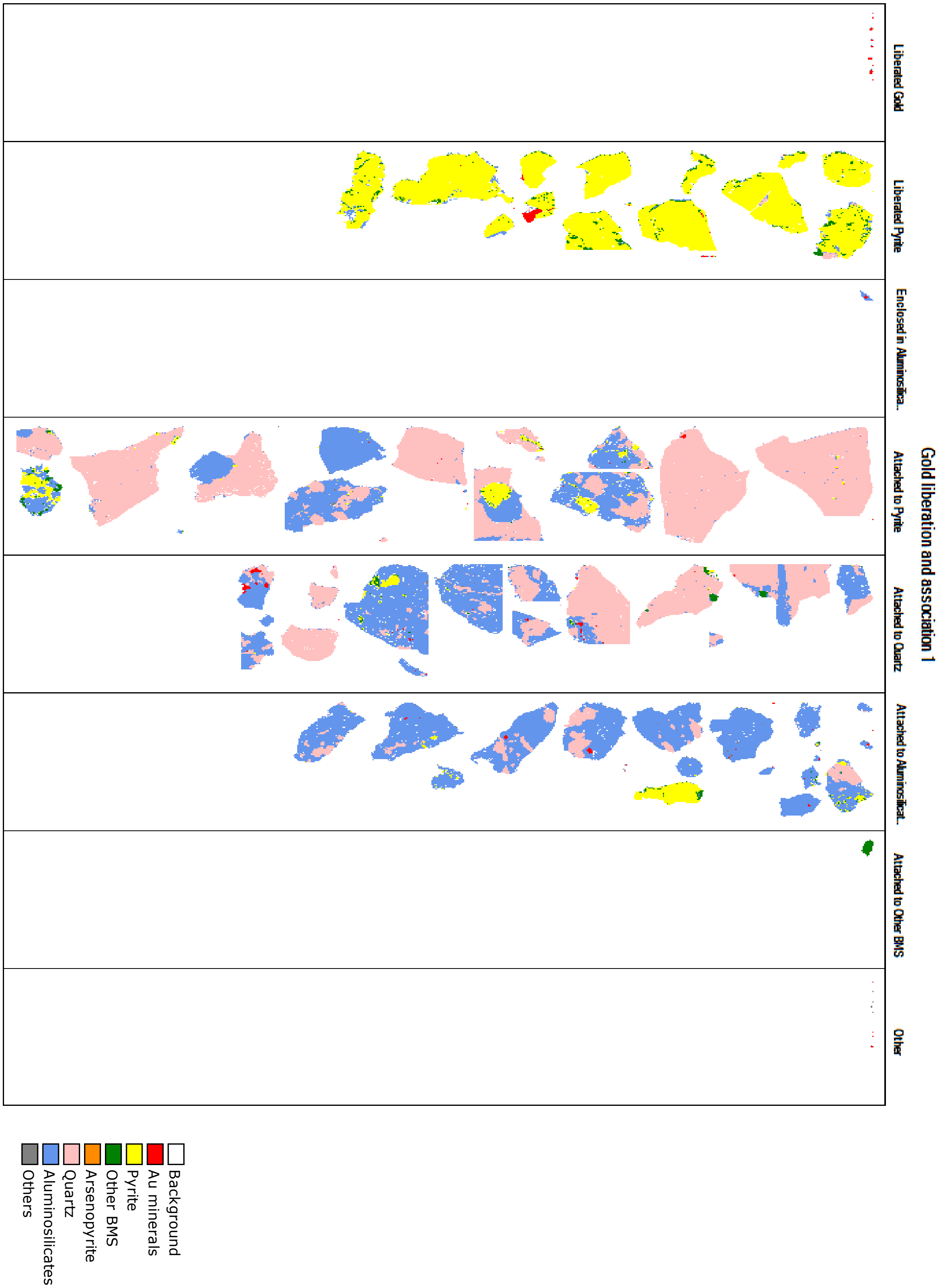

Figure 4.10: Sample B QEMSCAN images

4.1.3 DIAGNOSTIC LEACHING

Figure 4.11 gives results of diagnostic leach tests performed on sample A and B following the procedure on Table 3.1.

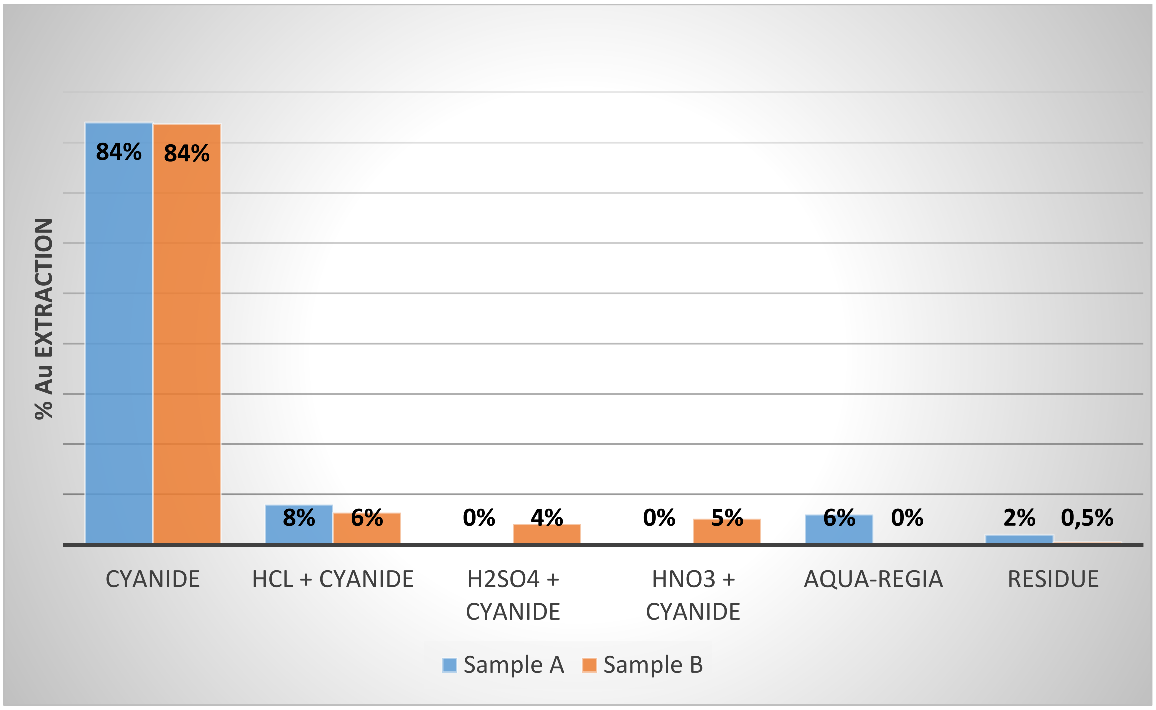

Figure 4.11: Diagnostic leach results

Diagnostic leaching was carried out using ore size fraction -300 to +100 microns (section 4.2.1.2)which is largely the grind size achieved by the mills used by ASGM operators before extractive processes are applied.

For sample A, the first leach achieved an extraction of 84%. After the first acid digestion step with HCl, the second cyanide leach achieved an 8% extraction of the initial gold assay value. Celep, Alp and Deveci (2008) postulates that HCl largely leaches pyrite minerals. The next 2 acid digestions with H_2SO_4 and HNO_3 coupled with cyanide leach steps yielded a 0% extraction. These acids digest base metal sulphides, thereby freeing up any locked gold. Finally aqua-regia leached 6% of the gold and 2% was left in the residue. Aqua-regia does not digest silicate minerals which indicates this gold was locked in sulphides which are digestible by the strong acid.

These results coupled with the QEMSCAN images show that the ore is mildly refractory with the bulk of gold on the surfaces of the minerals. 14% of the gold locked in sulphides which is digestible with *HCl* and aqua-regia creating pores for the gold dissolving lixiviant to seep through and leach the gold. The 2% left in the residue was locked in silicates which are indigestible by these acids. This is summarized in Figure 4.12 overleaf.

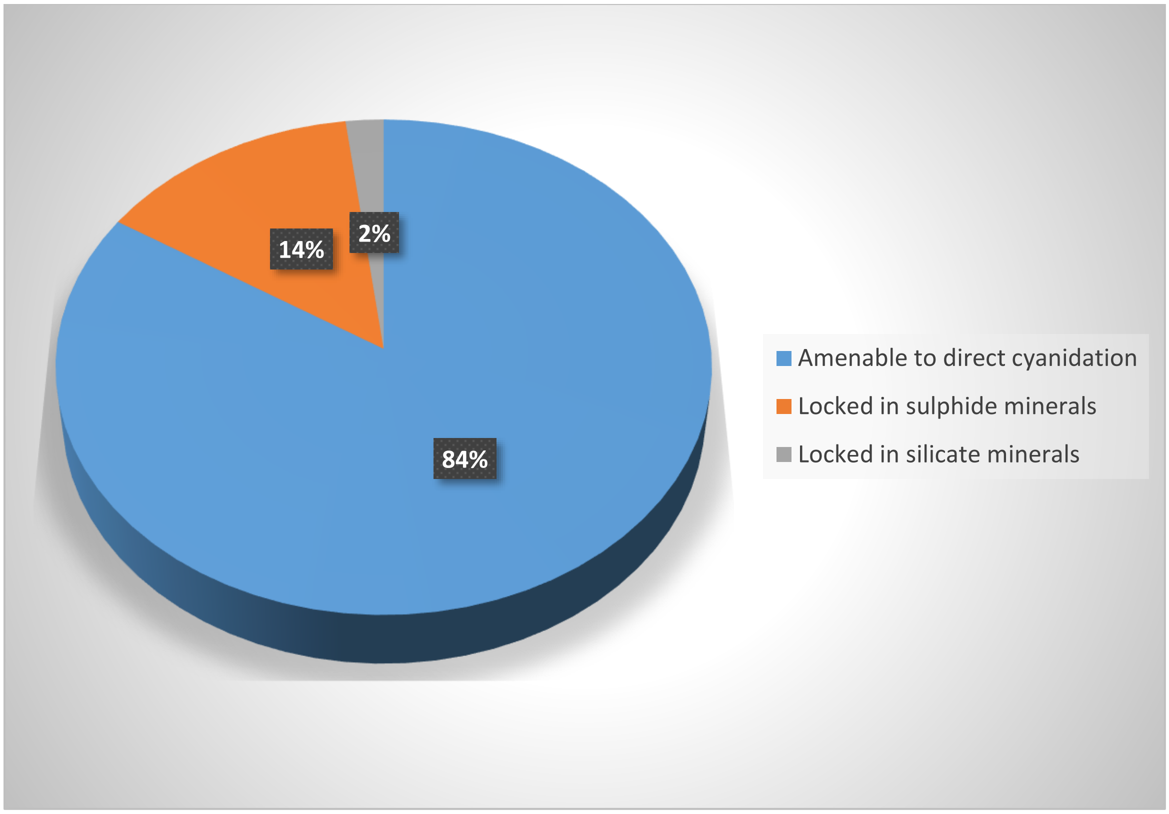

Figure 4.12: Sample A refractoriness

For sample B, the first leach achieved an extraction of 83.7%. HCl, H_2SO_4 and HNO_3 with their subsequent cyanide leach steps yielded 6.4%, 4.2% and a 5.2% gold extraction respectively as shown in Figure 4.11. Finally aqua-regia which is the most aggressive acid used in this exercise leached 0% of the gold and 0.5% was in the residue. These results show that the ore is mildly refractory. Given that HCl, H_2SO_4, $HNO_{3,}$ and aqua-regia do not digest silicates, and that gold in sample B is only hosted by pyrite and silicates. It can be deduced that 15.8% of the gold was locked in the pyrite while the remaining 0.5% was locked in silicates. Milling to -300 +100microns exposed 98.6% of gold associated with silicates and 75% of gold associated with sulphides. Figure 4.13 overleaf shows which minerals gold was locked in making it not dissolve in the first cyanidation step.

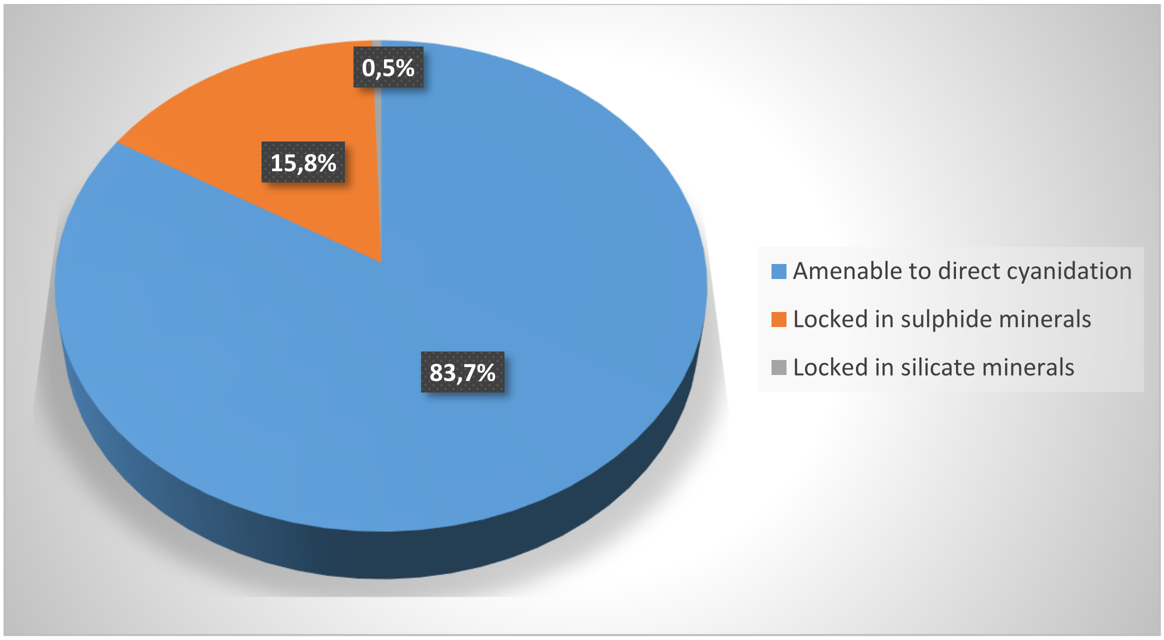

Figure 4.13: Sample B refractoriness

Diagnostic leaching is a tool that can be implemented in ASGM since they have limited to no access to equipment like QEMSCANs and XRDs due to their location and the analysis being costly. Diagnostic leaching can be used to generate the information shown in Figure 4.12 and Figure 4.13 which will tell them which gold is amenable to leaching before pretreatment and how much more gold they can extract after pretreatment. This can now be used in decision making since the information will be at hand and you can deduce the economics and feasibility of leaching the ore with or without pretreating. Care must be taken because the chemicals used in the process are toxic and need to be handled and disposed of in a proper safe manner.

4.2 CASE STUDY: ARTISANAL AND SMALL-SCALE GOLD MINING

DEFINITIONS

Artisanal miner: This group includes claim owners, people who work the mines, individuals who finance the rudimentary operation. For this case study, artisanal miners will refer to a subsistence miner who is not officially employed and works independently on a claim for shared profits i.e., mining, panning etc. The other parties will be unbundled as shown below for simplicity.

Artisanal mine: semi-mechanized gold mining and processing operation. Involve the use of rudimentary tools like shovels and machines like stamp mills.

Small-scale mine: mechanized operations which are structured like LSM but are smaller. Will have primary crushers and conveyors.

Processing Center: A center which just processes ore at a price. Are not involved in mining.

Financer: Individuals who fund/invest in artisanal mining operations for a negotiated return. These may be stand-alone individuals or owners of small-scale mines/processing centers.

Claim owner: Individual who has a mining right of a designated area.

Claim: A registered mining area.

Landowner: Someone who owns a piece of land which is not registered for mining (not a claim).

Site: Locale

Processing site: Location where ore processing is carried out since not all the processing equipment is mobile. Stamp mills, vat leach tanks and other processing equipment are located here. Ore is ferried from the mines to the processing site. NB: Not all processing sites are process centers.

A field work study was conducted to understand the operational mechanisms of ASGM practitioners at 2 processing sites, Kensington, Spring Farm in the Bulawayo province (Site A) and Gwanda in Matabeleland South Province (Site B), both in Zimbabwe. Site A is a licensed ore processing operation and is supplied ore mainly by a nearby artisanal mining operation who they have a mutually beneficial arrangement with. This mining operation was visited as part of the case study since their operations are linked. Site A also processes ore at a cost for other artisanal miners in the area. Site B is collectively owned and holds several mining claims. They are a formal mining operation who hold a mining and processing license. They mainly process their own ore but, on a few occasions, they process ore from artisanal miners in the surrounding area at a price or they keep their amalgamation tailings. Both sites are quite similar in terms of operations, and this is outlined below.

Small-scale mining and processing centers as described in most journals are formal mechanized operations that process a lower tonnage compared to LSM. The major distinction between them and artisanal mines is that they are more mechanized and have more finances at their disposal. Most small-scale operations have jaw crushers followed by mills. These are connected by a network of conveyors. Artisanal mines because of a lack of funds do not have conveyors or primary crushers. Site A and site B are formal operations but are not very distinct form the artisanal counterparts. They employ the same methods and equipment for mining. They cannot afford better machinery like ball mills like other small scale operations describe in texts by authors like Veiga *et al (*2009).

4.2.1 ASGM OPERATION

The case study was conducted over a period of 6 weeks of job shadowing and analyzing the processes. The operation starts with bush clearing and searching for the gold bearing rock (quartz) in a predominantly clay soil area. When rock is located mining commences following the path of the gold bearing seam. There was a passed down knowledge from artisanal miners that informs this kind of prospecting. They look for certain discolorations in the rock and for gold in the cleavages. Most of these activities were conducted before the job shadowing began at both sites; the mining shafts were already established. Mining and ore processing were carried out and these are detailed in this subsection as per the process flow starting from mining to extraction. For site A, the mining described will be that observed at the mining site which mainly supplies them.

4.2.1.1 MINING

The mining operation involves drilling, blasting, and hauling the ore from the shaft to the mills. Figure 4.14 is a picture of the run-off mine hauled from the shaft before comminution.

Figure 4.14: ROM ore from shaft (authors own)

Drilling and blasting were employed at both site A and B because of the hardness of the quartz. ANFO (Ammonium Nitrate Fuel Oil) explosives were the choice of explosive in both operations because they are the simplest and cheapest commercial explosive available. Most of the miners did not have the required blasting licenses to carry out these blasts, so all the blasts were conducted at night at site A to avoid authorities. This was also advantageous operationally because the miners got time to sleep during the nighttime after blasting when the shafts were still clearing of smoke, dust, and dangerous gases produced. Figure 4.15 shows a rock drill and a drill bit the miners use to bore holes to charge explosives.

Figure 4.15: Drilling Equipment (authors own)

Picks and shovels were used to load out the ore which was stockpiled separately from the waste material. As the shaft got deeper the miners employ the use of a hoist (shown in Figure 4.16) to haul up ore in metal buckets to the surface.

Figure 4.16: Shaft hoist with loading bucket attached (authors own)

Blasted rocks which were not fully separated from the compact surface in the shaft were loosened using jack hammers (shown in Figure 4.17) and then hauled up. If these rocks are left behind, they reduce efficiency of the next blast. They can become loose during drilling and charging. Cracks produce weak blasts which generate large chunks of ore which can't be hauled out and need to be re-blasted. This entails drilling and charging more explosives again incurring further costs in an already finance starved operation. Reduction of inefficiencies means less operational costs and more net profit at the end.

Figure 4.17: Jack Hammer (authors own)

When a hard surface was reached, the drilling and blasting process was repeated, followed by hauling. Visual inspections of the ore were carried out at 1-meter intervals to check for the presence of gold. This was done to avoid losses by mining non-gold bearing rocks.

At site A, 10 meters below the surface, ground water was encountered. This is a hazard because water loosens rocks on the shaft walls which can collapse the shaft or fall on miners working below causing injuries/death. So, the water was pumped out frequently and thick branches were used to secure the shaft walls. When a shaft collapses it is abandoned. Figure 4.18 shows a compressor and two petrol generators that power the operation for drilling, pumping out water, and operating the jack hammer.

Figure 4.18:Compressor and generators (authors own)

4.2.1.2 PROCESSING

The ore processing models for site A and B were mostly similar.

At site A, the mined ore was reduced in size using hammers to match the feed top size of the mills because they did not have a primary crusher. Both hammer and stamp mills are wet milling operations. The site A process flow diagram is shown in Figure 4.21. At the mining site there was a hammer mill which was used by the artisanal miners when the gold grade was visibly low. The hammer mill was connected to a cloth covered sluice to capture the concentrate by virtue of its higher density vs the tailings. The gold concentrate captured on the cloth was washed out into a bucket. This then goes through panning and amalgamation. The amalgam formed was roasted to leave behind the sponge gold. The tailings from the milling and sluicing flow to a Pond A where they are dewatered. Pond A was a at a higher level than the connected pond, Pond B. As the solids settled in the Pond A, the water rose and overflowed to Pond B. The recovered water from Pond B was recycled to the milling operation. The dewatered gravity tailings from Pond A were shoveled out, mixed with the tailings from the amalgamation process and transported by trucks to site A's processing site where they were leached in vat tanks using cyanide. In most instances when visual inspections were conducted and it was deduced that the ore is of a high grade, it was ferried straight to the processing site to undergo processing as shown in Figure 4.21. The ore was fed to the stamp mill using shovels and wheelbarrows. The stamp mill had a capacity of processing 5-10 tons of ore per hour. The stamp mill had a 1mm screen at the exit like the hammer mill, both producing milled ore with just over 70% of the ore in the -300 to +90-micron size range. The milled ore went through an extra gravity concentration step at the site processing plant. After sluicing, the tailing from sluicing went to a Knudsen concentrator which operates similar to a Knelson concentrator as shown in Figure 4.19. Gold grains which were heavier than the gangue were captured in the grooves.

Figure 4.19: a) Knudsen concentrator b) Inside the concentrator (author own)

Gravity concentrates from the sluice and Knudsen concentrator were enriched using panning and amalgamation. The amalgam formed was then roasted to get sponge gold. Tailings from the gravity concentrator went through dewatering phases similar to the ponds from the hammer mill process as shown in Figure 4.20 and the water was recycled back to the wet milling operation. The dewatered tailings were shoveled out and then moved to the vat tanks for cyanide leaching.

Figure 4.20: Dewatering ponds (authors own)

These processes are discussed in more detail from section (4.2.1.2.1) to (4.2.1.2.3).

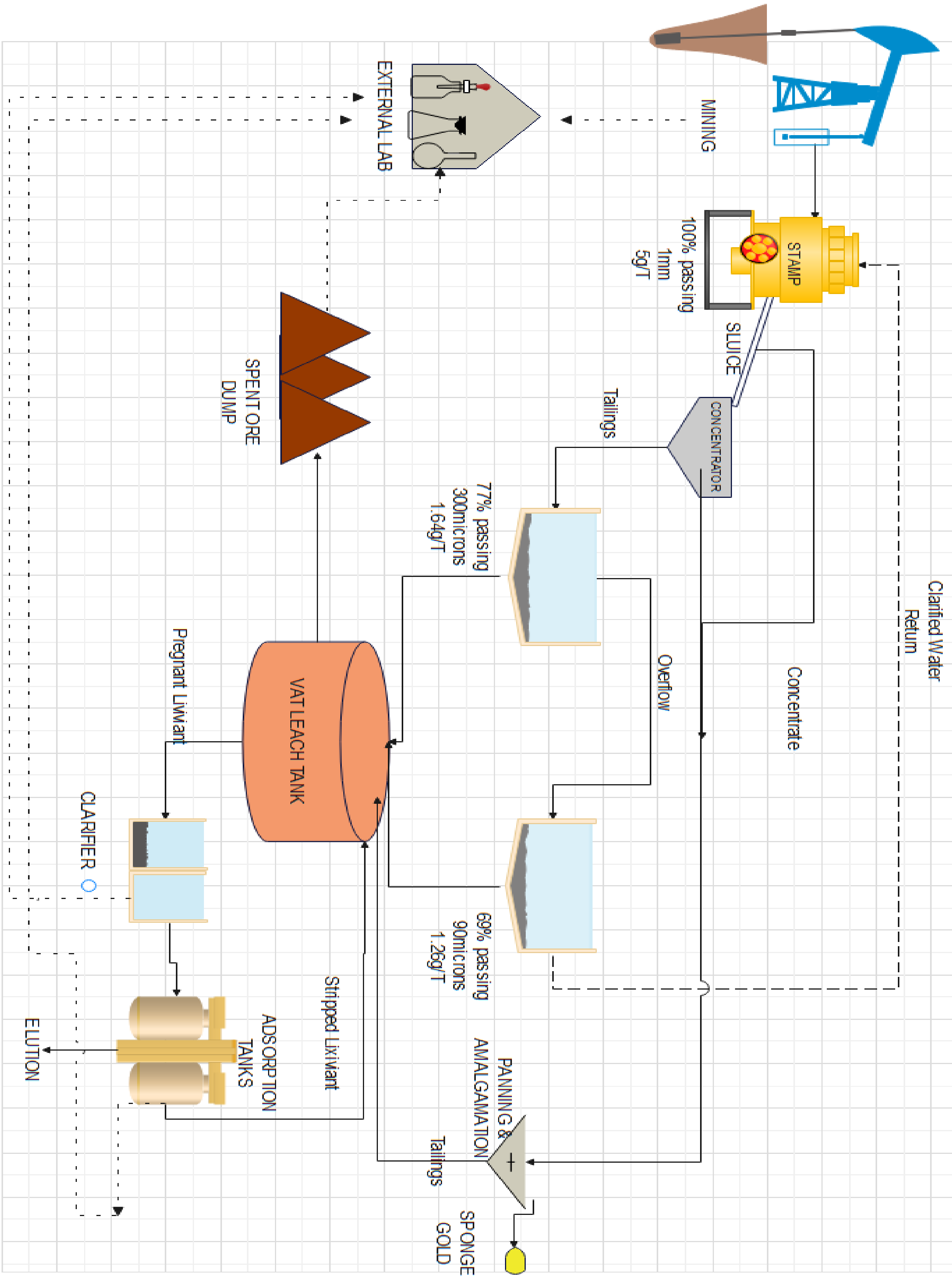

Figure 4.21: Site A Process Flow (authors own)

At site B, the mined ore was transported to the site B processing plants. It was then similarly fed to a stamp mill using shovels and wheelbarrows. The site B process flow diagram is shown in Figure 4.22 overleaf. The stamp mill and the gravity concentration process which follow it are similar to site A. Gravity concentrates were further upgraded using a James table. Borax was then added to the enriched concentrate, and it was then smelted. The gold separates from the gangue and can be tapped out since it settles at the bottom of the slag due to its higher density. They use mercury amalgamation after the James table if the concentrate is not sufficiently enriched for the borax process to be efficient. Tailings from the gravity concentrator go through dewatering phases and the water is recycled to the wet milling operation. The dewatered tailings and enrichment tailings then go for cyanide leaching.

