A study of alternative techniques to mercury amalgamation for gold extraction in artisanal and small-scale gold mining

By:

Archippe Ngwey Manzila

Supervisor:

Professor Jochen Petersen

Co-supervisor:

Doctor Thandazile Moyo

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Abstract

Artisanal and small-scale gold mining (ASGM) has many definitions depending on the context. However, the common theme that characterises gold mining operations that fall within this category is that they make use of rudimentary methods to mine and process gold. The ASGM sector is a source of livelihood for millions of people worldwide and continues to grow due to the ever-rising demand for gold, and high unemployment rates which have been exacerbated by the Covid-19 pandemic, particularly in developing countries.

Mercury amalgamation is the method of choice to recover gold in ASGM. This method consists of contacting the gold found within an ore with mercury to form an alloy i.e., the mercury-gold amalgam and subsequently burning off mercury to recover the gold in a form known as sponge gold. The popularity of this method has to do with its simplicity of application, low cost, and quick returns. However, mercury is a highly toxic substance; therefore, its use presents serious health risks for artisanal miners and their communities, and environmental risks for the ecosystems surrounding their operations. These risks arise primarily from the amalgam burning stage, whereby mercury is vapourised, and the dumping of mercury-rich tailings into local rivers. This mercury release affects human health by causing serious diseases that may lead to death. From an environmental perspective, mercury has been reported to severely pollute river ecosystems, inevitably finding its way to food chains.

Due to these issues, alternative technologies such as borax smelting, the Gemini table, thiosulphate, cyanide, chlorine, and urea leaching, to name a few, have been developed or adapted over the years to substitute mercury. However, most of these technologies have not been successfully implemented in artisanal mining operations. This lack of success is primarily due to their complexity and high cost, making them unattractive to artisanal miners.

This study investigates the application of cyanide and thiosulphate leaching as alternatives to mercury amalgamation for the recovery of gold in ASGM operations. Although cyanidation is practiced in ASGM, in some regions, it is only employed to treat tailings from the mercury amalgamation process. This is undesirable due to the fact that exposing mercury to cyanide results in the mobilisation of elemental mercury found in the tailings as mercury cyanide. This project investigates gold extractions that can be achieved with cyanide and alkaline thiosulphate systems and compares the results to those of mercury amalgamation.

This investigation was undertaken by conducting leach experiments using cyanide at 1 g/L, 3 g/L and 5 g/L, and ammonium thiosulphate at 0.1 M and 0.5 M, on 3 ore samples originating from artisanal mining locations. The experiments were conducted using batch stirred tanks reactors and the operating conditions (T= 26°C, solids loading: 30%, particle size: --300 +150 µm) were selected to mimic as closely as possible the conditions of artisanal mining processes.

The findings of the study revealed that cyanide leaching was the better performing technology compared to thiosulphate leaching as it achieved gold extractions of 71.6%, 69.7% and 67.8% for the 3 ores samples (Sample 1, Sample 2, and Sample 3, respectively) while thiosulphate leaching achieved gold extractions of 54.1%, 35.6% and 38.0% for the 3 ores, respectively.

Studying the minerology of the ores, using XRF, XRD, QEMSCAN, SEM-EDS and diagnostic leach, revealed the presence of sulphide minerals hosting refractory gold which contributed to the low gold extractions observed. Cyanide leaching proved to be a system that is easier to control compared to thiosulphate leaching, making it much more attractive to artisanal miners. It is recognised that cyanide is a toxic chemical, however, the method is already practiced in ASGM and cannot be simply wished away. Instead, steps must be taken for its safe and responsible use. Hence, this research makes recommendations on avenues that can be explored to reduce the risks associated with cyanide use.

It was also found that cyanide leaching outperformed mercury amalgamation which typically achieves gold recoveries of 30-50%. Thiosulphate leaching may be capable of achieving better gold recoveries than mercury amalgamation as well, as one of the ore samples achieved a gold extraction of 54.1%. However, this would depend on the ore type and reagent conditions as it was found that the 3 ore samples responded differently to leaching.

Nomenclature

Abbreviations

ASM	Artisanal and small-scale mining
ASGM	Artisanal and small-scale gold mining
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectrometry
LSM	Large scale mining
LOI	Loss on ignition
MP-AES	Microwave Plasma - Atomic Emission Spectroscopy
PSD	Particle size distribution
ppb	Parts per billion
ppm	Parts per million
QEMSCAN	Quantitative Evaluation of Minerals by Scanning electron microscopy
SADs	Strong acid dissociable cyanide complexes
SEM-EDS	Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy
tph	Tonnes per hour
USD	United States Dollar
WADs	Weak acid dissociable cyanide complexes
XRD	X-ray diffraction
XRF	X-ray fluorescence
ZAR	South African Rand

Chemical formula

Ag	Silver
Au	Gold
Ca	Calcium
Co	Cobalt
CN^-	Cyanide ion
Cu	Copper
Fe	Iron
Hg	Mercury
Mg	Magnesium
Na	Sodium
Na_2CO_3	Sodium carbonate
$Na_2S_2O_3$	Sodium thiosulphate
$NaHCO_3$	Sodium bicarbonate
NaOH	Sodium hydroxide
NaCN	Sodium cyanide
NH_3	Ammonia
NH_4^+	Ammonium
$(NH_4)_2S_2O_3$	Ammonium thiosulphate

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1. Introduction

1.1. Background to study

Artisanal and small-scale gold mining (ASGM) refers to operations that make use of rudimentary techniques to mine and process gold. The scale of operation and ore type can vary greatly; however, it is the low-tech nature of processing that qualifies it as artisanal (Veiga, 1997). For the purposes of this research, this will be the set definition although it must be acknowledged that, due to modernisation and the visible migration of skilled people into the sector, there are operations that employ basic mechanisation. The artisanal mining sector, as a whole, represents a source of livelihood for ~43 million people worldwide (Delve, 2020). Although the majority of miners in the sector are involved in industrial/construction minerals, about 15 million miners process ores that contain precious metals such as gold (Davies, 2014, Veiga et al., 2014b).

ASGM operations are typically conducted on underground, hard-rock primary deposits while in some regions, operations focus on secondary gold ores such as placer gold (alluvial, eluvial or colluvial material) which results from the liberation of gold during millions of years of weathering and hydraulic transport. This mechanism of gold placement contributes greatly to the success of ASGM operations since the ore is in a loosely agglomerated state, allowing for considerable savings in crushing and grinding (Marsden and House, 2009). ASGM operations are also quite often conducted in old gold mine shafts and mines that have been closed for reasons of poor safety, environmental regulations and low rate of return, however, still contain exploitable amounts of gold (Ledwaba and Mutemeri, 2018).

ASGM provides ~20% of the world's gold supply and the primary gold recovery method is mercury amalgamation. This technology is governed by the strong electrostatic force between electrons in mercury and gold which causes them to form a crystal lattice resulting in an alloy of the two compounds (Veiga, 1997). This alloy is called a gold-mercury amalgam. Processing methods can vary greatly in ASGM depending on the location and conditions in place, however, in a typical operation, as in Mozambique for example, the ore is first crushed in a mortar and pestle, then milled in a ball mill along with mercury for about an hour. Following this, the mill discharge is panned in rivers or open pits to remove gangue. The amalgam is then collected in a cloth and squeezed out to remove excess mercury before being burned in an open flame to vaporise mercury and obtain sponge gold (Drace et al., 2012, Ledwaba and Mutemeri, 2018, Veiga et al., 2014b). Alternatively, a variation of the process consists of coating copper plates with mercury which then amalgamates the gold as the ore is transferred down the plates. Mercury amalgamation is very popular amongst artisanal miners due to its simplicity and low cost (Veiga, 1997).

The use of mercury, however, presents very serious health and environmental risks. With an exception made for its metallic form which has a low solubility (64 µg/L) and poor absorption in the human gastrointestinal track (Veiga, 1997), mercury can be ingested by the human body in two primary ways: Firstly, during amalgam decomposition, typically conducted by burning in an open flame without condensers or retorts, Hg vapours are released directly into the atmosphere and can easily find their way into human lungs. In the respiratory tract, mercury is oxidised into Hg(II) complexes which can be absorbed by bodily fluids. From that point onward,

it can affect the kidneys after moderate exposure and, after long term exposure, cause serious damage to the nervous system which can lead to death. In the case of children in particular, stunted physical and mental development are key manifestations of nervous system damage (Appel and Na-Oy, 2012). Secondly, when tailings are dumped into water streams, a process called methylation occurs. In this process, mercury reacts with organic acids found in water forming methylmercury (Me-Hg) which pollutes the water and can be absorbed by fish. From there, Me-Hg easily finds its way into the human body from the consumption of fish and river water. It is estimated that the ASGM sector uses about 1400 tonnes/year of Hg which is virtually never recycled (Appel and Na-Oy, 2012). Hg emissions generated by the ASGM sector alone represent ~37% of all anthropogenic Hg released into the environment (Davies, 2014).

Furthermore, mercury amalgamation has been viewed as a one size fits all technology solution despite that ASM, just like other mining sectors, is extracting complex and mixed grade ores especially in the case of mining in disused/abandoned mines.

One of the major actions taken against mercury use was the UN Minamata Convention on Mercury. The text of the convention was signed in Japan, in 2013. The main objective set by the convention was to control and reduce the use of mercury in products and in industry with the goal of completely phasing it out by 2030 (Davies, 2014). This is discussed further in section 2.4.3. As much as this objective is noble, it would be difficult to realise if there are no viable technologies to replace mercury amalgamation. In addition, just as countries strive to completely phase out mercury as agreed at the Minamata Convention, thousands of people are driven to the sector every year due to economic hardship which has been worsened by the current Covid-19 pandemic. This ultimately leads to even more mercury emissions.

Given the concerning issues associated with mercury amalgamation, a few alternative methods shown in Table 1 (Davies, 2014, Grosse et al., 2003, Veiga et al., 2014a) have been developed or adapted over the years. These technologies are discussed in detail in section 2.3.2. The list of alternative methods provided in Table 1 is non-exhaustive.

Table 1: Alternative gold recovery methods

Method	How it works	Criticism
Gemini table	One direction shaking table, able to achieve rich gold concentrates without the use of mercury.	Cost per unit is ~8000 USD which is quite expensive for ASGM type of operations.
Sluice boxes	Use eddy currents to separate out gold from gangue. Easy to use and have low operating costs.	Require lots of hand sorting which is time consuming especially if large quantities of material are to be processed.
Centrifuges	Use gravitational force to initiate the separation of gold from gangue.	Expensive, have high electricity consumption and water requirement to prevent compaction of material.

Magnets	Particularly useful when the gangue contains iron to take advantage of its magnetism to separate out the gold.	Limited by the fact the that the ore must contain enough iron to induce magnetic separation.
Cyanidation	Uses cyanide as lixiviant. Has been found to be very effective for gold extraction with reported recoveries of ~95%.	Slower process compared to amalgamation. In addition, its use in conjunction with amalgamation results in the formation of mercury cyanide which is a toxic pollutant.
Borax smelting	Uses sodium tetraborate ($Na_2B_4O_7.10H_2O$) to lower the melting point of minerals allowing gold to accumulate at the bottom of the crucible to be easily removed.	Sophisticated process requiring significant training which could discourage artisanal miners who would rather use that time to secure their income with the tried and tested mercury amalgamation.
Thiosulphate leaching	Uses thiosulphate as lixiviant. Has low toxicity and is cheaper than cyanide. Has shown good results particularly in gold extraction from carbonaceous ores.	Presents issues of availability in remote areas as well as its requirement for pH and Eh control.
Chlorine leaching	Process developed by MINTEK called iGoli gold extraction system. Has shown good results with recoveries of up to 98%.	Critiqued for being too technical, and silver, which in many cases is found with gold, cannot be recovered since the presence of chlorine causes the formation of AgCl, a precipitate.

1.2. Problem statement

Despite the existence of mercury-free gold processing techniques (Table 1), their disadvantages or complexities result in mercury amalgamation prevailing due to it being relatively easy to apply and its low capital requirement. However, the inefficiencies of this method lead to poor gold recoveries which result in low profit margins for miners and ineffective use of gold deposits, representing a wastage of natural resource. This ultimately contributes significantly to poverty traps given the hand-to-mouth nature of ASGM.

In order to ensure viability of the ASGM sector, there is a need for technologies that are inexpensive, easily applicable, safe, environmentally friendly, and efficient in terms of gold recovery. It is quite difficult to achieve all of these requirements simultaneously since, in the mining industry, efficiency with safety and environmental safeguards rarely go hand in hand

with inexpensiveness. However, if such technologies could be developed, they would have a tremendous impact on the overall status and acceptance of the sector which is heavily criticised due to its safety and environmental impacts. This would ultimately lead to significant economic growth for artisanal miners and contribute towards the realization of the sustainable development goals (SGDs) 1,3,6,8,10 and 14 which aim to alleviate poverty, promote economic growth, good health, and preservation of the environment.

Cyanidation has the potential to be a suitable medium to long-term alternative to the mercury process in ASGM. This is due to the fact that it achieves high gold extractions and is a technology that quite a few artisanal miners are already familiar with since, in some regions, they have demonstrated a technical ability to employ the technology in vat and mill leaching of amalgamation tailings. It should be mentioned that this practice increases the mobilisation of mercury in rivers in the form of hazardous mercury cyanide complexes. Some examples of the application of cyanidation in ASGM are presented in section 2.5.1.4. In addition to the existing familiarity with cyanide, this technology can take advantage of the fact that much higher ore grades (10 g/t and higher) are often found in ASM compared to large-scale mining (LSM). Cyanide leaching is a well-studied technology in LSM, however, in the context of ASGM, more research needs to be done to understand the factors that affect the gold extraction process on actual ores found in ASM areas so that the technology can be directly compared to Hg amalgamation. More research is also needed to develop a method of cyanide disposal post leaching that is environmentally friendly and cost effective in the context of ASGM. Another promising technology is thiosulphate leaching which has shown promising results in terms of gold extraction. In addition, thiosulphate presents the advantage of being relatively safe and less toxic compared to cyanide (Aylmore, 2016), which is particularly important for ASGM where leakages of chemicals to the environment are more common. However, the technology still requires more research into reducing thiosulphate decomposition in aqueous solutions. This decomposition leads to challenges with hindered dissolution of gold due to a build-up of sulphur on the gold surface.

1.3. Objectives

Given the aforementioned challenges, the aim of this study is to investigate the application of cyanide leaching and thiosulphate leaching as alternatives to mercury amalgamation for the extraction of gold in the ASGM context.

This research aims to generate knowledge by addressing the following objectives:

- Contextualise the study by providing a socio-economic background of ASGM.
- Investigate and compare gold extractions that can be achieved by cyanide leaching and thiosulphate leaching.
- Compare process performances of the two alternative methods to mercury amalgamation in terms of gold extractions achieved.

Some of the key questions to be answered are:

- What is the impact of minerology on leaching with both cyanide and thiosulphate?
- What are the effects of varying the cyanide concentration in cyanide leaching?
- What are the effects of varying the particle size in cyanide leaching?
- What are the effects of varying [NH_3] and [Cu(II)] in thiosulphate leaching?
- How fast can gold be recovered in ASM with cyanidation and thiosulphate leaching compared to mercury amalgamation?

2. Literature review

2.1. Gold minerals

The method of extraction of any metal, in this case gold, from any ore body in which its concentration has been determined high enough for profitable extraction, depends heavily on the characteristics of the ore, and the mineral associations and phases within it. These characteristics are unique for each gold ore due to variations in the mode of occurrence of the deposit, size distribution of gold particles, type of host and gangue minerals and their associated size distribution, potential mineral alterations and more (Marsden and House, 2009).

The concentration of gold in the earth's crust is estimated at 0.003-0.005 g/t which is far lower than many other metals such as silver with a concentration of 0.07 g/t. Due to this low concentration, gold needs to be significantly upgraded (by an estimated factor of 3000-4000) by natural processes for it to reach concentrations high enough to make its commercialisation viable. Such natural processes include natural gravity concentration during ore formation processes as well as natural leaching by strong oxidising and acidic solutions which would cause the gold to be more concentrated after redeposition.

Gold is a siderophile compound meaning that it has a strong affinity for metals hence during rock formation, it is mainly associated with metallic phases, hydrothermal solutions as well as sulfidic phases. The gold contained in these hydrothermal solutions re-precipitates when these fluids come into contact with regions of high carbon or sulphide content which provide a reducing environment (Marsden and House, 2009). For example, during ore formation, gold precipitates after the hydrothermal solutions hosting it come into contact with pyrite according to the following reactions:

$$4\ FeS_2 + 6H^+ + 4\ H_2O \leftrightarrow 4\ Fe^{2+} + 7\ H_2S + SO_4^{2-} \quad [1]$$

$$AuCl_2^- + \frac{1}{2}H_2 \leftrightarrow [Au] + 2\ Cl^- + H^+ \quad [2]$$

$$AuCl_2^- + Fe^{2+} \leftrightarrow [Au] + Fe^{3+} + 2\ Cl^- \quad [3]$$

Gold mostly occurs in nature as a native element often found in association with silver. It does not commonly occur in oxides, sulphides and carbonates as opposed to most other metals and because of this, processes and technologies that selectively extract gold can be developed.

2.1.1. Native gold

Native gold typically contains about 85%-95% gold with the balance being, in most cases, silver. Native gold has a density of 15,000 kg/m^3 while gangue minerals found in association with it such as silicates have densities around 3,000 kg/m^3. This difference in densities offers a significant advantages for the recovery of gold in the sense that gravity concentration may be efficiently applied (Marsden and House, 2009).

When the proportion of silver found in association with gold is much larger (25%-55%), the mineral form in which gold occurs is referred to as electrum. It has a much lower density than

that of pure gold and the typical yellow colour of gold looks more pale as an expression of the high silver content (Macdonald, 2007).

2.1.2. Gold associated with sulphides

In sulphide minerals, gold is found within the structures of the sulphide mineral grains in the form of ultrafine solid solutions (example showed in Figure 1).

Typical gold grades in sulphide minerals are shown in Table 2.

Table 2: Gold content in sulphides (Marsden and House, 2009)

Mineral	**Grade**
Chalcopyrite	<0.2 – 7.7 g/t
Tetrahedrite	<0.2 – 72 g/t
Pyrite	<0.2 – 132 g/t
Arsenopyrite	<0.2 – 15,200 g/t

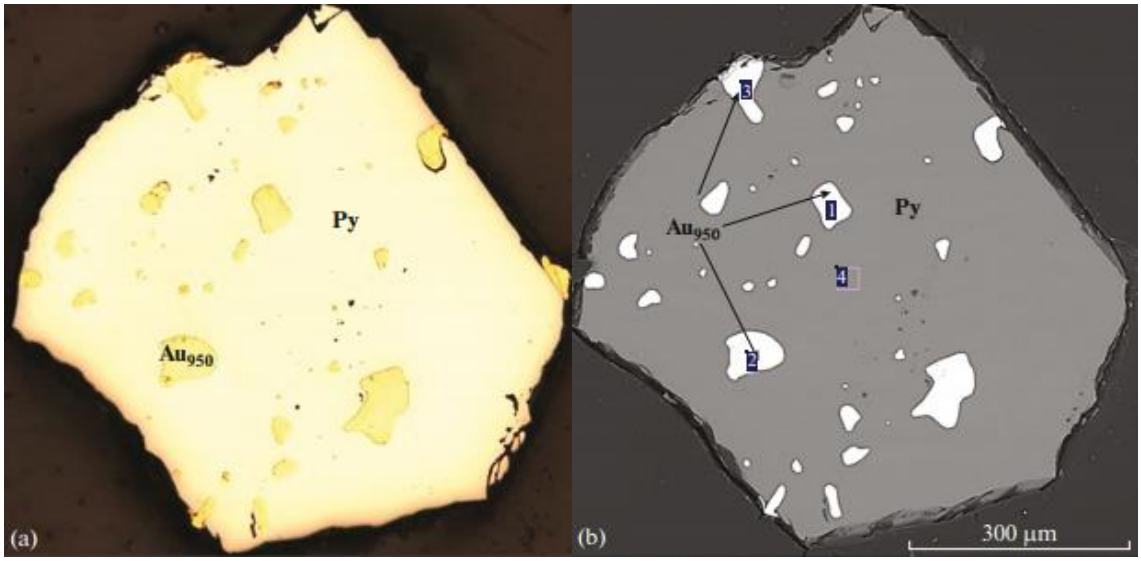

Figure 1: Gold inclusions in pyrite (a) optical image (b) SEM image (Palyanova, 2020)

It is important to understand this particular type of gold occurrence because, due to the occurrence of gold as solid solutions in these minerals, recovering the gold may become quite challenging particularly in the ASM context. This is discussed in section 2.3.4.

2.1.3. Gold tellurides and other gold minerals

Sylvanite ($(Au,Ag)_2Te_4$), petzite (Ag_3AuTe_2) and calaverite ($AuTe_2$) are the most commonly occurring gold tellurides. Gold has also been occasionally found in association with copper: auricupride ($AuCu_3$) and tetra-auricupride (AuCu) in which the gold content is typically less than 50%. Another rare occurrence is gold associated with bismuth forming the mineral called maldonite (Au_2Bi) which has been known to respond poorly to cyanidation.

2.2. Gold primary ores

2.2.1. Placer gold deposits

In these deposits, weathering and erosion are the primary agents that cause the liberation of gold. Once gold is liberated, gold particles are displaced from the primary deposit via hydraulic transport. The reason why this is possible at all, has to do with the inert and dense nature of gold. The primary deposit could be a gold-rich sulphide deposit or gold-quartz veins. It is important to highlight that these processes take time; weathering, erosion, hydraulic transport, and re-accumulation (concentration) of the gold particles and sediments take millions of years. And even when this is done, there needs to be a stable environment and bedrock to ensure that the gold accumulates in substantial amounts (Marsden and House, 2009).

Depending on how far the gold particles re-accumulate after being transported, different types of placers exist, of which the most important are:

- *Eluvial placers*: These placers are typically found closer to the parent rock and have been subjected to some level of weathering although less significant than the other placers leading to a lower gold grade in these types of placers.
- *Colluvial placers*: These placers are found much further from the parent rock meaning that the gold has been transported significantly and mostly found in the slopes surrounding the parent rock.
- *Alluvial placers*: They are found within water systems. The gold tends to accumulate in zones of slow current and underneath obstructions which can be in the form of potholes due to a sudden change of level of the riverbed, for example.

2.2.2. Free-milling ores

Free-milling ores are ores that can be readily treated by cyanidation and extractions as high as 95% can be achieved. These ores include primary palaeoplacers and quartz veins gold ores (Marsden and House, 2009).

2.2.2.1. Palaeoplacers & quartz-gold veins

Palaeoplacers are formed as a result of lithification which is a process by which a solid rock is formed by pressurised compaction and cementation of sediments. The sediments that consolidate to form palaeoplacers consist primarily of quartz, pyrite, micas, magnetite, platinum group metals and gold. One prominent example of a palaeoplacer is the Witwatersrand lakebed reef. Unlike alluvial placers, palaeoplacers are consolidated ores with gold unliberated. As a result, it is mandatory to crush and mill the ore, which is often hard to achieve due to the high quartz content, to sufficiently expose and liberate the gold for viable commercialisation (Marsden and House, 2009, Northern Miner, 1998).

Quartz-gold veins are volcanic hydrothermal veins in which gold and quartz are deposited mostly to occupy empty pockets of space along zones of rock fractures. The primary types include auriferous veins and gold-silver veins.

2.2.3. Oxidised ores

These are ores that have been strongly altered by weathering and hydrothermal fluids resulting in oxidation of the ore material. In these ores, gold is either liberated, which is directly proportional to the level of oxidation that has occurred, or present in association with geothite, magnetite and hematite which are oxidation products of sulphide minerals such as pyrite. Oxidised ores are known for their high permeability due to the structure of the ore being attacked and broken down by the oxidation processes. This increased permeability presents the advantage of achieving high gold extraction in heap and in-situ leaching operations.

2.2.4. Iron sulphides

2.2.4.1. Pyrite

Pyrite, also known as “fool’s gold” due to its yellow colour and metallic luster, is the iron sulphide mineral most widely found in association with gold. It also has a high stability in aqueous media (Marsden and House, 2009, The Editors of Encyclopaedia Britannica, 2019).

Pyrite has a high standard reduction potential and, for this reason, requires strong oxidising conditions for effective gold leaching via cyanidation. Under mildly oxidising conditions, it is unreactive and poor gold extraction is achieved especially if the gold exists as fine inclusions or solid solutions within the mineral grain. Its unreactivity may however, be an advantage if the gold is coarse and easily leachable by cyanide because pyrite does not undergo any side reaction with cyanide. Therefore, pyrite only becomes a problem if it hinders the liberation of gold existing within it as fine inclusions. As a remedy, it is typical to apply rigorous grinding and strong oxidising conditions. There are many ways in which gold may associate with pyrite and sulphide minerals in general, the different types of associations are shown in Figure 2. For types 1, 2 and 3, the gold can be easily extracted after adequately crushing and milling the ore while for types 4, 5 and 6, the gold might remain locked and require other techniques such as an oxidative pre-treatment step to increase extraction (Marsden and House, 2009).

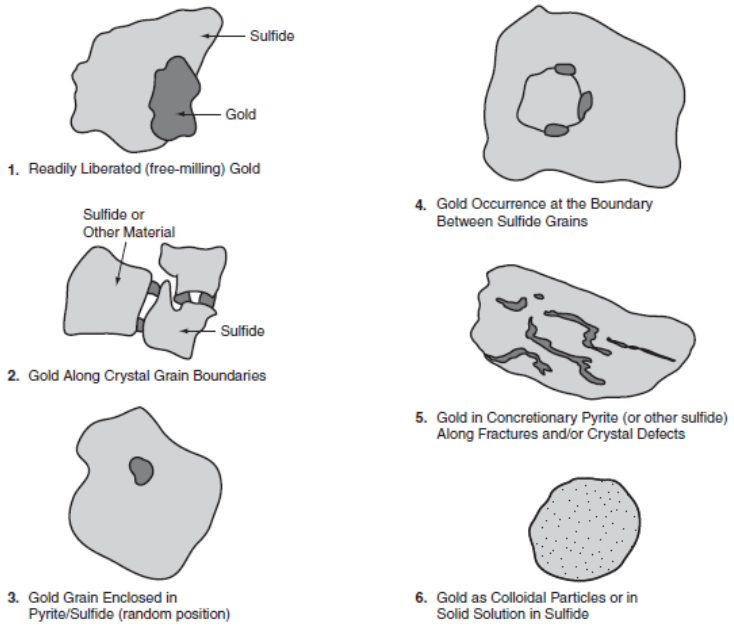

Figure 2: Gold associations in sulphide minerals (Marsden and House, 2009)

2.2.4.2. *Other types of iron sulphides*

These include mainly pyrrhotite ($Fe_{1-x}S$, x: 0 to 0.2) and marcasite (FeS_2) which can sometimes represent a considerable proportion of sulphide ores (up to 30%). The main consideration when it comes to these minerals is that, in cyanide leaching, they both significantly consume cyanide and oxygen, which is a serious issue to which oxidative pre-treatment has been found as a solution (Deschênes et al., 2003, Marsden and House, 2009).

2.2.5. Arsenic sulphides

2.2.5.1. *Arsenopyrite*

After pyrite, arsenopyrite is the second most common sulphide found in association with gold. The highest gold grades are found in arsenopyrite and Chryssoulis and Cabri (1990) have shown a direct proportionality between the gold grade and the amount of arsenic in pyrite. Gold and arsenopyrite share similar crystal chemistry and temperature of formation and because of this, more inclusions of gold as solid solutions are found in arsenopyrite compared to pyrite. Having said that, subjecting sulphide minerals to high temperatures as a result of a geological event can lead to a migration of the gold particles to the surface of the mineral grains and various fractures (Chryssoulis and Cabri, 1990, Marsden and House, 2009).

2.2.5.2. *Other arsenic sulphides*

Other notable arsenic sulphides are realgar (As_2S_2 or AsS) and orpiment (As_2S_3) which can be found in small amounts in many gold ore deposits that are already being exploited commercially. Orpiment is soluble in cyanide meaning that it may increase reagent consumption and, at the same time, leave behind undesired arsenic compounds in the leach solution. Realgar on the other hand does not impede cyanidation of gold particles.

2.2.6. Copper sulphides

Gold is rarely found solely in these ores. In almost all cases, pyrite is present in association with copper sulphide ores and together host the gold. Although the gold is typically of very low grade in copper sulphides (> 1 g/t), during ore processing, gold has a tendency to report with chalcopyrite and bornite as opposed to pyrite creating the opportunity to sell copper concentrates with a high gold content at a price just slightly under that of gold (90-97% gold price) (Organisation for Economic Co-operation and Development (OECD), 2017). Additionally, due to the fact that copper ores are typically processed at high tonnages, by-product gold production can be significantly large. Copper ores account for about 80% of all gold produced as by-product (Marsden and House, 2009).

The most important gold-bearing copper sulphide ore is chalcopyrite ($CuFeS_2$) which is typically found with pyrite and other sulphides. Secondary ores include chalcocite (Cu_2S), covellite (CuS) and bornite (Cu_5FeS_4) which are typically found in supergene sulphide enrichment zones which are zones where sulphides in deeper regions are upgraded or enriched by the deposition of valuable dissolved metals that are carried by aqueous fluids originating from the oxidation or weathering of the superficial zone of the ore deposit (hypogene) (Marsden and House, 2009, The Editors of Encyclopaedia Britannica, 2011).

2.2.7. Tellurides

These include maldonite, calaverite, krennerite, hessite and petzite as the primary tellurides found in gold ores. They are of high significance from an economic standpoint due to their high gold and silver content (12% - 44%) some of which occurs as native gold. Gold tellurides occur in the following geological settings (Gillen, 1982, Marsden and House, 2009):

- *Veins and fissures in tertiary rocks:* They mostly consist of quartz and carbonate minerals with dominance of krennerite over other tellurides which are all present as crystalline fine grained minerals. These veins exist in an environment where the wall-rock has been altered aggressively by water, carbon dioxide and sulphur. Native gold is quite rare in these veins while native tellurium exists in abundance.
- *Metamorphosed volcanic lava:* This ore type is significantly affected by structural deformation and experiences changes in mineral composition as a result of cooling of high-grade metamorphic rocks (retrograde metamorphism). As opposed to veins, they have a high native gold content while native tellurium is much less abundant and the predominant mineral form is calaverite over krennerite.

An important element to note about gold tellurides is that, in practice, they respond poorly to cyanide leaching and require to be oxidised first before leaching.

2.2.8. Carbonaceous ores

The main components of carbonaceous ores are hydrocarbon, humic acid and activated carbon, however their exact nature and mechanisms are still not well understood. The fact remains that, despite their relatively smaller surface area compared to pure activated carbon, carbonaceous material, with a carbon content as low as 5% in some ores, can significantly impede gold extraction (Afenya, 1991, Marsden and House, 2009).

Key to note about carbonaceous ores is that they contain organic material, called preg-borrowing or preg-robbing that can respectively absorb reversibly or irreversibly dissolved gold particles during leaching, resulting is poor gold extraction, particularly in cyanidation. For this reason, oxidative pre-treatment needs to be applied as well before leaching (Afenya, 1991).

2.3. Processing practices in ASGM

2.3.1. Main process flowsheet

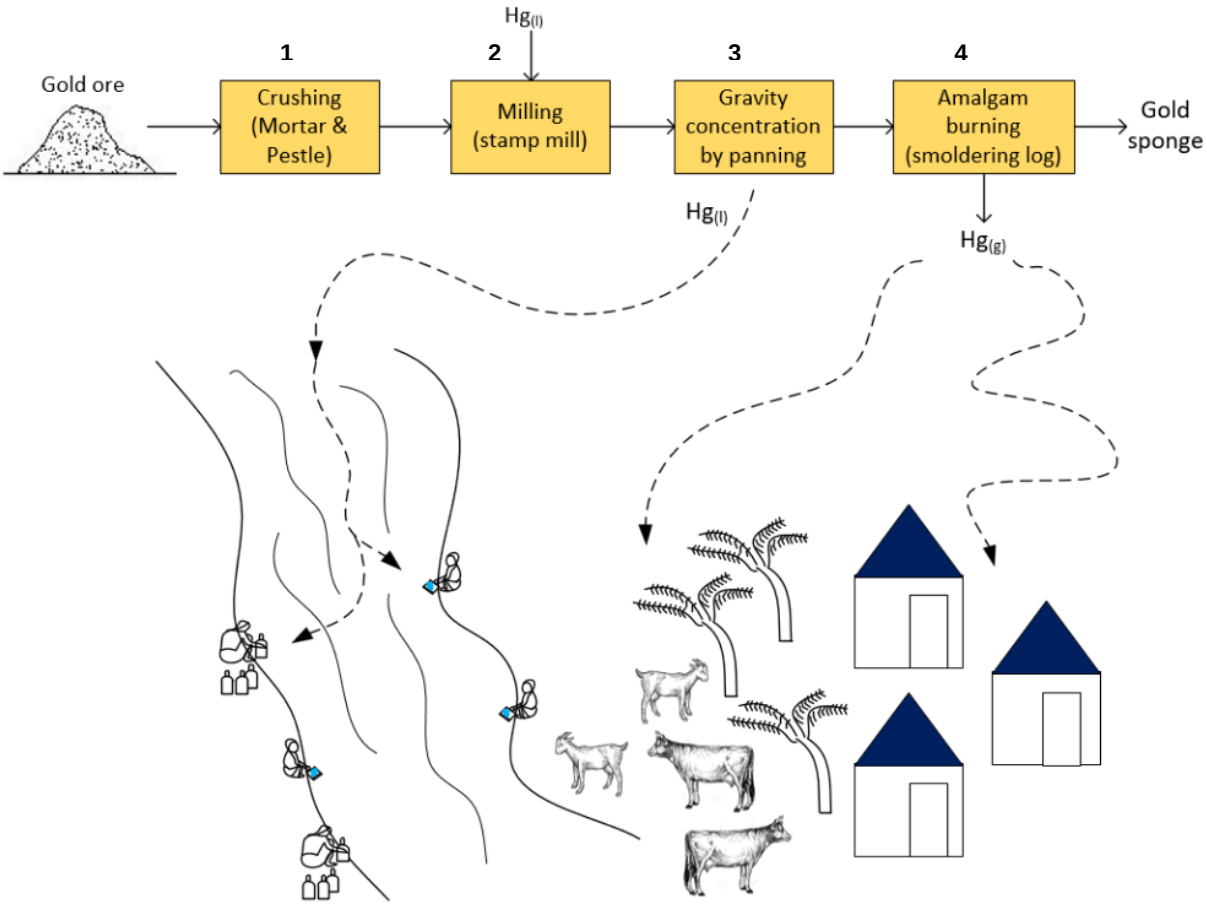

Figure 3: ASGM process flowsheet

The standard process for gold extraction in ASGM is presented in Figure 3, although the type and quality of equipment used may vary depending on the scale and capital invested in a particular operation. The process typically consists of (Figure 3) (Drace et al., 2012):

1. Mining the ore which can amount to tonnes depending on the size of the deposit. Ore mining is typically done by digging (10 m or deeper depending on the deposit) and manually or mechanically hoisting the ore in buckets. The ore is then crushed with a mortar and pestle as the first reduction step. In other cases, crushing by hand with a sledgehammer is also done.
2. Milling using a mill that is often specific to ASGM operations in a given country. For example, in Chile, the Chilean wet pan mill is often used while in Zimbabwe, toll milling is famous and currently used in many other countries in Africa as well. It is in this step that most miners introduce mercury in what is known as whole ore amalgamation.
3. Removing impurities contained in the mill discharge by panning the ore with water.
4. Burning off Hg in an open flame to obtain a gold sponge that can be either further refined or sold as is. The vapourised Hg is simply released into the atmosphere and mobilised to rivers and households, creating a serious source of Hg contamination for communities surrounding ASGM areas.

2.3.1.1. The issue with whole ore amalgamation

This method consists of simultaneously milling the ore and amalgamating it with mercury, whereas, ideally, the ore would first be milled, then concentrated using a gravity technique such as panning, and only after this step, be amalgamated with mercury. Whole ore amalgamation is a problem in that gold is not concentrated in its ore. And thus, when mercury is introduced to the whole ore, gangue materials such as clay minerals cause mercury to oxidise and lose its ability to bind effectively with gold. This process is known as mercury sickening. In addition to that, another process known as mercury flouring takes place and further impedes the amalgamation process. Mercury flouring is described as the dispersion of mercury into small droplets due to lack of coalescence (Veiga et al., 2014a).

Figure 4: Mercury droplet called "mercury flour" in tailings sample (Appel and Na-Oy, 2012)

Whole ore amalgamation can be applied in conjunction with other methods such as milling quickly followed by amalgamation using copper plates, whereby the copper plates are coated with mercury to instantly amalgamate the gold contained in the ore coming from the mill discharge (Veiga et al., 2014b). Copper plates are used due to the attraction of mercury to copper. This allows mercury to form a thin coating on the plates which can be scrapped off after amalgamating the gold.

About 46% of Hg introduced in mills is lost during whole ore amalgamation, before the amalgam burning stage (Veiga et al., 2014b). These droplets of mercury formed in the process are dumped with the tailings in river waters resulting in severe contamination as depicted in Figure 3.

2.3.2. Alternative technologies to Hg amalgamation

2.3.2.1. Gravity methods

Gemini table

It is a shaking table with a steel frame and a top surface made of fiberglass that moves in one set direction (Figure 5). The top surface has grooves that are designed in a unique fashion to efficiently trap gold particles. The speed can be varied depending on the ore treated. It produces high purity gold concentrates and is particularly effective on black sands that contain gold. The pre-concentrate is typically -20 mesh material. The common Gemini table can process a maximum of 27 kg ore/h and requires clean, constant and reliable water supplied at a constant feed pressure (Vieira, 2006). The GT60 Mk2 is the most common Gemini model.

Figure 5: Gemini table (911Metallurgist, n.d.)

- **Pros:** It produces gold concentrates of high purity that can be smelted straight away.
- **Cons:** The most significant disadvantage is its high cost, estimated at around 8,000 USD. Gemini tables require electricity and a reliable water supply to operate optimally which might be an issue in water scarce regions.

Sluice box

Sluice boxes are widely used in ASGM operations. This is mainly due to their ease of operation and affordability, especially when it comes to operating costs. They use an eddy current, that is formed as water flows through the sluice, to separate gold from gangue particles. Due to the higher density of gold, it will get trapped under the riffles while the gangue flows through with the water. They are equipped with mats below the riffles to hold the trapped gold; however, some gold is still lost as typical sluices in artisanal mining have a gold recovery efficiency of ~50% (Mitchell et al., 1997). To improve gold recovery, artisanal miners modify either the angle of the riffles or the sluice box itself or vary the feed flowrate. High recoveries are typically obtained at slurry flowrates in the range 250-1400 kg/m/min (Vieira, 2006). It is also important to carefully time mat clean up to prevent accumulation which might lead to further gold loss.

A notable example is the Cleangold sluice (Figure 6). This type of sluice is made of aluminium and has magnetic sheets that are specifically designed to trap magnetite, found in abundance

in gold placer deposits, which effectively holds fine gold that sits trapped below it (Davies, 2014, Vieira, 2006). The magnetite can then be easily scraped off the sluice into a pan after which magnets can be used to remove it, leaving behind a gold concentrate of high grade.

Figure 6: Cleangold sluice (Vieira, 2006)

- **Pros:** Easy to use, low cost (40–160 USD).
- **Cons:** Requires lots of hand sorting which can be time consuming.

Centrifugal concentrators

There are two main types of centrifugal concentrators, namely the Knelson concentrator and the Falcon concentrator (Figure 7). For ASM, the most suitable models are the Falcon B6 and Knelson 7.5 inches. This is due to their smaller capacities of 0.5 tph and 0.64 tph, respectively, which are more in line with the ore quantities processed in many ASM operations compared to other centrifuges such as the Icon 150 (Capacity: 2 tph) (Davies, 2014, Veiga and Gunson, 2020). The governing principle in these machines is the use of gravitational force to initiate the separation of gold from less dense gangue material.

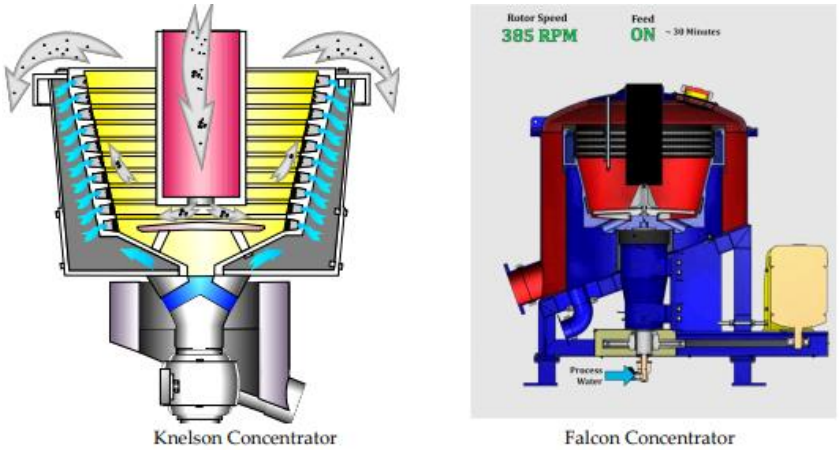

Figure 7: Knelson and Falcon concentrators (Veiga and Gunson, 2020)

Both concentrators have a rotating vessel which, in the case of the Knelson concentrator, has riffles (curved edges) along the wall of the cone. In the case of the Falcon concentrator, the riffles are found only in the upper vertical portion of the wall while the lower conical section is smooth. This difference in design is the fundamental reason for the different ways in which the

ore is fed in both of these devices. In the Knelson concentrator, the ore is fed directly into the fluidisation zone which is the high speed zone inside the bowl. This mean that the movement of gold particles is governed by the water flow which can be a problem in the sense that the smallest gold particles might remain within the feed flow instead of entering the IRS (inter-riffle spaces) and be lost. In the Falcon, the ore is fed into the segregation zone, situated along the conical section of the wall, which is a zone where the heavy particles segregate from the light particles (gangue) by forming a bed below them. It is only after this that the segregated heavy material enters the fluidisation zone. Due to this design, the heavy particles (gold in particular) which are in contact with the wall of the bowl can remain trapped within the IRS limiting the possibility of gold loss. For this reason, the Falcon concentrator tends to achieve recoveries higher than the Knelson (up to 100% for the Falcon and 90-95% for the Knelson (Ancia et al., 1997, Vieira, 2006)).

- **Pros:** They achieve high gold recoveries and due to the gravitational force utilised, they are able to achieve these recoveries at particle sizes as low as 38 µm (or even smaller). This is a general challenge that gravity based separation methods face whereby separation starts to become poor at particle sizes below 100 µm (Ancia et al., 1997).
- **Cons:** They are expensive (~4,000 USD (Veiga, 2008)), have a high water and electricity consumption and require a high level of skill to be operated efficiently. These challenges apply particularly to informal ASGM operations while small-scale operations may consider making the investment.

It is important to note that, in ASGM, gravity separation methods are not always used as mere steps to prepare the ore for subsequent processes as it would be the case in large scale mining. In many instances, they are standalone pieces of equipment whose outputs (gold concentrates) are sold directly as is by artisanal miners. In that sense, they can be considered gold recovery technologies on their own and directly compared to other technologies such as leaching.

2.3.2.2. Cyanide leaching

Cyanide leaching is a highly effective substitute to amalgamation which can achieve high gold recoveries. The chemistry and applications of cyanide leaching are discussed in detail in section 2.5.1. As much as cyanide is a toxic compound, many processes have been developed over the years to either recycle it or destroy it. These are discussed in detail in section 2.5.1.5.

- **Pros:** It provides high gold recoveries (~95% and higher). In addition, the process may not require new equipment for miners as they can adapt their current equipment such as the mills used for whole ore amalgamation, resulting in significant savings on capital costs (Davies, 2014).
- **Cons:** Cyanide is a toxic chemical. The main health risks after mild exposure are nausea, headache, and shortness of breath and after severe exposure, hypotension, seizures and potentially death (Johns Hopkins Center for Health Security, 2011). Cyanide toxicity is exacerbated when artisanal miners, after removing impurities in step 3 in Figure 3, proceed to collect Hg contaminated tailings and leach out the remaining

gold with cyanide. This results in the formation of mercury cyanide, a highly hazardous compound, that is dumped in rivers.

2.3.2.3. Thiosulphate leaching

Thiosulphate leaching of gold has been investigated over the years as a potential substitute for cyanidation due to its low toxicity. A thorough study of the thiosulphate system is provided in section 2.5.2.

- **Pros:** It is able to achieve high gold recoveries (as high as 80%).
- **Cons:** The chemistry of the process is quite technical and complicated which may discourage ASM miners.

2.3.2.4. Thiourea leaching

Thiourea ($(NH_2)_2CS$) is a less toxic reagent than mercury and cyanide that can extract gold. It requires a highly acidic environment (pH= 1) and the presence of ferric sulphate to maintain the potential between 390 and 420 mV so that the dimer formamidine disulphate, which is the gold extractant, can be formed. Sulfuric acid (H_2SO_4) is often used to help reach the highly acidic pH (Eisele et al., 1988, Veiga et al., 2014a).

Eisele et al. (1988) conducted a study that compared cyanide leaching to thiourea leaching. At 2 g/L each, cyanide leaching outperformed thiourea leaching (~90% vs ~70% extraction) and when the thiourea concentration was increased to 20 g/L, it only barely outperformed cyanide leaching at 2 g/L for 2 of the 14 ores used in the study.

Thiourea may be a better lixiviant than cyanide only in the special case where an acidic environment is needed in order to simultaneously extract another metal such as uranium. Besides this, thiourea may also be used for the treatment of antimony concentrates bearing gold, in which case gold would be extracted first due to faster kinetics compared to antimony (Eisele et al., 1988).

- **Pros:** Less toxic than mercury and cyanide.
- **Cons:** Strong acidity is a challenge in low-tech applications.

2.3.2.5. Chlorine leaching

This technology predates cyanide leaching and was first applied in 1848. It was popular for recovering fine gold and gold in sulfidic ores which were resistant to gravity techniques and amalgamation. Its popularity declined after the introduction of cyanidation which was less expensive and technical making it more attractive to artisanal miners. A revived interest in this technology came about after cyanidation started receiving lots of criticism especially following a series of man-made environmental disasters, such as the ones involving millions of tons of cyanidation tailings being dumped into rivers resulting in the destruction of ecosystems (Vieira, 2006).

One of the key processes using this technology is the iGoli process developed by MINTEK, South Africa, which involves leaching a concentrate (> 1000 g Au/t) with hydrochloric acid (HCl) and chlorine (Cl_2), after which gold is precipitated from the pregnant leach solution by

treating it with either sodium metabisulphite ($Na_2S_2O_5$) or ferrous sulphate ($FeSO_4$). Other agents such as oxalic acid, sodium nitrate and zinc may be used as well (Veiga, 2008, Vieira, 2006).

The CETEM-saltem process developed in Brazil is another process which involves mixing a concentrate with sodium chloride (NaCl) 1 M (may use seawater as well) whereby NaCl is converted, by electrolysis, to sodium hypochlorite (NaClO) and sodium chlorate ($NaClO_3$) while a gold chloride complex ($AuCl_4^-$) gets deposited on the cathode. It is estimated that in 4 h, a gold dissolution higher than 95% can be achieved (Veiga, 2008).

- **Pros:** The hydrochloric acid and chlorine needed in this process can be easily sourced from a generic swimming pool acid (33% HCl) and bleach (12% NaClO) in the iGoli process (Veiga et al., 2014a).
- **Cons:** The process is quite technical making it difficult to apply in ASGM.

2.3.2.6. Borax smelting

This method exploits the ability of sodium tetraborate (borax) as a flux to lower the melting point of minerals. The first step in this process is concentrating the ore which is achieved by panning and sluicing after the size reduction steps (i.e., crushing and milling). Following this, the concentrate is mixed with borax at a 1:3 ratio as well other fluxing agents depending on the mineralogy of the concentrate. The mixture is placed in a crucible or a simple clay bowl, then heated using a blow torch. Some miners add charcoal inside the clay bowl and place the borax-concentrate mixture in a plastic bag (Figure 8a). By the action of borax, all the minerals present in the ore melt down and undergo oxidation with the exception of gold which, after melting, is unaffected by the oxidation reaction and separates out from the other compounds at the bottom of the crucible (Davies, 2014). Figure 8b shows a good depiction of the gold collecting at the bottom of the bowl.

a)  b) 

Figure 8: a) borax mixed with concentrate b) Melted concentrate (Appel and Na-Oy, 2012)

- **Pros**: Borax is a relatively safe chemical, it might cause minor irritation to the eye if poorly handled, however, it is generally considered safe and non-toxic. Smelting using borax takes about just as much time as amalgamation, such that miners do not have to wait longer compared to their conventional method. Appel and Jønsson (2010) have shown that borax smelting can achieve gold recoveries as high as 98% in a study that compared it to amalgamation which reached 88%. Appel and Na-Oy (2012) suggest that the process is cheaper compared to amalgamation.

- **Cons**: Borax smelting does not work well on sulphur-rich and fine grained ores, which makes it not versatile. Another key issue is that the process requires skill. This means that miners would need to be trained, which would take some convincing and trust.

2.3.3. Challenges presented by physical parameters

In ASM, physical process parameters such as pH, agitation and temperature are harder to control compared to LSM where processes are more sophisticated. The main reason for this is that having many physical parameters to control essentially translate to more costs for the operation. For instance, if a process requires a specific temperature to operate efficiently, a heat exchange system would need to be designed for that purpose which is an added cost. This is an additional reason why amalgamation is popular in ASGM, besides the fact that the process is not too technical, it is also not a sensitive process that requires many parameters to be controlled. Miners amalgamate at the temperature of the day with just enough agitation in their mills to contact the mercury with the gold particles in the case of whole ore amalgamation or simply use a pan and contact the mercury with the gold in the concentrate by hand.

Despite the fact that most alternative technologies require more control over these parameters, they have the potential to achieve higher gold recoveries than amalgamation which only recovers about 30-50% of the gold (Veiga et al., 2009). Therefore, the added revenue from the increased recovery can potentially offset the cost of additives for pH and Eh control, for example. However, if in the end when everything balances out, the alternative technology is not significantly better than amalgamation from a financial point of view, artisanal miners will not feel the urge to switch to it. It is, therefore, important, when investigating these alternative technologies in the context of ASGM, not to limit studies at how much more gold they can recover compared to amalgamation but how much ore gold they can recover with minimum sensitivity to physical parameters.

2.3.4. Ore mineralogy limitations

In the past, ASGM consisted primarily of picking gold nuggets on riverbeds and panning gold from alluvial deposits. However, today the sector has expanded to operations on open pits, underground mines and more. This means that artisanal mining techniques are being applied to more and more complex ore bodies that present significant mineralogical limitations as a result of lower gold grades and varying mineralogy. These limitations are a particular challenge in ASGM given the lack of mineralogical tools to better understand these ore bodies, meanwhile LSM benefits from such tools to recover gold from relatively low grade ores.

2.3.4.1. Arsenopyrite

If a gold ore has been determined to have a particular grade and arsenopyrite content, the entire amount of gold present could be existing as invisible solid solutions within the arsenopyrite mineral (Marsden and House, 2009). This would make it very challenging for artisanal miners to use either cyanide leaching or gravity concentration to recover gold from such an ore.