The site has an onsite laboratory. Lixiviant samples from the leaching and adsorption tanks are collected and analyzed for dissolved gold in this laboratory using the Stannous test. They also send samples to an external lab to analyse quality of ore and as checks on the efficiency of their operation.

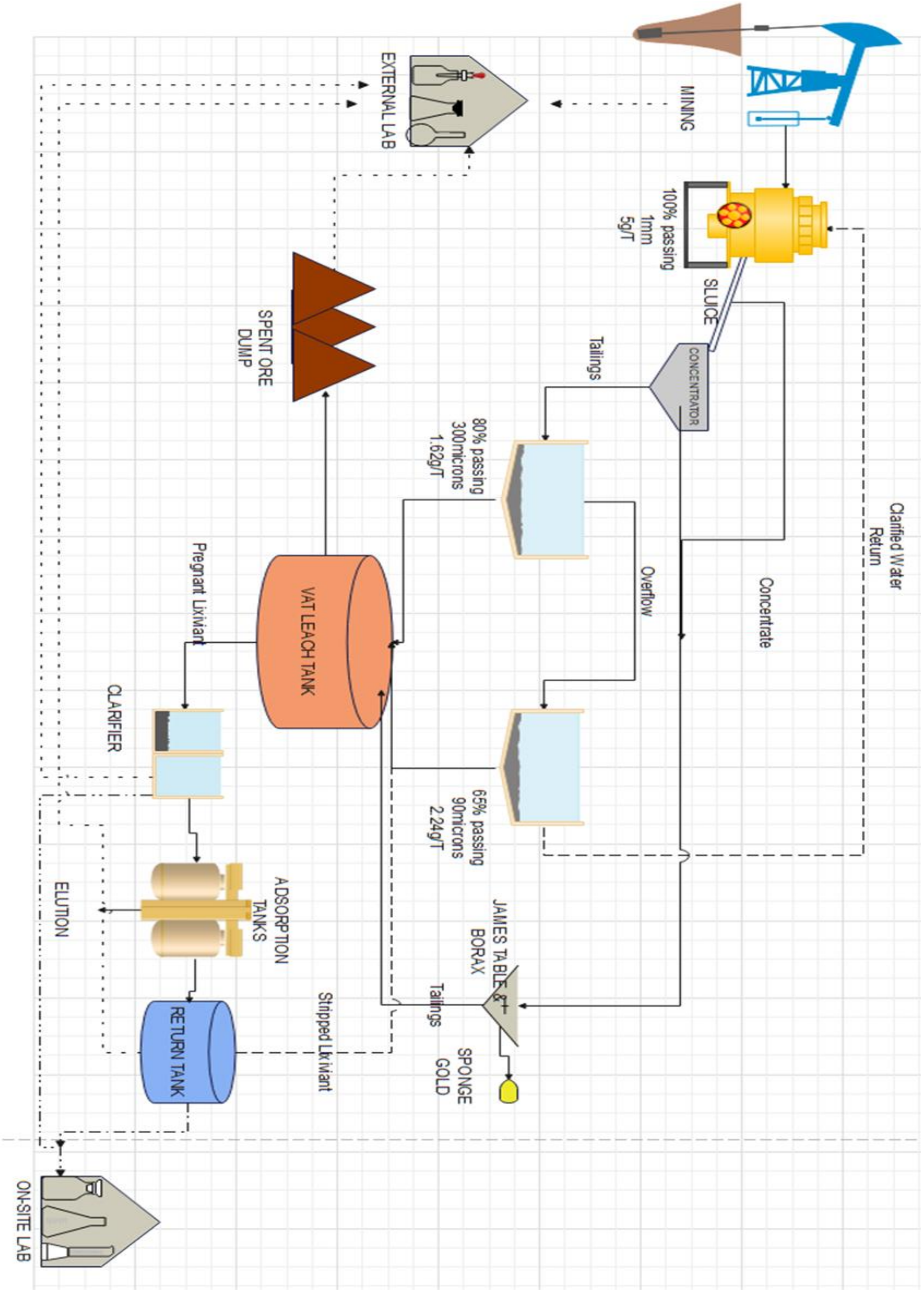

Figure 4.22: Site B Process Flow (authors own)

4.2.1.2.1 MILLING AND SLUICING

For the hammer mill at site A, the ore was fed to a hammer mill which was connected to a cloth lined sluice to capture the concentrate due to the difference in density between gold and the gangue it is associated with. This is a wet milling process, and the water was added with jugs which produces an uneven flow which is not desirable and leads to losses of concentrate as shown in the study conducted by Stoffersen *et al* (2018), in Mozambique when even flow produced a better concentrate than uneven flow. The hammer mill can process about 1 ton of feed per hour. The concentrate captured on the cloth was washed out into a bucket and awaited treatment by mercury-amalgamation. The tailings washed into a dewatering pond. The slurry flowed into Pond A first and by the sedimentation mechanism, the solids settle while water rises. A shallow trench connected Pond A to Pond B which was at a lower level. As the water level rose to the top of Pond A it flowed out to Pond B. Water recovered in Pond B was recycled to the milling operation. When the rising solid level reached surface level meaning Pond A was full, it was left for four hours to continue dewatering then the ore was shoveled out onto the surface to dry. When the sluicing tailings were dry, they were transported to the cyanidation tanks for leaching. Figure 4.23 shows the milling and sluicing operation with the tailings flowing into Pond A.

Figure 4.23: Hammer Mill and Sluice Site A (authors own)

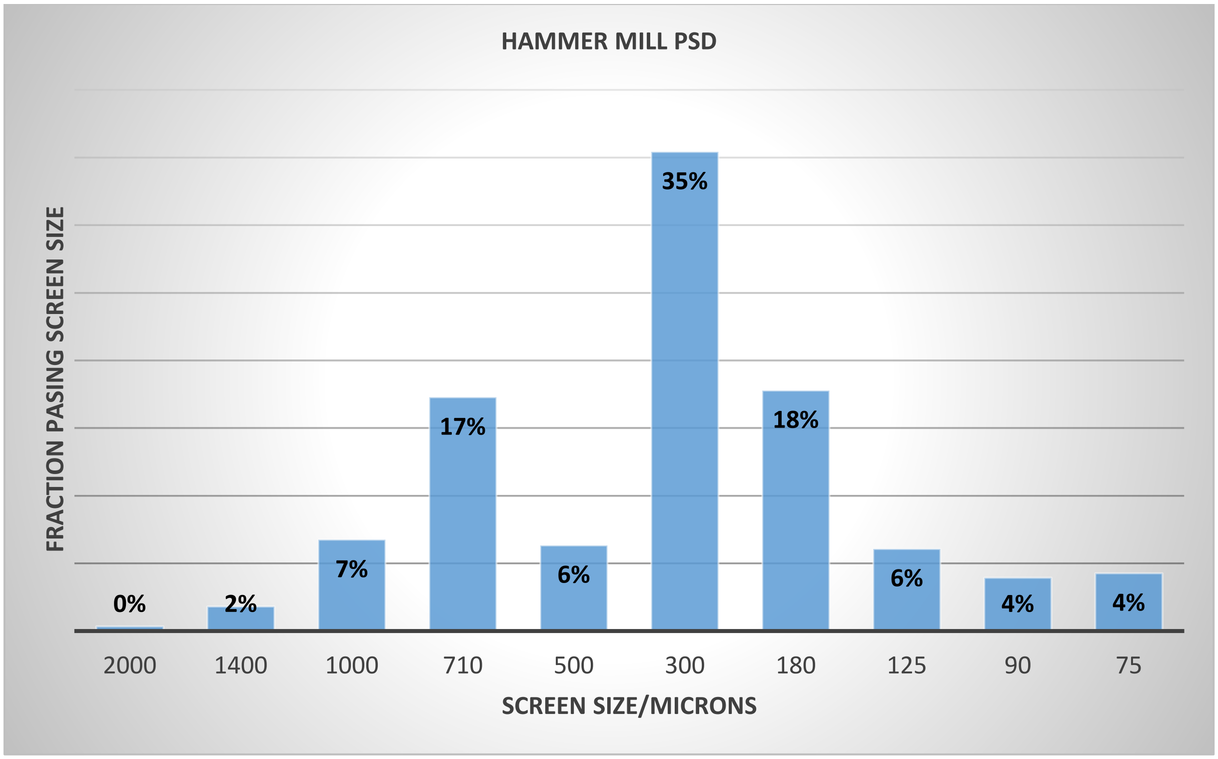

Figure 4.24: Product Size Fractions from the hammer mill at Site A

A sample of milled ore was collected from the hammer mill (feed for the sluice). The mill had a 1 mm sieve at the exit which governs the sizes that pass through. The process was a one pass operation, and the oversize was not recycled. The sizes above 1mm were due to a tear on the screen. Repairs on the screen were done when there was visibly too much oversize material being produced because it reduces the efficiency of sluicing (Vieira, 2006). Figure 4.24 shows that 67% of the milled ore from the hammer mill was passing 300 microns. This sizing was what informed the sizing of the ore which was to be tested in the lab with the different lixiviants.

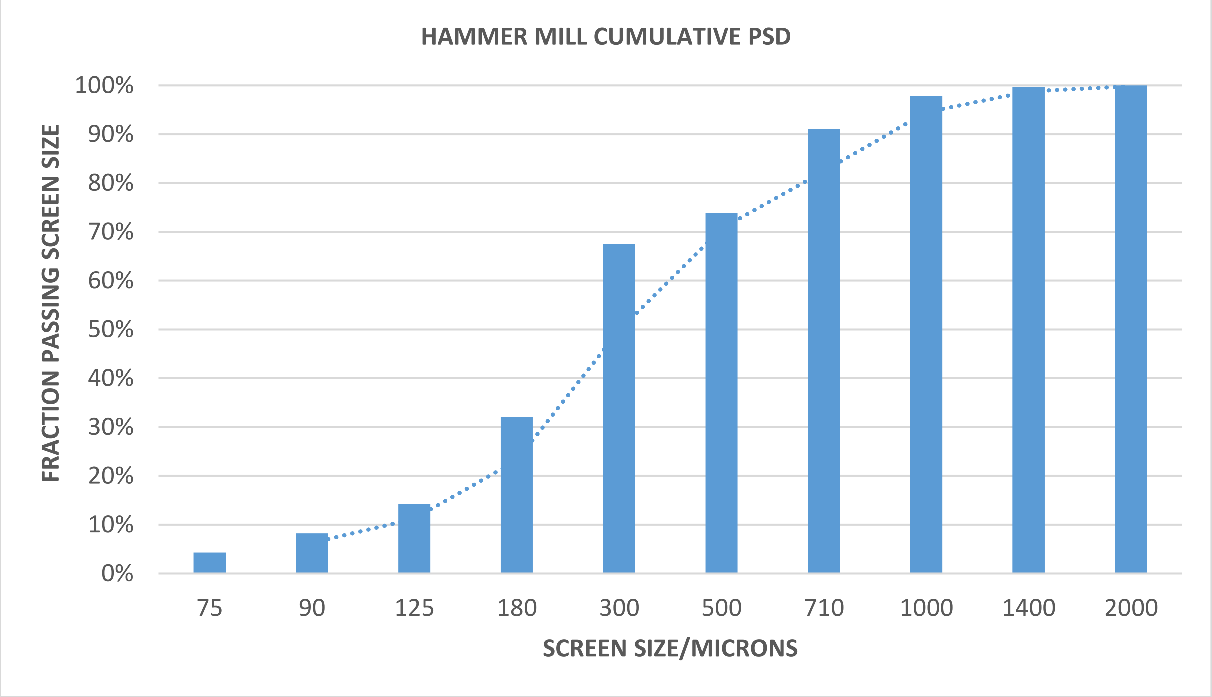

Figure 4.25: Cumulative Distribution of hammer mill product sizing

Figure 4.25 above shows the results of the product psd of the hammer in a cumulative graph.

Figure 4.26: Stamp mill Site B (authors own)

At both sites, sledgehammers were used to break down the ROM to below 10 cm before feeding it to the stamp mills. 3 people fed the ore in the wet milling process. The milled ore then passed through a sluice and a gravity concentrator which were set up in series to capture gravity concentrates. Gravity concentrates from the sluice and concentrator were enriched using a James table and then underwent mercury amalgamation/fluxing with borax. Gravity tailings and borax/mercury amalgamation residues were dewatered and moved to the cyanidation tanks for leaching. The water from the dewatering process was recycled to the wet milling operation. Figure 4.26 shows the stamp mill from site B which is powered by a diesel generator. The stamp mill at site A was connected to the city power.

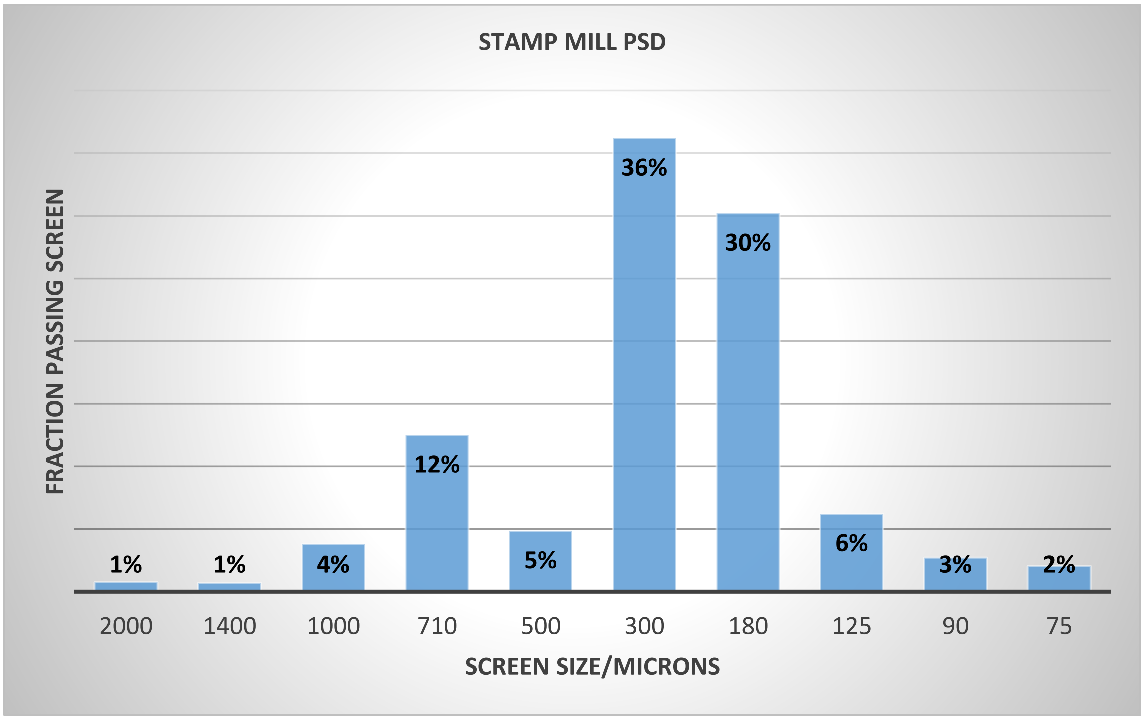

Figure 4.27: Product Size Fractions from Stamp Mill

Figure 4.27 shows the sizing of the stamp mill product. The hammer and stamp mills produced around 70% of milled ore in the 300-to-90-micron size range. This was quite coarse when compared to the ball mills used in Large Scale Mining with a target of 80% of milled ore passing 75 microns. This is an area of note since miners make the bulk of their revenue from the amalgamation process. The efficiency of this process step is dependent on the degree of gold liberation achieved from the milling process. Figure 4.28 overleaf shows the above results represented in a cumulative distribution.

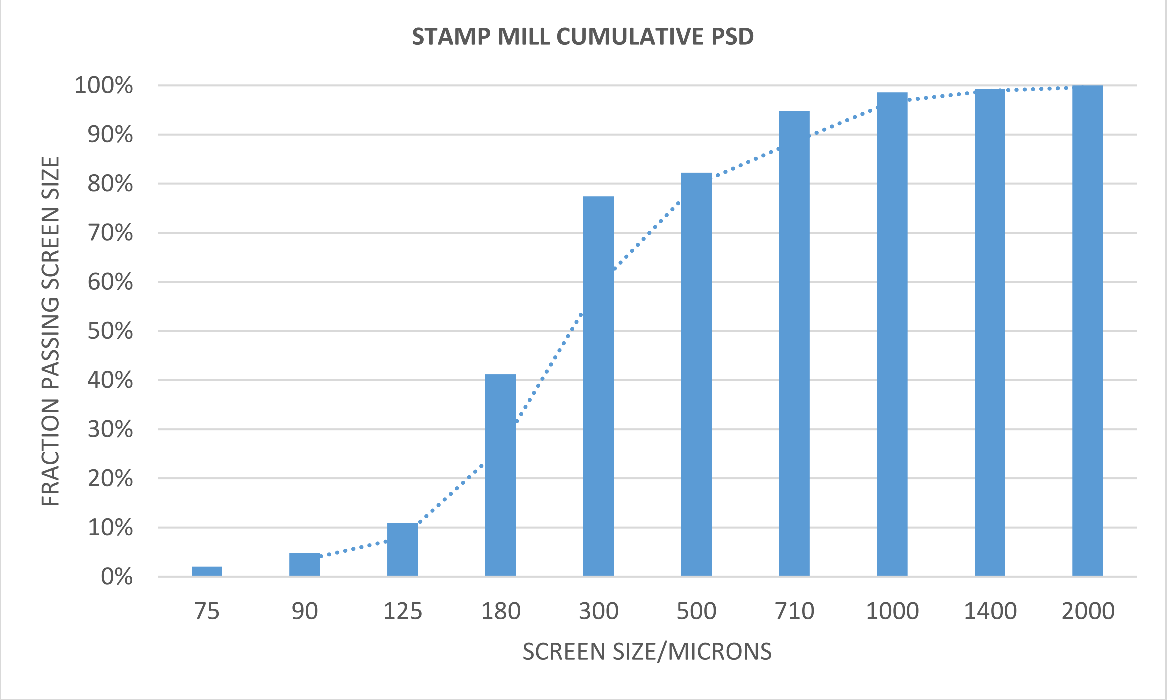

Figure 4.28: Stamp mill psd cumulative distribution

To achieve finer grind sizes the 1 mm screen needs to be replaced with a smaller one e.g., 100-micron screen. The retention time of the ore in the mill would increase and thereby reducing throughput drastically from a 5 TPH operation to below 2 TPH. The energy demands would go up and so does the cost, and the time taken to produce enough ore to be leached increases. The gravity separation processes would yield more because small size ranges in ore increase efficiency of gravity separation processes especially for centrifuges (Vieira, 2006). The leaching process ideally will be faster because fine grinding exposes more gold and surface area for leaching. However, finely ground ore impedes the seepage of the lixiviant through the ore in vat tanks. Therefore, more leaching time will be required. So, finer grinds would lead to greater recoveries of gold on one end but the costs and the residence times in the milling and leaching operations go up significantly.

4.2.1.2.2 MERCURY AMALGAMATION

The gravity concentrate was panned, removing the larger grains and gangue entrained in the gravity concentrate. Mercury was then added to the pan and mixed with the concentrate and was further panned. The flowy liquid mercury became more solid as the amount of gold captured increased. Thus, a mercury-gold amalgam is formed. Figure 4.29 shows the panning and mercury amalgamation process. Handfuls of the concentrate were added from the bucket containing the concentrate to the dish for panning and mercury amalgamation. The panning was done using the water in the wheelbarrow. Water is essential for panning, by sifting the pan in the water, the gangue being lighter moves to the edge of the pan and discarded while the heavy gold grains resist motion.

Figure 4.29: Panning and amalgamation of gravity concentrate (authors own)

From milling and sluicing just over 700kg of ore, the concentrate from sluicing was a third of a 20-liter bucket. Panning and mercury amalgamation were done until the whole concentrate captured from the cloth on the sluice was processed. The amalgam formed in this process was then roasted on a burning log in open air for approximately 1-2 minutes. The roasting process is dependent on the size of the amalgam. The sponge gold from the roasting was then weighed. Figure 4.30 shows sponge gold recovered after roasting; it weighed just about 1 gram.

Figure 4.30: Sponge gold (authors own)

4.2.1.2.3 VAT LEACHING

The gravity concentration and mercury amalgamation tailings were transported to the vat leach tanks for gold dissolution using cyanide.

Figure 4.31: Vat Leach Tanks Site A (authors own)

Site A had 3 vat tanks (pictured in Figure 4.31), each tank was 16.8 m^3 with dimensions of 4 m * 3.5 m * 1.2 m. Site B had 5 vat leach tanks which were 25 m^3 each. The design of all the tanks was the same. The tanks were made of bricks and impermeable cement. The bottom of the tank was lined with a filter made of 3 layers. The bottom layer was coarse gravel, on top of it was river sand and finally, woven fabric from cotton bales. Figure 4.32 shows a cross section of the vat leach tank. Unfortunately, information on the thickness of each layer could not be obtained.

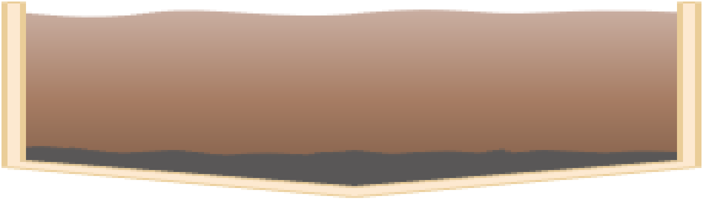

Figure 4.32: Cross section of vat leach tank (authors own)

20 tons of ore, 15 kg of sodium cyanide and 5 kg of sodium hydroxide were added to the tank with water to fill up the tank leaving a gap of about 5 cm between the top of the tank and the level of the lixiviant and ore. The lixiviant seeps through the ore dissolving gold and through the filter. The pregnant leach solution was tapped at the bottom corner of the vat tank and flowed by gravity to a clarifying pond.

Figure 4.33: Clarifier (authors own)

Figure 4.33 shows the clarifier which was partitioned into two tanks. The pregnant lixiviant from the vat leach tanks drained slowly into the receiving tank and the fine solids which were entrained with the lixiviant settled at the bottom. The pipes shown on Figure 4.33 which were feeding into the receiving tank were each from a separate vat tank. This made sampling easier to check how leaching was progressing in each vat tank. The barrier in between the tanks had holes near the middle which allowed for clarified fluid to enter the next tank. Maintenance was carried out after a cycle to remove the solids that would have settled at the bottom. The clarified pregnant lixiviant was pumped by a 0.5 horsepower pump to the carbon columns.

Figure 4.34: Carbon columns in Series (authors own)

Two adsorption columns worked in series improving adsorption efficiency as shown in Figure 4.34. The pregnant lixiviant flowed slowly from the bottom of the carbon column, contacting the activated carbon, and getting stripped of gold as it rose to the top of the first column and flowed out into the bottom of the second carbon column. The adsorption tanks each held 100 kg of activated carbon and they were kept under lock and key during operation to avoid theft. The stripped lixiviant, still under pressure, was recycled back to the vat leach tanks as shown in Figure 4.35. Site B was similar to site A but after the carbon columns they have holding tanks where the stripped lixiviant flowed to and were then pumped back to the vat leach tanks as illustrated in Figure 4.22. The holding tanks also served to store the lixiviant when the leaching operation was complete, and the vat tanks were drained so that the spent ore could be shoveled out. Site A during draining pumped and stored the lixiviant in 750-liter JoJo tanks.

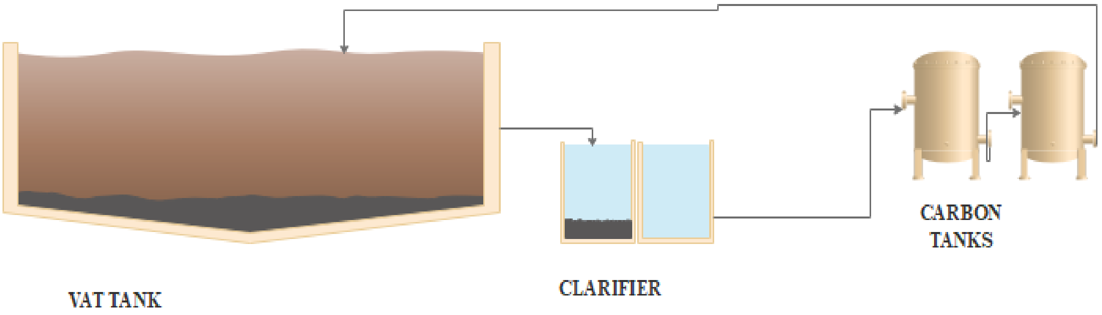

Figure 4.35: Leaching and Adsorption Circuit Site A (authors own)

The leaching and adsorption steps ran/operated in a closed circuit and the cycle took 3 to 5 days to complete.

The pregnant carbons which were kept under lock and key were collected when the cycle was complete. Armed security was always hired for this purpose because of instances of theft which previously occurred. For an extra layer of security, the date for the collection of the carbons was kept secret to avoid planned attacks. The site manager/owner was the only one privy to this information. The carbons were sent for a Zadra elution process and electrowinning off site. The plant used a solution of sodium hydroxide and cyanide at $140℃$ in a pressurised boiler to desorb the gold from the activated carbon. The other processes that followed including electrowinning were kept private. The carbons were weighed before and after the elution and electrowinning process which took just over 24 hours. The bullion was weighed and given to the owner together with the stripped carbons then the service was paid for. In other arrangements they kept a portion of the gold bullion as payment.

4.2.1.3 EFFICIENCY TESTS CONDUCTED AT SITE A AND B

From Site B's process, leachate flowed from the top of the tank where it was tapped at the bottom into a pipe which flowed into the clarifier. The site had 5 tanks and therefore 5 pipes, one from each tank, which bled into the clarifier. 3 tanks were running on the day. Tank 1 was on day 4 leaching and was being drained because the leaching operation was considered complete, tank 2 was on day 2 while tank 3 had just been loaded with ore and lixiviant. Samples were taken from the 3 tanks and analyzed using the stannous chloride gold test. In this test Tin (II)Chloride reacts with gold salts in solution forming a pink to dark purple precipitate depending on the concentration of gold in solution. The higher the concentration, the darker the precipitate. Observation of the precipitate was used by the operators to indicate the presence of gold in solution and to inform the decision to either continue with the leaching or to terminate and start on a new batch. Samples from the 3 tanks were collected and sent to an external lab for AAS analysis to compare with the ones from the stannous test. The results are shown in Table 4.1.