2.3.4.2. Oxidised ores

A major disadvantage of oxidised ores from a processing point of view is that, as a result of the alteration processes that they are subject to, they contain hydrated silica, clay minerals and gangue phases (oxide and hydroxide) in large amounts that become cyanide consumers due to their high solubility in cyanide. This unavoidably leads to high reagent consumption because less free cyanide is available to leach the targeted gold. Another key consideration about oxidised ores is that, due to the high clay minerals content, crushing and grinding leads to higher amounts of fine particles as opposed to other ore types such as free milling ores (Marsden and House, 2009). This is a particular problem for artisanal miners because fine grinding leads to loss of gold by gravity techniques.

2.4. Socioeconomics of artisanal mining

ASGM is source of livelihood for ~15 million people worldwide (Veiga et al., 2014b). It includes about 4.5 million women along with 600,000 children who are actively involved in gold mining activities (Drace et al., 2012). About 80 countries in the world have ASM operations taking place within their borders (Ledwaba, 2017).

Worldwide, the AGM sector produces around 300-400 t Au/year and accounts for 37% of all anthropogenic mercury emissions estimated at 1960 tonnes in 2010 (Veiga et al., 2014b). It is clear that the AGM sector is a significant contributor to the international gold trade, however it faces quite a lot of challenges, some of which along with proposed solutions are discussed in this section.

2.4.1. Challenges faced by artisanal miners

The intricacy and interconnection of the problems faced by the ASGM sector can be summarised by this statement quoted from Veiga (1997):

"*Researchers are interested in more research, economic groups are interested in properties discovered by artisanal miners, politicians seek for votes from environmentalists, Press wants sensationalism and miners do not care about pollution"*

All these issues feed into one another and ultimately work in cohort against the development of the sector.

2.4.1.1. Production

One of the major problems faced in the ASGM sector is the lack of knowledge on the dangers associated with the use of mercury amongst miners. As mentioned before, amalgam decomposition is typically done by burning off the mercury in an open flame. This results in the release of mercury directly into the atmosphere. Due to poor recycling of the mercury released, exorbitant amounts of mercury are required to keep up with production rates.

Another key problem that contributes to the high consumption of mercury is whole ore amalgamation, discussed in section 2.3.1.1., whereby the ratio of Hg used to Au produced is estimated at 5:1 (Hg:Au) (Telmer and Veiga, 2008).

ASGM operations are usually conducted on secondary gold ores which have formed as a result of centuries of weathering of primary gold ores. A high capital investment, which artisanal miners may not have access to, is required to profitably run operations on primary ores. When artisanal miners attempt to work with such ores, they quickly witness a drop in production level and when they seek help, mining companies are very reluctant to help. Companies with the engineering knowledge required have high consultation fees and university researchers usually propose advanced technical methods that are pricy and inaccessible to artisanal miners (Veiga, 1997).

2.4.1.2. Socio-economic and legislative status of ASM

Socio-economic

In South Africa, many of the current challenges faced by the mining industry have their roots in past injustices put in place and enforced by the apartheid regime. Historically Disadvantages South Africans (HDSAs) are still struggling to be active members of the mining economy and this is mainly due to past and current sizeable ownership of the mining industry and its profits by the rich minority (Ledwaba and Mutemeri, 2018). The structure of the mining laws in the apartheid regime was such that it asphyxiated the ASM sector by applying very restrictive laws and policies that mainly served the benefits of the LSM sector.

ASM only became recognised as a sector with the potential to empower HDSAs and possibly remedy the injustices of the past in South Africa as part of the Reconstruction and Development Programme (RDP) that came into effect after the transition to democracy, over two decades ago. Today, ASM is increasingly being considered as a sector that has a high potential to empower South Africans in the form of employment and entrepreneurship opportunities, mainly due to the poverty and high unemployment rates the country has faced over the last decade. The mining industry faced a net job loss of about 11,200 jobs in 2018 (Minerals Council South Africa, 2018) which is expected to increase due to the numerous challenges such as the significant fall of commodity prices (Ledwaba and Mutemeri, 2018).

Following an opposite trend to mining jobs, artisanal mining has grown significantly over the last two decades. The department of minerals resources has received numerous applications for mining licenses. However, it is difficult to estimate the exact number of artisanal miners involved in the sector since the majority operate without licenses. This includes mostly artisanal miners who run their operations in old mine shafts and closed mine dumps. This illegal mining is referred to as “zama-zama” mining. It is estimated that, over the last 10 years, about 30,000 people (SAHRC estimate) have been involved in illegal mining (Johnson, 2016).

Zama-zama mining is a major subject of debate amongst stakeholders. Despite its economic significance for HDSAs, it comes with a lot of crime due to gang violence, turf wars and unsafe working conditions. Johnson (2016) highlights that between 2012 and 2016, more than 300 miners have lost their lives as a result of these issues around violence and unsafe working practices. Figure 9 shows how drastically the causes of death in illegal mining have shifted over the years, noting that the overall number of casualties is higher in 2015. The numerous incidents that have been reported have tarnished the image of the ASM sector in the eyes of the government. However, it must be stressed that zama-zama mining thrived primarily because of the lack of employment opportunities in the formal LSM sector.

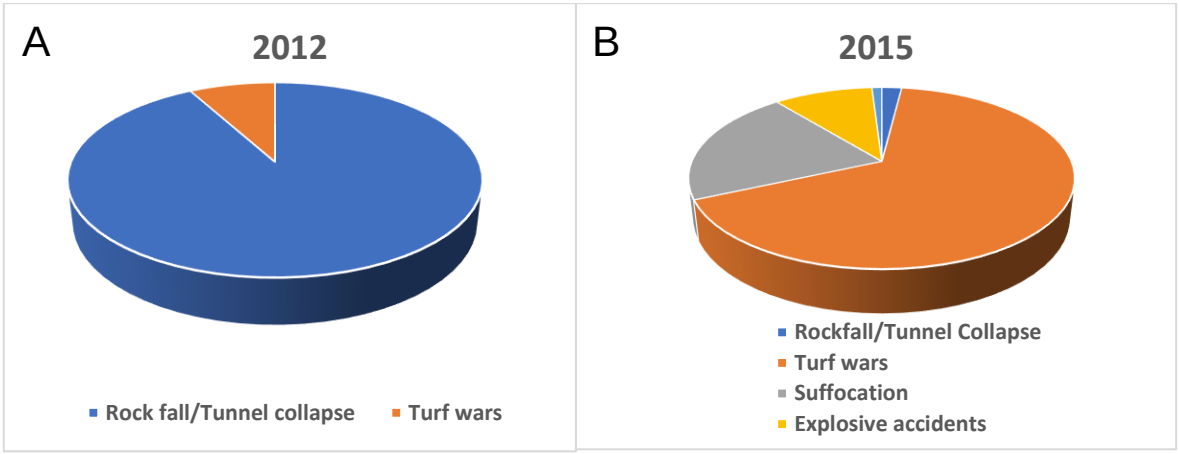

Figure 9: A) 2012 B) 2015 causes of death in ASGM (adapted from (Johnson, 2016))

Legislative

Since the transition to democracy, quite a few institutional frameworks (sets of formal policies, laws, and regulations) have been created to assist the growth of the sector in South Africa.

MPRDA

The Minerals and Petroleum Resources Development Act (MPRDA) came into effect in 2004. The preamble stipulates that the MPRDA (Government Gazette, 2002):

- Acknowledges that the mineral and petroleum wealth of the country belongs to all South African equally and that the State acts as the custodian.
- Recognises that the development of communities affected by mining is central.
- Reaffirms the State's key task to ensure equitable access and eradicate all forms of discrimination in the country's mineral and petroleum resources.

In its objectives, the act emphasises the need to (Government Gazette, 2002):

- Expand considerably opportunities for HDSAs, specifically including women, to access and benefit from the country's mineral and petroleum resources.
- Promote economic growth and employment for all South Africans.
- Ensure that citizens who are holders of mining rights actively contribute towards the socio-economic development of the areas surrounding their operations.

These objectives are all beneficial for the growth of the ASM sector, however, they come with many requirements. To obtain mining rights and permits some of the requirements are (Government Gazette, 2002):

- An environmental impact assessment and an environmental management programme.
- Consulting and notifying all the stakeholders (parties interested and affected).
- Proof of financial and technical resources.
- Commitment to prevent any pollution and ecological degradation during the mining activity.
- The mining area must not exceed 1.5 hectares (applies to mining permits only).

Failure to meet these requirements results in the rejection of applications by the minister. Mining rights have a validity of 30 years according to the MPRDA, while mining permits have a validity of 2 years. The application fee for a Mining Right is R 1000 and R 100 (currency in ZAR) for a Mining Permit.

Artisanal miners who follow the legal route, usually can only afford Mining Permits, however, it is quite difficult for miners to meet the requirements of the application process. The MPRDA, although recognising the need to promote artisanal mining, does not provide special provisions that cater for the ASM sector. Another issue is that of the limited land area provided by the Act which is particularly an issue for those who mine construction minerals (stones and aggregates which are much cheaper than valuable metals) since they require much more land to be profitable. In addition, the application procedure has been criticised for being very bureaucratic, cumbersome and requires to be done online which further discourages miners in the ASM sector who, for the majority, live in remote areas without internet access (Ledwaba and Mutemeri, 2018).

Support programmes in the ASM sector

These support programmes, which were mostly set in motion after the MPRDA, were developed by the government to assist the ASM sector on issues such as access to mineral rights and financial markets, better technologies and mining skills. These programmes include the ASM Training School and the Small Scale Mining and Beneficiation division established by Mintek in 2005 and 2002, respectively, the Small Scale Mining Board (SSMB) and the Small Scale Mining Directorate estabilised by the Department of Mineral Resources (DMR) in 2006 and 2004, respectively, to name a few (Ledwaba and Mutemeri, 2018).

Observing the implementation of these programmes reveal that most of them have not lived up to their expections and have provided very little support to the ASM sector in South Africa. Ledwaba and Mutemeri (2018) argue that these failures can be attributed to the lack of continuous support from the DMR, the fact that the programmes were state owned, underfunded and the lack of local stakeholder involvment in these programmes.

2.4.2. Solutions to assist ASGM sector

A few of the proposed solutions (some of which are already implemented around the world) to assist the sector include:

- Mercury retorts: The introduction of retorts has had a significant impact on ASGM operations using mercury. A retort is a piece of equipment which allows for the recovery and condensation of mercury vapours that are formed during amalgam burning for the production of sponge gold. Different designs exist, an example is shown in Figure 10. Retorts allow for a significant reduction in mercury emissions into the open air by preventing the loss of vapours which is beneficial from an environmental point of a view as well as the long-term health of artisanal miners by reducing inhalation of mercury. However, they do not address issues of spillages during process.

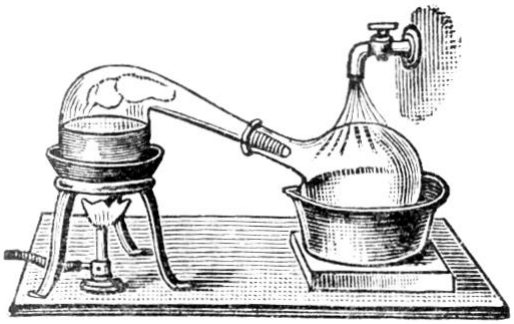

Figure 10: Mercury retort (Michaud, 2016)

  Amalgamation of gravity concentrates by miners instead of whole ores has been found to considerably reduce mercury consumption and losses associated with issues mentioned in section 2.4.1.1.

- Alternative technologies for mercury amalgamation: This is central for the long term success of the ASGM sector and must be done in a way that considers the economic situation of artisanal miners. Some of these technologies include leaching with thiosulphate, urea, chloride, cyanide, borax smelting and more (discussed in section 2.3.2). Most of these technologies were not primarily developed for the purpose of replacing amalgamation but have been adapted to serve as potential alternatives.

- Processing centres: They have been proposed as a creative solution to sensibly reduce the negative impacts of amalgamation on the environment. These centres are, by design, establishments that process gold for artisanal miners in a more structured and specialised space where emissions are controlled. However, in practice, most of these centres, which are mostly privately owned, only extract ~30% of the gold using inefficient methods such as crude grinding and whole ore amalgamation. This is done at a set fee. Miners often leave behind their tailings which are processed further in these centres and much higher extractions are achieved using cyanidation (Veiga et al., 2014b). This raises the question of whether this is really a solution for artisanal miners or for the engineering companies that run these centres.

- Education and training: Educating the miners on the detrimental effects of mercury on their health has been proposed as a key step in achieving any sort of sustainability in the sector. The problem, however, is that mercury is a slow killer and miners are more concerned with their current survival which is directly dependant on how much gold they can amalgamate. Therefore, education can only work if paired with other solutions which assist from an economic standpoint.

- Collective action or associative entrepreneurship amongst miners: Saldarriaga-Isaza et al. (2015) have proposed that this work structure has the potential to assist them significantly in accessing more efficient and cleaner production methods. By implementing co-management, which involves communication between the miners and the involvement of a third party, as a form of collective action, great individual contributions from the miners were achieved leading to improvements in their methods from a production and environmental point of view.

- Legal titles: The provision of legal titles from governments to artisanal miners who discover deposits would significantly assist the miners in developing more sustainable businesses for their families (Veiga, 1997).

2.4.3. Global initiatives for change in ASM

Given the impacts of the amalgamation process on health and the environment and economic hardship in ASGM, a few initiatives have been set in motion over the years to assist the sector.

2.4.3.1. Minamata Convention on Mercury (MC)

The convention took place in Japan and was named after the city of Minamata where a devastating health crisis took place as a result of Hg poisoning. The aim of this treaty that brought many countries together was to have a common commitment, put strategies in place and develop National Action Plans (NAP) to protect the environment as well as the global human health from the negative impacts of mercury with the ultimate goal of phasing it out by 2030. After many years of negotiations, the text of the convention was approved and signed in Kumamoto, Japan in 2013 by 128 signatories and came into full effect in 2017 (The International Institute for Sustainable Development (IISD), 2019). The treaty has been ratified by 131 countries as of 2021 (Minamata Convention on Mercury, 2021).

The success of the objectives of the convention relies heavily on every country's individual responsibility to apply the necessary changes. At the national level, each country needs to have existing legislations to control the trade of mercury, programs dedicated to first identify and then protect all communities at high risk of exposure to mercury as well as clear pathways for scientific and political cooperation at the international level (Sharma et al., 2019).

Unfortunately, to date, developing countries tend to overlook these keys factors for success. Sharma et al. (2019) studied the implementation of the objectives of the MC in India, one the largest current emitters of mercury globally. The authors observed that quite a few regulations pertaining to the provisions of the MC had been put in place, however, their implementation lacked strength. The same can be said about many other developing countries.

Some criticisms of the implementation of the MC objectives are firstly that they do not take into account the context and power dynamics, which dictate the trade and circulation of mercury, that exist in most mining communities. Secondly, there is a lack of involvement of local stakeholders when NAPs are designed which ultimately works against the effective enforcement of these national plans on the ground (Intergovernmental Forum on Mining Minerals Metals and Sustainable Development (IGF), 2017). For successful enforcement of these regulations, it is key that researchers, local stakeholders and policy makers work together, that lessons are learned from countries that have had some success with at least some of the provisions of the MC and that effective monitoring systems, informed by science, be put in place to track the use, emissions as well as the health and environmental impacts of mercury (Sharma et al., 2019). It must, however, be acknowledged that the MC, which only came into full effect in 2017, is still in its infancy and the implementation of its provisions will take time.

2.4.3.2. Fairmined

Fairmined is an independent organisation created by the Alliance for Responsible Mining (ARM), founded in 2004, that connects worldwide markets to mining communities that produce gold free of exploitation. Through Fairmined, companies buy gold from miners at a fairer price for miners and acknowledge their good production practices by paying them a premium which they can invest in their families and use to develop their communities.

A good example of the impact this initiative has had is an organisation in Colombia called Iquira. Obtaining a certification from Fairmined has helped them in increasing their awareness of the environmental impacts of mining, protecting their land which they also use for farming, working in a safe environment and having stable jobs. The Fairmined certification, on a global scale, helps in tracking the path followed by the gold from the miners all the way to the refineries and jewellery stores which contributes towards a sustainable future of the gold production chain at the artisanal and small-scale level. Another key element that this initiative has achieved is building a sense of responsibility in buyers for whom turning a blind eye on the source of their gold is now an option, not something they had no control over. In the same breath, this sense of responsibility can instil pride in gold buyers and miners as, for example, the 2015 Nobel Peace Prize medal was made with Fairmined certified gold (Alliance for Responsible Mining (ARM), 2016).

2.4.3.3. Forest-Smart Mining

This initiative was created by the World Bank as a part of its 2019 global initiative, called the Climate Smart Mining Initiative, to support the responsible circular economy of minerals and reduce their environmental impacts.

As much as activities such as agriculture and forestry have much greater impacts on forests globally compared to the ASM sector, it important to recognize the contribution of ASM to this issue since ASM operations are often run in conjunction with other land uses such as agriculture. It must be highlighted that the issue around forest protection is not just deforestation, mining activities often release effluents containing harmful chemicals that affect

forest ecosystems and biodiversity. Another key point is that artisanal miners do not necessarily target forests. However, they are driven to them by the alluvial deposits they target which in many cases are found in highly forested locations leading to deforestation (World Bank, 2019).

Forest-smart mining is mining that recognises the ways in which forests and various types of land uses are inter-connected. It aims to develop strategies to reduce the negative impacts of land use on forests. The application of forest-smart strategies in ASM is a difficult task given the very informal nature of the sector. Artisanal miners simply do not have the means and the incentive to change their methods in favour of forest-smart approaches (World Bank, 2019).

Some of the key principles of forest-smart mining are to (World Bank, 2019):

- Bring context in presenting mining deforestation by taking into account the large contribution of sectors such as agriculture to prevent hostility from mining stakeholders.
- Improving mining regulations and assist ASM operators, particularly in developing countries, such that forest-smart strategies can be implemented effectively in ASM.
- Investigate ways to create cooperation between LSM and ASM to help ASM develop strategies for forest protection.
- Ensure that an emphasis is placed on forest protection in environmental education agendas.
- Develop clear policies and legislations for land use, allocation, and ownership.

2.4.3.4. African Mining Vision (AMV)

At its 2009 summit, the African Union established the AMV as a way to express the commitment of all member countries to sustainable exploitation of natural resources. The AMV made ASM one of its key areas of focus after recognising its significant impact on the African economy (Intergovernmental Forum on Mining Minerals Metals and Sustainable Development (IGF), 2017).

Some of the areas of focus of the AMV for ASM are:

- Formalisation of the ASM sector.
- Integration of ASM into the African economic development plans and strategies with an emphasis on poverty reduction.
- Analysis and review of mining policies to assist the ASM sector.
- Promoting gender justice in ASM.

The AMV has, however, received lots of criticism on the slow implementation of its objectives since only 24 out of the 54 member countries are in some stage of national implementation. Lesotho is the only country that has made the most progress in adopting the AMV by developing its own Country Mining Vision. In recent years, there has been a loss of momentum in the AMV's spread over the continent. The AMV has, however, the potential to be a true game-changer for Africa's mineral sector by protecting it from the pressure of unfair mining contracts that it is often subjected to. The reason why the AMV has the potential to achieve this is that it extensively addresses the challenges that Africa faces in gathering its mineral

wealth for the sustainable development of its people and commits to reflect global standards for the fair governance of mineral sectors in Africa (Oxfam, 2017).

2.4.3.5. Cyanide code

The International Cyanide Management Code For The Manufacture, Transport and Use of Cyanide in the Production of Gold, simply referred to as the cyanide code is an industry standard code of practice in the use of cyanide in mining operations. The code was designed by a committee comprising of many stakeholders appointed by the United Nations Environment Programme and the International Council on Metals and the Environment (The cyanide Code, 2002).

Some of the key objectives of the code are:

- To protect exposed communities from the negative impacts of cyanide.
- To improve procedures for cyanide management.
- To be used by LSM, ASM, cyanide manufacturing and transporting companies.

The code is voluntary and aims to complement an organisation's existing policy and regulatory requirements. It addresses all steps of the cyanide life cycle, from production to its disposal after use (including tailings management) and decommissioning of cyanide plants. It also contains specific requirements for the involvement of stakeholders in cyanide management plans, cyanide related accident prevention, response to emergencies, training of miners and reporting by public groups on matters pertaining to cyanide (The cyanide Code, 2002).

A study, conducted by Nyanza et al. (2017), assessing the adherence of artisanal gold miners in northern Tanzania to the cyanide code, revealed that the majority of miners do not even know of, let alone adhere to the cyanide code. A strong correlation was found between site safety and increased knowledge of the code within miners and managers. There is, therefore, a clear need for better sensitisation and education on the existence of the code and safe practices in mining sites (Nyanza et al., 2017).

There are many more organisations and initiatives that should be mentioned such as the Organisation for Economic Cooperation and Development (OECD), the Southern African Development Community protocol on mining, the African Minerals Governance Framework, the African Minerals development Centre, Fairtrade, the Responsible Jewellery Council (RJC) that all aim to assist the ASM sector in various ways.

2.4.3.6. Link to Sustainable Development Goals (SDGs)

Many of the global problems that the SDGs aim to address, such as poverty, health, and environmental issues, can be found in communities surrounding ASM operations. For some of these issues, ASM makes positive contributions such as SDGs 1 and 8 which touch on economic growth, by providing a source of livelihood for millions of people, SDG 10 which touches on reducing inequality by allowing more people to have an income. However, for many other global problems, ASM has serious negative impacts, for example, on SDGs 3 and 6 which look at health and water quality, SDGs 13, 14 and 15 which are concerned with the environment and many more (de Haan et al., 2020). These negative impacts arise primarily

from the poor processing practices that exist in many ASM operations. The global initiatives presented above all provide support to ASM in their own ways and based on their reach and capacity, and by doing so, help steer ASM towards contributing more positively to the SDGs. The key SDGs highlighted in this section are presented in Figure 11.

Figure 11: SDGs supported by initiatives assisting ASM (United Nations, 2015)

2.4.4. A success story: Clean Tech Mine

Clean Tech Mine is an example of an operation that achieved something that is key when it comes to ASM operations, that is tailoring a process that is specific to the type of ore being processed and ensures the safety and empowerment of the miners. The mine is located in the Manica Province in Mozambique and employs about 100 miners. The mine was, unfortunately, forced to close down in 2020 for dumping large quantities of sludge into the Rovué River which feeds into the dam that provides electricity to the province (Magoum, 2020). It is, however, important to understand what made this mine such as successful operation when compared to other mines in the ASGM sector.

2.4.4.1. Processing method

At Clean Tech Mine, amalgamation, despite being popular in the province, was replaced by centrifugation and magnetic removal of gangue minerals.

The miners collect about 1-2 t of ore per day. The processing steps were as follows (Drace et al., 2012):

- An experienced miner panned with water small samples of the ore obtained to qualitatively determine the gold content and fed the information back to the miners who dig and extract the ore.
- Based on this, the miners could decide to continue mining the ore from a specific area or move to another where higher yield might be expected.
- The ore obtained was then transferred to a jaw crusher.

- The output was transferred to a ball mill.
- The pulp from the ball mill then went to a centrifuge which produced approximately 30-33 kg of concentrate from about 20 t of ore.
- The tailings were recovered and reprocessed via cyanidation.
- The centrifuge discharge was collected in basins. It contained predominantly gold, iron minerals and shavings (Figure 12a) which were removed with magnets. The magnets used were sourced from old radio speakers (Figure 13).
- The magnetic separation was repeated until all the visible gangue had been removed leaving behind a gold concentrate at a purity of 89-93% (Figure 12b).

Figure 12: a) Centrifuge discharge (left), b) 89-93% gold concentrate post magnetic separation (right) (Drace et al., 2012)

Figure 13: Magnets from radio speaker used for magnetite removal (Drace et al., 2012)

2.4.4.2. Positive impacts of the operation

Amongst many, some of the key positive take-away points from Clean Tech Mine are (Drace et al., 2012):

- The owner of the mine ensured a safe environment for the miners by eradicating mercury amalgamation.
- The processing route took advantage of the high magnetite content of their ore to apply magnetic separation as a concentration method.
- The final tailings were converted into bricks which can be used for construction work in the plant and also for sale.
- The owner of the mine reinvested the profit of his operation to improve the efficiency of the processing route followed in the mine.

- The miners were given food every day (breakfast and lunch).
- Full personal protective equipment (PPE) was provided to the miners.
- Miners had a fixed salary that did not depend on the weekly gold production.

2.4.5. Rationale

A fairer legislation that sets specific regulations and guidelines that cater for the context of the ASM sector would build trust between miners and the government. This would provide more incentive for miners to educate themselves on improving their methods of production, their personal safety, and the environmental impacts of their mining activities. This would ultimately allow miners to have access to national commodity markets leading to more revenue, access to loans from banks since economic risk factors will have been significantly reduced due to formalisation efforts, less violence in mining areas and less casualties due to unsafe working practices. The example of Clean Tech Mine paints a positive picture of how financial investments into the ASM sector can go a long way in ensuring a sustainable growth of the sector. An investment was made to acquire a jaw crusher, ball mill and a centrifuge and led to high gold yield which in turn allowed the miners to be remunerated fairly. It is important to understand that just as gold is a business, mercury is a business of its own. It cannot go away by itself, a strong multifaceted approach is key in designing pathways for its complete phase-out. In developing this approach, is it crucial to take into account the local mining context of ASM in terms of the minerology of the ore bodies typically found in ASM areas and the need for appropriate technology.

In grappling with these various ideas that aim to improve the ASM sector, it is also crucial that governments, investors, and all other interested parties understand the specific context of each mining community before even considering the possibility of success of a project. And this can only be achieved by actively involving the miners themselves and their communities. Experience shows that parachuted decisions have very low probabilities of success.