Table 4.1: Stannous Test vs AAS

TANK	STANNOUS CHLORIDE TEST	AAS (Au ppm)
1	Clear	0.15
2	Pink	1.98

3	Clear	0.17

The results above showed that their testing process, which took 30 minutes in total, is a good indicator even though it does not give quantitative results. There would be a need to standardize the colors with AAS results so that they can at least offer an estimate of the concentration of gold.

Further samples were taken from both sites to analyse the efficiency of the adsorption process. The results are in the Table 4.2 below, it is important to note that as the carbon gets saturated with gold, the adsorption efficiency drops.

Table 4.2: Adsorption Efficiency

SAMPLING POINT	CLARIFIER	ADSORPTION TANK	ADSORPTION EFFICIENCY
SITE B	1.9 ppm	0.49 ppm	74%
SITE A	1.98 ppm	0.13 ppm	93%

Site A had a very good adsorption efficiency and stripped 93% of the gold from the lixiviant while site B was at 74%. The difference in adsorption efficiency may be due to the activated carbon at site B having fewer active sites in comparison. This is because the adsorber was already in operation adsorbing gold from a previous tank which was in operation.

The extraction efficiency of the ASGM operation at site A was tested. To standardize the test, the ore used in this run was also used in the lab tests with the alternative lixiviants. The results are shown in Table 4.3 below.

Table 4.3: Site A extraction results

SITE	Site A
SAMPLE IDENTITY	Sample A
PSD OF ORE	Figure 4.27
EXTRACTION METHODS USED	Mercury Amalgamation and subsequent Cyanide leaching at NaCN(5g/l)
LEACH CYCLE	3 days
EXTRACTION	81%

In the field, at Site A, the processing was as in Figure 4.21. After mercury- amalgamation and 3 days of the leaching operation at a concentration of 5g/l NaCN in vat tanks, the total extraction was 81%. This extraction achieved in the field will be compared to test works conducted in the lab in section (4.6.4).

4.2.2 ASGM SOCIAL AND ORGANISATIONAL STRUCTURE

Typical of any business operation, ASGM be it formal or informal has a business structure and this forms the basis of decision making and influences the social interactions between the stakeholders. The organizational structure of site A and B are different and are outlined in this section.

Figure 4.36: Site A operational organogram

Site A had three individual parties in a mutually beneficial agreement. The first is the financer, who did not directly engage in the mining but funded the mining operation with the required mining equipment like the jackhammer, compressor, drilling equipment, etc. The financer also provided daily necessities/consumables like fuel, food, and mercury. The second is the landowner on whose land they were mining the gold ore, and lastly are the artisanal miners who worked the mines. The structure was flat with all three parties being equal and all decisions needing to be agreed on. The structure is shown in Figure 4.36.

The financer had a processing plant which was 15 km from the mine site and is shown in Figure 4.21. A hammer mill and sluice were set up at the mining site by the financer for mercury-amalgamation to be conducted on site for low grade ores while high grade ores would go to the processing site. There were 5 groups of artisanal miners with 4 members each. They all worked their own shafts which were 10 meters apart with the same arrangement.

From the job shadowing it was noted that even though the arrangement was for equal partnership, most of the power rested with the financer because the operations were heavily reliant on his funds, especially before high profit margins were realized. The financer preferred to process ore as soon as it got to one ton because processing large amounts once off would mean a lot of money in the miners' hands, and they could decide to become independent if they could afford to purchase their own equipment and necessities.

During the visit one of the mining groups struck it big recovering 143.86 grams of sponge gold (Figure 4.37) and moved to change the agreement set beforehand. Once they realized that they would not receive much since they had a huge debt to the financer (operational costs) and their share of the profit had to be split 4 ways between the artisanal miners they became angry and even more head strong to change the arrangement.

Figure 4.37: Sponge gold recovered (authors own)

This resulted in quite a huge argument where threats and insults were hurled by the miners. It was resolved to keep the profit share as previously agreed but the arrangement was restructured the following day with only that group of miners. The miners and the landowner would in future keep all the gold from mercury-amalgamation while the financer keeps the gravity tailings and all proceeds from the cyanidation process. These types of incidents fuel mistrust.

Most of the artisanal miners were from the local community and nearby surrounding areas so they interacted often. There was a general lack of trust and artisanal miners from one pit did not allow other miners from other pits near their ore, be it ROM or when it was being milled. They could not enter shafts which were not theirs. The miners slept guarding their ore and shafts. There was more leeway to the financer, but he was also not allowed to take any ore even for sampling unless mutually agreed that sampling was needed, or the ore was paid for. The landowner and the financer would also sleep at the mining site when ore which showed promise was blasted. This was done because miners were notorious for processing a portion of the ore during the cover of night and keeping the gold recovered to themselves. During the mercury amalgamation process, everyone is represented to avoid accusations of cheating and stealing. The general lack of trust made the word-of-mouth agreements seem hollow.

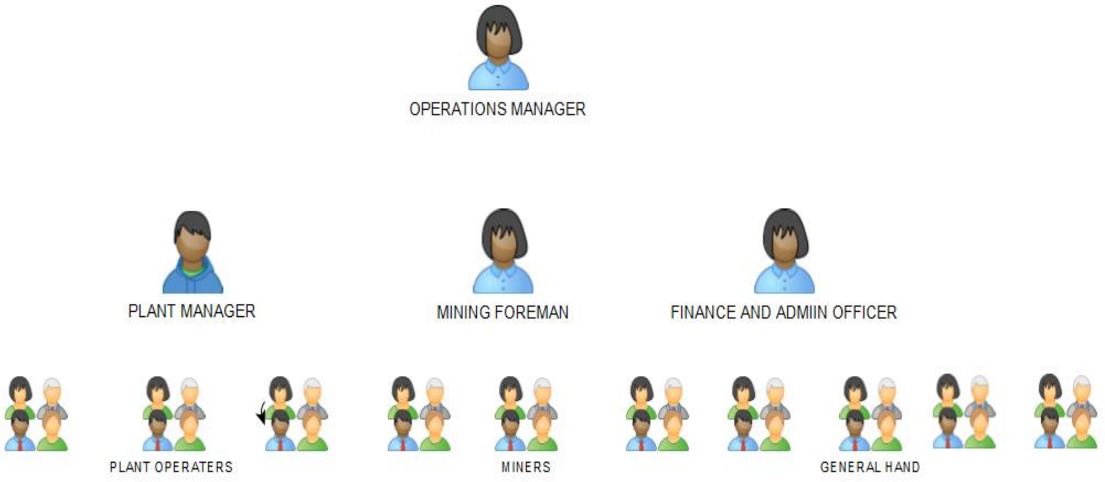

Figure 4.38: Site B organizational structure

Site B had the structure of most businesses as shown in Figure 4.38. The operation was jointly owned by a group of women who had several small-scale mining claims and processing centers across the country. One of the partners was mandated to oversee at least one operation at the different sites. Below that there are employees. There were 2 operations foremen, 1 in charge of the processing plant and the other in charge of the mining operations. The finance and administration officer also sat at their level. Below them were miners, general hands, and plant operators. All the employees got paid a monthly salary which was fixed. The workers came from different parts of the country and were employed because they have experience in these operations. They stayed in a camp at the processing site, and this also served as extra security.

4.2.3 ASGM ECONOMIC STRUCTURE

The economic structure of site B was straight forward. All the gold extracted, and all profits made belonged to the business and employees were paid wages/salaries. Profit shares went to the group of business partners. Site A had a separate profit share for the amalgamation process and the cyanidation process. This is detailed below.

4.2.3.1 MERCURY AMALGAMATION PROFIT SHARE

Gold recovered from gold-mercury amalgamation process was sold and the financer was paid back his expenses which were all documented, leaving the net profit. This is the norm in most ASGM operations as is detailed in a study by Chipangura (2019). From the net profit, the financer got 25%, the miners 37.5%, and the landowner receive 37.5% as shown in Figure 4.39 as per the arrangement.

One gram of sponge gold from this process was sold at $43 at the site to gold buyers. In Bulawayo town, the selling price was $57/g to gold buyers. Once purified to 99.9% the market price was $75/g which could be gotten if sold to Fidelity Gold Refinery (FGR) which is a state-owned gold buyer. That was the price during the time of the field work in November 2021. These prices fluctuate depending on the gold markets. The sponge gold profit from the ore processed at an offsite processing center shown on Figure 4.37 was also shared according to the arrangement described even though initially there was a huge disagreement. For that particular group of miners, the arrangement was re-done. The miners and the landowner would in future keep all the gold from mercury-amalgamation while the financer keeps the gravity tailings and all proceeds from the cyanidation process. This arrangement favors the financer because most of the gold is extracted from the cyanide process. According to the information from the mineralogy which shows that for high degrees of liberation that would favor high recoveries with mercury amalgamation, they needed to grind the ore finer. However, they could not afford such an operation. So, they will share the 30 -33% traditionally achieved from amalgamation while the financer gets the largest profits from cyanidation. This also confirms that artisanal miners are more inclined to processes where they can actually see gold being extracted and recovered like mercury amalgamation as compared to technologies that dissolve gold like cyanide leaching.

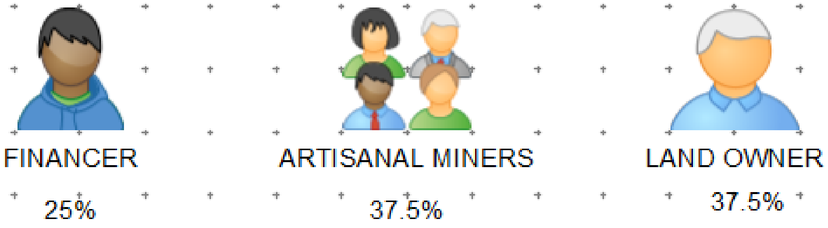

Figure 4.39: Profit sharing from amalgamation

4.2.3.2 VAT LEACHING PROFIT SHARE

Gravity tailings and mercury amalgamation tailings were usually processed at the financers processing plant. The gold recovered from the cyanidation process which was fully funded by the financier was shared after the gold was recovered from elution and electrowinning. 75% of the net profit went to the financer, 12.5% to owners of the land and 12.5% to the miners as shown in Figure 4.40 below. The gold from elution was quite pure and was sold at $75/g to FGR, meaning the profit margins were higher. The elution cost was also included as part of the costs of the financer and got deducted before profit share.

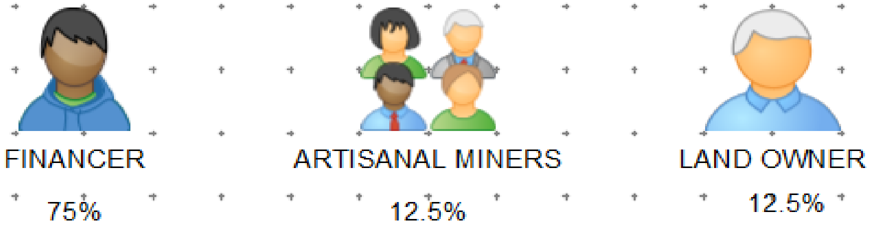

Figure 4.40: Profit sharing from leaching

If an external processing center was used for crushing and amalgamation, that center kept the tailings as payment for services. This was usually the case at most operations where the financer/process center kept all the profit from the leaching process while the miners kept gold recovered from mercury amalgamation (Chipangura, 2019; Hlungwani, Yingi and Chitongo, 2021). So, they usually opted for processing centers when they were sure that their ore is rich in free gold which is easily liberated by milling and recovered by mercury-amalgamation. This was because other more mechanized processing centers used jaw crushers and stamp mills, with a conveyor system to move ore from one stage to the next making the process faster. The financer was usually against this because he realized more profit from the leaching process. In cases where a claim is fully owned by a rich individual who chooses to have artisanal miners, they work the mines/riverbeds and share the profit from the amalgamation process 50/50 and the claim owner still gets to keep the tailings (Chipangura, 2019; Hlungwani, Yingi and Chitongo, 2021). In light of these other arrangements, the profit-sharing arrangement at site A is more favorable to the artisanal miners and the landowner.

The processing operation employed by the ASGM sites uses a combination of a mercury amalgamation and cyanide leaching process to extract gold. The goal of this research is to eliminate mercury usage in this sector. Also, the cyanidation of amalgamation tailings which have residual mercury lead to the formation of mercury-cyanide which is even more toxic than either mercury or cyanide. Therefore, the leach studies conducted will be conducted on run off mine samples which have been milled to the mode size of ASGM ore which is used in extractive processes. This is to test if the same or higher recovery can be achieved without the need to use mercury.

4.3 IGOLI PROCESS

The iGoli process uses hydrochloric acid and sodium hypochlorite to leach gold as detailed in section (3.4). The extractions were very low and reported below the detection limit of the analytical instrument, and thus they cannot be reported with confidence. Iron leached was analyzed because of the significant quantity of iron in the ore and the knowledge that the iGoli lixiviants target iron compounds preferentially to gold (Mahlatsi and Guest, 2003). The results showed a 55% extraction of the total iron in the ore. This is detailed in the appendices, section (7.1). It should be noted that the iGoli process was designed for enriched gravity concentrates as a direct substitute for mercury amalgamation.

4.4 CYANIDE LEACHING BASELINES

Figure 4.41 shows the results of the cyanide baseline experiments conducted at 4 concentrations, 20 g/l, 5 g/l, 3 g/l, and 1 g/l. The experiments were conducted at 400 rpm using sample A.

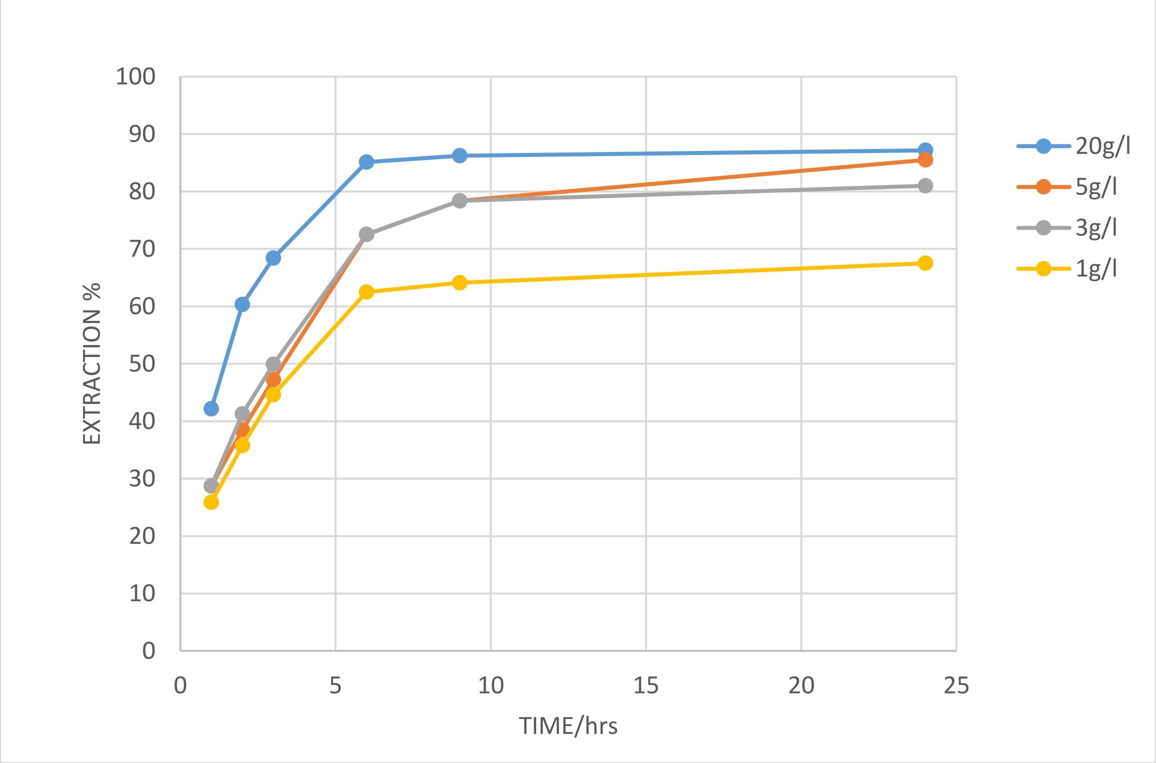

Figure 4.41: Gold extraction at varied cyanide concentrations, at room temperature and agitated at 400 rpm for 24 hours.

The leaching rate was at its highest at a high cyanide concentration of 20 g/l, leaching 42% of the gold in the first hour and the leaching being appreciably complete after 6 hours with 85% of the gold extracted. No significant extraction occurred after the 6-hour mark with only a 2% increment in extraction after 24 hours. 5 g/l and 3 g/l cyanide concentrations had similar extractions of 29% after an hour and 73% at the 6th hour mark. The 1 g/l was at 26% in the first hour and leached up to 64% of the gold after 9 hours and only achieved a 3% increase to 68% at the 24-hour mark. 5 g/l was at 86% and 3 g/l was at 81% after 24 hours. These final extractions are plotted below in Figure 4.42 against cyanide concentration.

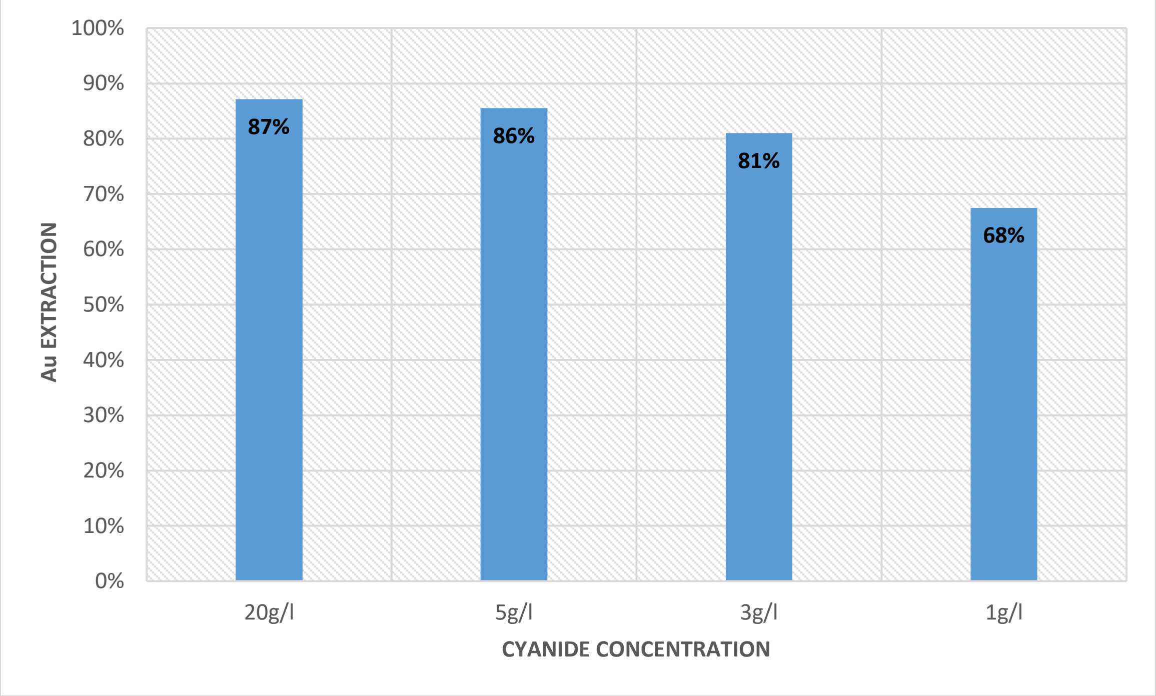

Figure 4.42: Cyanide concentration vs gold extraction after 24 hours

As shown in Figure 4.42, at 1 g/l cyanide concentration, the extraction was low at 68% but when a higher concentration of 3g/l was used, the extraction increased to 81%. Beyond that, a 66% increase in cyanide concentration from 3 g/l to 5 g/l resulted in only a 5% increase in gold extraction. Furthermore, increasing the cyanide concentration to close to seven-fold from 3 g/l to 20 g/l only resulted in a 6% increase in gold dissolution from 81% to 87%. It should also be noted that based on the results from the Cynoprobe (Table 4.4), the cyanide was not completely depleted at 1 g/l cyanide after the 24-hour operation. According to Rees, K.L and van Deventer (2000), the reason being that sulphide minerals in the ore that host the gold are preg-robbing at low cyanide concentrations and will adsorb the gold from the lixiviant, thereby having a low extraction. To prevent this phenomenon, a pre-treatment process with H_2SO_4 to digest the sulphides can be employed or a higher cyanide concentration can be used. The results shown in Figure 4.42 signify that gold extraction can be run optimally at 3g/l cyanide, so increasing cyanide concentration can work without an acid digestion pre-treatment process that might be more costly and complicated for the regular ASGM practitioner. Beyond 3g/l, an increase in cyanide concentration led. to an insignificant increment in gold extraction vs the concentration of lixiviant used. Operating at high cyanide concentrations poses significant risks and hazards given the inadequate SHE practices at ASGM operations in addition to increased costs associated with use of high amounts of reagents.

Table 4.4: Cynoprobe results

CYANIDE CONCENTRATION BEFORE LEACHING OPERATION	AVERAGE CYANIDE CONCENTRATION AFTER LEACHING (CYNOPROBE)	CYANIDE USED FOR LEACHING
1 g/l	0.2 g/l	0.8 g/l
3 g/l	2.3 g/l	0.7 g/l
5 g/l	4.2 g/l	0.8 g/l

4.4.1 LEACHING KINETICS

Kinetic models provide the link between reaction rate and reaction conditions e.g., lixiviant concentration. Of note are the Shrinking Core Model (SCM) and the Shrinking Sphere Model (SSM) which can describe most of the ore leaching reaction kinetics.

The SCM assumes each particle is a sphere and the reaction is considered to take place first on the outer surface of ore particles (Ferrier *et al.*, 2015; Didyk-mucha, Pawlowska and Sadowski, 2016). The reaction then progresses inwards as the reacting particles shrink in the leaching process, leaving behind a shell of porous/permeable inert solid (Ferrier *et al.*, 2015; Didyk-mucha, Pawlowska and Sadowski, 2016). The kinetics of the leaching process involves:

1. the external diffusion of the lixiviant to the solid surface/boundary layer,
2. diffusion into the boundary layer to the solid surface
3. the internal diffusion into the porous layer from the solution to the core surface and vice versa,
4. leaching reaction on the core surface (Rutto and Enweremadu, 2012; Didyk-mucha, Pawlowska and Sadowski, 2016).

The leaching rate is controlled by diffusion of the lixiviant through the porous layer or the leaching reaction at the mineral surface of un-reacted particles (Rutto and Enweremadu, 2012). The relationship between time and conversion achieved from a mass balance analysis are linked by Equation 9:

Equation 9: SCM

$$\frac{t}{\tau} = 1 - 3(1-X)^{\frac{2}{3}} + 2(1-X)$$

Where t is time at any particular point in reaction, X is the conversion at that particular instance and τ is the reciprocal of residence time (Rutto and Enweremadu, 2012).

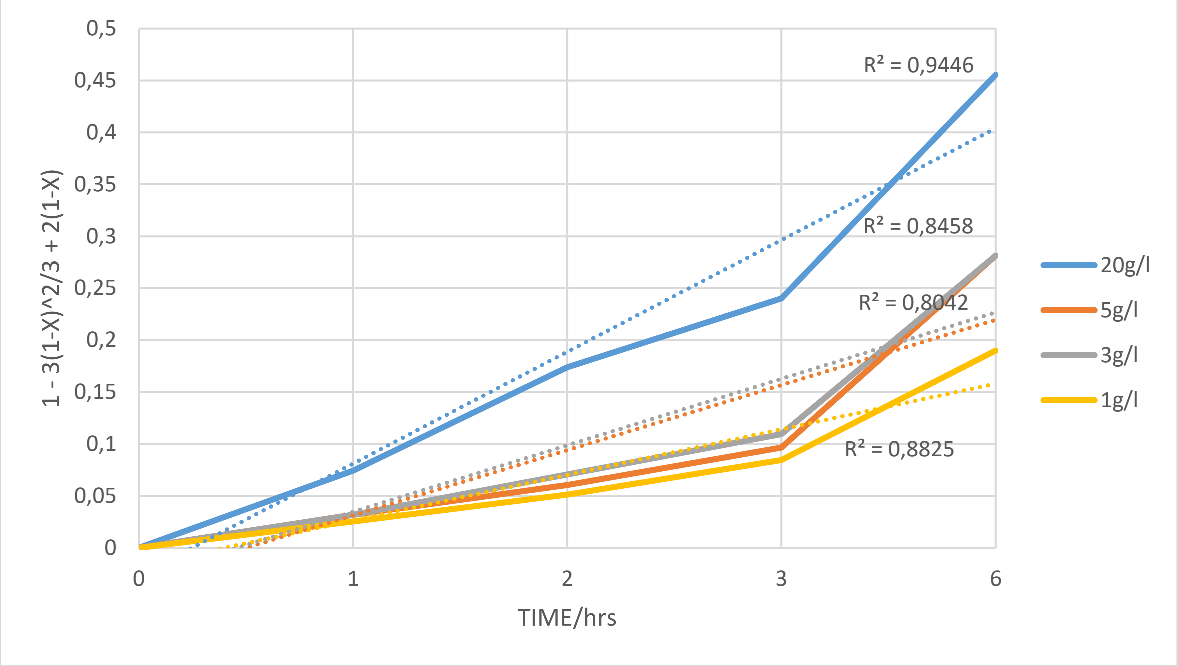

Figure 4.43: Shrinking core model over the first 6 hours.

Figure 4.43 shows the results when the data from cyanide baseline experiments were mapped onto a shrinking core model. The gold leaching kinetics were not a perfect fit for the SCM model.

The SSM like the SCM assumes the particles are spherical and they shrink as the reaction progresses, but unlike SCM, no porous layer forms outside the reacting core (Petersen, 2009). The relationship between conversion and time from a mass balance analysis are given by Equation 10.

Equation 10: SSM

$$\frac{t}{\tau} = 1 - (1 - X)^{1/3}$$

(Petersen, 2009)

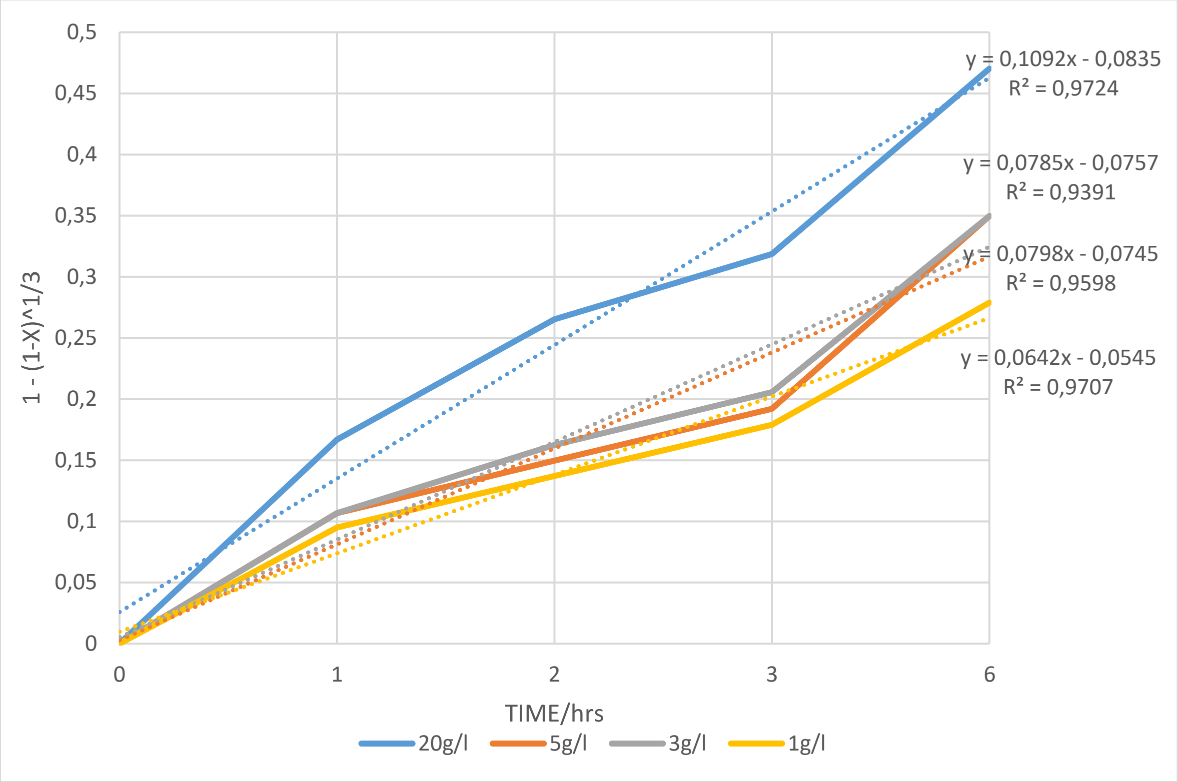

Figure 4.44: Shrinking sphere model over the first 6 hours.

Figure 4.44 shows the results when the data from cyanide baseline experiments were mapped onto a shrinking sphere model. The shrinking sphere model can describe the initial dissolution process of gold using cyanide. This confirms the QEMSCAN imaging (Figure 4.8) and the diagnostic leach results (section 4.1.3) which reflected that after milling to +100 to -300 microns, the bulk of the gold is on the surface of the minerals it is associated with and not locked inside.

The residence time $[\frac{1}{\tau}]$ which is the slope of the equations was plotted against concentration for the cyanide baselines. The results are shown in Figure 4.45 below.

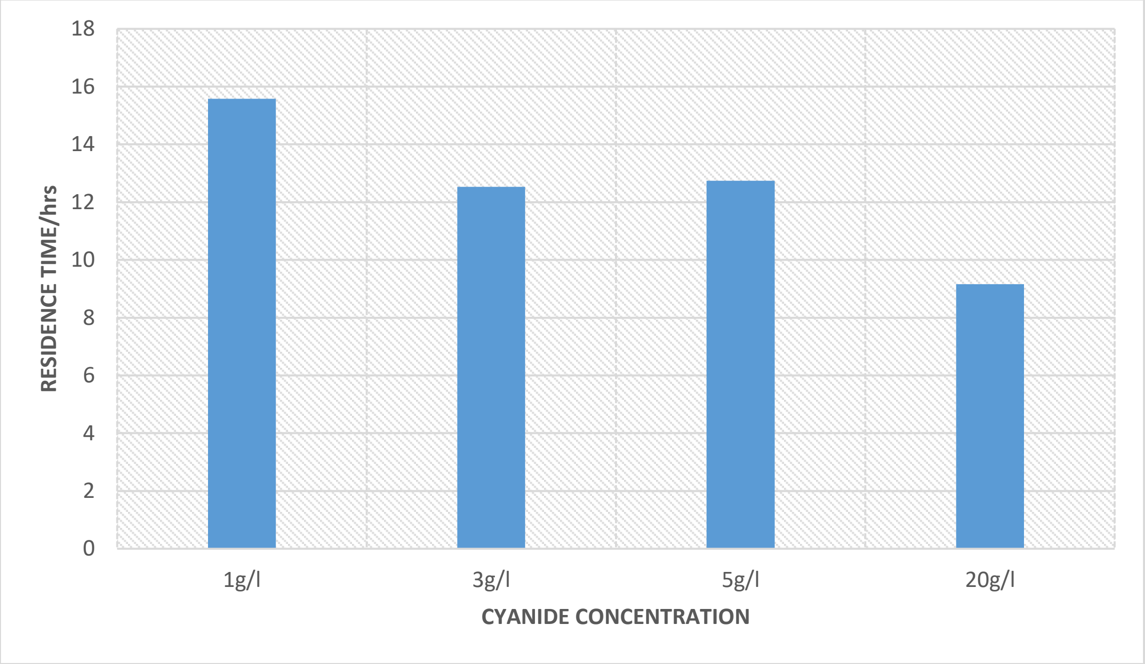

Figure 4.45: Residence time vs concentration at agitation 400 rpm and room temperature

Figure 4.45 shows the effect of cyanide concentration on time taken for the reaction to reach completion when agitating at 400 rpm. As shown, increasing cyanide concentration led to a reduction in residence time. To compare, 20 g/l cyanide requires 9 hours for reaction completion while 1 g/l cyanide requires 15.5 hours.

For comparison with the ASGM process at 5 g/l cyanide (section 4.2.1.3), the residence time was 3 days. From Figure 4.42 we can tell there was only a difference of 1% in extraction when the concentration was increased from 5 g/l to 20 g/l cyanide in the lab operation when all other factors were kept constant. Therefore, the biggest variance between the residence times in the lab operation versus the ASGM field operation was due to the effect of agitation.

4.5 CYANIDE-GLYCINE SYNERGISTIC LIXIVIANT

These experiments were carried out varying the concentration of cyanide and glycine on sample A. Sample B was only used to confirm whether the trend applied with a different gold ore. The effect of agitation was also studied and below are the results.

4.5.1 CYANIDE-GLYCINE AT 400rpm

The tests at 400 rpm were run on sample A. The results in this section are extractions of gold tested while varying the glycine concentrations and holding the cyanide concentration constant at 1 g/l, 3 g/l and 5 g/l in 3 experiments.

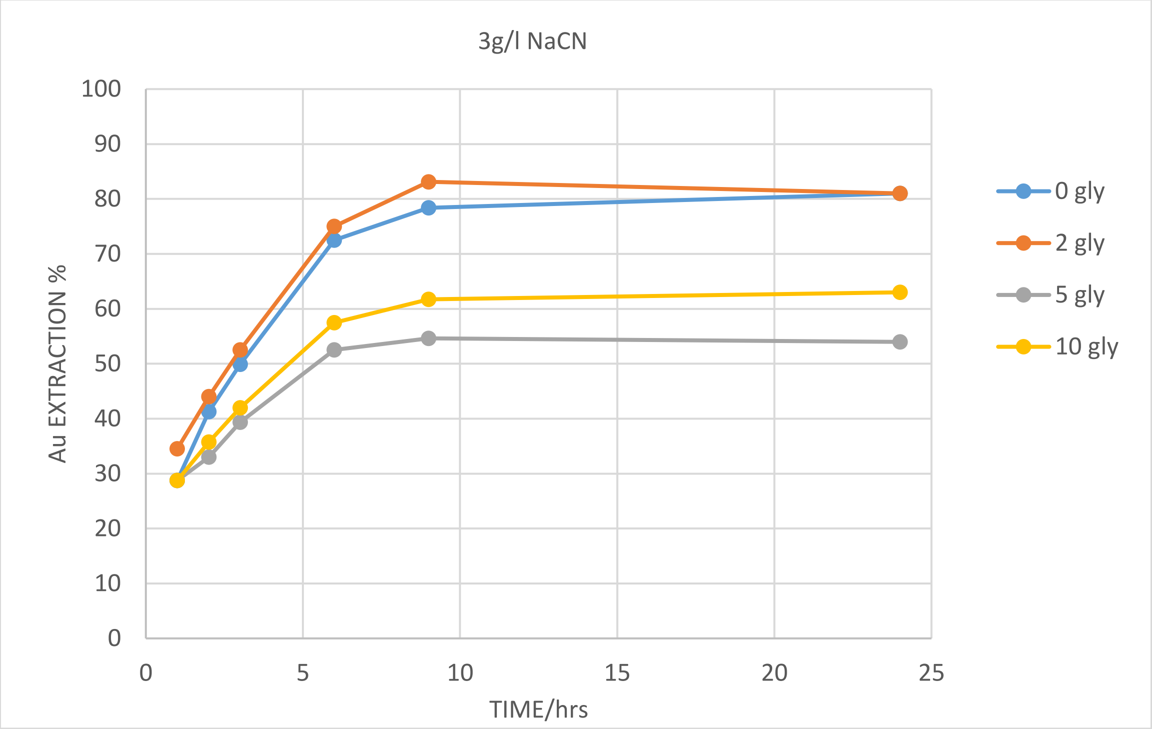

Figure 4.46: Gold extraction with 3 g/l cyanide, varying glycine concentration, agitating at 400 rpm at room temperature for 24 hours.

Figure 4.46 shows results of a leach experiment that ran at 3 g/l $NaCN$, and agitated in a bottle roller at 400rpm. The glycine concentration was varied between 0 and 10 g/l. At 2 g/l cyanide concentration, the leaching reaction proceeded the fastest and reached its highest extraction after 9 hours at 83% gold extraction with the leaching operation looking relatively complete. Proceeding all the way to 24 hours led to a small drop of in extraction to 81% like 0 g/l glycine. Further increasing the concentration of glycine to 5 g/l and 10 g/l resulted in the decline of gold extraction as shown in Figure 4.46. These observations do not agree with what was observed by Oraby, Eksteen and Tanda (2017), who achieved higher gold extractions when glycine concentration was increased. It should be noted that the pH was dropping slightly with the addition of glycine. The pH values noted are shown in Table 4.5 below:

Table 4.5: Glycine Concentration vs pH

GLYCINE CONCENTRATION (g/l)	pH
0	10.5
2	10.2
5	9.9
10	9.7

Glycine is an acid and has COOH on one end of its chain. When dissolved in alkaline aqueous media it readily releases the H^+ ion as shown in Equation 11.

Equation 11: Glycine dissolution

$$NH_2CH_2COOH \xrightarrow{water} NH_2CH_2COO^- + H^+$$

This will cause the pH to drop as evidence in experimental work (Science Lab.com, 2012). The more glycine you add the lower your pH will be. In a cyanide system, it is critical to keep the pH above 9.5 because below that you start forming HCN gas from the NaCN in solution(Cyanide Code, 2021). If pH keeps lowering to 7, 99% of the cyanide will exist as HCN(g) which is toxic and has a high vapour pressure at ambient conditions meaning that it can easily volatilize and become a serious health hazard (Cyanide Code, 2021). Loss of cyanide means a reduction in cyanide concentration which affects gold dissolution as shown on Figure 4.42 and discussed. Therefore, it is imperative to keep an eye on the pH when adding glycine.

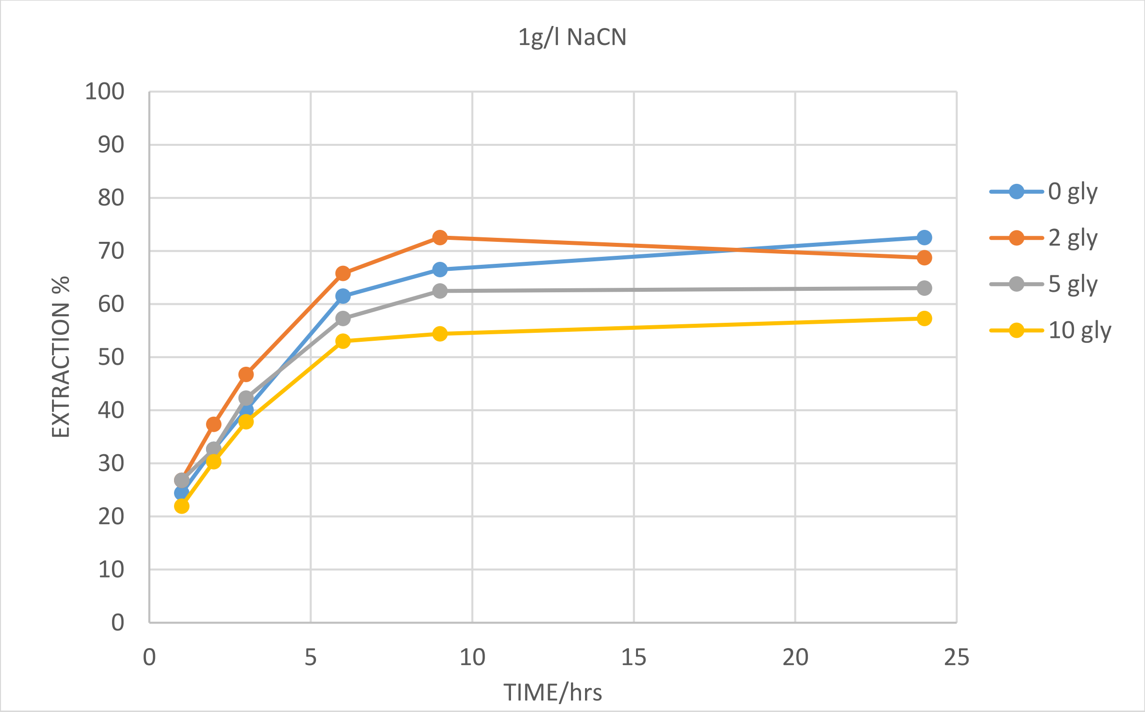

Figure 4.47: Gold extraction with 1 g/l cyanide, varying glycine concentration, agitating at 400 rpm at room temperature for 24 hours.

Figure 4.47 shows results from a gold leaching experiment that ran at 1 g/l $NaCN$, and agitated in a bottle roller at 400rpm. The glycine concentration was varied. The pH of the operation was the same as those shown on Table 4.5. Like the trend seen in Figure 4.46, the extraction went down with increase in glycine concentration, with 2 g/l glycine having fastest leaching rate through the first 9 hours achieving a 72.5% extraction but then fell below 0 g/l glycine after the full 24 hours. After 24 hours, the highest extraction was with no glycine at 73% extraction, 2 g/l glycine is 69%, 5 g/l glycine at 63% and 10 g/l glycine at 57%.

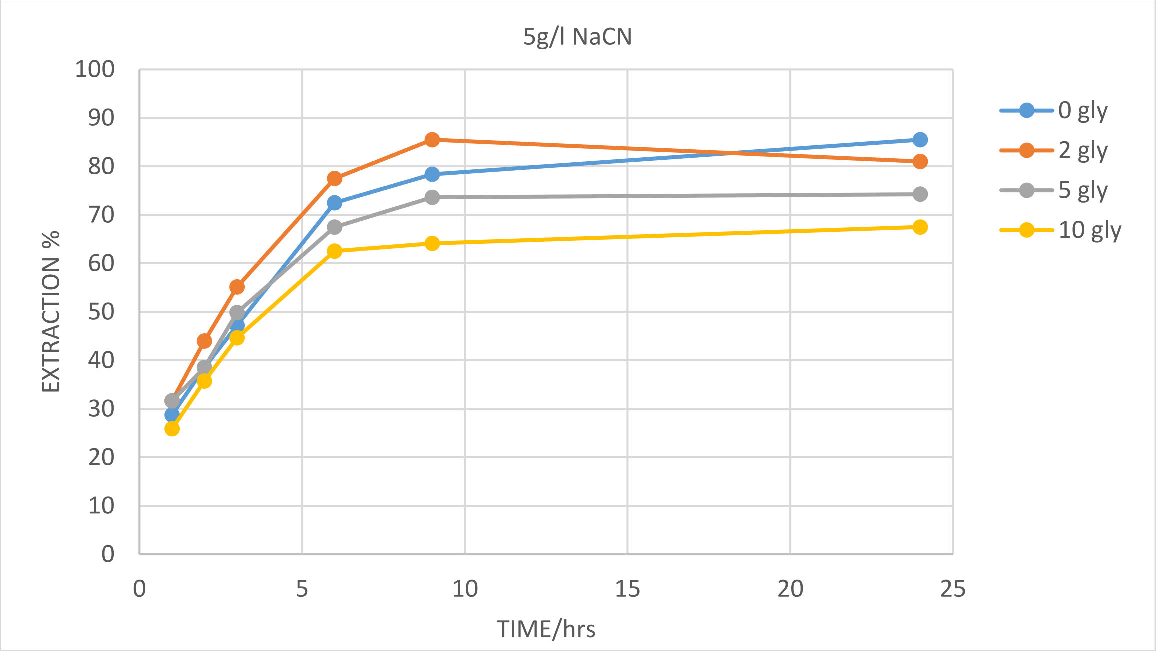

Figure 4.48: Gold extraction with 5g/l cyanide, varying glycine concentration, agitating at 400 rpm at room temperature for 24 hours.

The experiment was repeated at 5 g/l NaCN as shown in Figure 4.48. Just like the experiments ran at 1 g/l $NaCN$ (Figure 4.47) and 3 g/l $NaCN$ (Figure 4.46), the gold extraction dropped with an increase in glycine concentration with the exception of 2 g/l glycine which performed the best in the first 9 hours but dropped off after. In the first hour of the experiment, the lixiviant with lower glycine concentration (2 and 5 g/l glycine) had a 6% higher extraction than the 10 g/l glycine. As the experiment proceeds, there is a distinct demarcation between the 3 glycine concentrations. At the 3-hour mark all 3 glycine operations showed linear extractions of about 10% gold extraction per hour. The 2 g/l glycine line was 5% higher than the 5 g/l which was 5% higher than the 10 g/l. After 24 hours, the experiment with no glycine achieved 86% extraction, 2 g/l glycine 81%, 5 g/l glycine 74%, and 10 g/l glycine 68%. A marked drop off in gold dissolution with increase in glycine concentration over the 24-hour leaching period was noted.

It should be stated that it was observed over all the 3 experiments that 2 g/l glycine had the higher initial extraction rates and higher extractions after 9 hours in the 3 experiments at 400 rpm. This trend is summarized in Figure 4.49 overleaf.

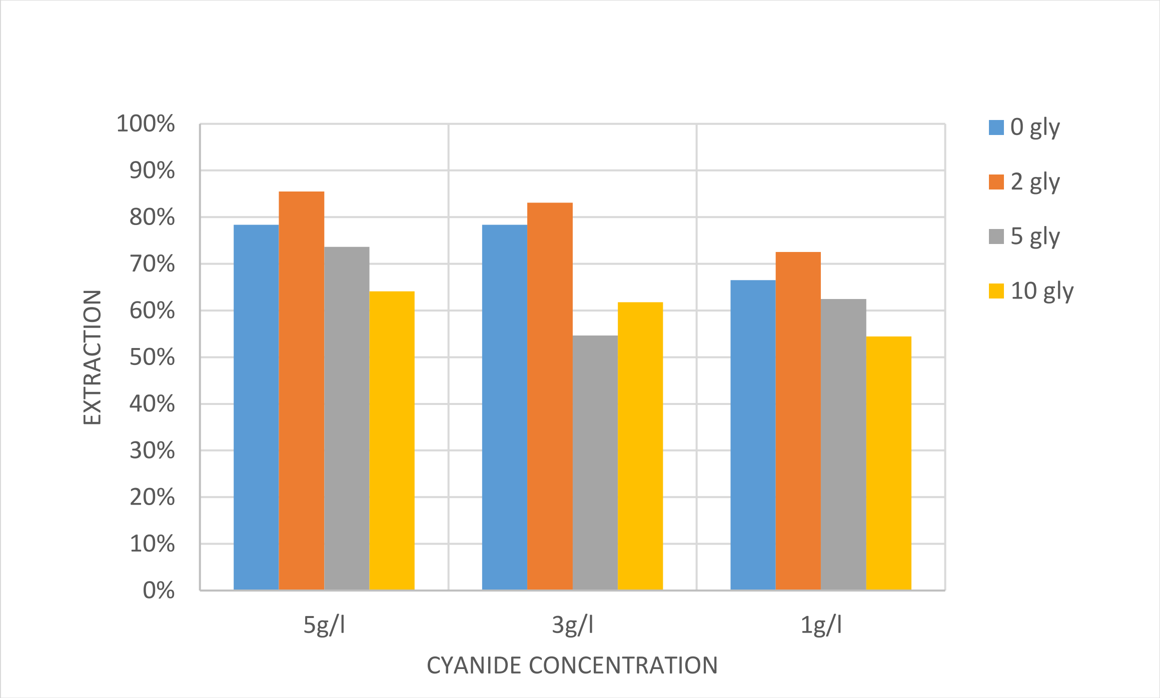

Figure 4.49: Effect of glycine concentration vs extraction over the first 9 hours

The extraction at 2 g/l glycine was the highest after 9 hours across all 3 experiments at 400 rpm and seems relatively complete. Running the experiment further resulted in a reduction in extraction which may be due to the preg-robbing nature of the ore since it contains sulphides. Increasing the concentration of glycine beyond 2 g/l did not lead to an increase in extraction.

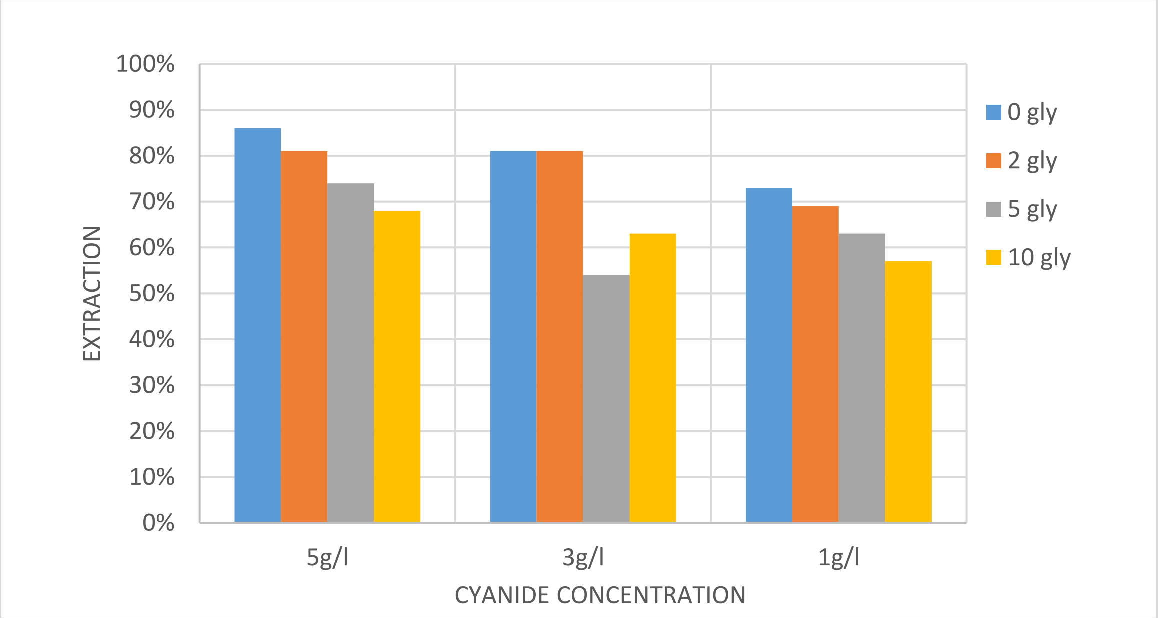

Figure 4.50: Effect of glycine concentration vs extraction after 24 hours

Figure 4.50 summarizes the final extractions achieved after 24 hours for all the experiments ran at 400 rpm as a function of cyanide and glycine concentration. As already discussed, the trend is that of a decline in gold dissolution when glycine concentration is increased in a 24-hour operation with 2 g/l glycine working best over a 9-hour period.

The kinetics of this process are like the ones for the cyanide baselines (section 4.4.1). The same ore and similar conditions are used with a narrow size distribution. This means the shrinking sphere model can describe the leaching kinetics. Increasing glycine concentration would also lead to longer residence times since the trends of a drop off in extraction on addition of glycine are similar to those of a drop off in gold extraction when cyanide concentration is reduced as calculated and discussed in section (4.4.1).

4.5.2 CYANIDE-GLYCINE AT 150rpm

To test the effect of agitation, the speed was lowered from 400 rpm to 150 rpm. The experiments were all conducted at 3 g/l cyanide because it was found to be optimal. The glycine concentration was varied. Sample A and sample B were both used to confirm if a similar trend would apply when different ores are used. Figure 4.51 and Figure 4.52 are graphical representations of these results.

Also, the concentration of bicarbonate was doubled in these experiments to counteract the acidity of glycine and raise the pH. Table 4.6 below shows the pH values variance with increase in glycine concentration.

Table 4.6: Glycine concentration vs pH

GLYCINE CONCENTRATION (g/l)	pH
0	10.8
2	10.5
5	10.3
10	9.9

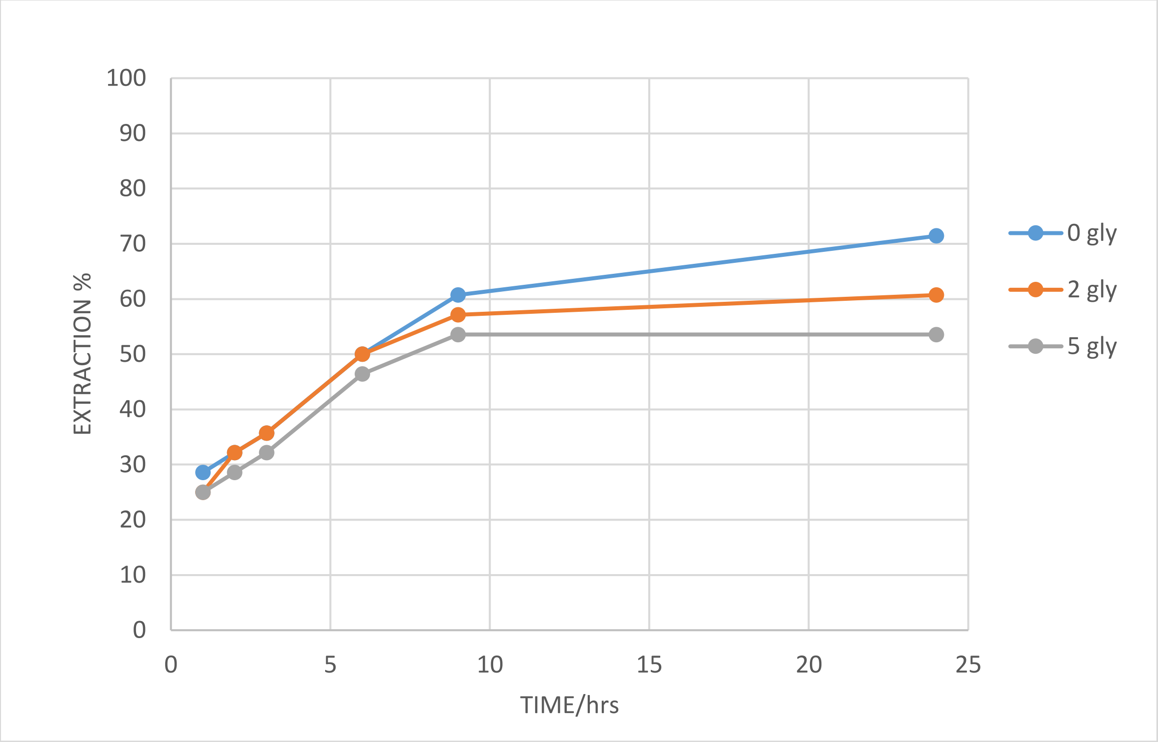

Figure 4.51: Gold extraction at 3 g/l cyanide, varying glycine concentration (sample A), agitating at 150 rpm at room temperature for 24 hours.