2.5. Gold extraction technologies investigated

2.5.1. Cyanide leaching

The property of cyanide solutions to dissolve gold was first recognised in 1783 by Scheele, a German-Swedish chemist, then subsequently studied by many scientists such as Elsner and Faraday in the 1850s. Cyanidation became a predominant method for gold extraction around the late 19th century and remains a process widely used today (Marsden and House, 2009).

2.5.1.1. Cyanide solution chemistry

The main salts of cyanide are sodium, potassium, and calcium cyanide. As shown in Table 3, sodium and potassium cyanide have a higher solubility in water, although they have lower amounts of available cyanide than calcium cyanide. In addition, their availability in a purer form makes them easier to handle than calcium cyanide (Marsden and House, 2009).

Table 3: Properties of cyanide compounds (Marsden and House, 2009)

Compound	Available Cyanide (%)	Solubility in water at 25°C (g/100 cc)
NaCN	53.1	48
KCN	40.0	50
$Ca(CN)_2$	56.5	Decomposes

In solution, cyanide hydrolyses according to the following reaction:

$$CN^- + H_2O \leftrightarrow HCN + OH^- \quad [4]$$

HCN then dissociates in water as shown in the reaction below (Smith and Martell, 1976):

$$HCN \leftrightarrow H^+ + CN^- \quad [5]$$

At ambient temperature, the acid ionisation constant (K_a) and pK_a are 6.2 x 10^{-10} and 9.31 respectively, which suggest that hydrogen cyanide (HCN) does not readily ionise in solution, it is a weak acid. This means that the solution pH must be higher than 9.31 to deprotonate HCN into free cyanide (CN^-), which is the desired cyanide specie in solution for gold complexation. Figure 14 shows cyanide speciation as a function of pH at equilibrium.

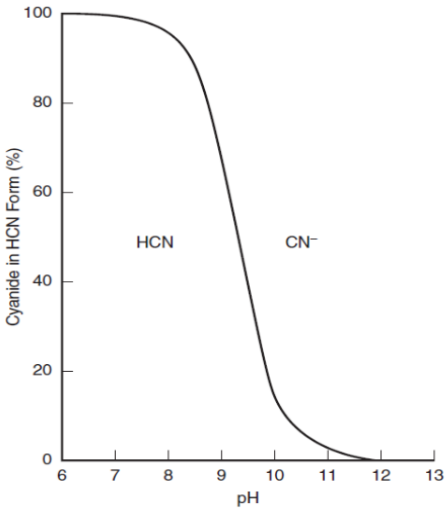

Figure 14: HCN formation as a function of pH (Marsden and House, 2009)

It can be seen that at a pH of 9.3, about half of the HCN is present as HCN and the other half as CN^-. The more the pH increases, the more HCN gets deprotonated and at a pH of about 10, 90% of the cyanide is present in the form of CN^- and conversely at pH of around 8, 90% of the cyanide is present in the form of HCN. This is of particular importance in cyanide chemistry since HCN, a toxic gas, has a high vapour pressure at ambient conditions meaning that it can easily volatilize and become a serious health hazard. Secondly, operating at a pH above 10 minimizes the loss of free cyanide which is necessary for the gold complexation reaction. In addition, it is important to consider the fact that that although CN^- is the more desired form of cyanide in solution, both species (HCN and CN^-) can react with oxygen according to reaction 6 and 7 to form cyanate (CNO^-) which is an undesired form of cyanide that cannot complex gold and can further reduce the amount of available free cyanide.

$$4\,HCN + 3\,O_2 \leftrightarrow 4\,CNO^- + 2H_2O \quad [6]$$

$$3CN^- + 2O_2 \leftrightarrow 3CNO^- + 2OH^- \quad [7]$$

However, these reactions are very slow and occur to a significant extent only when strong oxidants such as ozone and hydrogen peroxide are used. It is quite important to be aware of these losses and side reactions that might take place in cyanide systems since, waste of reagent can easily inflate costs of production which is a deciding factor in the approval of a technology amongst artisanal miners.

2.5.1.2. Gold dissolution in cyanide systems

The overall dissolution of gold in a cyanide system which is an oxidative dissolution process is described by the following reaction:

$$2Au + 4CN^- + O_2 + 2H_2O \leftrightarrow 2Au(CN)_2^- + H_2O_2 + 2OH^- \quad [8]$$

The electrochemical process occurring on the gold particle surface is described in Figure 15.

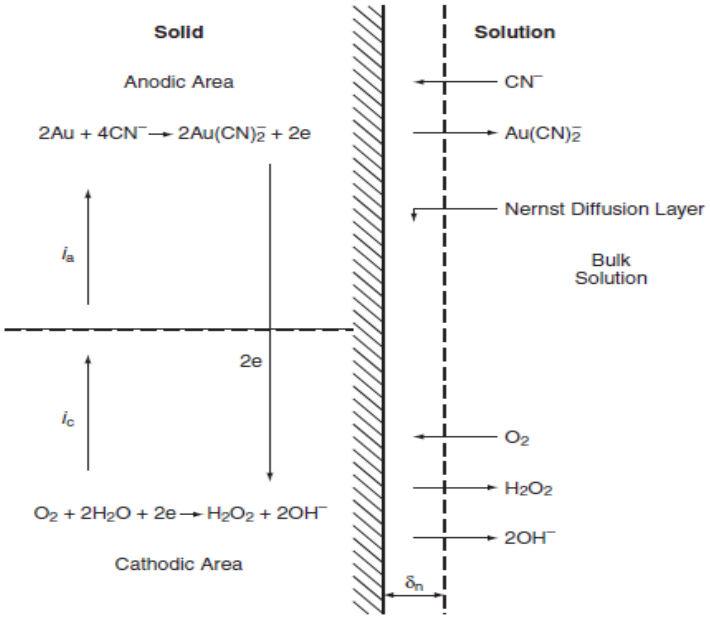

Figure 15: HCN and CN- formation as a function of pH (Marsden and House, 2009)

2.5.1.3. Kinetics of gold leaching

The kinetics of gold dissolution (Eq. 8) can be affected by:

- Concentration of cyanide and oxygen in the system
- pH
- Temperature
- Exposed surface area of gold
- Level of agitation in the system

Cyanide and oxygen concentration in system

The rate of the gold dissolution reaction (being an oxidative dissolution) is significantly dependent on the diffusion rates of cyanide and oxygen. When the diffusion rates of the two species are equal, the reaction reaches a rate where it can be limited by the diffusion rate of either cyanide or oxygen. At this point, it is found that (using the diffusion rate equation of both compounds and their respective diffusivities):

$$\frac{[CN^-]}{[O_2]} = 6 \qquad [9]$$

It has been shown that the ratio $[CN^-]/[O_2]$ can vary from 4:1 to 7:1 (Heath and Rumball, 1998), however it is typically preferred to operate at ratio of at least 6:1 to prevent the concentration of cyanide from being rate-limiting ((Marsden and House, 2009).

In the reaction system, the concentration of cyanide can easily be controlled by simply adding more of the salt, particularly in systems with species that compete for cyanide. The same cannot be said for the oxygen concentration since oxygen has a low solubility in water (8.2 mg/L) in ambient conditions (25°C, 1 atm) which further decreases with increasing ionic

strength as well as if temperature is increased. Increasing the amount of dissolved oxygen is typically achieved by pressure leaching since the increased pressure allows for better dissolution of oxygen. In reactors operating at ambient pressure, dissolved oxygen concentrations can be increased by the use of pure oxygen or hydrogen peroxide which come with increased costs.

It can be seen on Figure 16 that increasing the dissolved oxygen concentration leads to higher extraction rates. However, it also shows that similar results of final gold recovery can be achieved with lower oxygen concentrations by extending the leaching time.

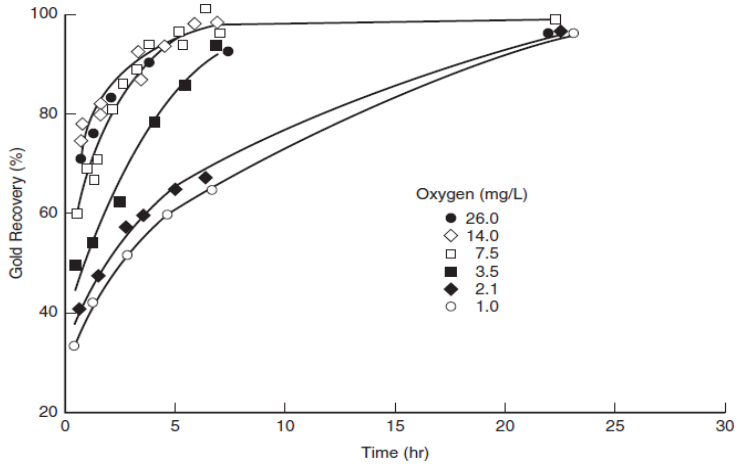

Figure 16: Effect of oxygen concentration in gold extraction from calcine using KCN ((Marsden and House, 2009))

This information provides useful knowledge in making economic decisions for the leaching process in the sense that, the economics associated with longer leaching time to reach a certain extraction can always be weighed against those of increasing the dissolved oxidant concentration in the system.

pH

As mentioned above, operating at pH values above 9.5 is key to prevent the loss of cyanide to HCN gas which is a safety hazard due to its high toxicity on top of the fact that reagent loss translates to increased costs to meet the required extraction. Perry et al. (1999) have shown that aqueous HCN can leach gold, however it does not achieve this at a rate fast enough to compete with CN^-. And thus, the dissolution rate of gold in cyanide solutions is directly proportional to the free cyanide concentration.

Ultimately, many factors can have an impact on the overall effect of pH on the dissolution process. These include: the type of salt used for pH modification, the dissolution of other metals present in the ore, the viscosity of the solution, etc. To prevent cyanide loss, pH modifiers (alkali) are typically added before cyanide to set the pH between 10 and 11. In most applications, sodium hydroxide (NaOH) or calcium hydroxide ($Ca(OH)_2$) are used. $Ca(OH)_2$ is usually preferred due to its cheaper cost and NaOH, being a dispersant, can sometimes cause the dissolution of silicates which can negatively affect post-leaching processes. To attain the desired pH range (10-11), the $Ca(OH)_2$ concentration in solution ranges between 0.15 to 0.25 g/L. An even cheaper alternative is calcium oxide (CaO).

Temperature

It has been shown that increasing the system temperature up to 85 °C causes the gold dissolution to increase as depicted on Figure 17. This temperature effect is due to the increased diffusion rates of the species in the reaction. However, as mentioned in the section looking at Cyanide and oxygen concentration in system in 2.5.1.3, increasing the temperature causes the solubility of oxygen to decrease, therefore, above 85 °C the increased gold dissolution associated with the higher temperature is outweighed by the reduced oxygen dissolution. This is why a dip is observed on the extraction curve above 85 °C (Marsden and House, 2009).

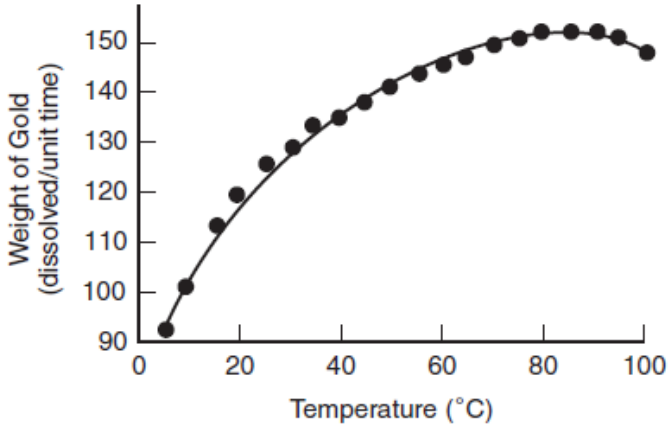

Figure 17: Effect of temperature on aerated dissolution of gold in KCN solution (Marsden and House, 2009)

In addition, Figure 17 also shows that increasing the temperature from 25 °C to 85 °C results in about 20% increased recovery of gold. The profit from the increased recovery need to be weighed against the cost of increasing temperature to have a clear idea whether or not it is worth it. In most instances, increasing the temperature is only justified for the treatment of high-grade concentrates.

Exposed surface

The amount of available exposed gold surface plays a key role in the success of the overall dissolution process. The extent of gold surface exposure is related to the particle size distribution (PSD) of the ore which is, in turn, dictated by how well the crushing and milling was conducted. Whether fine PSDs are more advantageous for the dissolution process is greatly dependant on the type of ore treated. In most instances, finer PSD leads to a higher dissolution rate, however, if the ore holds heavy cyanide consuming species that become exposed as the PSD decreases, more cyanide will be directed to those species, leading to an overall decreased rate of dissolution. Different particles sizes are preferred depending on the type of leaching applied (Marsden and House, 2009). It is important to note that size reduction is directly linked to energy costs which are significant operating costs in a mine.

Agitation

The level of agitation impacts the dissolution rate by affecting the thickness of the diffusion layer between the particles and the lixiviant solution. Good mixing, which is typically achieved by mechanical agitation, first homogenises the solution then reduces the diffusion layer thickness, leading to higher dissolution rates. In systems such as dump leaching, increasing the lixiviant flow rate has been found to have a similar impact as agitation due to the enhanced mass transfer occurring in the system. However, higher flow rates lead to a lower gold concentration in the pregnant leach solution which might not be desired in downstream processes. Therefore, level of agitation and slurry flowrates need to be assessed carefully when designing the leaching process (Marsden and House, 2009).

2.5.1.4. Applications of cyanidation in artisanal gold mining

Cyanidation appears to be the most promising candidate to replace Hg amalgamation. The process can easily leach out gold grains finer than 0.2 mm in one day using a cyanide concentration varying between 50 and 10,000 mg/L.

The leaching can be followed by precipitation using Zinc, according to the following reaction (Eq. 10), to recover the gold. Zinc precipitation is most efficient when working with a high gold grade.

$$2Au(CN)_2^- + Zn \rightarrow Zn(CN)_4^{2-} + 2\,Au \qquad [10]$$

Activated carbon (AC) (5-10 kg Au/t AC) can also be used to adsorb the gold post leaching. One significant advantage of this method is the fact that it does not require a filtration step since the AC is completely mixed with the pulp. However, most artisanal mining sites do not actually work with carbon in pulp (CIP) but instead decant then use a carbon in leach (CIL) system.

Examples of application of cyanidation in ASM

North Sulawesi, Indonesia cyanidation laboratory experiment

3 tests were conducted to assess the efficiency of cyanidation against gravity concentration and other methods such as mill leaching and the use of magnetic sluices.

The first test consisted of a four-step concentration process using a lab scale Knelson gravity concentrator. The ore, at a gold grade of 6.02 g/t, was first crushed using a jaw crusher (d_{80} = 5 mm) and split to maintain homogeneity in the samples. After each concentration step, the tailings were reground to liberate more gold. The final tailings obtained after the 4 stages were treated by cyanidation for 24h to further recover the gold. It was found that the first concentration only achieved a gold recovery of 8%. The total recovery after the 4 stages amounted to 29%. The cyanidation step added a 49% gold recovery leading to an overall gold recovery of 78%.

The second test compared the Knelson concentrator, two sluices (one Cleangold magnetic sluice and a homemade magnetic sluice referred to as HMMS) and conventional cyanidation. For this test, the samples fed for each method had a gold grade of 11.5 to 12.6 g/t and d_{80} =

0.25 mm. Leaching was achieved in a bottle roll test at 30% solids loading and 1 g/L NaCN concentration for 6 h. The gold recoveries achieved by the Knelson concentrator, the Cleangold sluice, the HMMS and cyanidation were 5%, 7%, 8% and 84% respectively.

The third test investigated the efficiency of mill leaching using cyanide (~1 g/L) on a gold ore (d_{80} = 5 mm) of grade ranging from 14.7 to 17.5 g/t. The mill was loaded with the gold ore, water, lime for pH control, sodium cyanide and rods for grinding. It was operated for 2 h before the rods were removed and AC introduced. The mill was then restarted and operated for a total of 24 h. After 2 h, a recovery of 77.9% was achieved and a total recovery of 93.6% was obtained after the 24 h experiment time limit (Veiga et al., 2009).

Portovelo, Ecuador field experiments

Two tests were conducting using two different set-ups, an agitated tank and a ball mill that is typically used for amalgamation operations. The ore used in these tests first went into a grinding stage using a Chilean mill to obtain a size fraction d_{80} = 0.150 mm. As an initial concentration stage, a sluice box was used, yielding a pre-concentrate with a gold grade of 17.3 g/t.

For the first test, which made use of a mechanically agitated tank, the pre-concentrate (41% solids loading) was leached using a cyanide solution of high concentration (5 g/L) and lime was added to raise the pH to about 11 to prevent the generation of $HCN_{(g)}$. After about 7 h of leaching, AC was added to the slurry. The analysis of samples revealed that, after 7 h, a gold dissolution of 62% was achieved and after 31 h, a total dissolution of 94% was reached.

In the second test, the ball mill was loaded with steel balls to grind the pre-concentrate. The test was conducted at a high solids loading of 70%. A high cyanide concentration of 6 g/L was used and the pH was maintained at 10.5. After about 2 h of leaching, AC was introduced after removing the steel balls. At the end of the test, about 6 h later, the AC, the remaining solution and tailings were sent to be analysed by AAS. A gold recovery of 95% was achieved after 8 h (6 h of leaching + 2 h during grinding). It was argued that the increased recovery can be attributed to the grinding stage that caused a higher gold liberation (Veiga et al., 2009). In addition to that, the increased recovery can also be attributed to the improved mass transfer as a result of the continued rotation of the ball mill.

2.5.1.5. Post-leaching cyanide treatment

Cyanide is a toxic chemical that has the potential to cause serious harm to humans if exposed but also severe pollution to the environment, particularly water streams in proximity to leaching operations. The average lethal cyanide dose has been estimated between 50 and 200 mg for an adult human (Young and Jordan, 1995) and the established cyanide concentration limit in the air, by international standards, is set at 4.7 ppm (Estay, 2018). If this technology has to be proposed as a medium to long term remedy for mercury amalgamation, a clear method for its treatment post-leaching needs to be derived. Cyanide is considered to be in the P-class of hazardous wastes which are considered to be acute hazardous wastes generated by commercial processing plants. This group includes other chemicals such as arsenic, fluorine, endrin, etc. The chemicals in this class have the most regulations put in place to control their management and handling (Young and Jordan, 1995).

Most technologies that have been developed for the treatment of wastewaters have focused on the removal of heavy metals or toxic chemicals as cations. There was, therefore, a need to investigate treatment methods for anions such as cyanide which are toxic as well.

The main methods for cyanide remediation are divided into two groups: first, separation processes which aim to recover the cyanide with the purpose of re-use. Such processes include physical methods such as membrane separation, distillation and hydrolysis, and complexation methods such as the AVR (acidification, volatilization and reneutralisation) process, the SART (Sulfidization, Acidification, Recycling and Thickening) process and solvent extraction. Secondly, destruction processes which focus on breaking up the covalent bond between the carbon and nitrogen atoms in cyanide with the objective of forming less or non-toxic compounds. Destruction processes include mainly oxidation methods such as bio-oxidation and chemical addition (Young and Jordan, 1995). Table 4 summarises the applicability of the various methods.

Table 4: Effectiveness of various cyanide separation (Young and Jordan, 1995)

SEPARATION	Effective for separating						
Remediation Process	Free Cyanide?	Thio-cyanate?	WAD Metal Complex?		SAD Metal Complex?		Need Further Treatment?
			Cd/Zn	Cu/Ni	Fe	others	
Electrodialysis	yes	yes	yes	yes	yes	yes	No but costly
Reverse Osmosis	yes	yes	yes	yes	yes	yes	No but costly
Electrowinning	no	no	some	most	no	most	yes
Hydrolysis/Distillation	yes	no	no	no	no	no	yes
AVR	yes	some	yes	yes	most	some	some
Cementation (est.)	no	no	no	most	some	yes	most
Fe Complexation	yes	little	no	no	no	no	yes
Precipitation Flotation	yes	little	most	most	yes	no	most
Ion Flotation	some	?	some	yes	yes	yes	most
Solvent Extraction (est.)	some	little	yes	yes	yes	yes (Au)	some
Mineral Adsorption (est.)	most	some	most	yes	yes	yes	some
Untreated Activated Carbon	no	some	some	yes	yes	yes	some
Cu-treated Activated Carbon	yes	yes	yes	yes	yes	yes	little
Untreated Resin	no	some	yes	yes	yes	yes	little
Cu-treated Resin	yes	some	yes	yes	yes	yes	little

est. = estimated

Separation methods have the potential to offset the cost of disposal, however, if no recycling is implemented, the recovered stream will need to be further treated before being released into the environment due to the high cyanide concentration. On the other hand, destruction methods break down cyanide which is great to meet environmental regulations, however, they are of no benefit whatsoever to the process itself making them a high expense. It must be highlighted, as well, that the effectiveness of these methods is often case specific as it is related to the type of cyanide species in solution, whether dealing with weak acid dissociable cyanide complexes (WADs) or strong acid dissociable cyanide complexes (SADs) (Young and Jordan, 1995).

Many other methods have been investigated such as Caro's acid and tailings washing which are unfortunately quite costly in terms of capital and operating costs. The cheapest method seems to be natural attenuation/degradation in tailing ponds. With this method, cyanide can naturally oxidise and degrade to carbon dioxide, nitrates, and ammonia. However, some cyanide species can have a strong resistance to break-down by natural degradation and lead to severe cyanide contamination in soils and water streams. These include primarily cyanides of copper, iron, and nickel. It is, therefore, imperative that pH and concentrations of WADs in effluent streams are monitored carefully, and that ponds and impoundments are designed adequately to prevent seepage. In addition, ponds must be designed with enough volume allowance to prevent overflow in case of storm (Stapper et al., 2021).

Dealing with cyanide is of high importance in ASGM where excessively high concentrations are used translating to high cyanide concentrations in effluent streams. In mining communities, one of the first signs of river contamination is death of livestock which can cause factions and disputes. It is, therefore, even more important for these treatment methods to be understood and easy to implement. A promising method which could be applied in the ASGM context is the SART process given its ability to recover cyanide and return it directly into the process as well as produce by-product metals in saleable form. This ability to recycle cyanide alone would be of great benefit to artisanal miners by sensibly reducing their operating costs. The process is also quite flexible in the sense that it can be modified by removing certain units based on the requirements of a given operation.

2.5.2. Thiosulphate leaching

Thiosulphate ($S_2O_3^{2-}$) is a reagent considered relatively safe, clean, less toxic, and less harsh on the environment compared to other reagents such as cyanide and mercury. It has also shown great results in terms of its extractive properties in gold leaching operations (Aylmore, 2016).

2.5.2.1. Chemistry of thiosulphate leaching

The dissolution of gold in a thiosulphate system is an electrochemical process described by the following overall reaction:

$$4\,Au_{(s)} + O_2 + 2\,H_2O + 8\,S_2O_3^{2-} \rightarrow 4\,Au(S_2O_3)_2^{3-} + 4\,OH^- \quad [11]$$

The process involves the oxidation of gold (Au) and reduction of oxygen (O_2) at the anode and cathode, respectively. The reaction is, however, typically slow and requires the presence of copper (Cu(II)) and ammonia (NH_3) as catalysts (Bin et al., 2017).

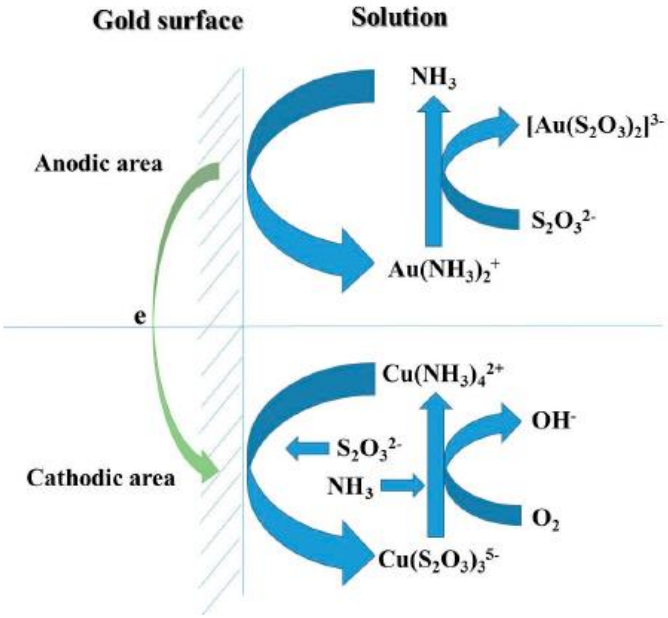

Figure 18: Electrochemical process of thiosulphate leaching (Bin et al., 2017)

Figure 18 describes the electrochemical process as it takes place on the gold surface. In the anode, NH_3 complexes with Au to form the $Au(NH_3)_2^+$ complex. NH_3 then gets substituted by $S_2O_3^{2-}$ resulting in the formation of $Au(S_2O_3)_2^{3-}$ which is the more stable complex (Bin et al., 2017, Zhang et al., 2004). NH_3 plays the key role of acting a catalyst in the reaction involving gold and $S_2O_3^{2-}$ and also helps stabilise Cu(II) in alkaline environment.

Anodic reactions:

$$Au \rightarrow Au^+ + e^- \quad [12]$$

$$Au^+ + 2\,NH_3 \rightarrow Au(NH_3)_2^+ \quad [13]$$

$$Au(NH_3)_2^+ + 2\,S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + 2\,NH_3 \quad [14]$$

In the cathode, $Cu(NH_3)_4^{2+}$ undergoes reduction to $Cu(S_2O_3)_3^{5-}$. The dissolved O_2 then oxidises it back into $Cu(NH_3)_4^{2+}$. $Cu(NH_3)_4^{2+}$ therefore acts as a catalyst for O_2 reduction.