A similar trend to section (4.5.1) of a drop off in extraction on increase in glycine concentration was observed as shown in Figure 4.51. The lixiviant with cyanide only performed the best with 71% extraction, followed by 2 g/l glycine at 61%, while the lowest extraction was at the highest glycine concentration of 5 g/l at 54%. It should be noted that the lower speed led to a slower and lower extraction rate across all concentrations of lixiviants. Reducing the speed of agitation leads to a longer residence time to achieve the same extraction.

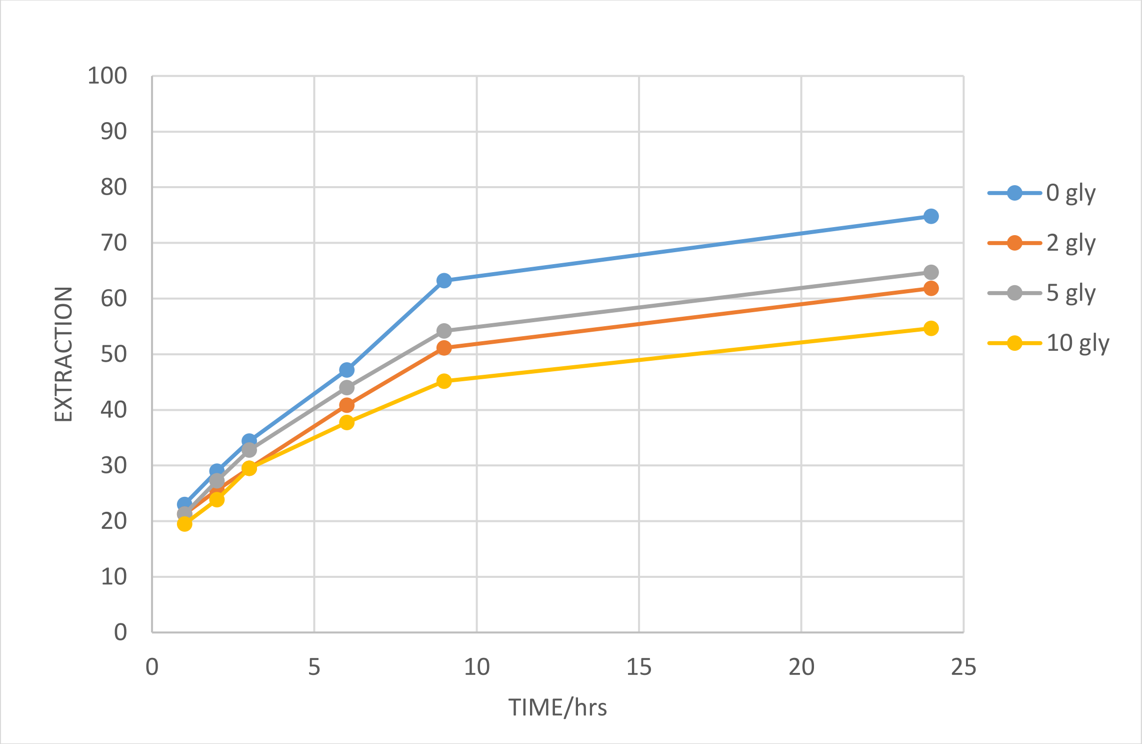

Figure 4.52: Gold extraction at 3 g/l cyanide, varying glycine concentration (sample B), agitating at 150 rpm at room temperature for 24 hours.

The results of the experiment repeated with sample B are shown in Figure 4.52. The results are like those shown Figure 4.51. On 2 different samples, the results are similar with a reduction in extraction efficiency when glycine concentration is increased in the leaching lixiviant at 150 rpm.

The top size of gold grains was 25 μm for sample A and 45μm for sample B. For cyanidation and lixiviants that dissolve gold, large gold grains mean more time required to achieve complete dissolution. In a standard leaching operation, incomplete leaching of liberated large gold grains will report as ore refractoriness (Marsden and House, 2009). They would require more time to completely dissolve. When comparing Figure 4.51 and Figure 4.52 it can be seen that sample A leaching was almost complete since the extraction lines were plateauing between the 9th and 24th hour while the extraction for sample B was still incomplete and all the extraction lines were trending upwards in the same period. This could be the effect of gold grain size since sample B has larger gold grains than sample A which require more residence time.

4.5.3 CYANIDE-GLYCINE AT 0rpm

After running cyanide-glycine at a high agitation of 400 rpm and at a medium agitation speed of 150 rpm, the last experimental runs were conducted at zero agitation with sample A, since sample B had been confirmed to produce similar results.

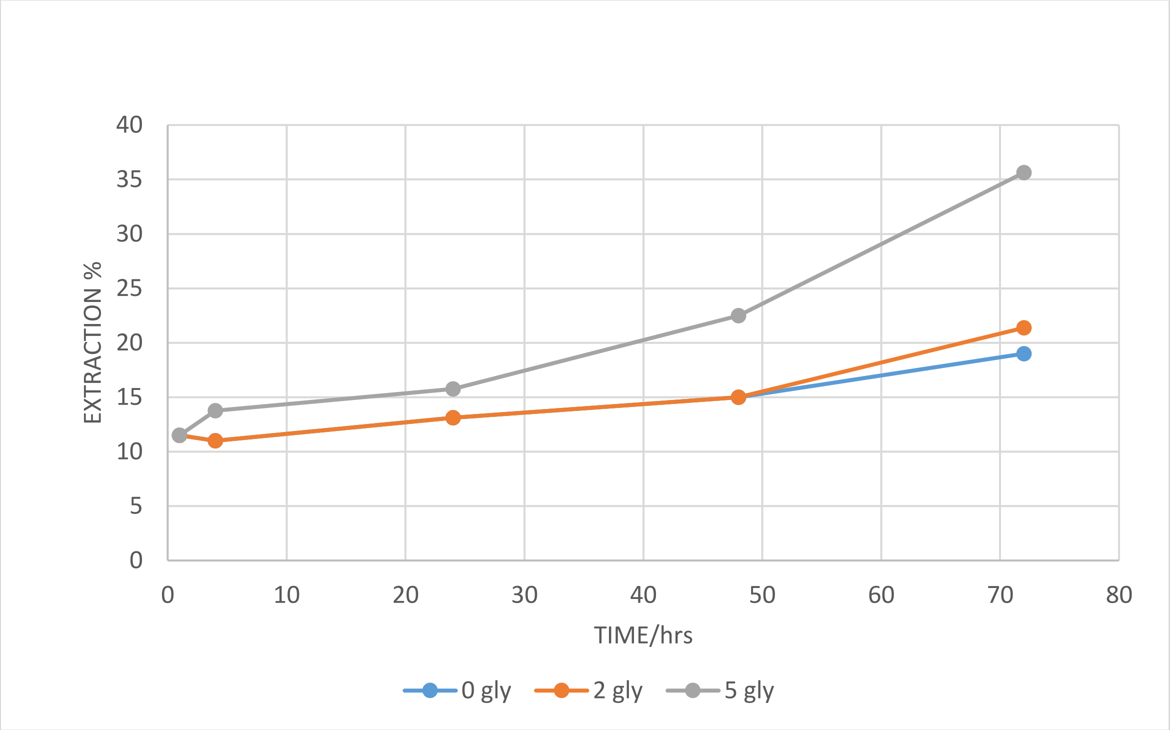

Figure 4.53: Gold extraction with 3g/l cyanide, varying glycine concentration, not agitated at room temperature for 72 hours.

Figure 4.53 shows results of a leach experiment ran at 3g/l $NaCN$, and zero agitation. The glycine concentration was varied. Unlike the agitated experiments, it was noted that increasing glycine concentration improved the leaching. This is the opposite of what was observed when the slurry was agitated. It should be noted that the pH was still following a similar trend on addition of glycine as in Table 4.6. At a concentration of 5 g/l glycine, the extraction was at 13.8% in the first four hours while 0 and 2 g/l glycine were both at 11%. After 72 hours the margin widened with 5g/l glycine dissolving 36% of the gold, 2 g/l glycine 21%, and 0 glycine 19%. The experiment was run for only 3 days because that is the residence time used in ASGM for the vat each operation.

In non-agitated systems, increasing glycine concentration led to an increase in gold extraction. This aligns with the results observed in a study by Eksteen and Oraby (2015), who achieved higher gold dissolutions by increasing amino acid concentration in heap or in-situ leaching. The difference in results between agitated and non-agitated systems may be due to that amino acid surfactants exhibit thickening behavior when the pH is lowered (Vu *et al.*, 2020). The thickening can impede dissolution of air into the lixiviant which in turn lowers the extraction since the dissolution of gold in cyanide and glycine is oxygen dependent as shown in Equation 7: Cyanide leaching and Equation 6: Amino acid leaching. However, this thickening behavior was noted at pH's lower than 7 for amino acids tested by Vu *et al* (2020), when they were studying the thickening mechanisms for an amino acid-derived surfactant compositions. The operating pH's in the cyanide-glycine tests were never below 9.5. Therefore, drop in pH could not be a factor but thickening may be due to a shear thickening property which is exhibited by some organic compounds. When not agitated, the extractions were improved by glycine addition which might be due to the glycine not thickening, allowing for atmospheric oxygen dissolution. Adding H_2O_2 to the slurry as a source of oxygen might improve the extraction when glycine concentration is increased in agitated systems. The reaction is shown below in equation 12.

Equation 12: Hydrogen peroxide reaction

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

4.6 FURTHER DISCUSSIONS

4.6.1 ORE ASSEMBLAGES AND THEIR EFFECT ON EXTRACTION

The diagnostic leaching test work on sample A revealed that 84% of the gold was amenable to direct cyanidation while 16% was encapsulated in the host minerals and required a digestion step to free up (Figure 4.12). From the QEMSCAN images (Figure 4.8) of sample A most of the gold particles are on the surface of the milled ore and not encapsulated in the minerals it is associated with. This is further confirmed by the kinetic study conducted (section 4.4.1) that shows that the dissolution of gold is described by a shrinking sphere model. This is because the bulk of the gold is on the surface with 16% encapsulated. If the bulk of the gold particles were encapsulated in the minerals, the kinetics would be described by a shrinking core model.

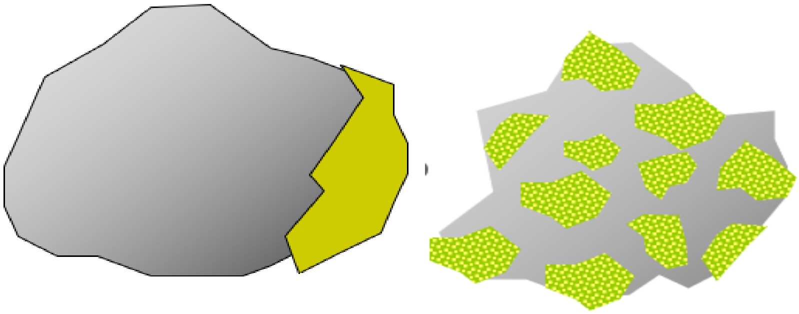

Figure 4.54: a) Gold particle on the surface of gangue mineral b) Majority of gold particles encapsulated in gangue mineral (adapted from (Petersen, 2009)*)*

Figure 4.54 shows the type of mineral assemblaes being described, a) will be described by SSM while b) is SCM. Sample A is similar to a). In the case of ASGM operations which have a 2 stage extraction operation, mercury amalgamation and vat leaching, it is better to process this type of ore. Mercury needs to be in contact with the gold to form a mercury-gold amalgam. Gold which is encapsulated in minerals would need to be milled finer to achieve a similar recovery which is not ideal for ASGM practitioners as previously discussed. For vat leaching, the dissolution of gold using cyanide is a slow process which is rendered even slower when agitation is not employed. For gold particles which are exposed, the cyanide lixiviant easily contacts the gold and starts leaching. For encapsulated gold particles assuming the gangue material its associated with is porous, the lixiviant needs to diffuse from the outer surface of the mineral to the gold surface and react. The lixiviant then has to diffuse back to the surface and to the bulk lixiviant. Considering that sample A with the bulk of gold particles on the surface requires a 3 day residence time, ore with encapsulated particles would require more. If encapsulated in an inert non porous solid, neither amalgamation nor cyanide leaching can extract the gold unless its ground finer to expose it.

4.6.2 OBSERVATIONS OF SOCIO-ECONOMIC RELATIONS IN ASGM

There are close ties between artisanal miners, small scale mines and process centers which dictate how the ore is processed. These ties are based on finances, food, mining supplements, and processing benefits afforded to the artisanal miners by small-scale and processing centers for rights to process their ore for a share of profit or for right to their amalgamation tailings.

From observations during shadowing, this system works if the artisanal miners are making enough to survive but not too much to be able to finance their own mining, milling and mercury-amalgamation operations. The profit-sharing agreements seem to be more beneficial to the financer as he gets the largest share of the profit from the cyanidation process which extracts the bulk of gold from the ore as discussed in section (4.2.3.2). It is also imperative to note that the financer shoulders all the costs even before any revenue is realised. The artisanal miners and the land owners do not possess the necessary funds to bank roll the mining or the processing operational costs. Most landowners are poor farmers who discovered they have gold bearing rock on their land but do not have the requisite skills or finances to operate independently. Studies by Moyo (2023) brought to light that the current livelihood discourses in Zimbabwe, indicate that communities who depend on agriculture as their main source of livelihood usually adopt artisanal and small-scale mining as a key alternative source of livelihood. In Zimbabwe, by law, you cannot convert agricultural land or any land into a mining site without registering it first and paying for licenses and rights (Chipangura, 2019)(Hlungwani, Yingi and Chitongo, 2021). These processes are expensive and daunting, as noted by Chipangura (2019), who carried out an ethnographic case study through interviewing stakeholders in ASGM, in Penhalonga, Eastern Zimbabwe. This also disqualifies them from any loans from banks coupled with the fact that most people in rural areas do not have title deeds for their land to loan against. Owing to these barriers, illegal gold mining has proliferated among the groups that cannot meet the legal requirements (Hlungwani, Yingi and Chitongo, 2021). That is why they lean into agreements with artisanal miners and third parties who can finance the operation. The financer has limited funds, so he only funds the operation and does not pay the miners salaries. Also, because of poor knowledge and skills, the risks of a loss are high as there is reliance of visual inspections rather than scientific data from sampling and analysis. This is evidenced when they only managed to recover a gram of sponge gold after processing 700kg of ore (section 4.2.1.2.2). So, he relies on the profit-sharing arrangements which are beneficial to him since any gold recovered pays for his operational expenses first and no artisanal miners or the landowners are paid from gold recovered until a net profit is realised. This means the miners are working for food unless they reach depths with profitable ores.

The relationships are ridden with mistrust and all the parties will always seek to get an upper hand when the conditions are more favourable to them. This was evident as discussed in section (4.2.2), when the miners had made what they believed was a huge haul and they forcefully moved to change the agreement to one that would see them get a larger share. The only thing that binds these relationships and agreements made together are that all parties are co-dependant and need each other. This mistrust seems to be a recurring theme in ASGM as a claim owner in a study conducted by Chipangura (2019), claimed that artisanal miners are dishonest and they steal ore.

The positive side is that because the group is small, the decision making is fast, and disputes are urgently dealt with because they communicate directly with each other without any bureaucratic or organisational barriers. Disagreements may get very heated but cooler heads usually prevail. There was an openness to technologies that would result in higher extractions and more profits without requiring a lot of capital.

4.6.3 EFFECT OF AGITATION

From Figure 4.55 and Figure 4.56, its clear that there is a linear relationship between extraction rate and agitation.

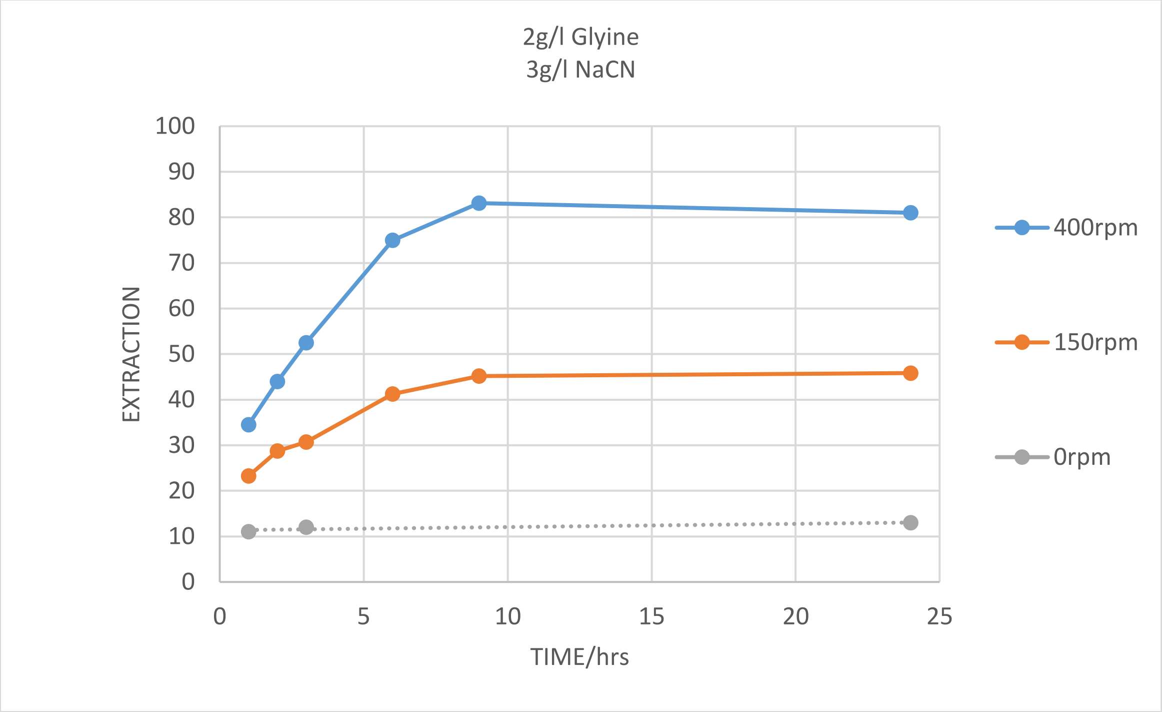

Figure 4.55: Effect of agitation at 2 g/l glycine, 3 g/l cyanide, varied agitation at room temperature for 24 hours.

The extractions are faster at 400 rpm with 83% of gold leached after 9 hours, while at 150rpm extraction is at 45%. In a non-agitated reactor, the extraction is 12.5% after 9 hours and 13% after 24 and its still rising. Increasing the agitation favors a high extraction rate.

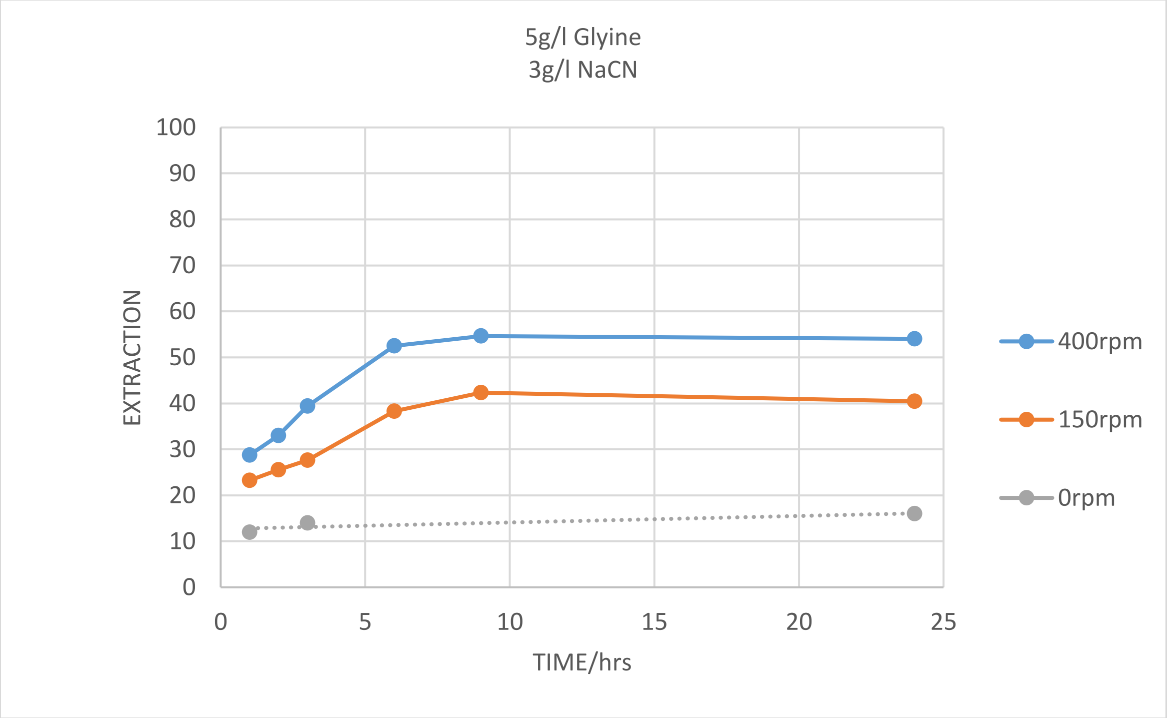

Figure 4.56: Effect of agitation at 5 g/l glycine, 3 g/l cyanide, varied agitation at room temperature for 24 hours.

Figure 4.56 shows results like Figure 4.55. High extraction rates are achieved at higher agitation with more favorable leaching kinetics. This is due to the higher ore and lixiviant contacting. Not agitating gives extractions which are not significant.

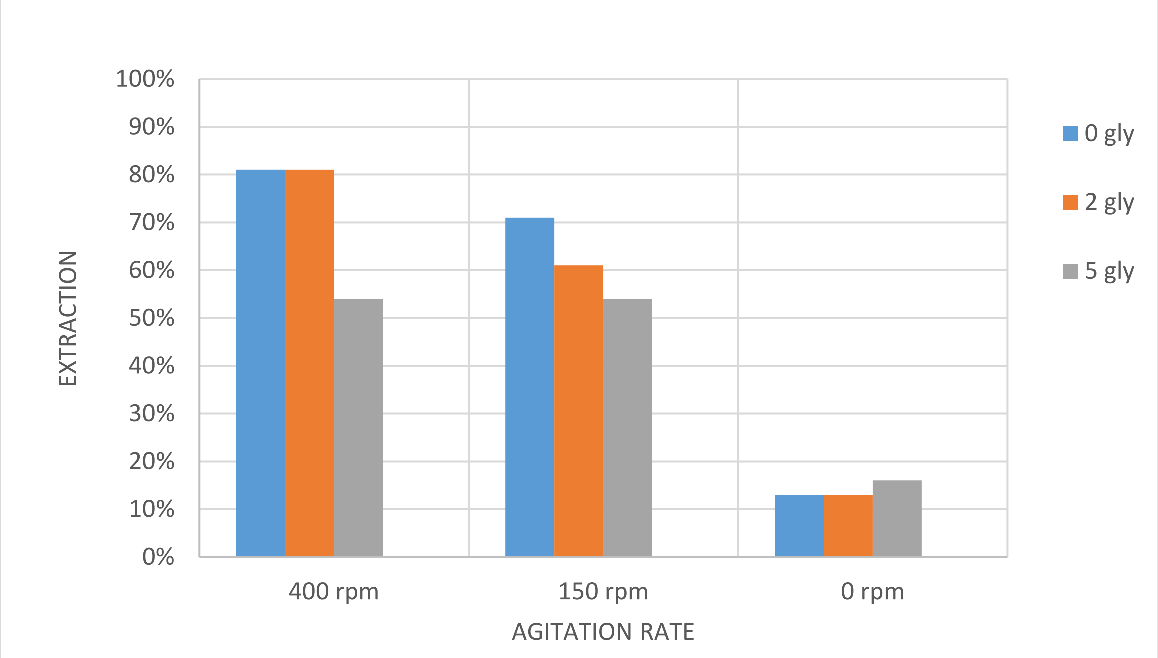

Figure 4.57: Effect of agitation

Figure 4.57 summarizes the effect of agitation on the leaching experiments conducted. Agitation is critical parameter to get meaningful extraction rates. From Figure 4.57 it is clear to see that reducing the agitation rate leads to a reduction in the extraction kinetics and ultimately lower extractions in the allotted 24-hour period.

4.6.4 ASGM OPERATION VS LABORATORY OPERATION

In the field an extraction of 81% was achieved operating at 5 g/l $NaCN$ concentration for 3 days using the same ore as sample A (Section 4.2.1.3). To design a process going forward in the lab that can mimic the field operations, 2 methods were explored. A bottle roller operation at 4 cyanide concentrations (section 4.4) and a non-agitated BSTR. The 24-hour bottle roller operation at 400 rpm at 3 g/l $NaCN$ yielded an 81% gold extraction similar to what was achieved in the field, but this extraction was achieved in 24 hours. The non-agitated BSTR at 3 g/l cyanide achieved a 19% extraction after 3 days which is very low compared to the ASGM process. None of the processes were a perfect match because the system used combines two gravity concentration steps and mercury amalgamation with a cyanide leaching step which is in between an agitated process and a non-agitated one because they cycle the lixiviant and strip it of gold using carbon columns as described in section 4.2.1.2.

From the lab tests, similar gold extractions can be achieved with cyanide alone without the need for mercury amalgamation.