Cathodic reactions:

$$Cu(NH_3)_4^{2+} + 3\,S_2O_3^{2-} \rightarrow Cu(S_2O_3)_3^{5-} + 4\,NH_3 \quad [15]$$

$$4\,Cu(S_2O_3)_3^{5-} + 16\,NH_3 + O_2 + 2\,H_2O \rightarrow 4\,Cu(NH_3)_4^{2+} + 4\,OH^- + 12\,S_2O_3^{2-} \quad [16]$$

As depicted in the reactions above, the chemistry of the Au-O_2-Cu(II)-NH_3-$S_2O_3^{2-}$ system is quite complex which has resulted in difficulties in upscaling the thiosulphate technology to heap and in situ leaching of gold deposits (Zhang et al., 2004).

It is important to take note of the side reaction of Cu(II) with $S_2O_3^{2-}$ (Eq. 17) resulting in the formation of a series of sulphur species such as tetrathionate and more. The impact of these polysulphides will be elaborated in section 2.5.2.3.

$$2\,Cu(NH_3)_4^{2+} + 8\,S_2O_3^{2-} \rightarrow 2\,Cu(NH_3)_2^{+} + S_4O_6^{2-} + 8\,NH_3 \quad [17]$$

2.5.2.2. Gold dissolution kinetics in thiosulphate systems

Kinetics

Aylmore (2016) studied and compared the rate of gold dissolution in both cyanide and thiosulphate systems under various conditions and observed that thiosulphate leaching has slower kinetics and only starts to compete against cyanidation when a catalyst such as Cu(II) is added instead of solely using O_2 as oxidant. The author also observed that the ammonium thiosulphate ($(NH_4)_2S_2O_3$) significantly outperformed sodium thiosulphate ($Na_2S_2O_3$).

A similar behaviour was observed by Zhang et al. (2004) in an experiment conducted on colloid gold, as depicted on Figure 19. Cyanidation with O_2 as an oxidant outperformed all thiosulphates systems (curve a) by achieving 95% dissolution of gold in 2 min. However, amongst the thiosulphate systems, the best performance was achieved with the highest concentration of Cu(II) (curve b) with 90% dissolution achieved after 1 h.

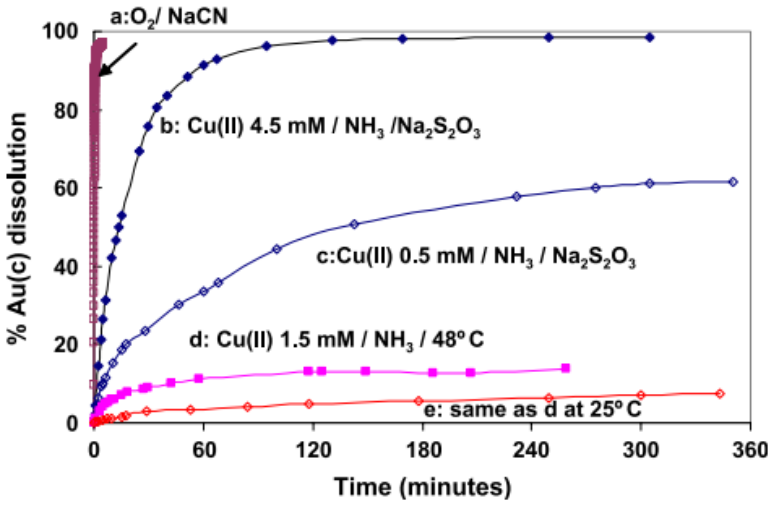

Figure 19: Dissolution of gold in various leaching systems (Zhang et al., 2004)

Copper ammoniacal thiosulphate system

As mentioned earlier, the presence of Cu(II) plays a key role in the dissolution process. Its key benefit has been well explained by Breuer and Jeffrey (2002) in an electrochemical study conducted using rotating electrochemical quartz crystal microbalance (REQCM). A kinetic plot (Figure 20) generated using REQCM first shows the gold leaching rate for a gold sample leached with thiosulphate in an air-saturated environment. It can be seen at first glance that the reaction proceeds very sluggishly with a mixed potential of 65 mV which indicates that in order to reduce O_2 on the gold surface, a significantly high overpotential is essential. When Cu(II) was used in conjunction with ammonia and thiosulphate, the mixed potential rises to the high positive value of 238 mV. The leaching is much faster as shown on Figure 20 and thus confirms the key catalytic role of Cu(II) which acts as a redox mediator meaning that it facilitates electron transfer between the dissolved oxygen and the oxidising mineral.

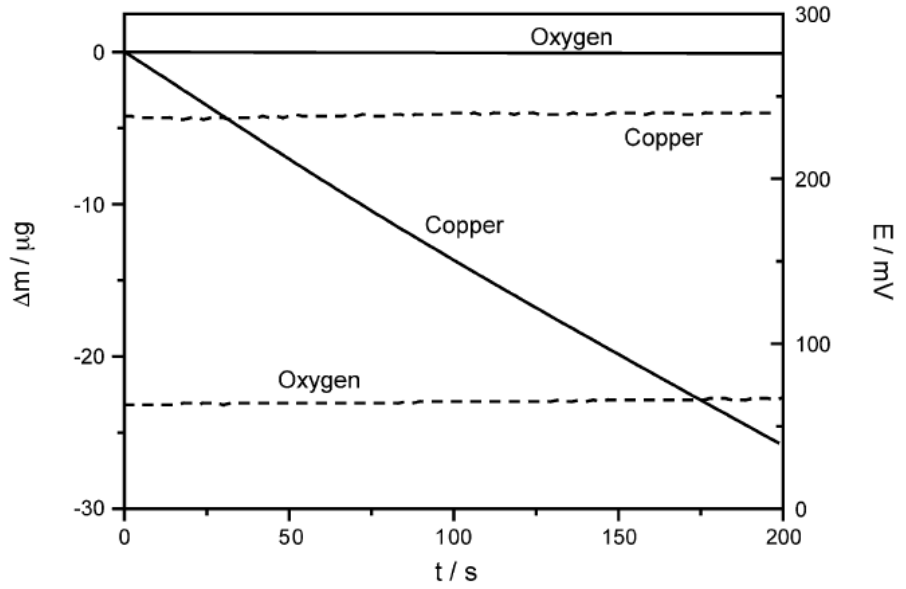

Figure 20: Kinetic plot of gold leaching rate in ammoniacal thiosulphate in presence of either O_2 or Cu(II) as an oxidant (Breuer and Jeffrey, 2002)

Jeffrey et al. (2008) reconfirmed this beneficial impact of Cu(II) on the gold dissolution process as part of a different study that focussed on passivation in thiosulphate leaching. It was shown (Figure 21), that the leaching of gold occurred at much higher rates in the presence of both Cu(II) and NH_3 compared to purely thiosulphate systems. The leach rates were determined at 80 mV which is a mixed potential within the region established for the thiosulphate gold leaching system in the presence of Cu(II) and NH_3.

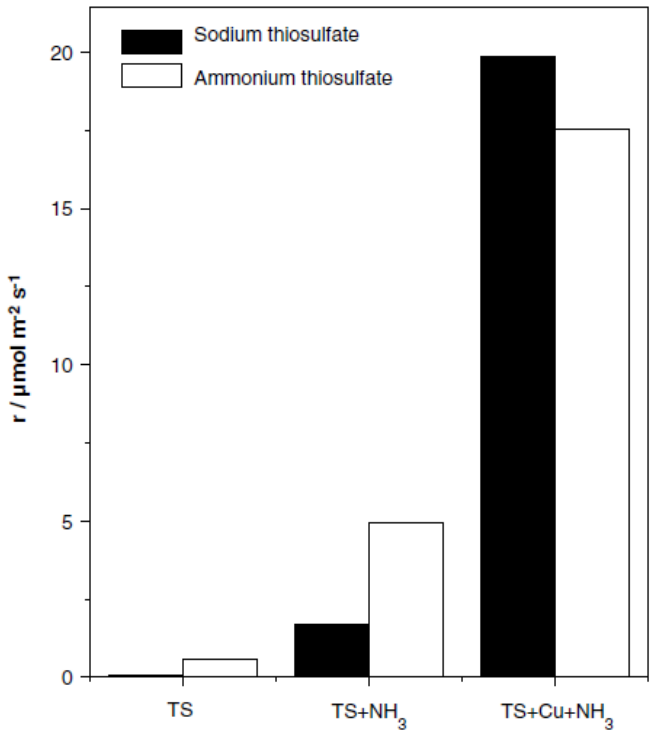

Figure 21: Leaching rates for gold in ammonium or sodium thiosulphate (TS), with addition of NH_3 and addition of Cu(II) and NH_3 at 80 mV (Jeffrey et al., 2008)

When Cu(II) is present, NH_3 is required to stabilise it in solution by forming $Cu(NH_3)_4^{2+}$. Jeffrey et al. (2001) have shown that for an efficient process, the concentration of Cu(II) needs to be lower than that of thiosulphate. The authors reported a $S_2O_3^{2-}$/Cu(II) ratio in the range 10 to 1000, stating that this demonstrates that the diffusion of thiosulphate to the gold surface is significantly faster than that of Cu(II). This means that if the concentration of Cu(II) is too low, the gold dissolution will be impeded since the diffusion of Cu(II) will have become a limiting factor.

As aerated leaching proceeds, the concentration of Cu(II) first drops as it is reduced by reacting with thiosulphate (Eq. 15). Dissolved O_2 in the system then oxidises it back, regenerating $Cu(NH_3)_4^{2+}$ (Eq. 16). The Cu(II) concentration eventually reaches a steady state concentration which is obtained from the relative rates of the two reactions and at this point, the rates of both reactions are equal. At this stage, if the rate of Cu(II) reduction increases, the steady state concentration of Cu(II) will decrease accordingly. Jeffrey et al. (2001) proposed that the concentration of Cu(II) should be kept higher than 5 mM for fast kinetics.

Role of O_2 in dissolution process

As mentioned in section 2.5.2.1, $Cu(NH_3)_4^{2+}$ undergoes reduction to $Cu(S_2O_3)_3^{5-}$ and O_2 is needed to convert Cu(I) to Cu(II) by oxidising $Cu(S_2O_3)_3^{5-}$ back into $Cu(NH_3)_4^{2+}$. Since Cu(II) is the redox mediator on the mineral surface, is it key for it to remain available during the dissolution process such that the gold can be leached effectively.

Another important point is that despite the fact that the presence of O_2 allows for Cu(II) to be regenerated via the reaction in Eq. 16, it also speeds up the Cu(II) and $S_2O_3^{2-}$ redox reaction

(Eq. 17) and by doing so causes the concentration of Cu(II) to drop faster and increases $S_2O_3^{2-}$ consumption. For this reason, it is important to maintain the flowrate of O_2 at a low level such that a steady concentration of Cu(II) can be reached (Aylmore, 2016). Evidence of this is shown on Figure 22 which shows the gold extraction as well as the reagent consumption as the oxygen level (DO: dissolved O_2) is decreased from 4 mg/L to 2 mg/L. It can be seen that that reducing the DO level improved the gold extraction as a result of higher availability of Cu(II) and reduced reagent consumption.

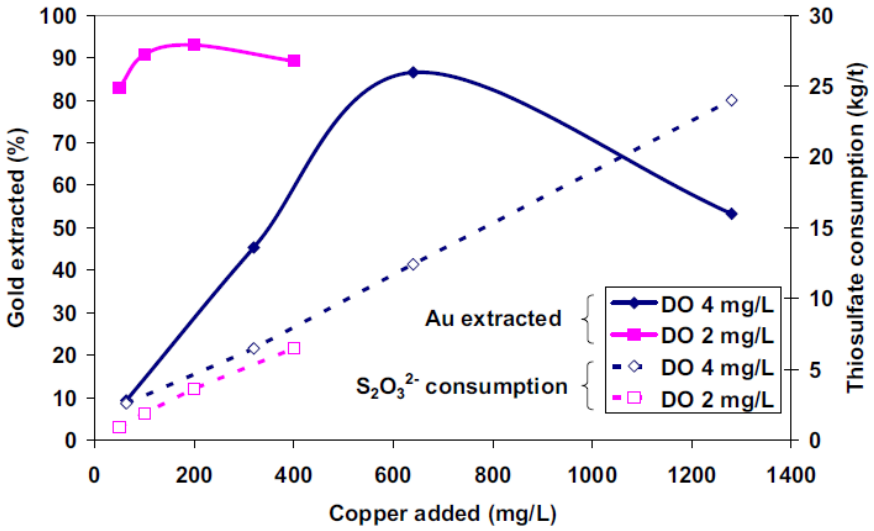

Figure 22: Gold extraction and thiosulphate consumption at varying total Cu(II) and DO levels for the leaching of an oxide ore (Aylmore, 2016)

Effect of pH

Working at high pH in gold leaching using thiosulphate as a lixiviant has been shown to be advantageous (Aylmore, 2016). However, the ore type and mineralogy of the ore plays a big role on how much of an impact pH has on the process. Aylmore (2016) proposed that the positive impact of working at high pH is significant when dealing with oxide and sulphide ores (pH 9.5-10.0) while carbonaceous ores seem not to be impacted by pH. This is shown on Figure 23 below.

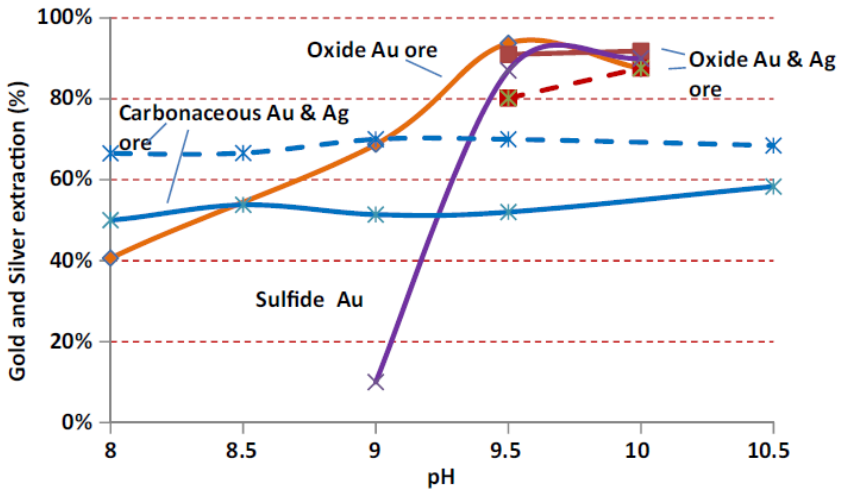

Figure 23: Impact of pH on gold and silver extraction for various ore types (Aylmore, 2016)

The positive impact of high pH can be attributed to the fact that by increasing the pH, more free NH_3 is made available and by doing so more Cu(II) is present in solution, improving the leaching process (Senanayake, 2004b). This conclusion is also supported by Jeffrey et al. (2008) who, in a comparison between sodium thiosulphate and ammonium thiosulphate leaching performances, showed that sodium thiosulphate, which normally performs worse, achieved better leaching kinetics as a result of increasing the pH to 11.4 from a value of 9.8 when working with ammonium thiosulphate.

Aylmore et al. (2014) have shown that a high pH also allows for the break-down, by hydrolysis of the degradation products of thiosulphate (tetrathionate, etc.) which have been shown to impede the leaching process. Having said that, increasing the pH also gives rise to the possibility of increasing reagent consumption (thiosulphate and ammonia). It is therefore key to carefully adjust the pH depending on the leaching system and ore type.

Effect of temperature

Similar to pH, the effect of temperature in thiosulphate leaching has a lot to do with the type of gold ore being leached. In the case of oxide ores, Abbruzzese et al. (1995) conducted an experiment that showed that increasing the temperature did not improve the leaching and was in fact detrimental. After 3 hours of leaching, the extraction dropped from 79% (at 25 °C) to 56% (at 60 °C). A plot of these results is shown on Figure 24.

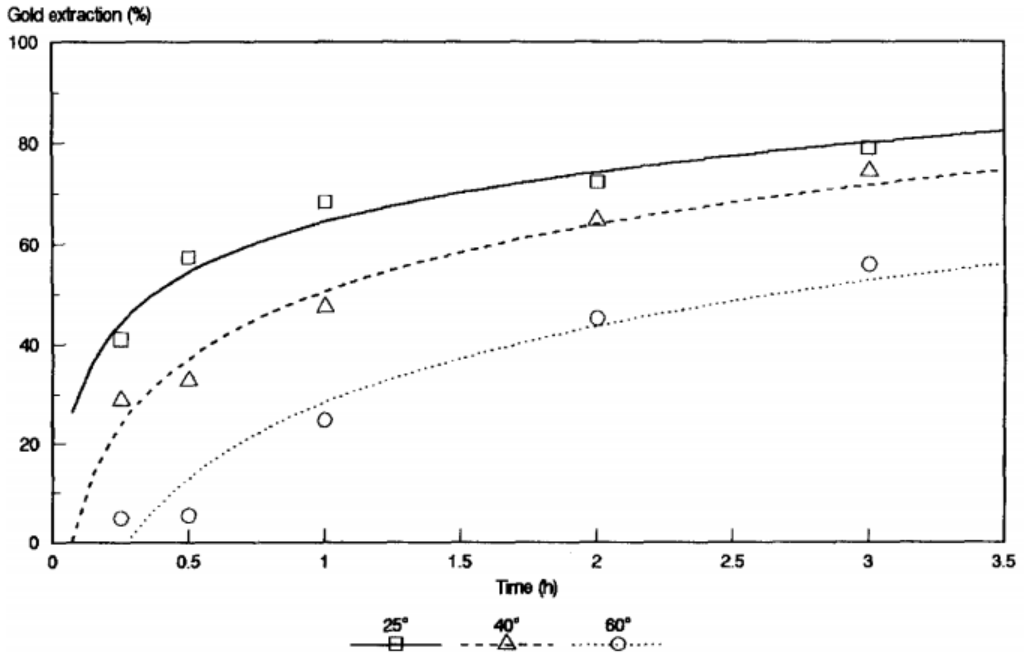

Figure 24: Effect of temperature on thiosulphate leaching of gold from an oxide ore (Abbruzzese et al., 1995)

The decreased recovery observed at temperatures above 25 °C was attributed to passivation said to occur due to the formation of cupric sulphide originating from the reaction (Eq. 18) between copper and thiosulphate, a thermal reaction facilitated by the elevation of temperature (Abbruzzese et al., 1995).

$$Cu^{2+} + S_2O_3^{2-} + H_2O \rightarrow CuS + SO_4^{2-} + 2\,OH^- \quad [18]$$

The fast kinetics of cupric sulphide formation at high temperature (~60 °C) result in the formation of a film that coats the gold surface and, by doing so, hinders its dissolution.

Increasing the temperature also promotes thiosulphate decomposition (Eqs. 19 & 20), meaning that less thiosulphate is available to complex the gold, resulting in a decrease in gold dissolution. To compensate for that loss, the amount of reagent will need to be significantly increased.

$$2\,S_2O_3^{2-} + H_2O + \frac{1}{2}O_2 \rightarrow S_4O_6^{2-} + 2\,OH^- \quad [19]$$

$$3\,S_2O_3^{2-} + 3\,H_2O \rightarrow 4\,SO_3^{2-} + 2\,S^{2-} + 6\,H^+ \quad [20]$$

Aylmore (2016) presents how different ores behave with regards to temperature (Figure 25). Sulphide ores for example, seem to respond positively to a temperature increase but only up to 40 °C after which the temperature loses its effect. The general trend for other ore types is that increasing temperature either does not impact the process at all or negatively affects it.

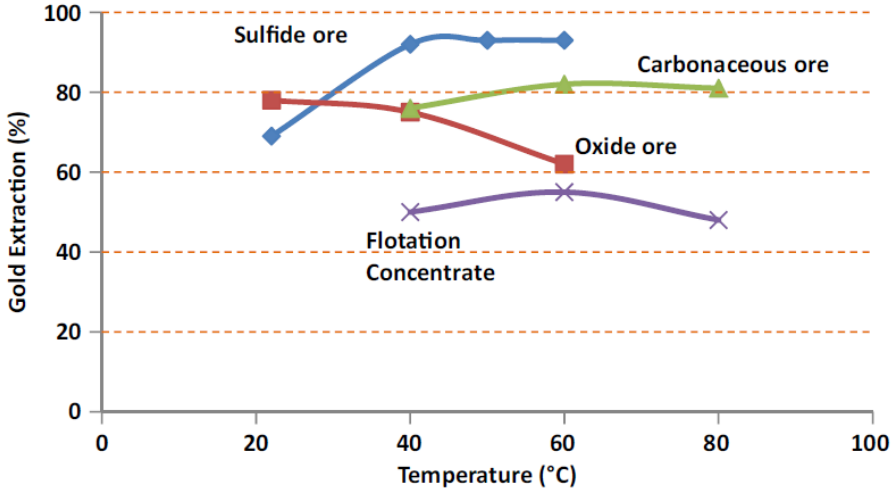

Figure 25: Effect of temperature on thiosulphate leaching of gold on various ore types (Aylmore, 2016)

Gold passivation

A key consideration is that gold dissolution can be hindered by a build-up of sulphur on its surface as a result of thiosulphate decomposition and this phenomenon depends greatly on the type of cation in solution. Baron et al. (2013) suggest that the addition of thiourea and ammonia prevent the formation or adsorption of the sulphur species that build up on the gold surface. They also showed that the leaching trends in the presence of these additives were much higher, which proved that the additives prevented any interference on the gold dissolution that would have been affected by the sulphur species.

The dissolution behaviour in thiosulphate media with NH_3 showed in the study conducted by Aylmore (2016) further supports the findings of Baron et al. (2013) that the presence of an additive such as NH_3 prevents the formation of sulphur species resulting from thiosulphate decomposition and by doing so prevents any interference on the leaching process resulting in higher dissolution rates. In the same breath, having less thiosulphate decomposition occurring

means that more thiosulphate is available to complex the gold which translates to a more efficient reagent consumption.

Influence of different thiosulphate salts

Another key factor that affects the leaching system is the type of cation that is in association with thiosulphate ($MS_2O_3^-$, M^+= Na^+, K^+, NH_4^+, Ca^{2+}). Aylmore (2016) highlighted that it plays a key role in stabilising the oxidation products.

A similar observation was made by Feng and Van Deventer (2010) who conducted a study comparing the influence of calcium, sodium and ammonium thiosulphate respectively on a pure gold sample, a pyrite concentrate and a sulphide ore. The study showed that what caused the difference in leaching behaviours between the different salts is the thiosulphate ion capacity of ion-pair formation with the respective cations under study. A plot of this comparison (on the pure gold sample) is shown on Figure 26 where it can be seen that the highest gold dissolution was achieved with calcium thiosulphate followed by ammonium thiosulphate; sodium thiosulphate performed the worst. It was concluded that the high gold dissolution achieved with calcium thiosulphate can be attributed to the divalent nature of calcium (Ca^{2+}) which helped in forming stronger ion-pairs and at the same time providing better stabilisation of the gold thiosulphate ions compared to its monovalent counterparts. This behaviour is linked to the higher stability constants that have been determined for divalent cations (such as Ca^{2+}) thiosulphate complexes. Ammonium (NH_4^+), being a larger ion that sodium (Na^+) is likely to have led to the formation of much stronger and more stable ion-pairs with the gold thiosulphate ions.

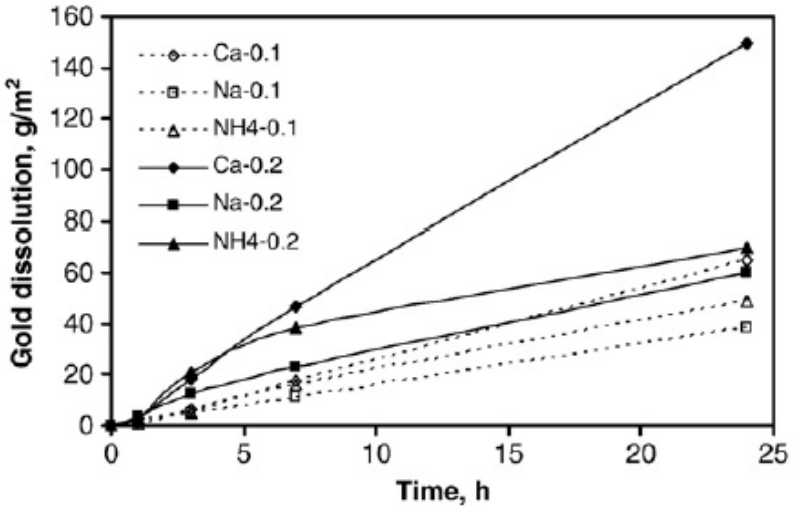

Figure 26: Leaching of pure gold sample with the 3 thiosulphate salts at 0.1 M and 0.2 M concentration (Feng and Van Deventer, 2010)

Feng and Van Deventer (2010) also highlighted that the leach curves on Figure 26 show the occurrence of an induction period at the beginning of the leaching process which indicate some form of hindered dissolution taking place. After the induction period, a roughly linear leaching behaviour can be observed in the case of calcium and sodium thiosulphate while the

ammonium thiosulphate leach curve shows a decrease in leaching rate as time proceeds indicating a more pronounced hindered dissolution.

The experiment conducted on the pyrite concentrate showed different results (Figure 27). Despite calcium thiosulphate showing faster leaching in the first 7 h, after 24 h, ammonium thiosulphate showed slightly higher dissolution rates.

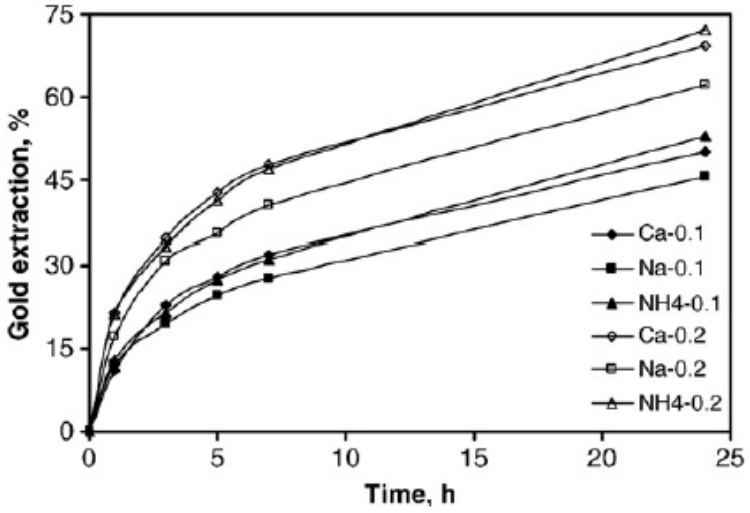

Figure 27: Leaching of pyrite concentrate with the 3 thiosulphate salts at 0.1 M and 0.2 M concentration (Feng and Van Deventer, 2010)

Feng and Van Deventer (2010) suggest that this behaviour is likely due to the fact that ammonium thiosulphate offers an added availability of free ammonia via the conversion of ammonium to ammonia which, as mentioned before, plays a key role in catalysing the gold and thiosulphate complexation and stabilising Cu(II). Although an equal amount of ammonia was initially added at the start of the experiment with the three salts, it inevitably decreased over time due to evaporation in the calcium and sodium thiosulphate systems hence the flip in leading extraction rate to ammonium thiosulphate at the 7 h mark.

The other reason why ammonium thiosulphate performed better with regards to the concentrate has to do with the fact that the gold leaching process with ammoniacal thiosulphate is greatly influenced by the behaviour of the sulphides minerals present beyond looking solely at the gold dissolution behaviour. Dissolving the sulphides minerals inevitably allows the gold to be better exposed to the lixiviant, and by doing so improves gold extraction. From the pyrite and chalcopyrite reactions in ammoniacal thiosulphate systems (Eqs. 21 & 22 respectively) it can be seen that increasing the concentration of ammonia would improve the leaching of the sulphides.

$$2FeS_2 + \frac{15}{2}O_2 + 8\,NH_3 + (4+n)H_2O \rightarrow Fe_2O_3.nH_2O + 4\,(NH_4)_2SO_4 \quad [21]$$

$$2CuFeS_2 + \frac{17}{2}O_2 + 12NH_3 + (2+n)H_2O \rightarrow 2Cu(NH_3)_4SO_4 + 2(NH_4)_2SO_4 + Fe_2O_3.nH_2O \quad [22]$$

The improved leaching of the sulphide minerals was visualised by the authors by looking at the amount of copper that was leached after the 24 h leaching period. The Cu concentration for the ammonium thiosulphate, calcium thiosulphate and sodium thiosulphate systems (all at 0.1 M) was 4090 mg/L, 3460 mg/L and 3380 mg/L respectively. This suggests that the higher amount of ammonia available in the ammonium thiosulphate system led to an improved leaching of the sulphides minerals which exposed more gold leading to higher gold extraction as presented on Figure 27.

In the final experiment conducted by Feng and Van Deventer (2010) that involved the sulphide ore (Figure 28) it was found that calcium thiosulphate performed better amongst the three salts. This was attributed to the fact that, unlike in the pyrite concentrate, the sulphide content in the sulphide ore was lower meaning that the leaching had little dependency on the interaction between the gold and sulphides species. This then resulted in attributing the higher gold extraction achieved with calcium thiosulphate to the stronger ion-pair formation as explained in the case of the pure gold sample.

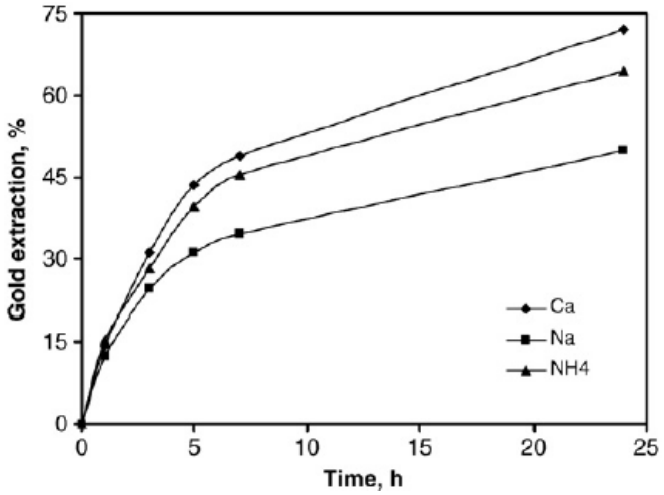

Figure 28: Leaching of sulphide ore with the 3 thiosulphate salts at 0.1 M concentration (Feng and Van Deventer, 2010)

Across all experiments involving the pure gold sample, the pyrite concentrate and the sulphide ore, sodium thiosulphate performed the worst. Overall, calcium thiosulphate shows the best results in terms of extraction, however depending on the sulphide content ammonium thiosulphate showed slightly better results due to the higher amount of ammonia available.

It is also important to note that across all experiments, ammonium thiosulphate showed a higher pH stability compared to the other two. This is attributed to the buffering effect of ammonium/ammonia.

2.5.2.3. Stability of thiosulphate and impact of Cu(II) on stability

Polythionates such as tetrathionate are the typical products of thiosulphate degradation that are formed according to Eq. 17 due to the presence of Cu(II) which destabilises thiosulphate causing it to oxidise into these species. Cu(II) here acts as a catalyst for the reaction. These polythionates are detrimental to the leaching process in the sense that thiosulphate is being utilised to form these polythionates instead of being used to complex the targeted species i.e.,

gold. This leads to high reagent consumption which translates to high operating costs. Secondly, Cu(II) which plays a key role as redox mediator is being depleted by the side reaction resulting in decreased gold dissolution rate. Thirdly, Zhang and Dreisinger (2002) have shown that these polythionates are very poisonous to ion-exchange resins which are used to recover gold from thiosulphate post-leaching. This is shown in Figure 29 (Dowex and IRA are types of base resins) where it can be seen that gold loading dropped dramatically by almost 90% as the concentration of tetrathionate increased to 0.02 M. The authors have proposed that the reason behind this behaviour is that tetrathionate has a strong absorption capacity to resins and thus competes with the gold-thiosulphate complex for ion-exchange sites until most sites are taken up by tetrathionate, at which point the resin is said to be poisoned.

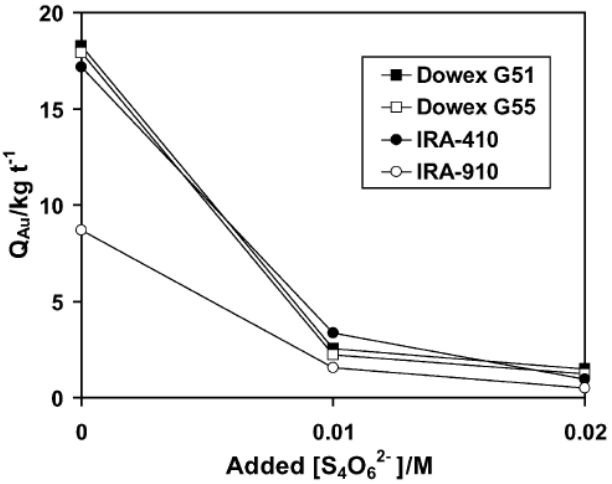

Figure 29: Effect of tetrathionate concentration on gold loading on various resins (Zhang and Dreisinger, 2002)

To provide guidelines of how to control the concentrations of the various species involved in thiosulphate leaching of gold with regards to the thiosulphate oxidation reaction that forms polythionates, Senanayake (2004a) studied how the rate of thiosulphate oxidation varied as a function of the Cu(II) concentration as well as the presence of NH_3 and O_2. The results are shown in Figure 30.

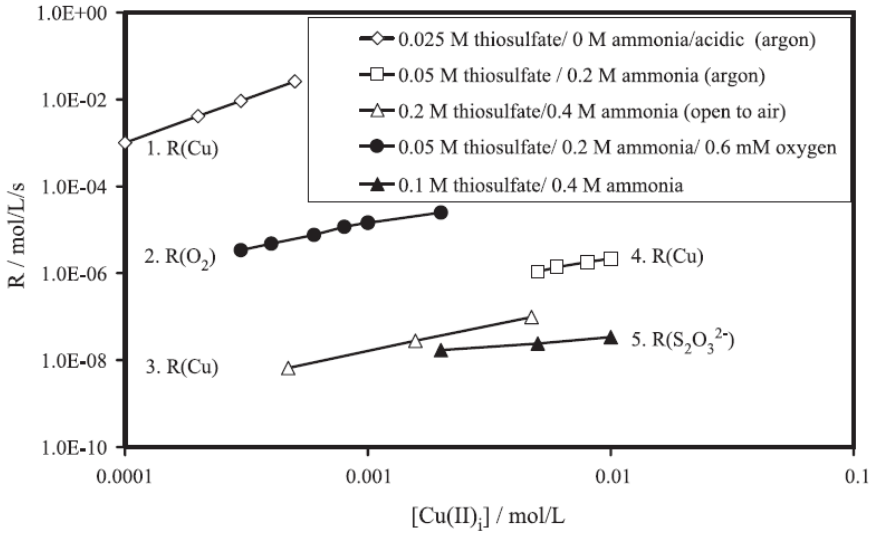

Figure 30: Rate of thiosulphate oxidation as a function of [Cu(II)] (Senanayake, 2004a)

It can be seen that the rate of oxidation of thiosulphate to form tetrathionate decreases at higher NH_3 concentration (looking at lines 1 and 4), lower O_2 concentration (lines 2 and 3) and lower Cu(II) concentration (On lines 1 to 5, lowering [Cu(II)] decreased the rate). One way to deal with tetrathionate is alkaline decomposition which is achieved by operating at pH 11. This will cause tetrathionate to decompose to thiosulphate and sulphite.

3. Materials and methods

The experimental approach followed to investigate cyanide and thiosulphate leaching as alternatives to mercury amalgamation is presented in this chapter. A description of the materials, methods and different analytical techniques applied will be provided.

The main experimental matrix was conducted in 4 phases:

- Mineralogical analysis of the ores
- Cyanide leach tests
- Thiosulphate leach tests
- Mercury amalgamation tests

3.1. Materials

3.1.1. Gold ores

3 gold ore samples originating from Zimbabwe were used to conduct the experiments. They were mined from 3 different artisanal mining locations as grab samples and were not systematically collected. They will be referred to as Sample 1, Sample 2, and Sample 3 throughout the chapters. For the 3 ore samples, bulk gold grades were obtained by fire assay, and elemental compositions were determined by ICP-OES. LECO analysis was conducted to determine total sulphur and carbonaceous content. The samples went through a series of ore preparation steps, before being used in the experiments, which are presented below.

Sample preparation

The 3 ore samples were received as mined rocks and first went through a crushing stage using a jaw crusher (Figure 31a). This was followed by dry milling using a rod mill (Figure 31b). The ores were then sieved (Figure 31c) using three sieves of 300 µm, 212 µm and 150 µm aperture. Once they were separated into the different size ranges (Figure 32a), they were split using a rotary splitter (Figure 32b) to ensure proper mixing and homogeneity of the ores such that the samples used in the experiments could accurately represent the bulk ores for each size fraction.

a)  b)  c) 

Figure 31: a) Jaw crusher b) Rod mill c) Sieves

a)  b) 

Figure 32: a) Ore sample separated into different size fractions b) Rotary splitter

Table 5 shows the ore masses obtained in each size range after sieving for each ore type, as well as the bulk gold grades of the 3 ores. The gold grades were determined by fire assay.

Table 5: Ore size ranges

Ore deposit	Bulk grade (g/t)	Size range (µm)	mass (g)	mass fraction (%)
Sample 1	7.6	+300	4462.4	70.3%
		-300 + 212	352.7	5.6%
		-212 + 150	549.3	8.7%
		-150	983.5	15.5%
		Total	**6347.9**	100.0%
Sample 2	20.4	+300	4689.8	73.1%
		-300 + 212	309.7	4.8%
		-212 + 150	323	5.0%
		-150	1089.1	17.0%
		Total	**6411.6**	100.0%
Sample 3	18.7	+300	3924.5	76.5%
		-300 + 212	181.5	3.5%
		-212 + 150	161.5	3.1%
		-150	862.1	16.8%
		Total	**5129.6**	100.0%

In ASGM, the PSD typically used in leaching operations is below 250 µm (Veiga et al., 2009). To conduct the experiments in a range close to this value whilst at the same time have enough material available, it was decided, for each ore, to further mill the samples at +300 µm (Table 5), which represented more than 70% of the ore mass, and recombine the milled ores in the size ranges -300 +212 µm and -212 +150 µm into a new size range -300 +150 µm. By doing this, 1.5 kg of ore in the adequate size range for each of the 3 ore samples were obtained (Table 6).

Grade analysis by fire assay was done for the 3 size ranges (shown in Table 6), as well. The 3 ores, Sample 1, Sample 2, and Sample 3 at -300 +150 µm PSD had grades of 5.9 g/t, 16.3 g/t and 14.2 g/t, respectively. These values were used in all calculations for gold extraction.

Table 6: New size ranges after recombining

Ore deposit	Grade (g/t)	Size range (µm)	mass (g)	mass fraction (%)
Sample 1	4.7	+300	399	16.7%
	5.9	-300 +150	1500	62.6%
	4.4	-150	496	20.7%
Sample 2	22.4	+300	419	16.2%
	16.3	-300 +150	1500	58.1%
	21.4	-150	663	25.7%
Sample 3	11.4	+300	900	32.2%
	14.2	-300 +150	1500	53.7%
	16.3	-150	395	14.1%

Based on the gold grades and mass fractions of the ores in each size range, the gold distribution in each ore was determined and is presented in Table 16 (Appendix B: Gold distribution). 69%, 51% and 56% of the gold is found within the -300 +150 µm PSD for Sample 1, Sample 2, and Sample 3, respectively.

Elemental composition

For the 3 ores, compositions of key elements were obtained by fire assay and ICP-OES, and are presented in Table 7.

Table 7: Bulk ore elemental composition

	Au	Cu	Co	Fe	Ca	Mg
	g/t	g/t	g/t	%	%	%
Sample 1	7.60	128.14	50.93	7.27	1.18	2.37
Sample 2	20.40	102.21	24.10	4.12	7.86	0.78
Sample 3	18.70	96.71	25.64	3.95	4.56	1.31

3.1.2. Reagents

For cyanide leaching experiments, sodium cyanide (97%) was used. Sodium carbonate (99.5%) and sodium bicarbonate (≥ 95%) were used to ensure that pH is maintained above 9.3 to prevent the formation of hazardous hydrogen cyanide gas (Mintek, 1999). For thiosulphate leaching experiments, ammonium thiosulphate (98%), copper sulphate ($CuSO_4.5H_2O$: 98.5%) and ammonia (30% in water) were used. Mercury (100%) was also used to conduct mercury amalgamation tests for the purposes of assessing the performance of the other two reagents against it. All reagents were sourced from Merck expect for mercury which was sourced from Bellray.

3.2. Apparatus

3.2.1. Batch stirred tank reactor (BSTR)

3 jacketed BSTRs with a volume of 1 L (Figure 33) were used to conduct the leach experiments. A solids loading of 30% was chosen to mimic what is typically done in ASGM operations (Veiga et al., 2009). The solution inside the reactors were agitated using mounted mechanical stirrers with impellers rotating at 300 rpm. This allowed for constant mixing of the solution inside the reactors. Constant mixing is important to maximise contact time between the lixiviant and the mineral particles which in turn maximise the capacity of the lixiviant to dissolve the targeted metal, i.e., gold in this case. It also prevents the accumulation of solids at the bottom of the reactors which would render the process inefficient since some gold particles would not be exposed to the lixiviant. The agitation speed of 300 rpm was chosen based on leach experiments conducted by Breuer and Jeffrey (2002). The BSTRs were also used to conduct a laboratory scale vat leaching experiment described in section 3.3.1.2.

Temperature was kept at ambient temperature (26 °C) using a water bath, for all experiments. This was done because ASGM operations are typically conducted at the atmospheric temperature of the day (20 °C-30 °C) to minimise additional costs of heating and cooling. A case could be made not to control the temperature in the laboratory, however laboratory temperatures are not ambient due to maintenance of a microclimate through air conditioning. The use of a water bath was therefore necessary. In addition, it was decided to work at a constant and known temperature so that the leaching behaviour would only be dependent on the cyanide and thiosulphate concentrations which were the key parameters varied in this study. The 3 reactor set-up, shown in Figure 33, allowed for simultaneous leaching of the 3 ores under study.

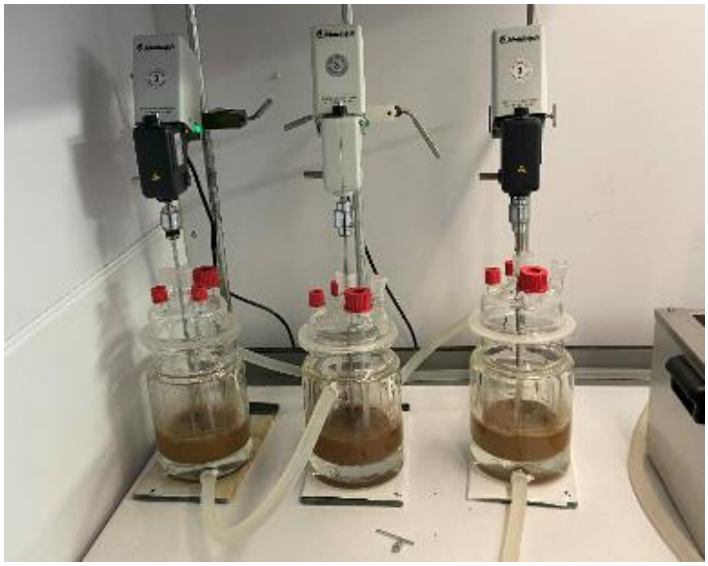

Figure 33: BSTR set-up

3.2.2. Centrifuge

Due to the high solids loading, obtaining clear liquid samples from which gold concentration could be determined by MP-AES was a challenge. As a remedy, a centrifuge (Figure 34a) was used to depress all solid particles such that it would be possible to easily pipette out the superficial clear liquid as shown in Figure 34b & c.

a) 

b) 

c) 

Figure 34: a) Centrifuge, pregnant leach solution sample b) before centrifugation c) after centrifugation

3.2.3. Cynoprobe

Although the focus of the leaching experiments was to assess the extraction behaviour of gold, it was important to understand the rate at which cyanide is consumed throughout the leaching process. To achieve this, a lab cynoprobe (Figure 35), developed by MINTEK, was used. It uses an electrochemical amperometric method to measure the concentration of free and weak acid dissociable cyanide which are cyanide species that can be liberated at low pH (4.5) such as HCN, CN^- and metal complexes such as Cu, Ni and Ag complexes (MINTEK, n.d.). The cynoprobe consists of an electrolytic cell (80 mL capacity) in which the cyanide solution is contacted with a silver electrode. Electrons transferred in this process generate a current that is measured. The cynoprobe then develops a linear relationship between the measured current and the cyanide concentration from which the latter can be determined. Of the 12 mL leach sample collected during experiments, 4 mL were used for cyanide analysis. The 4 mL solution was diluted by a factor of 20 to make the 80 mL solution required by the cynoprobe.

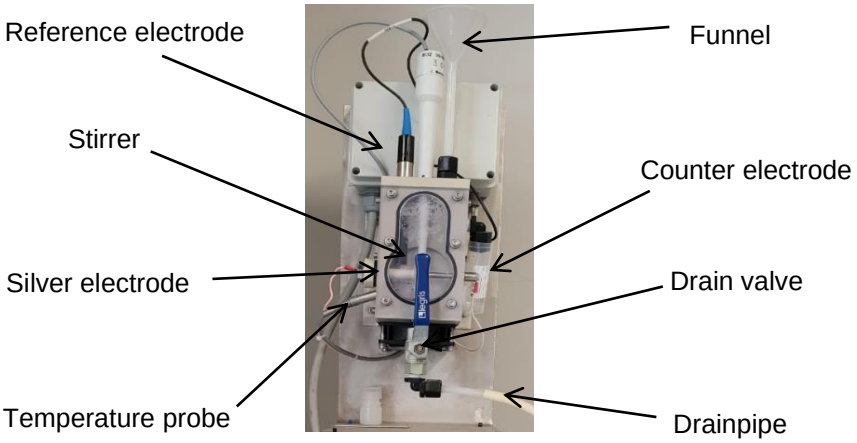

Figure 35: Mintek Lab Cynoprobe

3.3. Methods

The experimental plan designed to investigate the performance of cyanide leaching and thiosulphate leaching is presented below in sections 3.3.1 and 3.3.2, respectively. Section 3.3.3 presents the experimental approach followed for mercury amalgamation tests used as basis for comparison.

3.3.1. Cyanide leaching

3.3.1.1. Leach tests

Cyanide concentration in ASGM is often kept very high (10 g/L or higher) simply because it is believed that the more the better for the process. However, for this series of experiments, it was decided to operate at 3 set concentrations (1 g/L, 3 g/L and 5 g/L) which fall within a more reasonable range prescribed by other researchers (Veiga et al., 2009). The three concentrations selected provide enough excess of cyanide such that the reagent concentration is not a limiting factor. Calculations pertaining to this are presented in Appendix A: Stoichiometric calculations of reagent requirement for Au leaching. For all leaching experiments, 12 mL leach samples were collected at different time intervals.

The conditions of the cyanide leaching experiments are summarised in Table 8.

Table 8: Cyanide leaching experiment conditions

Parameters	Specifications
Reagent concentration	1 g/L, 3 g/L, 5 g/L
Temperature	26 °C
Particle size	-300 + 150 µm
pH	10-11
Aeration	Air ingression from an open reactor
Mass of ore used	100 g/stirred tank reactor
Solids loading	30%

3.3.1.2. Vat leach test

Since cyanide vat leaching is a common practice in ASGM, it was decided to conduct an experiment mimicking it in a laboratory environment so that it could be compared to the agitated cyanide leaching experiments. For this test, the same reactors, and experimental conditions (-300 +150 µm PSD, 30% solids, 26°C) used for the agitated leach tests were applied; however, the impellers were removed so that the solution could sit still. At 30% solids, the solution covered the solids and was at a level high enough to account for evaporation. Leach samples were taken close to the surface of the settled solids. This test was conducted at a cyanide concentration of 5 g/L for the 3 ores under study.

3.3.2. Thiosulphate leaching

In this set of experiments, 3 parameters were varied: Cu(II) concentration, $(NH_4)_2S_2O_3$ concentration and NH_3 concentration. As highlighted in section 2.5.2, Cu(II) and NH_3 play key roles in the leaching process in thiosulphate systems. To be able to compare leaching performance between cyanide and thiosulphate, the particle size was kept the same for both sets of experiments. The concentrations of $(NH_4)_2S_2O_3$ selected are in enough excess to not be a limiting factor in the leaching process. Calculations to ascertain this can be found in Appendix A: Stoichiometric calculations of reagent requirement for Au leaching.

Table 9 presents a summary of the conditions at which the various tests were run.

Table 9: Thiosulphate leaching experiment conditions

Parameters	Specifications
Reagent concentration	0.1 M & 0.5 M $(NH_4)_2S_2O_3$ 0.5 M & 1 M NH_3
Temperature	26 °C
Particle size	-300 + 150 µm
pH	10-11
Oxidant/catalyst	1 mM & 10 mM $CuSO_4$
Mass of ore used	100 g/stirred tank reactor
Solids loading	30%

Table 10 shows the experimental matrix for the thiosulphate leach tests. To investigate the effect of $(NH_4)_2S_2O_3$ concentration, the data from tests 1 and 2 will be compared. To investigate the effect of Cu(II) concentration, tests 1 and 3 will be compared as well as tests 2 and 5. Finally, to assess the effect of NH_3 concentration, tests 2 and 4 will be compared.

Table 10: Experimental matrix of thiosulphate leaching tests

Test	1	2	3	4	5
$[(NH_4)_2S_2O_3]$	0.1 M	0.5 M	0.1 M	0.5 M	0.5 M
$[NH_3]$	0.5 M	0.5 M	0.5 M	1 M	0.5 M
$[Cu^{2+}]$	1 mM	1 mM	10 mM	1 mM	0 mM

3.3.3. Mercury amalgamation

A mercury amalgamation experiment was conducted in a laboratory environment. The 3 ores under study were panned using a plastic basin and the concentrates were then amalgamated with mercury (Figure 36). The experiment was, however, unsuccessful due to the small quantity of ore available (~200 g of ore used). Since the ore grade varies between 7 and 20 g of gold per tonne of ore, a 200 g sample, which further decreases in quantity after panning, would not be enough to yield a recoverable gold-mercury amalgam. Figure 37a shows how no amalgam was found in the cloth used to separate out the amalgam by removing excess mercury and no gold sponge was recovered after roasting (Figure 37b). Amalgam roasting was done in a fume hood to contain the mercury vapours generated.

Figure 36: Mixing of mercury and ore concentrate

a) b)

Figure 37: a) no visible amalgam ball recovered b) burning of small particles potentially being amalgam particles

Due to these limitations, Mr Wilson Masuku, a master's candidate in Chemical Engineering at the University of Cape Town, whose research focus is in ASGM as well and who was already well placed in the field, conducted a Hg amalgamation field experiment whose results were used in this study as benchmark. The material used was similar to Sample 3. Although it was not representative of Sample 1 and 2, it was used as a reference point to compare the results of this study to those obtained for an ore typical of artisanal mining areas. A summary of the field work report can be found in Appendix C: Field work summary report. Approximately 100.7 g of gold was recovered from processing 3 t of ore.

3.4. Analysis techniques

3.4.1. pH

Measuring pH was of particular importance in cyanide leaching experiments, given the hazardous nature of HCN gas which forms at a pH below 9.3. A Metrohm pH meter was used with the probe calibrated for alkaline regions using standards at pH 7.01, 9.21 and 12.00. This was done at the start of each day dedicated to the preparation of lixiviants.