4.6.5 NEW TECHNOLOGIES TRANSLATED TO ASGM PRACTICE

From the technologies tested, cyanide leaching is the best performing process in agitated systems which enhance extraction and reduce the residence time of the operation significantly. Cyanide-glycine had a distinct improvement over cyanide only in a non-agitated system, but it was still low. 3 g/l cyanide and 5 g/l glycine almost doubled the extraction achieved by 3 g/l cyanide alone in a 72-hour operation as shown in Figure 4.58. The leaching operation employed by ASGM practitioners and process centers does not agitate the slurry. The lixiviant is fed at the top of a vat tank until all the ore is submerged in the lixiviant. The lixiviant is allowed to slowly seep through the ore by gravity, contacting, and thereby dissolving gold from the ore. This makes looking at the cyanide-glycine process attractive here. Amino acids have been shown to enhance extraction in heap leaching by Eksteen and Oraby (2015), who studied the leaching and adsorption of gold using low concentration amino acids and hydrogen peroxide, and found that gold dissolution increases by increasing amino acid concentration and pH.

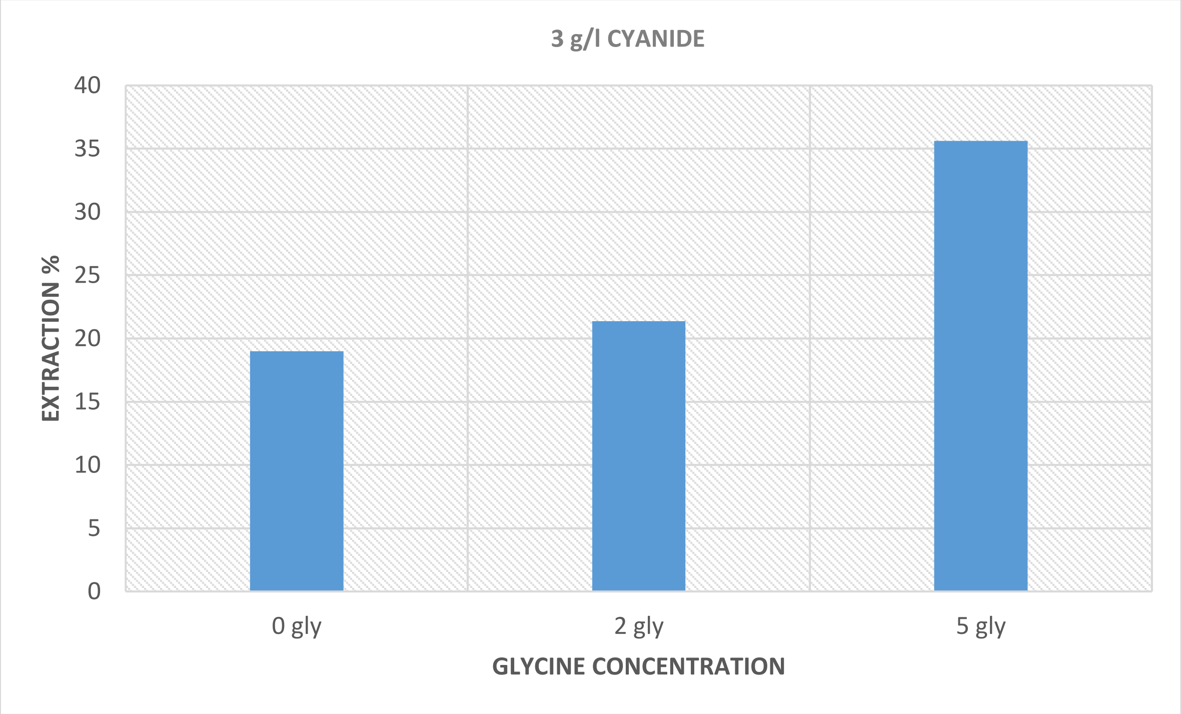

Figure 4.58: Gold extraction at zero agitation

Increasing the pH to 12 coupled with the circulation of the lixiviant is expected to increase the extractions achieved by cyanide-glycine in the non-agitated test works. Consequently, the residence time of 3 days used by the miners can possibly be reduced to 36 hours because of the higher leaching rate of cyanide-glycine when not agitated.

Using a suction pump under the vat tanks can allow the miners to mill their ore a bit finer without having to worry about it hindering the flow of the lixiviant. A pump from the holding tanks can be linked to a perforated pipe which will be laid across the top of the vat tank so that the lixiviant can be sprayed evenly across the whole surface are of the ore. The pumps and the spraying can greatly enhance extraction.

The iGoli process which was the other technology tested yielded poor results. Apart from the poor results, the lixiviants used in the iGoli process produce toxic acid fumes. It therefore becomes unfavorable for ASGM where open vat tanks are used. Moving to closed reactors and fume extraction systems would be too costly for the capital-deprived miners.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The main thrust of this study was to test the efficacy of two alternative technologies, the cyanide-glycine and the iGoli process, to mercury amalgamation in the ASGM context.

The mineralogical analysis coupled with the diagnostic leach gave an insightful understanding of the ore. Just over 80% of the gold can be leached by direct cyanidation/cyanide-glycine without the use of mercury.

The iGoli process does not work for ASGM in whole ore amalgamation and might at best be considered to substitute mercury amalgamation. However, the quantities of concentrate produced per batch are not substantial enough to warranty investment into setting up the iGoli process. Also, the trust deficit among miners may not favor employing a technique that dissolves all the gold before any intermediate yields (like the sponge gold in the mercury amalgamation process) are obtained.

The cyanide-glycine method has shown two note-worthy trends. The dissolution of gold trends downwards with an increase in glycine concentration in agitated systems. On the other hand, the dissolution of gold significantly increases as the glycine concentration is increased in a non-agitated system. This bodes well for ASGM extraction operation which allows the lixiviant to seep through the ore then goes for adsorption and flow back to the leaching tank instead of agitating the lixiviant and the ore. In a non-agitated system at a fixed cyanide concentration, increasing glycine concentration from 0 to 5g/l almost doubled extraction. The advantage is that for the same extraction, you can reduce the quantity of cyanide used and eliminate the use of mercury since the ore can dissolve the liberated gold as well.

The case study revealed that there is mistrust between the stakeholders in ASGM. There is a general awareness among most of artisanal miners that there is more gold in the ore than is recovered via amalgamation as evidenced by most artisanal miners preferring to have a share in both amalgamation and cyanide leaching. Therefore, with some information dissemination, demonstration of successful extractions, there is a chance of receptiveness to new and more gainful processing approaches. However, there is a need to build trust. The cyanide-glycine technology needs to be investigated further against higher cyanide concentrations at a high pH. If these tests are successful, it means that it will be safer for the environment, miners, and surrounding communities as the same extraction can be achieved at lower cyanide concentrations. No extra capital will be required as it can be implemented with the current equipment they have. However, the profit shares don't favor the miners in the leaching process at 12.5%, whereas mercury amalgamation works in their favor since they are offered higher profit percentages (37.5%) there. To promote a leach-based solution to the mercury problem would therefore require a revision of the profit shares of the new system. If this can be negotiated as a long-term solution, then miners can become more involved, educated, and ultimately make more money which can sustain them and their families and thus make ASGM a more sustainable industry.

5.2 RECOMMENDATIONS

- Conduct lab tests at lower glycine concentrations such as 0.5 g/l, 1 g/l, 1.5 g/l and see if the trend is similar or that there is an optimum concentration of glycine which when exceeded leads to a reduction in extraction.
- Conduct cyanide-glycine tests at pH values higher than 12.
- Conduct field experiments at ASGM sites using the findings of this study. This will give a measure of the applicability of the gold extraction technologies investigated and the challenges and opportunities that may exist in uptake.

- Conduct further experiments using the iGoli on gravity concentrates and compare it to results from this study.
- Investigate other alternative technologies that can easily fit, given the knowledge of ASGM operations.

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7 APPENDICES

7.1 IGOLI PROCESS

The iGoli process was designed by Mintek for small-scale miners. It uses a combination of hydrochloric acid and sodium hypochlorite to leach enriched gold gravity concentrates. The technology was tested on sample A.

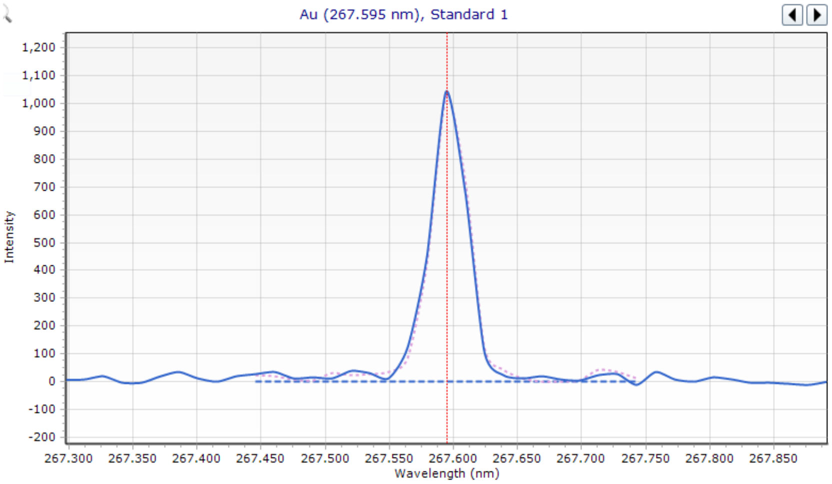


Figure 7.1: Emission signal for the 0.1 ppm Au calibration standard

Figure 7.1 shows the emission signal for the 0.1 ppm Au calibration standard on MP-AES. A well-defined peak (analyte signal) can be distinguished from the baseline.

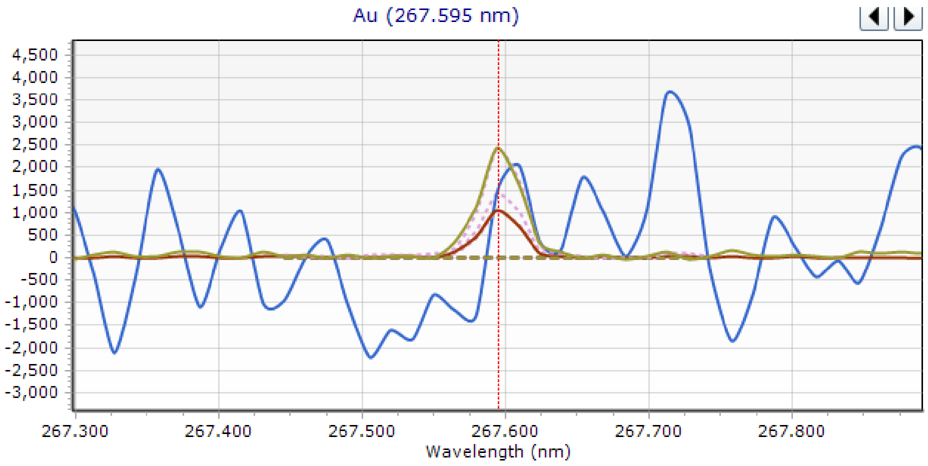


Figure 7.2: Overlay of the 0.1 ppm standard (red), 0.2 ppm check (green) and the sample (blue)

Figure 7.2 shows an overlay of the 0.1 ppm standard (red), 0.2 ppm check (green) and the sample (blue). There is no distinct Au signal from the sample (other samples similar). A similar background signal was observed on the ICP-OES. Gold could be present at lower concentration levels than what we can detect on the MP-AES/ICP-OES or there may be no gold dissolved in these samples.

The iGoli process lixiviants did not dissolve gold when the experiment ran on whole. The iGoli process was designed to treat a panned concentrate to replace mercury amalgamation but was never intended for whole ore leaching. On the other hand, it did leach iron from the pyrite mineral which was in the ore. The results on leaching copper and iron compared to diagnostic leaching and cyanide-glycine are shown in Table 7.1.

Table 7.1: Fe and Cu leach results

Leach Technology	**Iron (Fe)**	**Copper (Cu)**
iGoli	55%	47%
iGoli (50% increase in lixiviants)	60%	79%
Diagnostic Leach	75%	93%
Cyanide-Glycine	13%	70%

It is known that HCl destroys pyrite minerals (Celep, Alp and Deveci, 2008), in conjunction with hypochlorite which is a very strong oxidant. Therefore, the results showed a high iron leaching percentage at 55% whereas cyanide only achieves 13%. When 50% more of the iGoli lixiviants are used, the Fe extracted goes up to 60%.

7.2 CALCULATIONS

7.2.1 EXTRACTION

The gold concentration in leaching media was reported in mg/l from the Analytical Lab. Extraction was calculated following the steps detailed below.

i) Calculate the mass of gold in the mass of ore to be leached,

$$mass\ of\ gold\ in\ ore\ (m) = gold\ concentration\ (\%) * mass\ of\ ore$$

- Gold concentration from fire assay

ii) Measure the volume of the lixiviant.

iii) Calculate the concentration at which 100% extraction is achieved.

$$concentration\ of\ gold\ in\ lixiviant\ at\ 100\%\ extraction = \frac{mass\ of\ gold\ in\ ore}{volume\ of\ lixiviant}$$

iv) From the Lab results, calculate extraction.

$$\%\ extraction = \frac{gold\ concentration\ from\ lab\ sample}{concentration\ of\ gold\ in\ lixiviant\ at\ 100\%\ extraction}$$

v) Care should be taken to adjust the concentration since the lixiviant volume reduces during sampling. For example, if initial volume of lixiviant is 500ml and mass of gold in ore is 10mg,

$$\begin{aligned} concentration\ of\ gold\ in\ lixiviant\ at\ 100\%\ extraction &= \frac{10mg}{500ml} \\ &= \boldsymbol{20mg/l} \end{aligned}$$

After a 20ml sample, the new concentration at 100% extraction will be,

$$concentration\ of\ gold\ in\ lixiviant\ at\ 100\%\ extraction = \frac{10mg}{480ml}$$
$$= \mathbf{20.8mg/l}$$

vi) Example, 3 samples 20ml each were extracted in the first, second and third hour without replacement of lixiviant. The concentrations of the samples received from the lab are as follows 2 mg/l, 5 mg/l, and 10 mg/l respectively. Calculate the % extraction of each.

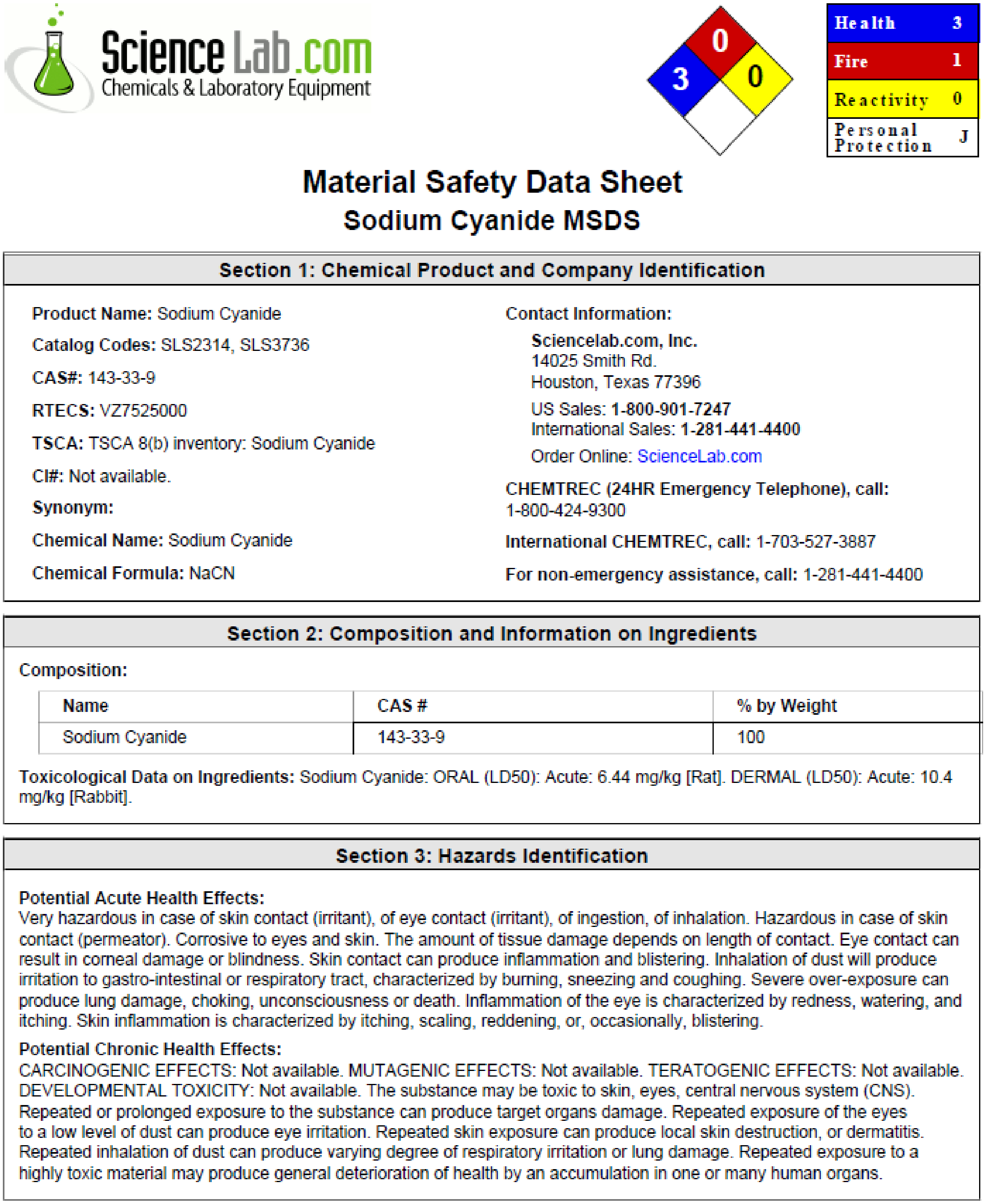
$$1st\ hour\ \%\ extraction = \frac{2}{20} = 10\%$$

$$2nd\ hour\ \%\ extraction = \frac{5}{20.8} = 24\%$$

$$3rd\ hour\ \%\ extraction = \frac{10}{21.7} = 46\%$$

7.3 MATERIAL AND SAFETY DATA SHEETS

7.3.1 SODIUM CYANIDE



ScienceLab.com
Chemicals & Laboratory Equipment

Health	**3**
Fire	**1**
Reactivity	**0**
Personal Protection	**J**

Material Safety Data Sheet
Sodium Cyanide MSDS

Section 1: Chemical Product and Company Identification

Product Name: Sodium Cyanide

Catalog Codes: SLS2314, SLS3736

CAS#: 143-33-9

RTECS: VZ7525000

TSCA: TSCA 8(b) inventory: Sodium Cyanide

CI#: Not available.

Synonym:

Chemical Name: Sodium Cyanide

Chemical Formula: NaCN

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Sodium Cyanide	143-33-9	100

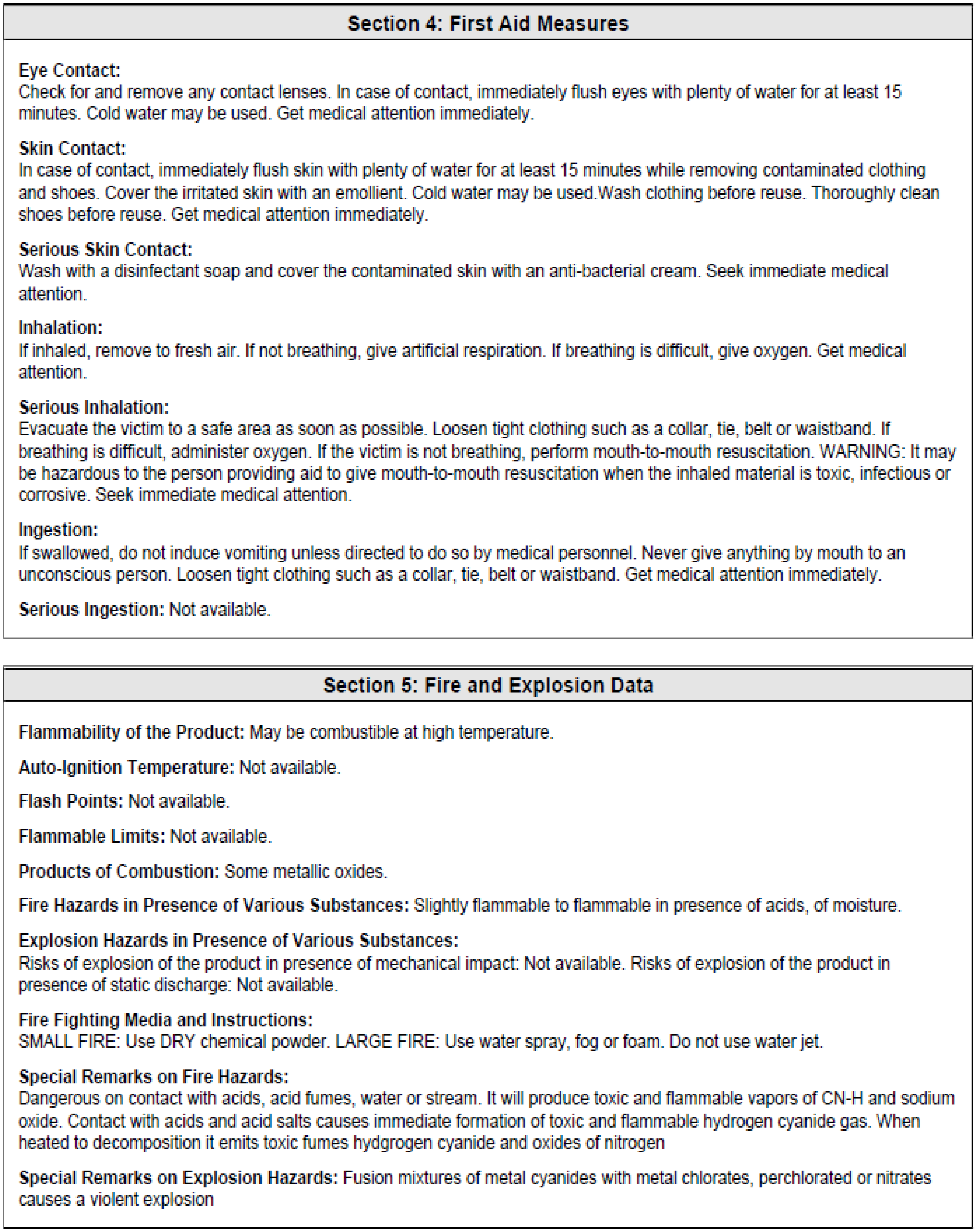
Toxicological Data on Ingredients: Sodium Cyanide: ORAL (LD50): Acute: 6.44 mg/kg [Rat]. DERMAL (LD50): Acute: 10.4 mg/kg [Rabbit].

Section 3: Hazards Identification

Potential Acute Health Effects:
Very hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Hazardous in case of skin contact (permeator). Corrosive to eyes and skin. The amount of tissue damage depends on length of contact. Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering. Inhalation of dust will produce irritation to gastro-intestinal or respiratory tract, characterized by burning, sneezing and coughing. Severe over-exposure can produce lung damage, choking, unconsciousness or death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

Potential Chronic Health Effects:
CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance may be toxic to skin, eyes, central nervous system (CNS). Repeated or prolonged exposure to the substance can produce target organs damage. Repeated exposure of the eyes to a low level of dust can produce eye irritation. Repeated skin exposure can produce local skin destruction, or dermatitis. Repeated inhalation of dust can produce varying degree of respiratory irritation or lung damage. Repeated exposure to a highly toxic material may produce general deterioration of health by an accumulation in one or many human organs.

(Science Lab.com, 2005)



Section 4: First Aid Measures

Eye Contact:
Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention immediately.

Skin Contact:
In case of contact, immediately flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Cover the irritated skin with an emollient. Cold water may be used.Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention immediately.

Serious Skin Contact:
Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

Inhalation:
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Serious Inhalation:
Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. WARNING: It may be hazardous to the person providing aid to give mouth-to-mouth resuscitation when the inhaled material is toxic, infectious or corrosive. Seek immediate medical attention.

Ingestion:
If swallowed, do not induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention immediately.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: May be combustible at high temperature.

Auto-Ignition Temperature: Not available.

Flash Points: Not available.

Flammable Limits: Not available.

Products of Combustion: Some metallic oxides.

Fire Hazards in Presence of Various Substances: Slightly flammable to flammable in presence of acids, of moisture.

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available. Risks of explosion of the product in presence of static discharge: Not available.

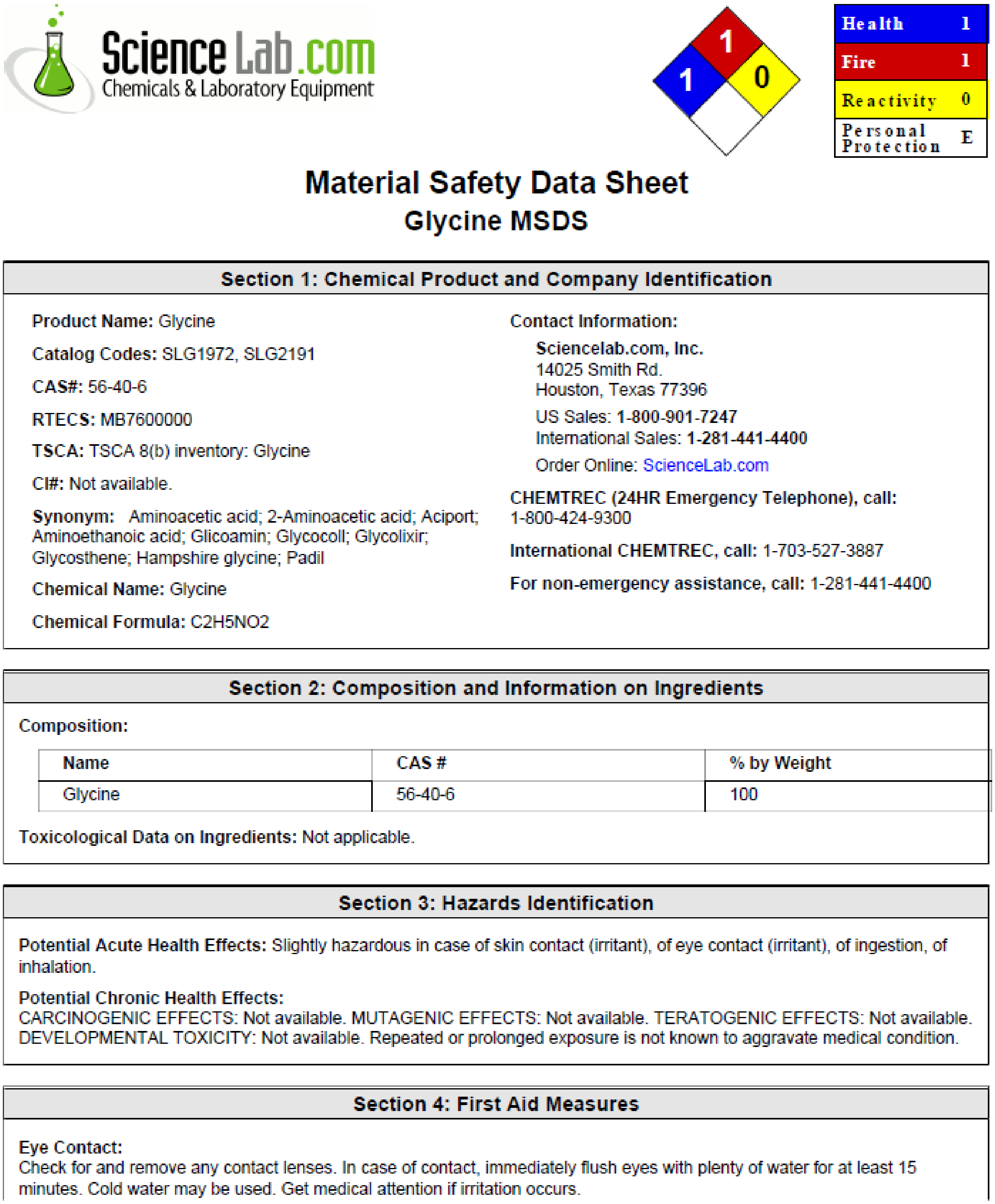
Fire Fighting Media and Instructions:
SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use water spray, fog or foam. Do not use water jet.

Special Remarks on Fire Hazards:
Dangerous on contact with acids, acid fumes, water or stream. It will produce toxic and flammable vapors of CN-H and sodium oxide. Contact with acids and acid salts causes immediate formation of toxic and flammable hydrogen cyanide gas. When heated to decomposition it emits toxic fumes hydgrogen cyanide and oxides of nitrogen

Special Remarks on Explosion Hazards: Fusion mixtures of metal cyanides with metal chlorates, perchlorated or nitrates causes a violent explosion

(Science Lab.com, 2005)

7.3.2 GLYCINE



ScienceLab.com
Chemicals & Laboratory Equipment

Health	1
Fire	1
Reactivity	0
Personal Protection	E

Material Safety Data Sheet
Glycine MSDS

Section 1: Chemical Product and Company Identification

Product Name: Glycine

Catalog Codes: SLG1972, SLG2191

CAS#: 56-40-6

RTECS: MB7600000

TSCA: TSCA 8(b) inventory: Glycine

CI#: Not available.

Synonym: Aminoacetic acid; 2-Aminoacetic acid; Aciport; Aminoethanoic acid; Glicoamin; Glycocoll; Glycolixir; Glycosthene; Hampshire glycine; Padil

Chemical Name: Glycine

Chemical Formula: $C2H5NO2$

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Glycine	56-40-6	100

Toxicological Data on Ingredients: Not applicable.

Section 3: Hazards Identification

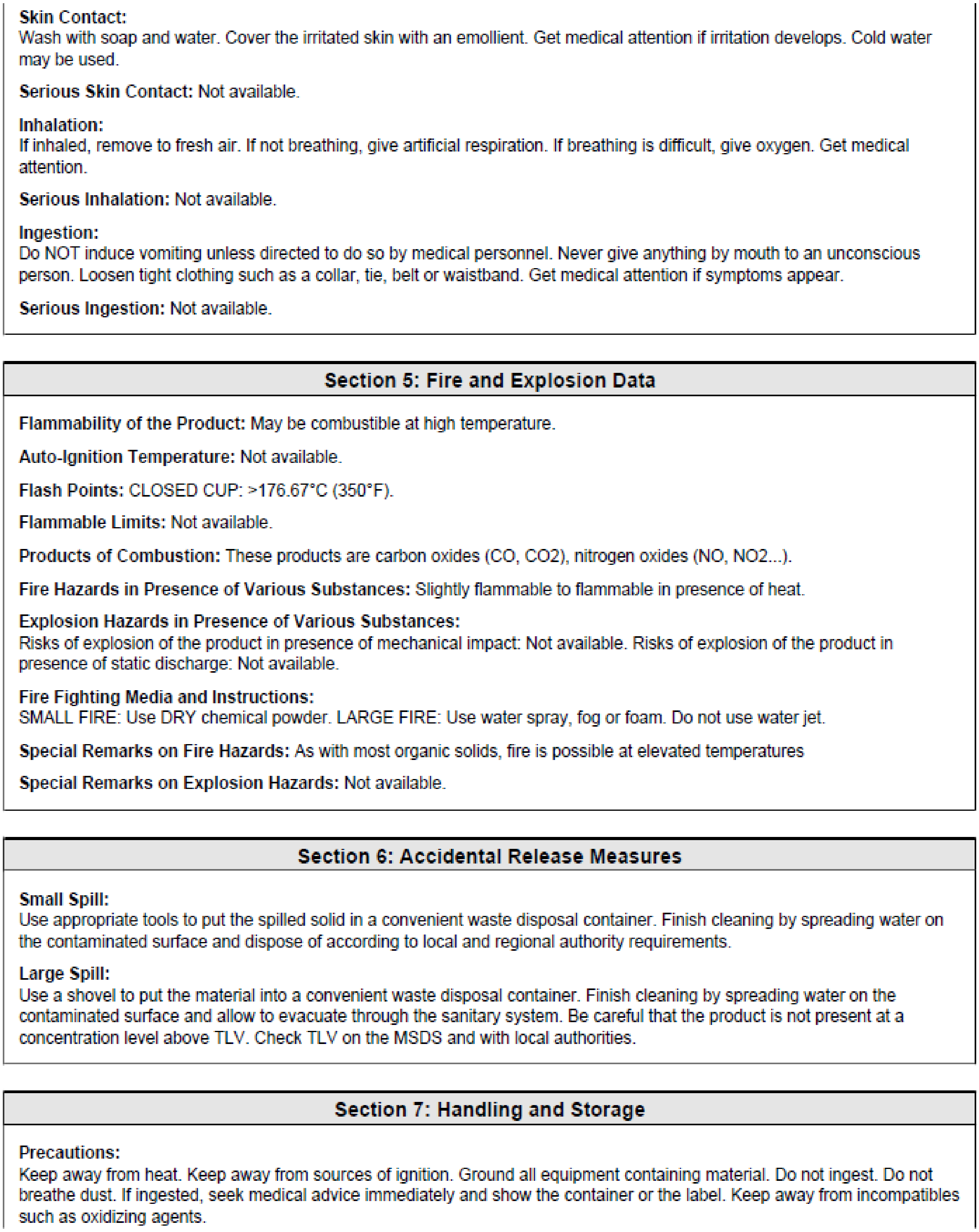
Potential Acute Health Effects: Slightly hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation.

Potential Chronic Health Effects:
CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. Repeated or prolonged exposure is not known to aggravate medical condition.

Section 4: First Aid Measures

Eye Contact:
Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention if irritation occurs.

(Science Lab.com, 2012)



Skin Contact:
Wash with soap and water. Cover the irritated skin with an emollient. Get medical attention if irritation develops. Cold water may be used.

Serious Skin Contact: Not available.

Inhalation:
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Serious Inhalation: Not available.

Ingestion:
Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. Loosen tight clothing such as a collar, tie, belt or waistband. Get medical attention if symptoms appear.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: May be combustible at high temperature.

Auto-Ignition Temperature: Not available.

Flash Points: CLOSED CUP: >176.67°C (350°F).

Flammable Limits: Not available.

Products of Combustion: These products are carbon oxides (CO, CO2), nitrogen oxides (NO, NO2...).

Fire Hazards in Presence of Various Substances: Slightly flammable to flammable in presence of heat.

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available. Risks of explosion of the product in presence of static discharge: Not available.

Fire Fighting Media and Instructions:
SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use water spray, fog or foam. Do not use water jet.

Special Remarks on Fire Hazards: As with most organic solids, fire is possible at elevated temperatures

Special Remarks on Explosion Hazards: Not available.

Section 6: Accidental Release Measures

Small Spill:
Use appropriate tools to put the spilled solid in a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and dispose of according to local and regional authority requirements.

Large Spill:
Use a shovel to put the material into a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and allow to evacuate through the sanitary system. Be careful that the product is not present at a concentration level above TLV. Check TLV on the MSDS and with local authorities.

Section 7: Handling and Storage

Precautions:
Keep away from heat. Keep away from sources of ignition. Ground all equipment containing material. Do not ingest. Do not breathe dust. If ingested, seek medical advice immediately and show the container or the label. Keep away from incompatibles such as oxidizing agents.

(Science Lab.com, 2012)

7.3.3 HYDROCHLORIC ACID

Version: 4.0
Revision Date: 02-02-2015

SAFETY DATA SHEET

1. Identification

Product identifier: HYDROCHLORIC ACID

Other means of identification
Synonyms: Muriatic Acid, Hydrogen Chloride, Aqueous
Product No.: 9385, 9538, 9165, V226, V187, V078, V001, 6900, 2624, 2515, H999, H987, H616, 5861, 2062, 5814, 2626, 2612, 5800, 9625, 5587, 9551, 9544, 9539, 9535, 9530, 9529, 5367, H613, 37825, 25496, 20620, H613

Recommended use and restriction on use
Recommended use: Not available.
Restrictions on use: Not known.

Manufacturer/Importer/Supplier/Distributor Information

Manufacturer
Company Name: Avantor Performance Materials, Inc.
Address: 3477 Corporate Parkway, Suite 200
Center Valley, PA 18034
Telephone:
Customer Service: 855-282-6867
Fax:
Contact Person: Environmental Health & Safety
e-mail: info@avantormaterials.com

Emergency telephone number:
24 Hour Emergency: 908-859-2151

Chemtrec: 800-424-9300

2. Hazard(s) identification

Hazard Classification

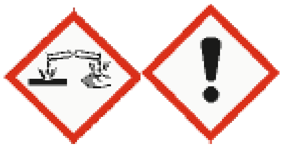
Physical Hazards

Corrosive to metals	Category 1

Health Hazards

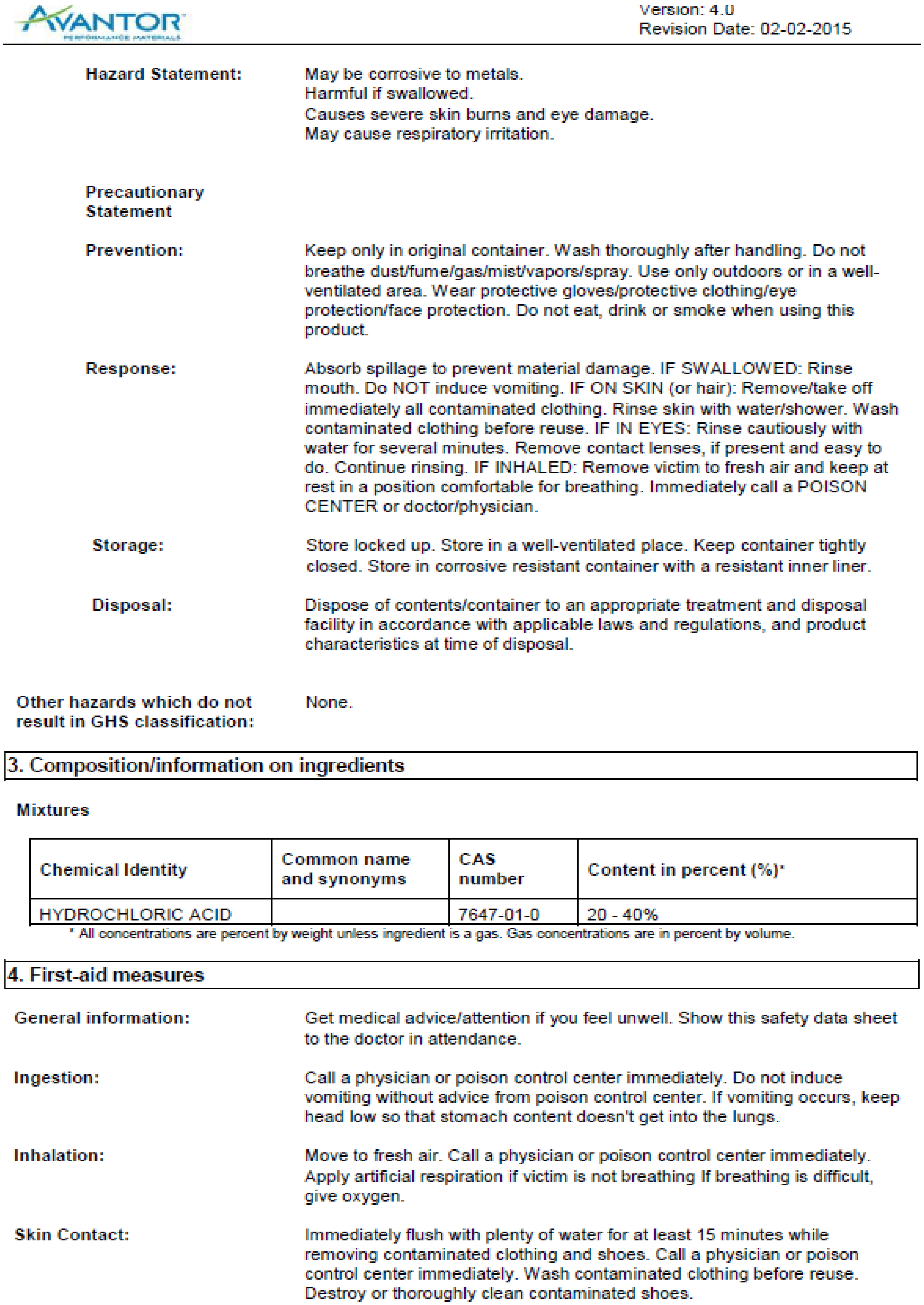
Acute toxicity (Oral)	Category 4
Skin Corrosion/Irritation	Category 1
Serious Eye Damage/Eye Irritation	Category 1
Specific Target Organ Toxicity - Single Exposure (Inhalation - vapor)	Category 3

Label Elements
Hazard Symbol:



Signal Word: Danger

(Avantor Performance Materials, 2015)



AVANTOR PERFORMANCE MATERIALS

Version: 4.0
Revision Date: 02-02-2015

Hazard Statement:	May be corrosive to metals. Harmful if swallowed. Causes severe skin burns and eye damage. May cause respiratory irritation.
Precautionary Statement	
Prevention:	Keep only in original container. Wash thoroughly after handling. Do not breathe dust/fume/gas/mist/vapors/spray. Use only outdoors or in a well-ventilated area. Wear protective gloves/protective clothing/eye protection/face protection. Do not eat, drink or smoke when using this product.
Response:	Absorb spillage to prevent material damage. IF SWALLOWED: Rinse mouth. Do NOT induce vomiting. IF ON SKIN (or hair): Remove/take off immediately all contaminated clothing. Rinse skin with water/shower. Wash contaminated clothing before reuse. IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing. Immediately call a POISON CENTER or doctor/physician.
Storage:	Store locked up. Store in a well-ventilated place. Keep container tightly closed. Store in corrosive resistant container with a resistant inner liner.
Disposal:	Dispose of contents/container to an appropriate treatment and disposal facility in accordance with applicable laws and regulations, and product characteristics at time of disposal.
Other hazards which do not result in GHS classification:	None.

3. Composition/information on ingredients

Mixtures

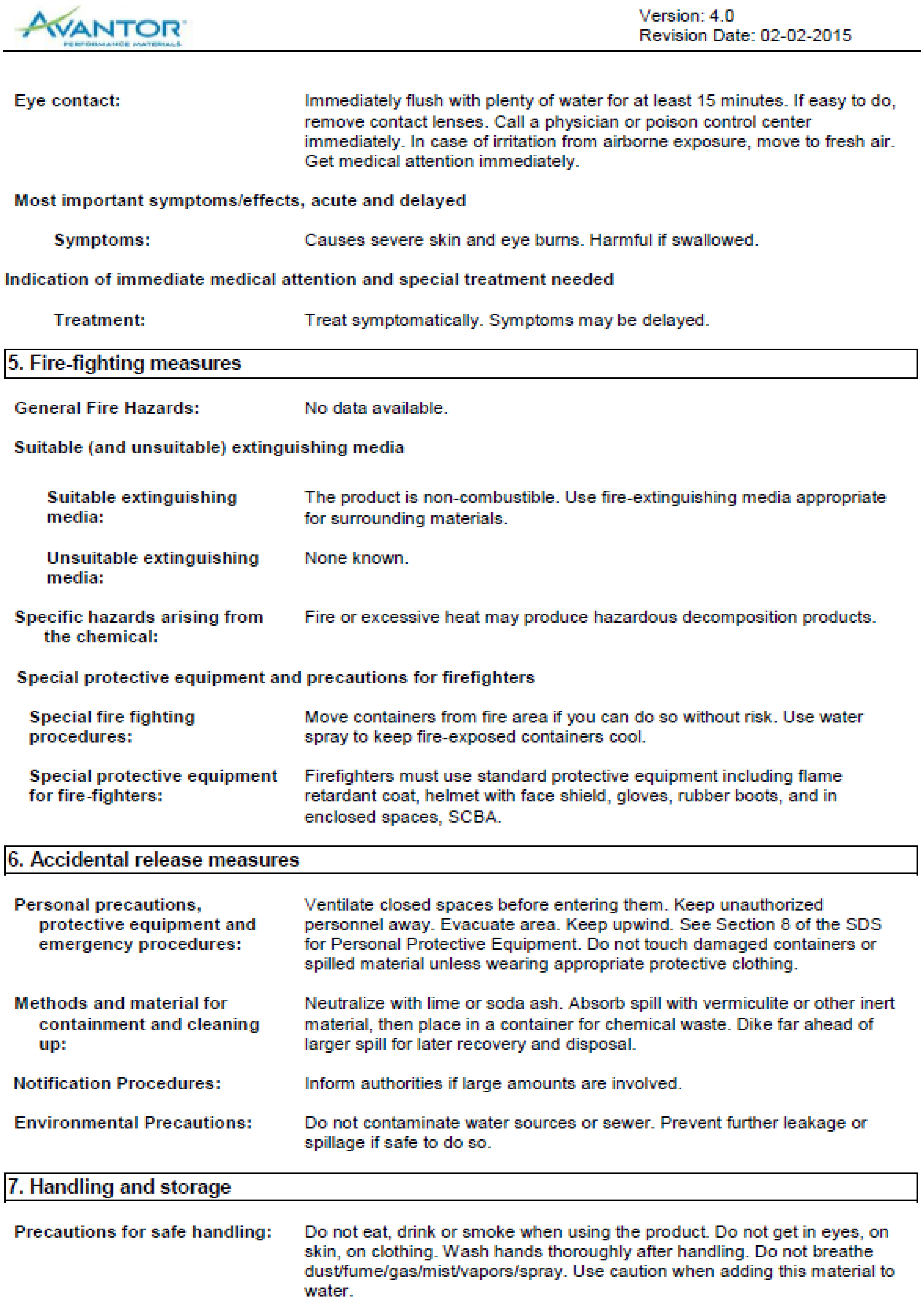
Chemical Identity	Common name and synonyms	CAS number	Content in percent (%)*
HYDROCHLORIC ACID		7647-01-0	20 - 40%

* All concentrations are percent by weight unless ingredient is a gas. Gas concentrations are in percent by volume.

4. First-aid measures

General information:	Get medical advice/attention if you feel unwell. Show this safety data sheet to the doctor in attendance.
Ingestion:	Call a physician or poison control center immediately. Do not induce vomiting without advice from poison control center. If vomiting occurs, keep head low so that stomach content doesn't get into the lungs.
Inhalation:	Move to fresh air. Call a physician or poison control center immediately. Apply artificial respiration if victim is not breathing If breathing is difficult, give oxygen.
Skin Contact:	Immediately flush with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Call a physician or poison control center immediately. Wash contaminated clothing before reuse. Destroy or thoroughly clean contaminated shoes.

(Avantor Performance Materials, 2015)



AVANTOR PERFORMANCE MATERIALS

Version: 4.0
Revision Date: 02-02-2015

Eye contact:	Immediately flush with plenty of water for at least 15 minutes. If easy to do, remove contact lenses. Call a physician or poison control center immediately. In case of irritation from airborne exposure, move to fresh air. Get medical attention immediately.

Most important symptoms/effects, acute and delayed

Symptoms:	Causes severe skin and eye burns. Harmful if swallowed.

Indication of immediate medical attention and special treatment needed

Treatment:	Treat symptomatically. Symptoms may be delayed.

5. Fire-fighting measures

General Fire Hazards:	No data available.

Suitable (and unsuitable) extinguishing media

Suitable extinguishing media:	The product is non-combustible. Use fire-extinguishing media appropriate for surrounding materials.
Unsuitable extinguishing media:	None known.
Specific hazards arising from the chemical:	Fire or excessive heat may produce hazardous decomposition products.

Special protective equipment and precautions for firefighters

Special fire fighting procedures:	Move containers from fire area if you can do so without risk. Use water spray to keep fire-exposed containers cool.
Special protective equipment for fire-fighters:	Firefighters must use standard protective equipment including flame retardant coat, helmet with face shield, gloves, rubber boots, and in enclosed spaces, SCBA.

6. Accidental release measures

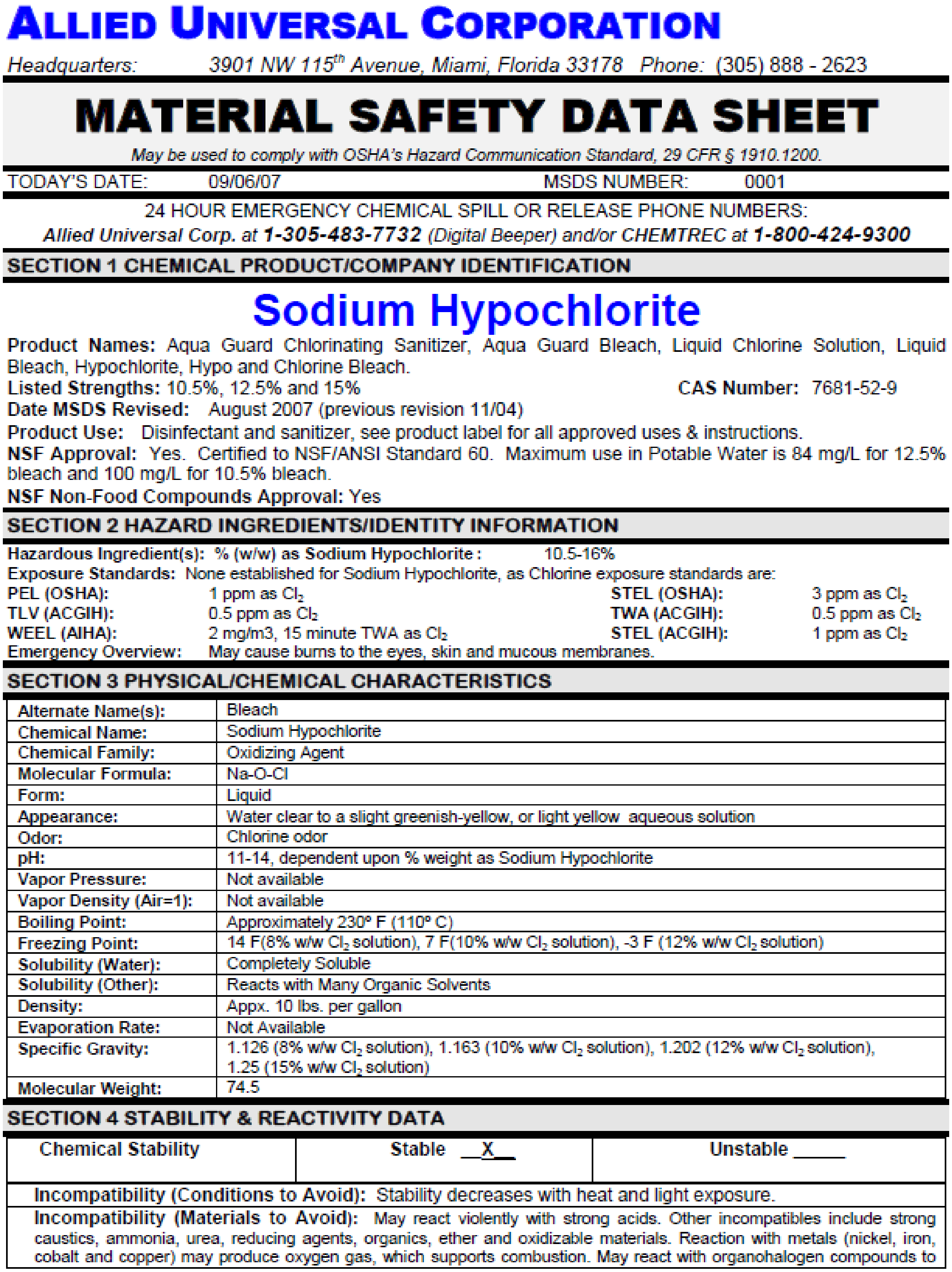
Personal precautions, protective equipment and emergency procedures:	Ventilate closed spaces before entering them. Keep unauthorized personnel away. Evacuate area. Keep upwind. See Section 8 of the SDS for Personal Protective Equipment. Do not touch damaged containers or spilled material unless wearing appropriate protective clothing.
Methods and material for containment and cleaning up:	Neutralize with lime or soda ash. Absorb spill with vermiculite or other inert material, then place in a container for chemical waste. Dike far ahead of larger spill for later recovery and disposal.
Notification Procedures:	Inform authorities if large amounts are involved.
Environmental Precautions:	Do not contaminate water sources or sewer. Prevent further leakage or spillage if safe to do so.

7. Handling and storage

Precautions for safe handling:	Do not eat, drink or smoke when using the product. Do not get in eyes, on skin, on clothing. Wash hands thoroughly after handling. Do not breathe dust/fume/gas/mist/vapors/spray. Use caution when adding this material to water.

(Avantor Performance Materials, 2015)

7.3.4 SODIUM HYPOCHLORITE



ALLIED UNIVERSAL CORPORATION

Headquarters: 3901 NW 115th Avenue, Miami, Florida 33178 Phone: (305) 888 - 2623

MATERIAL SAFETY DATA SHEET

May be used to comply with OSHA's Hazard Communication Standard, 29 CFR § 1910.1200.

TODAY'S DATE: 09/06/07 MSDS NUMBER: 0001

24 HOUR EMERGENCY CHEMICAL SPILL OR RELEASE PHONE NUMBERS:
*Allied Universal Corp. at **1-305-483-7732** (Digital Beeper) and/or CHEMTREC at **1-800-424-9300***

SECTION 1 CHEMICAL PRODUCT/COMPANY IDENTIFICATION

Sodium Hypochlorite

Product Names: Aqua Guard Chlorinating Sanitizer, Aqua Guard Bleach, Liquid Chlorine Solution, Liquid Bleach, Hypochlorite, Hypo and Chlorine Bleach.

Listed Strengths: 10.5%, 12.5% and 15% **CAS Number:** 7681-52-9

Date MSDS Revised: August 2007 (previous revision 11/04)

Product Use: Disinfectant and sanitizer, see product label for all approved uses & instructions.

NSF Approval: Yes. Certified to NSF/ANSI Standard 60. Maximum use in Potable Water is 84 mg/L for 12.5% bleach and 100 mg/L for 10.5% bleach.