3.4.2. Solids analysis

3.4.2.1. Fire assay

This technique was used to determine the Au grade of the 3 ore samples. Fire assay analysis consists of first pulverising a solid sample, then mixing it with a fluxing agent to achieve efficient melting of the ore sample, and finally separating the gold from gangue phases. The ore-flux mixture is heated in a furnace and a collector (in most cases either Ni or Pb) is used to absorb the gold. After allowing the collector to cool, a process known as cupellation takes place to recover the gold. This is done either by oxidising the collector (in the case of Pb) such that it is absorbed into the cupel and gold can be recovered in the form of a bead and analysed by ICP or, in the case of Ni, dissolving the collector in HCl and recovering the gold by filtration (SGS Minerals Services, 2013).

3.4.2.2. LECO elemental analysis

LECO analysis was used to determine the total sulphur and carbon content of the ores. However, it can also determine hydrogen, nitrogen, and oxygen content. This analysis technique detects and measures the concentration of combustion gases by relying on the use of thermal conductivity and infrared absorption (Gazulla et al., 2012).

3.4.2.3. X-ray fluorescence (XRF)

XRF is an analysis technique that measures the composition of major as well as trace elements within a sample in concentrations varying from ppm to ppb. This analysis was done on the 3 ores samples. XRF instruments comprise of an X-ray source and a detector. The X-ray generated by the source is aimed at the surface of a sample, in some instances a filter may be applied to the X-ray tube to modify the X-ray beam. When the latter hits the surface of a sample, secondary X-rays, which are specific to an element, are generated and captured by the detector. An analyser, which processes the X-rays captured, generates intensity peaks of the X-rays which then identify the element and allow the analyser to calculate the elemental composition. XRF results were produced together with data from loss on ignition (LOI) which is a method used to measure the water and organic matter content of a sample by burning it at high temperatures and weighing it before and after burning to determine the weight loss (Santisteban et al., 2004).

3.4.2.4. X-ray diffraction (XRD)

XRD works in a similar way to XRF in the sense that an X-ray beam is projected on the surface of a sample and secondary X-rays are generated, collected by a detector, and processed by an analyser. However, XRD is specifically used to quantify minerals and identify mineral

structures within a sample using an X-ray of single wavelength. The analysis was therefore conducted to obtain more information on the different minerals present in the 3 ore samples.

3.4.2.5. QEMSCAN analysis

QEMSCAN is an analysis tool that quantifies minerals and elements within an ore sample using an electron beam technology referred to as scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The instrument used was an FEI FEG QEMSCAN 650F which is equipped with two Bruker ZFlash 6130 EDS detectors. The analysis was conducted on the 3 ore samples to shed light on the mode of occurrence of the gold within them. Two unsized standard blocks were prepared for each ore. For each sample, 1 g of the sample aliquot was mixed with carbon black powder and resin and thereafter cured in 30 mm by 10 mm cylinder moulds. The samples then went through various grinding and polishing steps. They were dried and carbon coated using a Quorum Q150T E carbon coater. The QEMSCAN equipment was set to perform at an accelerating voltage of 25 kV and beam current of 10 nA. Particle mineral analysis (PMA) was then performed on each sample at a field size of 1000 µm and 3.0 point spacing. In the software, there is a mineral library called a species identification protocol (SIP) list which contains a list of mineral species where each mineral has assigned elemental concentrations and/or peak intensities. The surface of the polished block is divided into pixels and X-ray spectra and back-scattered electron (BSE) data are used to match each pixel to a mineral specie. The data is then processed by checking that the minerals are correctly classified and by validating the data against XRD and XRF data.

3.4.2.6. Diagnostic leach

Diagnostic leaching is a method that can be used to make a qualitative assessment of the mode of occurrence of gold within an ore and provide some information on the extent of its refractoriness. With this information, a pre-treatment method can be designed to adjust or manipulate certain process parameters to try to maximise gold extraction during the leaching stage (Celep et al., 2008). In a diagnostic leach, mineral species and phases in the ore can be selectively decomposed by specific reagents. Table 11 shows the different chemicals that can be used to decompose various minerals.

Table 11: Treatment methods for diagnostic leaching (Celep et al., 2008)

Treatment	Minerals likely to be destroyed
NaCN	Gold
Na_2CO_3	Gypsum and arsenates
HCl	Calcite, Dolomite, Galena, Pyrhotite, Goethite
$HCl/SnCl_2$	Hematite, Calcine, Ferrites
H_2SO_4	Cu-Zn sulphides, Labile pyrite
$FeCl_3$	Sphalerite, Labile Sulphides, Tetrahedrite
HNO_3	Pyrite, Marcasite, Arsenopyrite,
Oxalic Acid Washes	Oxide Coatings Silicates
HF	Silicates
Acetonitrile elution	Gold adsorbed on carbon

The sequence of the leach tests is presented on Table 12. Since the main goal of this method is to understand the refractoriness of the gold, the focus in stage 1 is to remove any gold that can be recovered by gravity concentration and collect the tailings which will go through the

series of increasingly aggressive leach tests. After each leaching stage, leach samples were collected and sent for ICP-OES analysis and the solids were then prepared for the next leach stage by washing and drying. The diagnostic leach study was done on the 3 ore samples using BSTRs at 300 rpm, 26 °C and 30% solids (for cyanide leach) and 10% solids (for acid leach). Each leach test in the sequence was ran for 24 h.

Table 12: Diagnostic leach sequence

Stage	Treatment method
1	Gravity concentration by panning
2	Cyanide leach (20 g/L NaCN)
3	Hydrochloric acid leach (12% HCl)
4	Cyanide leach (20 g/L NaCN)
5	Sulphuric acid leach (48% H_2SO_4)
6	Cyanide leach (20 g/L NaCN)
7	Nitric acid leach (33% HNO_3)
8	Cyanide leach (20 g/L NaCN)
9	Reverse aqua regia leach (HNO_3: 55%, HCl: 32%, ratio 5:1)

3.4.3. Solutions analysis

3.4.3.1. Microwave Plasma Atomic Emission Spectroscopy (MP-AES)

MP-AES was used to determine the concentrations of Au and Cu in solution following the leach tests. This method presents the advantage of being able to detect gold at a concentration as a low as 2.1 µg/L which is particularly beneficial if there is no prior knowledge of the gold extraction to expect. An Agilent 4200 MP-AES was used to conduct the analyses. This atomic spectrometer runs on air using a nitrogen generator to conduct elemental analysis and can simultaneously analyse many elements.

3.4.3.2. Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES)

ICP-OES was used to determine the concentrations of key elements targeted in the series of diagnostic leach tests. These include Au, Cu, Fe and As. It was also used to determine the composition of base metals in the ore samples. A Varian ES 730 ICP-OES was used to conduct the analysis. This spectrometer uses an argon plasma to excite the atoms of the elements in a liquid sample, and the light that is emitted as the atoms return to their group state is captured by the analyser. The intensity of the light generated can then be related to the concentration of a given element.

4. Results and discussion

In this section, the results of the experiments conducted, as planned out in section 3.3, are presented and discussed. These results aim to provide a better understanding of the mechanisms in which cyanide and thiosulphate leaching can be applied effectively to leach gold in the particular context of ASGM as well as how these methods compare to mercury amalgamation. To introduce this section, a summary of the mineralogical data of the 3 ores, which will inform the interpretation of the leaching results, is presented.

4.1. Ore characterisation

4.1.1. Bulk mineralogy

XRF results (Table 13) showed high proportions of SiO_2 (Sample 1: 57.6 wt.%, Sample 2: 62.8 wt.% and Sample 3: 63.4 wt.%), CaO (Sample 1: 2.2 wt.%, Sample 2: 11.6 wt.% and Sample 3: 7.9 wt.%), Fe_2O_3 (Sample 1: 10.7 wt.%, Sample 2: 5.6 wt.% and Sample 3: 6.9 wt.%), Al_2O_3 (Sample 1: 13.8 wt.%, Sample 2: 5.3 wt.% and Sample 3: 7.5 wt.%) and LOI % (Sample 1: 5.4 wt.%, Sample 2: 10.8 wt.% and Sample 3: 7.6 wt.%). The major mineral proportions identified by XRF were corroborated by the XRD and QEMSCAN bulk minerology data (Table 14) which showed that the 3 ores are predominantly made of quartz, feldspar, chlorite, mica, calcite and Fe-Ti oxides.

Table 13: XRF data

Sample	Fe_2O_3 %	MnO %	Cr_2O_3 %	TiO_2 %	CaO %	K_2O %
Sample 1	10.7	0.2	0.1	0.7	2.2	1.1
Sample 2	5.6	0.1	0.1	0.5	11.6	0.2
Sample 3	6.9	0.1	0.1	0.6	7.9	0.5

Sample	P_2O_5 %	SiO_2 %	Al_2O_3 %	MgO %	Na_2O %	LOI %	Total
Sample 1	0.1	57.6	13.8	4.3	2.4	5.4	98.5
Sample 2	0.1	62.8	5.3	1.4	0.7	10.8	99.1
Sample 3	0.1	63.4	7.5	2.9	1.1	7.6	98.6

Table 14: XRD and QEMSCAN bulk mineralogy data

Minerals	XRD (values in mass %)			QEMSCAN (values in mass %)		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
Quartz	34.0	67.0	64.0	36.8	59.8	51.1
Feldspar	33.0	7.0	12.0	19.8	8.5	12.0
Chlorite	25.0	5.0	10.0	24.6	5.8	14.2
Mica	6.0	2.0	3.0	8.6	1.4	3.6
Calcite	2.0	19.0	11.0	1.1	14.1	7.0
Pyroxene	-	-	-	2.4	1.0	2.7
Amphibole	-	-	-	0.5	3.0	4.0
Talc	-	-	-	0.1	0.01	0.2
Fe-Ti oxides	-	-	-	5.8	5.7	4.4
Apatite	-	-	-	0.2	0.2	0.2
Sulphides	-	-	-	0.01	0.33	0.03
Other	-	-	-	0.2	0.5	0.3

QEMSCAN analysis revealed the presence of sulphide minerals which, although small in amounts, are notable since they can host significant amounts of gold in the form of ultrafine solids solutions, as highlighted in section 2.1.2, and recovering gold from them via leaching is often difficult since it is locked inside the sulphide mineral matrix.

4.1.2. QEMSCAN using SEM-EDS

By manual search, gold was visually examined in the 3 ores (Figure 38, Figure 39, and Figure 40). This indicates that some of the gold present in these ores exists in its native form as free gold and can therefore be extracted effectively by leaching and gravity separation as well. The gold particles in Figure 38, Figure 39, and Figure 40 had a diameter of 4 µm, 5 µm, and >1 µm, respectively.

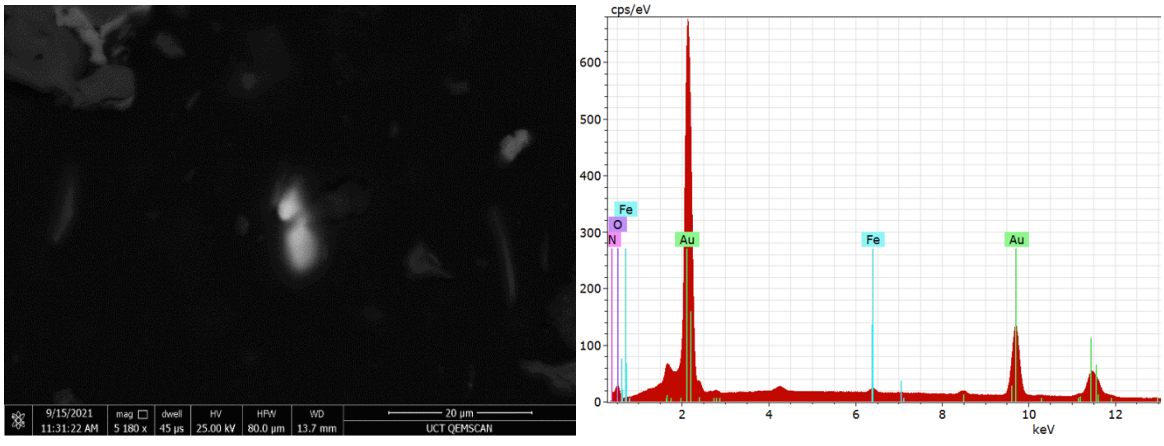

Figure 38: SEM-EDS image of gold particle in Sample 1

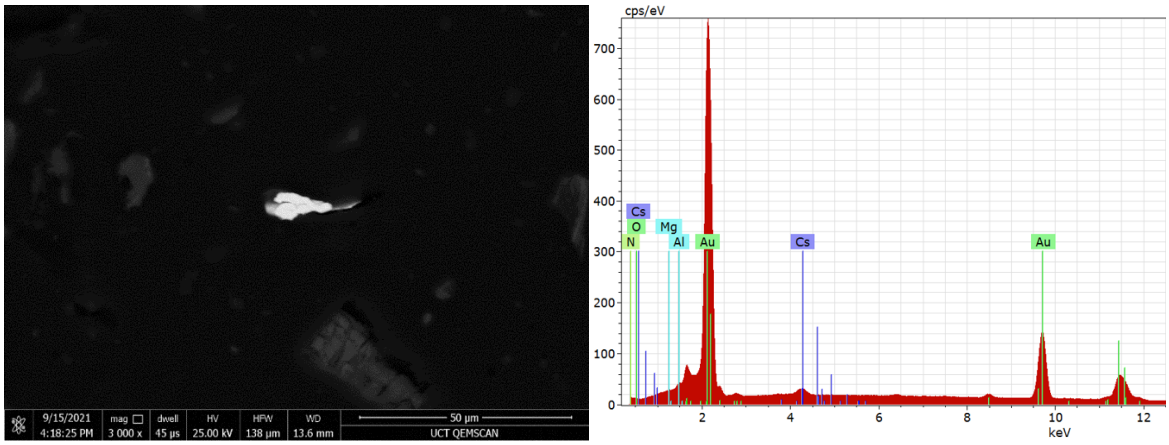

Figure 39: SEM-EDS image of gold particle in Sample 2

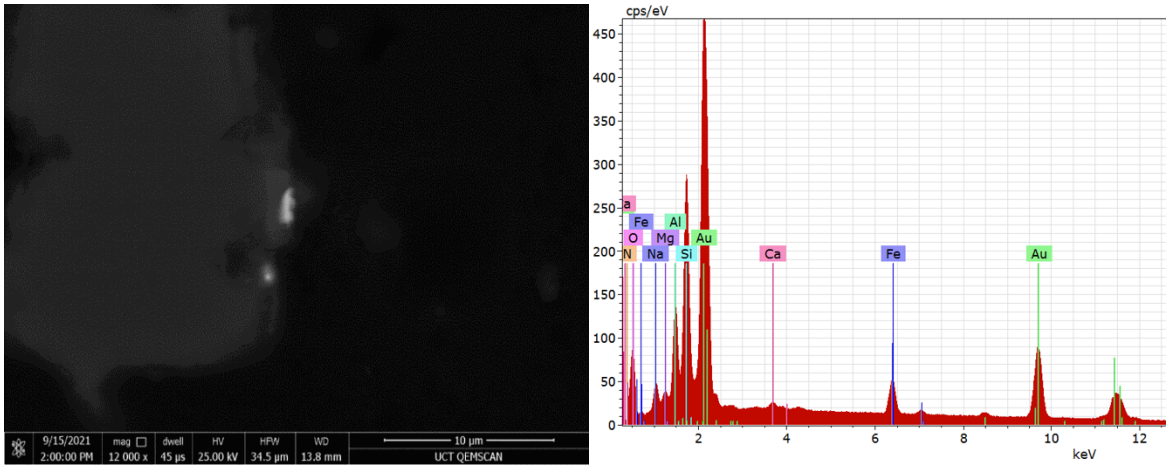

Figure 40: SEM-EDS image of gold particle in chlorite boundary in Sample 3

Evidence of the presence of sulphide minerals (pyrite and arsenopyrite) in Sample 1 and Sample 3 was found as shown in Figure 41. These sulphide minerals can host significant amounts of gold in the form of ultrafine particles and recovering gold from them via direct leaching is often difficult since it is locked inside the sulphide mineral matrix, which is inert to most gold leaching chemistries.

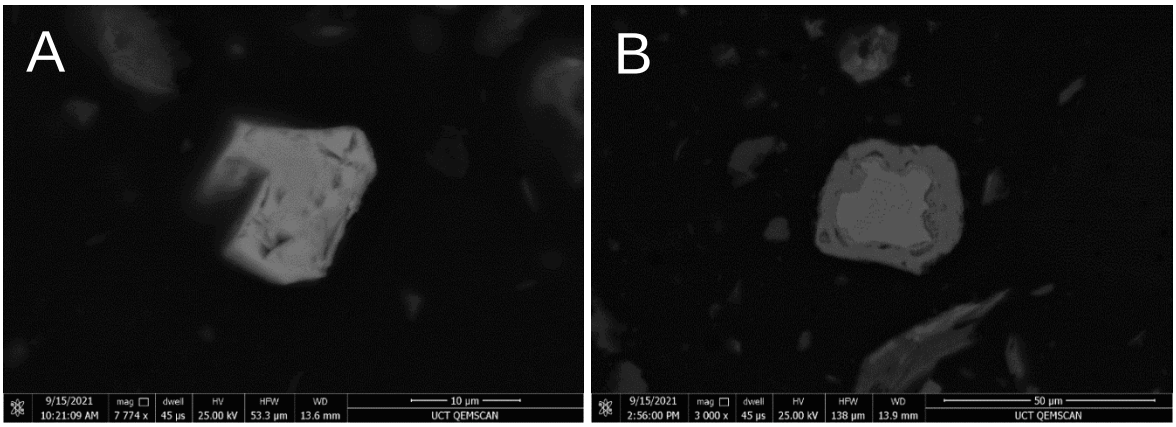

Figure 41: A) Arsenopyrite in Sample 1 B) Pyrite surrounded by iron oxide layer in Sample 3

4.1.3. Diagnostic leach

The diagnostic leach tests were conducted following the procedure presented in Table 12. Stage 2, the first cyanide leach test after panning (Figure 42 A) showed a final gold extraction of 0.81 mg/L, 1.5 mg/L and 1.3 mg/L for Sample 1, Sample 2, and Sample 3, respectively. The gold extracted at this stage is not considered refractory since it was recovered by conventional cyanidation. In stage 3, some more gold was extracted by HCl leach (0.18 mg/L, 0.33 mg/L and 0.12 mg/L for Sample 1, Sample 2, and Sample 3, respectively) which means that the previous cyanidation step, which was done at a high cyanide concentration of 20 g/L, did not recover all the gold. This indicates that this portion of the gold leached by HCl was refractory to cyanide and possibly being hosted by sulphides such as pyrrhotite as indicated in Table 11. The HCl leach also extracted As, especially in Sample 2, as well as Cu and Fe.

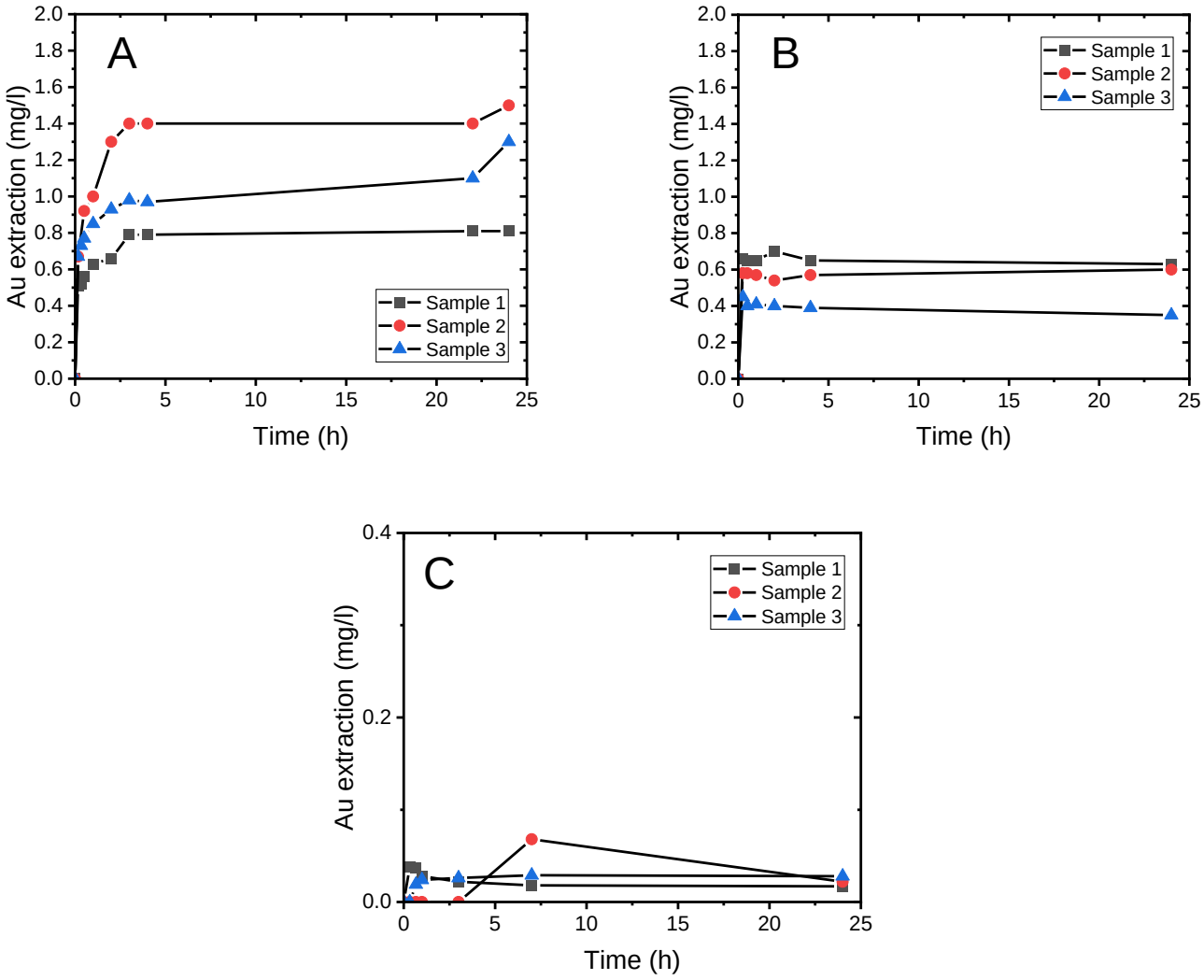

Figure 42: Cyanide leaching using 20 g/L NaCN A) stage 2 B) stage 4 C) Stage 6

Stage 4, the second cyanide leach test (Figure 42 B) achieved some gold extraction although much less than the first cyanide leach (0.63 mg/L, 0.60 mg/L and 0.35 mg/L for Sample 1,

Sample 2, and Sample 3, respectively). The HCl leach unlocked and leached some refractory gold which was then leached by cyanide in stage 4. H_2SO_4 leach results in stage 5, did not release any additional gold which is expected since the primary role of acid digestion is to digest materials that lock up gold, such that the gold that has been exposed can be recovered by cyanidation. This can be confirmed by comparing the cyanidation results of stage 4 (Figure 42 B) to those of stage 6 (Figure 42 C). In stage 4, the gold extractions for the 3 ores plateaued over the entire leaching period (24 h) meaning that cyanide did not have access to any additional gold beyond what it managed to extract. However, the chemical attack by H_2SO_4 in stage 5 further unlocked some gold which was then recovered by cyanidation in stage 6 (Figure 42 C). The final gold extractions by cyanide leach in stage 6 were, however, very low at 0.02 mg/L, 0.02 mg/L and 0.03 mg/L for Sample 1, Sample 2, and Sample 3, respectively. No more gold was recovered in the remaining tests indicating that the ores had been spent and the maximum amount of gold was recovered. Table 15 shows the concentrations of key elements that were dissolved during acid digestion although it is important to note that the key results of this diagnostic leach are those of the cyanide leaching tests that followed each acid digestion step.

Table 15: Metal concentrations in acid leach samples (NQ: not quantified, detection limit = 0.05 mg/L)

Stage #	Treatment	Ore	Element analysed by ICP-OES (mg/L)			
			As	Au	Cu	Fe
3	HCl leach (12%)	Sample 1	5.5	0.18	2.3	2545
		Sample 2	28.8	0.33	3.9	2341
		Sample 3	7.7	0.12	0.55	970
5	H_2SO_4 leach (48%)	Sample 1	53.1	NQ	4.8	1043
		Sample 2	16.1	NQ	2.3	264
		Sample 3	7.6	NQ	3.7	620.2
7	HNO_3 leach (33%)	Sample 1	NQ	NQ	35.7	634
		Sample 2	NQ	NQ	0.89	35.4
		Sample 3	NQ	NQ	30.7	500.4
9	Reverse aqua regia leach (HNO_3 55% & HCl 32%) 5:1	Sample 1	NQ	NQ	3.8	20.7
		Sample 2	NQ	NQ	2.6	18.6
		Sample 3	NQ	NQ	2.4	21.7

Figure 43 shows the cumulative total Au extracted in each of the stages for which Au concentration could be measured, for all 3 samples. The cumulative total Au extracted from the tailings obtained after panning (stage 1) were 4.4 mg Au/ Kg ore, 10.4 mg Au/ Kg ore and 6.8 mg Au/ Kg ore for Sample 1, Sample 2, and Sample 3, respectively. These totals amount to 75%, 64% and 48% of the Au originally present in Sample 1, Sample 2, and Sample 3, respectively. These percentages are a quantitative representation of the extent of refractoriness of these ores. The implication of this for ASM, where ores similar to the ones

used in this study are found, is that miners would be losing 48–75% of gold in their tailings by only relying on panning and Hg amalgamation of concentrates.