NSF Non-Food Compounds Approval: Yes

SECTION 2 HAZARD INGREDIENTS/IDENTITY INFORMATION

Hazardous Ingredient(s): % (w/w) as Sodium Hypochlorite : 10.5-16%

Exposure Standards: None established for Sodium Hypochlorite, as Chlorine exposure standards are:

PEL (OSHA):	1 ppm as Cl_2	**STEL (OSHA):**	3 ppm as Cl_2
TLV (ACGIH):	0.5 ppm as Cl_2	**TWA (ACGIH):**	0.5 ppm as Cl_2
WEEL (AIHA):	2 mg/m3, 15 minute TWA as Cl_2	**STEL (ACGIH):**	1 ppm as Cl_2

Emergency Overview: May cause burns to the eyes, skin and mucous membranes.

SECTION 3 PHYSICAL/CHEMICAL CHARACTERISTICS

Alternate Name(s):	Bleach
Chemical Name:	Sodium Hypochlorite
Chemical Family:	Oxidizing Agent
Molecular Formula:	Na-O-Cl
Form:	Liquid
Appearance:	Water clear to a slight greenish-yellow, or light yellow aqueous solution
Odor:	Chlorine odor
pH:	11-14, dependent upon % weight as Sodium Hypochlorite
Vapor Pressure:	Not available
Vapor Density (Air=1):	Not available
Boiling Point:	Approximately 230° F (110° C)
Freezing Point:	14 F(8% w/w Cl_2 solution), 7 F(10% w/w Cl_2 solution), -3 F (12% w/w Cl_2 solution)
Solubility (Water):	Completely Soluble
Solubility (Other):	Reacts with Many Organic Solvents
Density:	Appx. 10 lbs. per gallon
Evaporation Rate:	Not Available
Specific Gravity:	1.126 (8% w/w Cl_2 solution), 1.163 (10% w/w Cl_2 solution), 1.202 (12% w/w Cl_2 solution), 1.25 (15% w/w Cl_2 solution)
Molecular Weight:	74.5

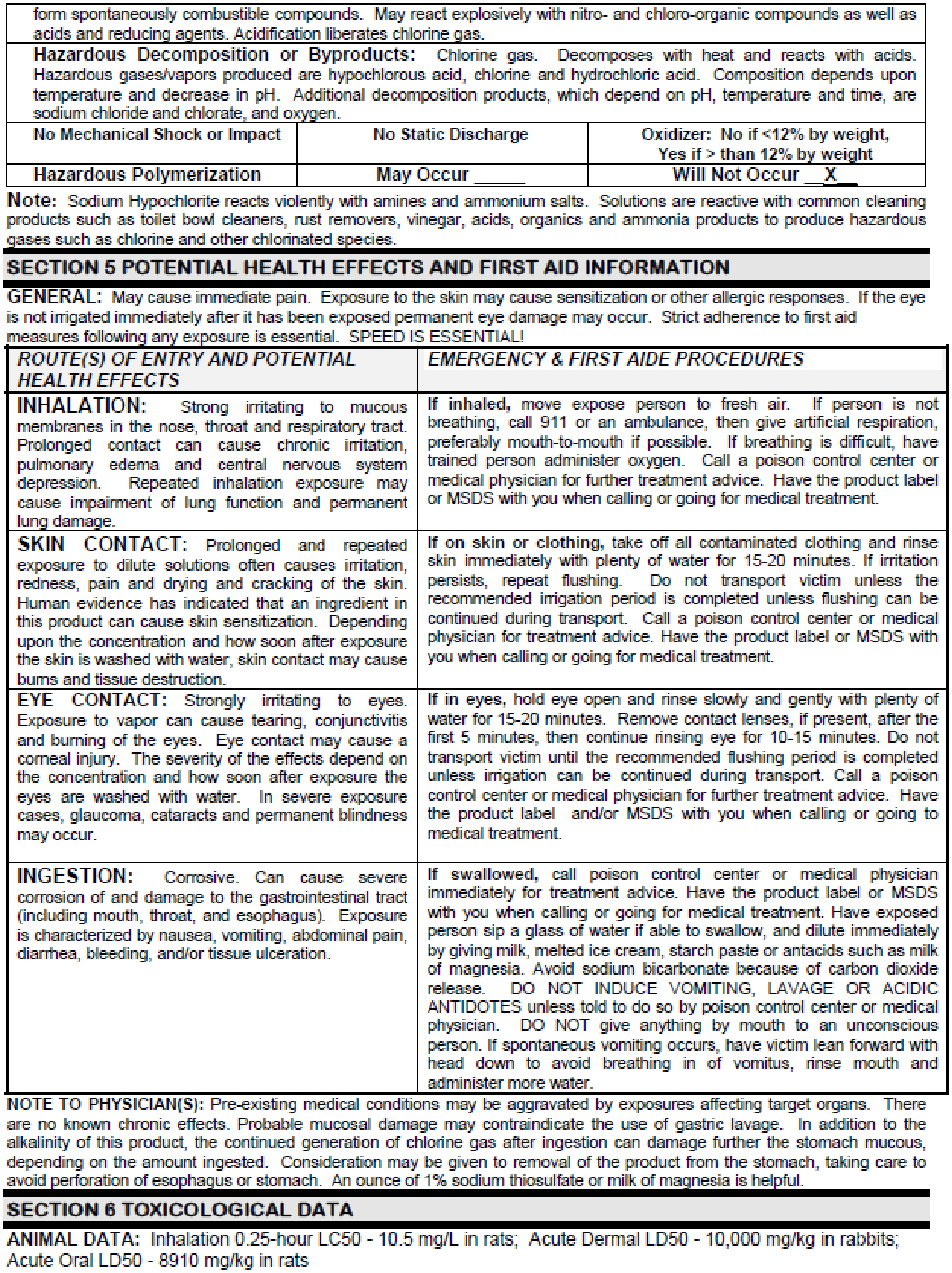
SECTION 4 STABILITY & REACTIVITY DATA

Chemical Stability	**Stable __X__**	**Unstable _____**

Incompatibility (Conditions to Avoid): Stability decreases with heat and light exposure.

Incompatibility (Materials to Avoid): May react violently with strong acids. Other incompatibles include strong caustics, ammonia, urea, reducing agents, organics, ether and oxidizable materials. Reaction with metals (nickel, iron, cobalt and copper) may produce oxygen gas, which supports combustion. May react with organohalogen compounds to

(Corporation, 2007)



form spontaneously combustible compounds. May react explosively with nitro- and chloro-organic compounds as well as acids and reducing agents. Acidification liberates chlorine gas.
Hazardous Decomposition or Byproducts: Chlorine gas. Decomposes with heat and reacts with acids. Hazardous gases/vapors produced are hypochlorous acid, chlorine and hydrochloric acid. Composition depends upon temperature and decrease in pH. Additional decomposition products, which depend on pH, temperature and time, are sodium chloride and chlorate, and oxygen.

No Mechanical Shock or Impact	**No Static Discharge**	**Oxidizer: No if <12% by weight,** **Yes if > than 12% by weight**
Hazardous Polymerization	**May Occur _____**	**Will Not Occur __X__**

Note: Sodium Hypochlorite reacts violently with amines and ammonium salts. Solutions are reactive with common cleaning products such as toilet bowl cleaners, rust removers, vinegar, acids, organics and ammonia products to produce hazardous gases such as chlorine and other chlorinated species.

SECTION 5 POTENTIAL HEALTH EFFECTS AND FIRST AID INFORMATION

GENERAL: May cause immediate pain. Exposure to the skin may cause sensitization or other allergic responses. If the eye is not irrigated immediately after it has been exposed permanent eye damage may occur. Strict adherence to first aid measures following any exposure is essential. SPEED IS ESSENTIAL!

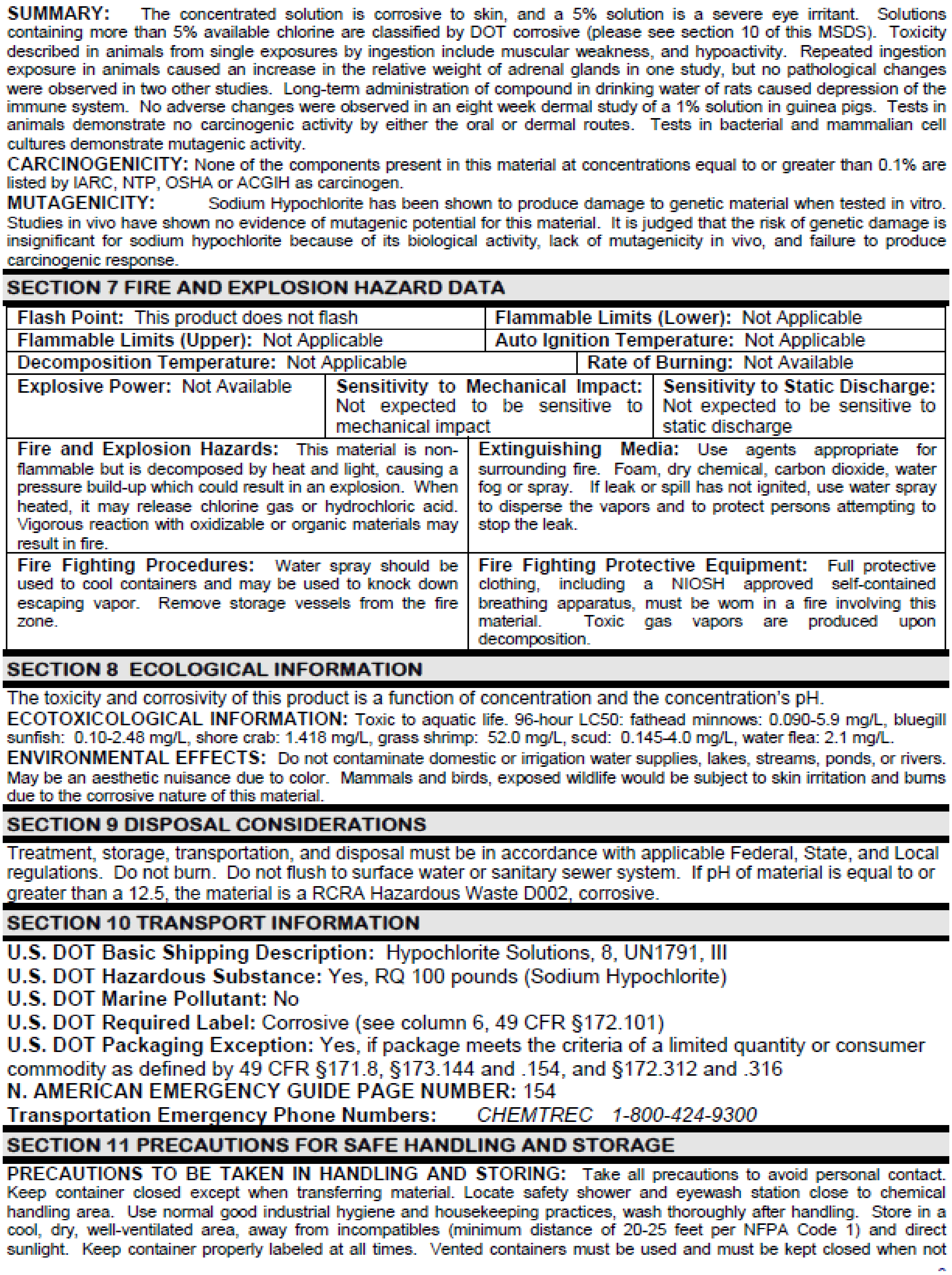
ROUTE(S) OF ENTRY AND POTENTIAL HEALTH EFFECTS	*EMERGENCY & FIRST AIDE PROCEDURES*
INHALATION: Strong irritating to mucous membranes in the nose, throat and respiratory tract. Prolonged contact can cause chronic irritation, pulmonary edema and central nervous system depression. Repeated inhalation exposure may cause impairment of lung function and permanent lung damage.	**If inhaled,** move expose person to fresh air. If person is not breathing, call 911 or an ambulance, then give artificial respiration, preferably mouth-to-mouth if possible. If breathing is difficult, have trained person administer oxygen. Call a poison control center or medical physician for further treatment advice. Have the product label or MSDS with you when calling or going for medical treatment.
SKIN CONTACT: Prolonged and repeated exposure to dilute solutions often causes irritation, redness, pain and drying and cracking of the skin. Human evidence has indicated that an ingredient in this product can cause skin sensitization. Depending upon the concentration and how soon after exposure the skin is washed with water, skin contact may cause burns and tissue destruction.	**If on skin or clothing,** take off all contaminated clothing and rinse skin immediately with plenty of water for 15-20 minutes. If irritation persists, repeat flushing. Do not transport victim unless the recommended irrigation period is completed unless flushing can be continued during transport. Call a poison control center or medical physician for treatment advice. Have the product label or MSDS with you when calling or going for medical treatment.
EYE CONTACT: Strongly irritating to eyes. Exposure to vapor can cause tearing, conjunctivitis and burning of the eyes. Eye contact may cause a corneal injury. The severity of the effects depend on the concentration and how soon after exposure the eyes are washed with water. In severe exposure cases, glaucoma, cataracts and permanent blindness may occur.	**If in eyes,** hold eye open and rinse slowly and gently with plenty of water for 15-20 minutes. Remove contact lenses, if present, after the first 5 minutes, then continue rinsing eye for 10-15 minutes. Do not transport victim until the recommended flushing period is completed unless irrigation can be continued during transport. Call a poison control center or medical physician for further treatment advice. Have the product label and/or MSDS with you when calling or going to medical treatment.
INGESTION: Corrosive. Can cause severe corrosion of and damage to the gastrointestinal tract (including mouth, throat, and esophagus). Exposure is characterized by nausea, vomiting, abdominal pain, diarrhea, bleeding, and/or tissue ulceration.	**If swallowed,** call poison control center or medical physician immediately for treatment advice. Have the product label or MSDS with you when calling or going for medical treatment. Have exposed person sip a glass of water if able to swallow, and dilute immediately by giving milk, melted ice cream, starch paste or antacids such as milk of magnesia. Avoid sodium bicarbonate because of carbon dioxide release. DO NOT INDUCE VOMITING, LAVAGE OR ACIDIC ANTIDOTES unless told to do so by poison control center or medical physician. DO NOT give anything by mouth to an unconscious person. If spontaneous vomiting occurs, have victim lean forward with head down to avoid breathing in of vomitus, rinse mouth and administer more water.

NOTE TO PHYSICIAN(S): Pre-existing medical conditions may be aggravated by exposures affecting target organs. There are no known chronic effects. Probable mucosal damage may contraindicate the use of gastric lavage. In addition to the alkalinity of this product, the continued generation of chlorine gas after ingestion can damage further the stomach mucous, depending on the amount ingested. Consideration may be given to removal of the product from the stomach, taking care to avoid perforation of esophagus or stomach. An ounce of 1% sodium thiosulfate or milk of magnesia is helpful.

SECTION 6 TOXICOLOGICAL DATA

ANIMAL DATA: Inhalation 0.25-hour LC50 - 10.5 mg/L in rats; Acute Dermal LD50 - 10,000 mg/kg in rabbits; Acute Oral LD50 - 8910 mg/kg in rats

(Corporation, 2007)



SUMMARY: The concentrated solution is corrosive to skin, and a 5% solution is a severe eye irritant. Solutions containing more than 5% available chlorine are classified by DOT corrosive (please see section 10 of this MSDS). Toxicity described in animals from single exposures by ingestion include muscular weakness, and hypoactivity. Repeated ingestion exposure in animals caused an increase in the relative weight of adrenal glands in one study, but no pathological changes were observed in two other studies. Long-term administration of compound in drinking water of rats caused depression of the immune system. No adverse changes were observed in an eight week dermal study of a 1% solution in guinea pigs. Tests in animals demonstrate no carcinogenic activity by either the oral or dermal routes. Tests in bacterial and mammalian cell cultures demonstrate mutagenic activity.

CARCINOGENICITY: None of the components present in this material at concentrations equal to or greater than 0.1% are listed by IARC, NTP, OSHA or ACGIH as carcinogen.

MUTAGENICITY: Sodium Hypochlorite has been shown to produce damage to genetic material when tested in vitro. Studies in vivo have shown no evidence of mutagenic potential for this material. It is judged that the risk of genetic damage is insignificant for sodium hypochlorite because of its biological activity, lack of mutagenicity in vivo, and failure to produce carcinogenic response.

SECTION 7 FIRE AND EXPLOSION HAZARD DATA

Flash Point: This product does not flash	**Flammable Limits (Lower):** Not Applicable	
Flammable Limits (Upper): Not Applicable	**Auto Ignition Temperature:** Not Applicable	
Decomposition Temperature: Not Applicable	**Rate of Burning:** Not Available	
Explosive Power: Not Available	**Sensitivity to Mechanical Impact:** Not expected to be sensitive to mechanical impact	**Sensitivity to Static Discharge:** Not expected to be sensitive to static discharge
Fire and Explosion Hazards: This material is non-flammable but is decomposed by heat and light, causing a pressure build-up which could result in an explosion. When heated, it may release chlorine gas or hydrochloric acid. Vigorous reaction with oxidizable or organic materials may result in fire.	**Extinguishing Media:** Use agents appropriate for surrounding fire. Foam, dry chemical, carbon dioxide, water fog or spray. If leak or spill has not ignited, use water spray to disperse the vapors and to protect persons attempting to stop the leak.	
Fire Fighting Procedures: Water spray should be used to cool containers and may be used to knock down escaping vapor. Remove storage vessels from the fire zone.	**Fire Fighting Protective Equipment:** Full protective clothing, including a NIOSH approved self-contained breathing apparatus, must be worn in a fire involving this material. Toxic gas vapors are produced upon decomposition.	

SECTION 8 ECOLOGICAL INFORMATION

The toxicity and corrosivity of this product is a function of concentration and the concentration's pH.

ECOTOXICOLOGICAL INFORMATION: Toxic to aquatic life. 96-hour LC50: fathead minnows: 0.090-5.9 mg/L, bluegill sunfish: 0.10-2.48 mg/L, shore crab: 1.418 mg/L, grass shrimp: 52.0 mg/L, scud: 0.145-4.0 mg/L, water flea: 2.1 mg/L.

ENVIRONMENTAL EFFECTS: Do not contaminate domestic or irrigation water supplies, lakes, streams, ponds, or rivers. May be an aesthetic nuisance due to color. Mammals and birds, exposed wildlife would be subject to skin irritation and burns due to the corrosive nature of this material.

SECTION 9 DISPOSAL CONSIDERATIONS

Treatment, storage, transportation, and disposal must be in accordance with applicable Federal, State, and Local regulations. Do not burn. Do not flush to surface water or sanitary sewer system. If pH of material is equal to or greater than a 12.5, the material is a RCRA Hazardous Waste D002, corrosive.

SECTION 10 TRANSPORT INFORMATION

U.S. DOT Basic Shipping Description: Hypochlorite Solutions, 8, UN1791, III
U.S. DOT Hazardous Substance: Yes, RQ 100 pounds (Sodium Hypochlorite)
U.S. DOT Marine Pollutant: No
U.S. DOT Required Label: Corrosive (see column 6, 49 CFR §172.101)
U.S. DOT Packaging Exception: Yes, if package meets the criteria of a limited quantity or consumer commodity as defined by 49 CFR §171.8, §173.144 and .154, and §172.312 and .316
N. AMERICAN EMERGENCY GUIDE PAGE NUMBER: 154
Transportation Emergency Phone Numbers: *CHEMTREC 1-800-424-9300*

SECTION 11 PRECAUTIONS FOR SAFE HANDLING AND STORAGE

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORING: Take all precautions to avoid personal contact. Keep container closed except when transferring material. Locate safety shower and eyewash station close to chemical handling area. Use normal good industrial hygiene and housekeeping practices, wash thoroughly after handling. Store in a cool, dry, well-ventilated area, away from incompatibles (minimum distance of 20-25 feet per NFPA Code 1) and direct sunlight. Keep container properly labeled at all times. Vented containers must be used and must be kept closed when not

(Corporation, 2007)

7.4 IMPORTANCE OF RESEARCH

Figure 7.3: Sustainable Development Goals

The study is closely associated with the sustainable development goal (SDG) 8 which is decent work and economic growth. This is achieved in the study by:

- Improving occupational health and safety
- Making production sustainable and eliminating mercury use in ASGM (World Bank, 2020).

The success of the study will contribute towards the development of at least 1 alternative process to replace mercury in gold extraction which has severe environmental impacts in terms of atmospheric emissions during the roasting of the amalgam and solid/liquid waste generated. The study will therefore relate to SDG 6, 13, 14, and 15 which focus on climate action, life below water, and life on land, respectively.

7.5 ETHICS ASSESSMENT FORM

Application for Approval of Ethics in Research (EiR) Projects
Faculty of Engineering and the Built Environment, University of Cape Town

ETHICS APPLICATION FORM

Please Note:

Any person planning to undertake research in the Faculty of Engineering and the Built Environment (EBE) at the University of Cape Town is required to complete this form **before** collecting or analysing data. The objective of submitting this application *prior* to embarking on research is to ensure that the highest ethical standards in research, conducted under the auspices of the EBE Faculty, are met. Please ensure that you have read, and understood the **EBE Ethics in Research Handbook** (available from the UCT EBE, Research Ethics website) prior to completing this application form: http://www.ebe.uct.ac.za/ebe/research/ethics1

APPLICANT'S DETAILS		
Name of principal researcher, student or external applicant		Wilson Masuku
Department		Department of Chemical Engineering
Preferred email address of applicant:		MSKWIL004@myuct.ac.za
If Student	Your Degree: e.g., MSc, PhD, etc.	MSc Chemical Engineering
	Credit Value of Research: e.g., 60/120/180/360 etc.	Type text h180
	Name of Supervisor (if supervised):	Thandazile Moyo
If this is a researchcontract, indicate the source of funding/sponsorship		Julian Baring Scholarship
Project Title		Verification and validation of mercury-free technologies in the artisanal and small-scale gold mining sector.

I hereby undertake to carry out my research in such a way that:

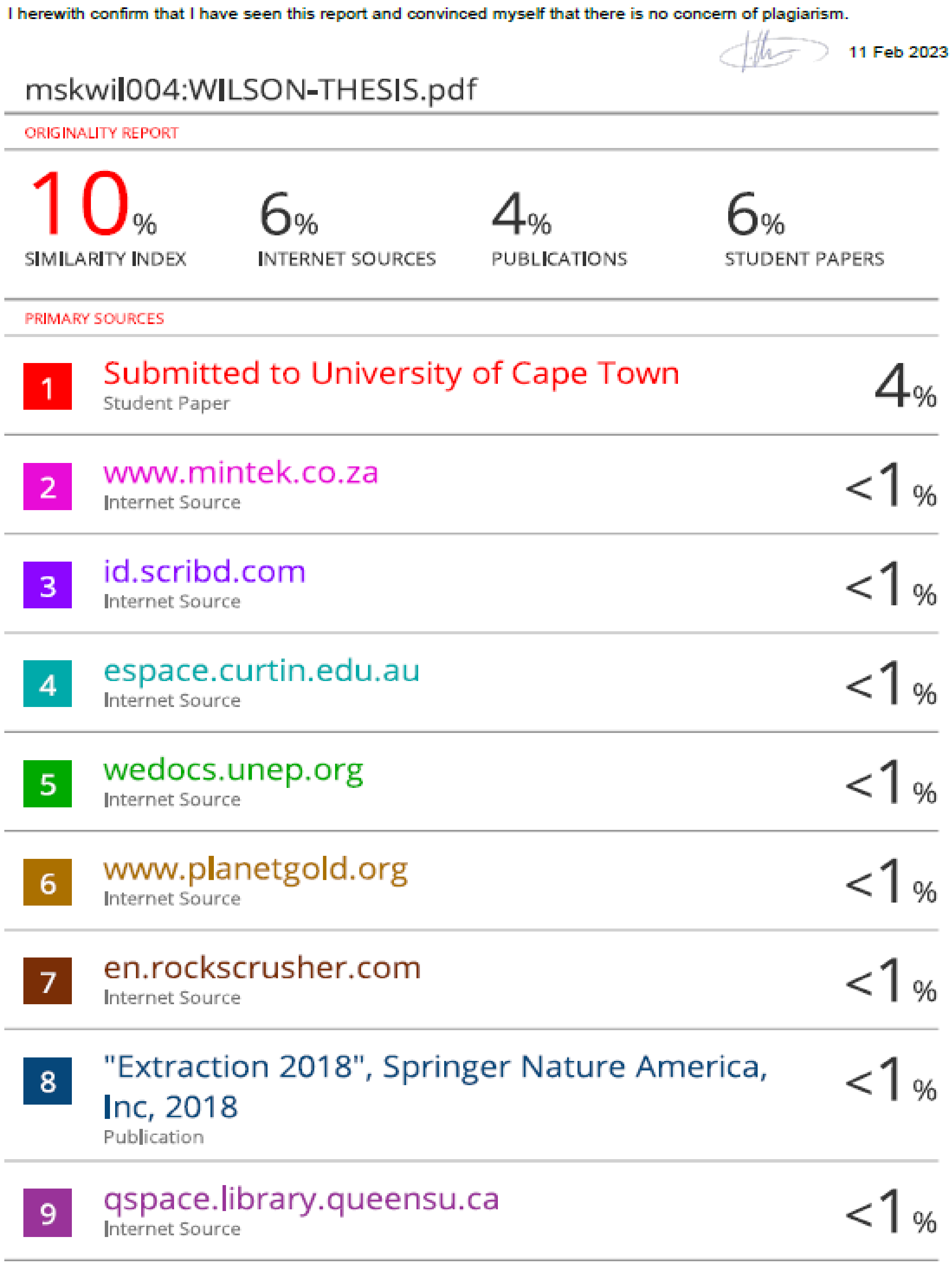
- there is no apparent legal objection to the nature or the method of research; and
- the research will not compromise staff or students or the other responsibilities of the University;
- the stated objective will be achieved, and the findings will have a high degree of validity;
- limitations and alternative interpretations will be considered;
- the findings could be subject to peer review and publicly available; and
- I will comply with the conventions of copyright and avoid any practice that would constitute plagiarism.

APPLICATION BY	Full name	Signature	Date
Principal Researcher/ Student/External applicant	Wilson Masuku		11/08/2021

SUPPORTED BY	Full name	Signature	Date
Supervisor (where applicable)	Thandazile Moyo		11/08/2021

APPROVED BY	Full name	Signature	Date
HOD (or delegated nominee) Final authority for all applicants who have answered NO to all questions in Section 1; and for all Undergraduate research (Including Honours).	Elaine Opitz		08/10/2021
Chair: Faculty EIR Committee For applicants other than undergraduate students who have answered YES to any of the questions in Section 1.			

7.6 SIMILARITY REPORT



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11 Feb 2023

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