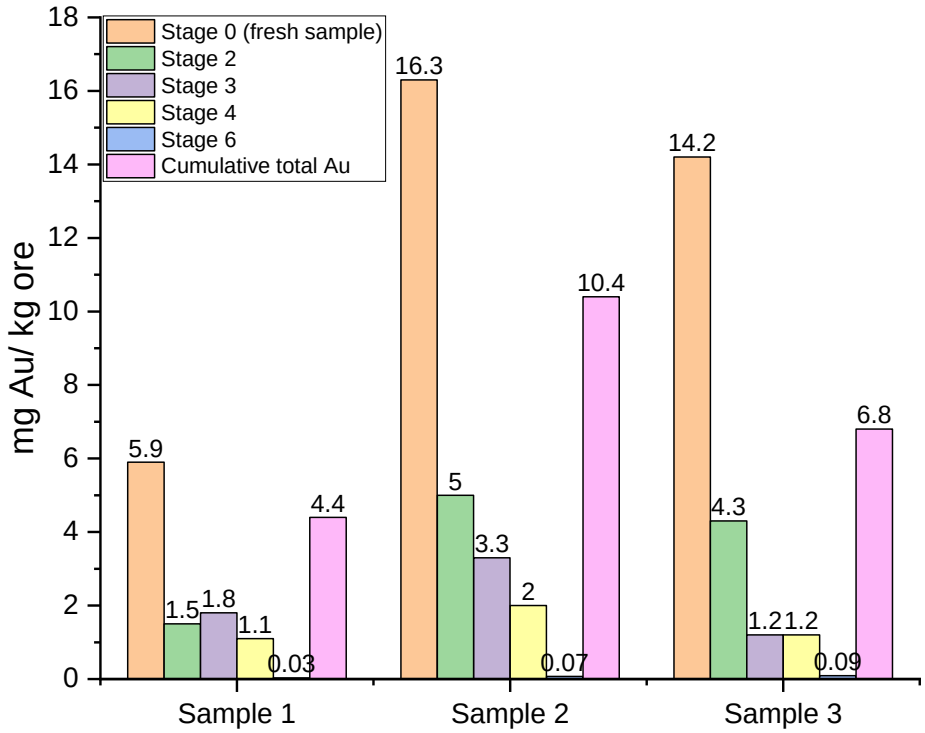

Figure 43: Au extraction for each stage of the diagnostic leach, for each sample

The concentrate obtained in stage 1 (Table 12, page 64) was not assayed for gold but instead, used to conduct a Hg amalgamation experiment (described in section 3.3.3) which was unsuccessful. This means that the gold from stage 1 was lost and not quantified, therefore making it impossible to close the mass balance. A fresh sample could not be used due to limited ore quantity. However, the diagnostic leach was able to qualitatively and quantitatively prove that some of the gold in these ores is refractory and would, therefore, not be recoverable by cyanidation. It also showed, as hinted by the QEMSCAN results, that the refractory gold was indeed hosted by sulphide minerals which were dissolved by the acids used in the diagnostic leach.

4.2. Cyanide leaching

4.2.1. Results

4.2.1.1. Preliminary experiments

A cyanide leach trial run was conducted on the 3 ores under study at a particle size of -150 µm which is not the particle size set for the main experimental matrix (-300 + 150 µm). This served the purpose of first testing out the experimental set-up to avoid wasting the ore which was of limited quantity and, secondly, getting a sense of the leaching performance at a finer PSD. The experiment was run at 20% solids loading and a cyanide concentration of 1 g/L.

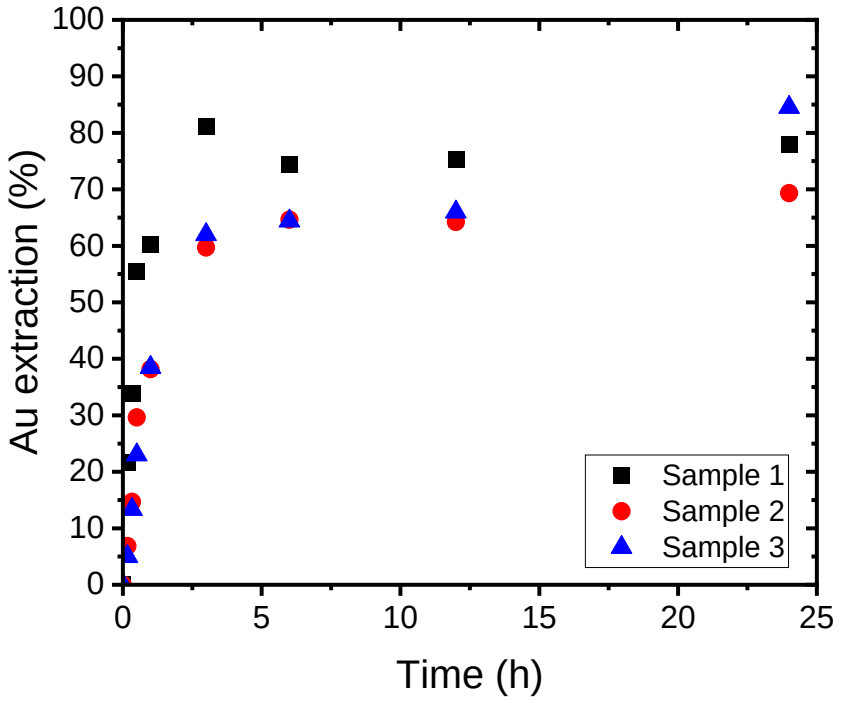

Figure 44: Au extraction at 1 g/L NaCN (20% solids, - 150 µm PSD, 300 rpm, 26°C)

It can be seen from Figure 44, that the gold extraction is quite fast at the start of the experiment up to the 5 h mark, after which it starts to plateau. At the 24 h mark, Sample 1 and Sample 3 achieved the highest extraction at 77.9% and 84.5%, respectively. Sample 2, the highest grade ore, reached an extraction of 69.3%. It is important to note that, in the first hour of leaching, shown in Figure 45, Sample 1, the lowest grade ore, showed faster leaching.

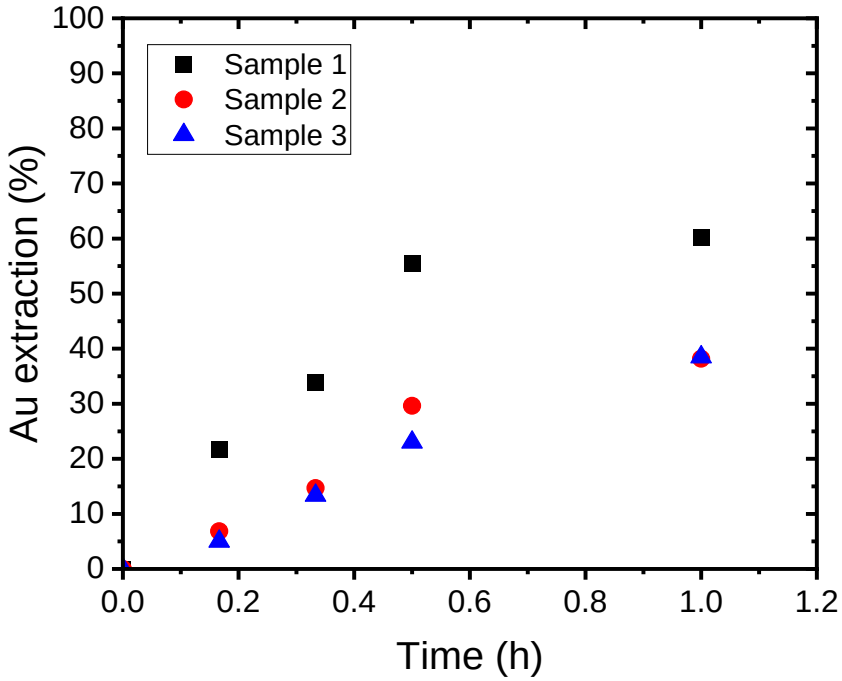

Figure 45: Au extraction during 1st hour of leaching at 1 g/L NaCN (20% solids, - 150 µm PSD, 300 rpm, 26°C)

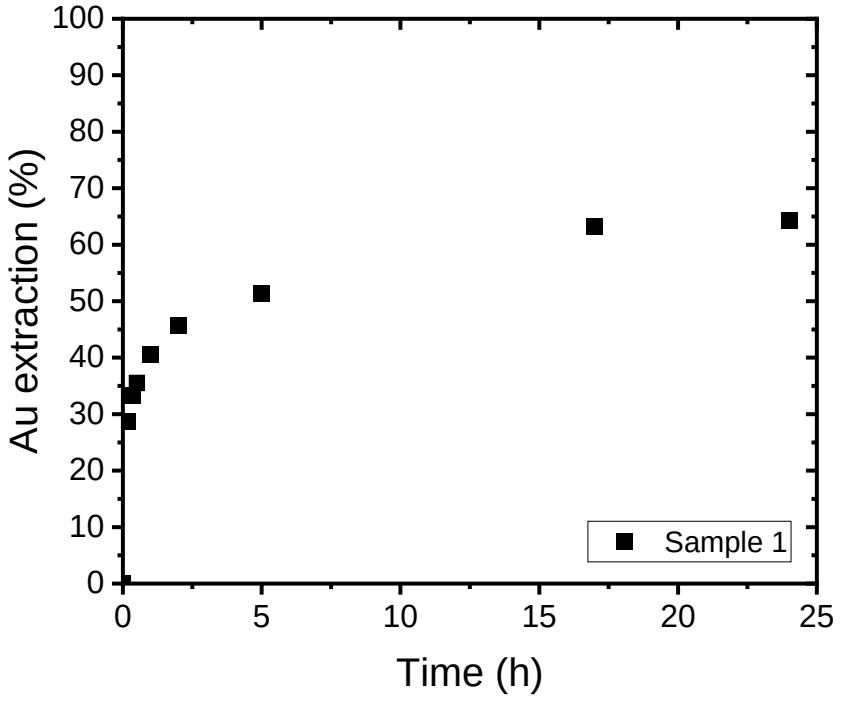

Figure 46: Au extraction at 1 g/L NaCN (30% solids, -300 +150 µm PSD, 300 rpm, 26°C)

The second trial experiment was conducted on Sample 1 at -300 + 150 µm PSD, 30% solids loading and a cyanide concentration of 1 g/L. It can be seen from Figure 46, that extraction seems to slow down after the 5 h mark which is similar to what was observed in Figure 44.

After 24 h, the final gold extraction was 64.3% which is lower than the 77.9% extraction achieved at -150 µm PSD for Sample 1 (shown in Figure 44). This indicates that gold was less liberated in the coarser material.

4.2.1.2. Main experiments

Au extraction

Following the trial runs, the main cyanide leaching experiments were conducted. The plots in Figure 47, Figure 48 and Figure 49 compare the leaching behaviours of the 3 ores at the 3 cyanide concentrations.

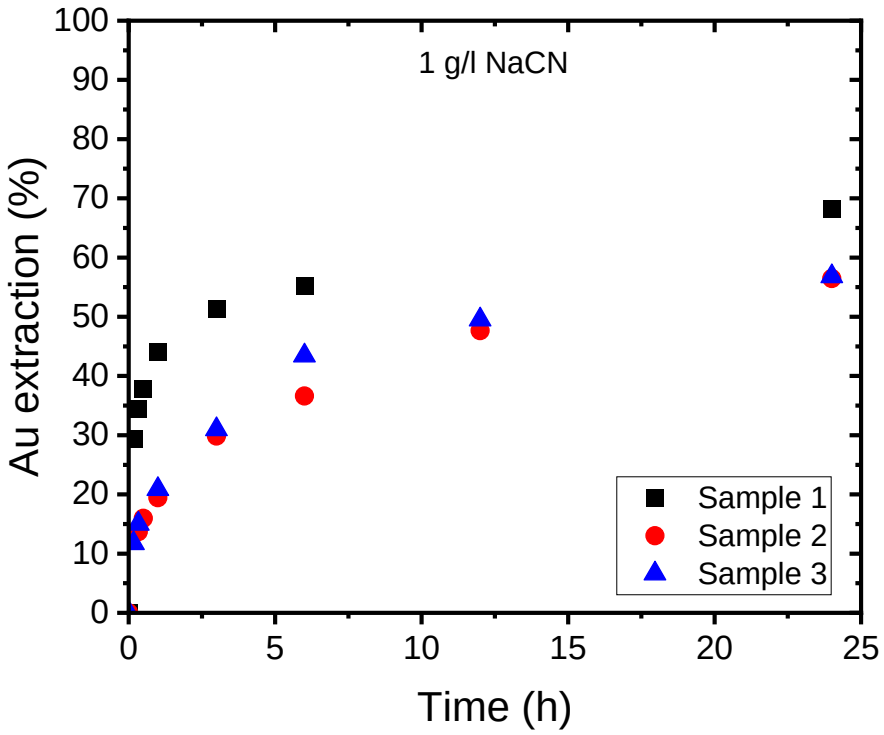

Figure 47: Au extraction at 1 g/L NaCN (30% solids, -300 +150 µm PSD, 300 rpm, 26°C)

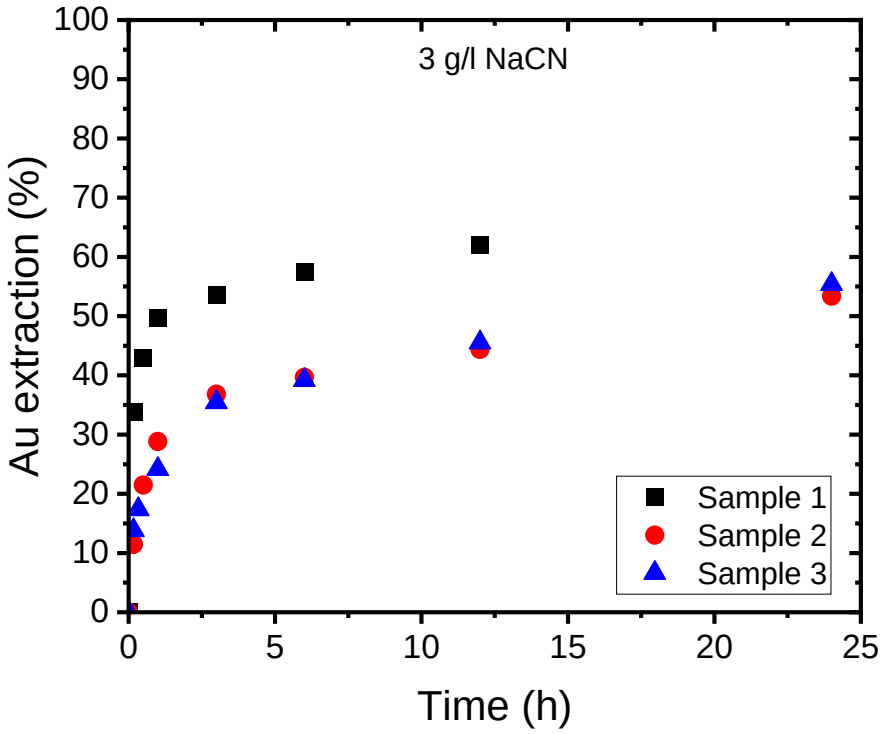

Figure 48: Au extraction at 3 g/L NaCN (30% solids, -300 +150 µm PSD, 300 rpm, 26°C)

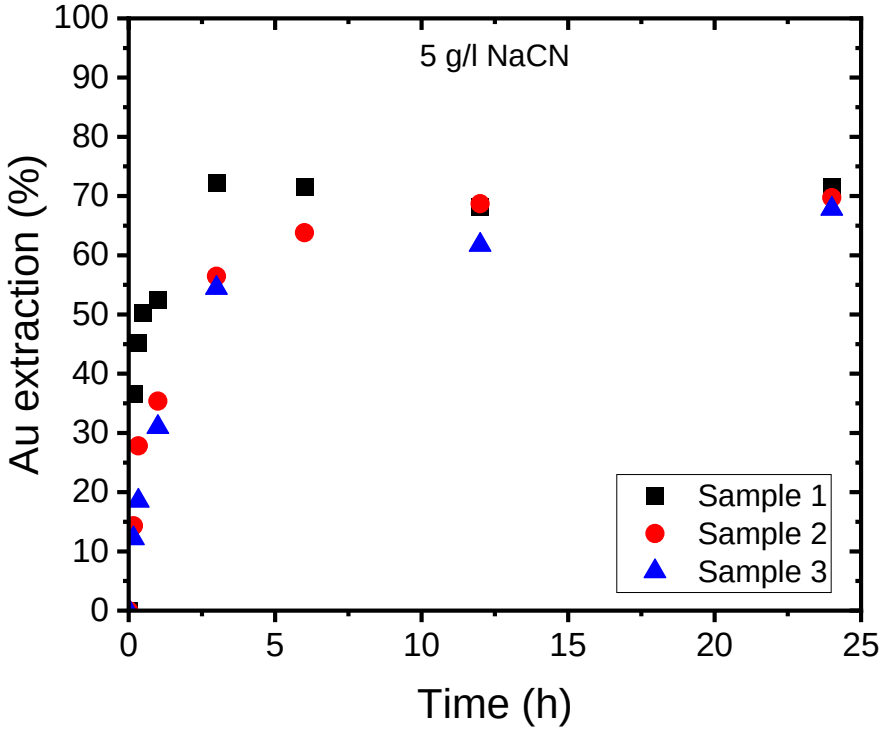

Figure 49: Au extraction at 5 g/L NaCN (30% solids, -300 +150 µm PSD, 300 rpm, 26°C)

At 1 g/L NaCN, Sample 1 achieved the highest gold extraction at 68.2% while Sample 2 and Sample 3 achieved 56.4% and 56.8% respectively, after 24 h of leaching. At 3 g/L NaCN, Sample 1 still achieved the highest extraction at 62.0% while Sample 2 and Sample 3 achieved 53.4% and 55.4% respectively. Extractions at 3 g/L NaCN appear to be slightly lower than those achieved at 1 g/L NaCN. It is important to note here that for Sample 1, at 3 g/L NaCN, gold extraction data was plotted only up to 12 h of leach time as the extraction achieved at 24 h was considered an outlier. At 5 g/L NaCN, Sample 1 reached an extraction of 71.6% while Sample 2 and Sample 3 achieved 69.7% and 67.8%, respectively. It can be observed, however, that there is a slight decrease in gold concentration for Sample 1 at 5 g/L NaCN, after 3 hours of leaching. Sample 2 and Sample 3 (highest grade ores) showed similar initials kinetics at the 3 cyanide concentrations.

Figure 50, Figure 51 and Figure 52 show how each ore responded to the leaching at the 3 concentrations chosen for the experiments.

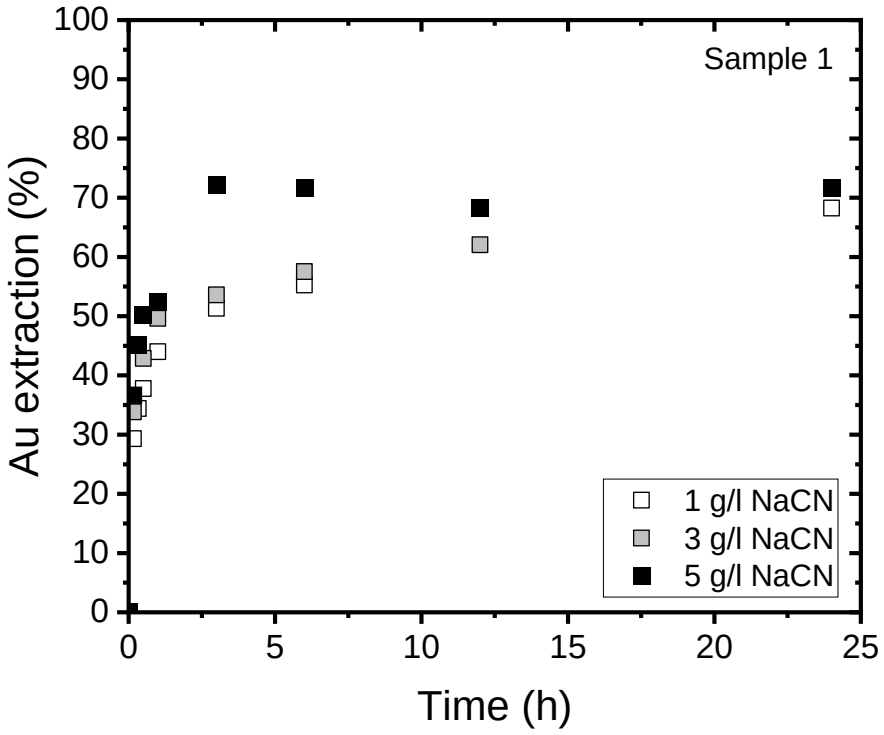

Figure 50: Au extraction at 3 concentrations for sample 1 (30% solids, -300 +150 µm PSD, 300 rpm, 26°C)

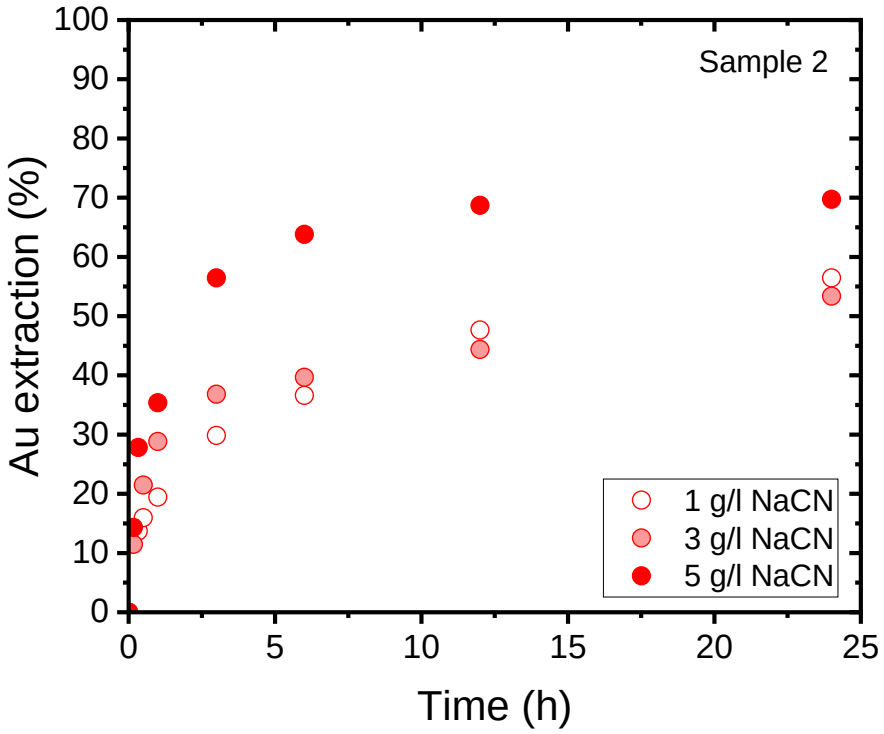

Figure 51: Au extraction at 3 concentrations for Sample 2 (30% solids, -300 +150 µm PSD, 300 rpm, 26°C)

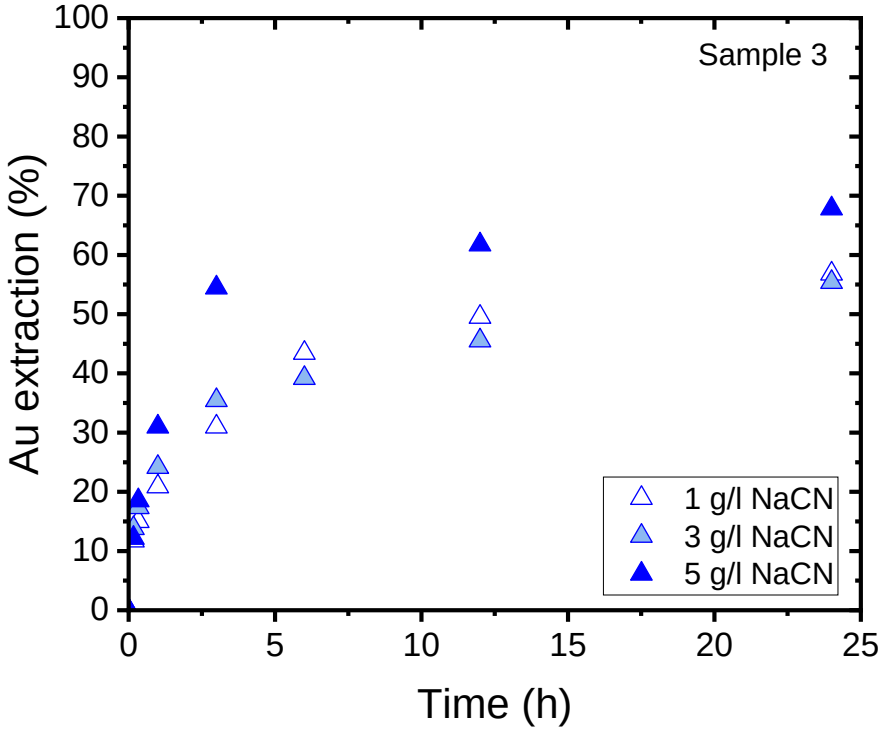

Figure 52: Au extraction at 3 concentrations for Sample 3 (30% solids, -300 +150 µm PSD, 300 rpm, 26°C)

It can be seen from Figure 50, Figure 51 and Figure 52 that Sample 1 had the fastest initial kinetics at the 3 cyanide concentrations, achieving gold extractions of 51.3%, 53.6% and 72.2% within the first 3 hours of leaching at 1 g/L, 3 g/L and 5 g/L NaCN, respectively. In the same time period, Sample 2 achieved 29.9%, 36.8% and 56.4% while sample 3 achieved 31.0%, 35.4% and 54.5% at 1 g/L, 3 g/L and 5 g/L NaCN, respectively.

Reproducibility of experiments

To test the reproducibility of these experiments, a second run of cyanide leaching of Sample 1, Sample 2, and Sample 3 at 3 g/L, 1 g/L and 5 g/L, respectively, was conducted and compared to the results of the main experimental matrix. Figure 53, Figure 54 and Figure 55 present these comparisons.

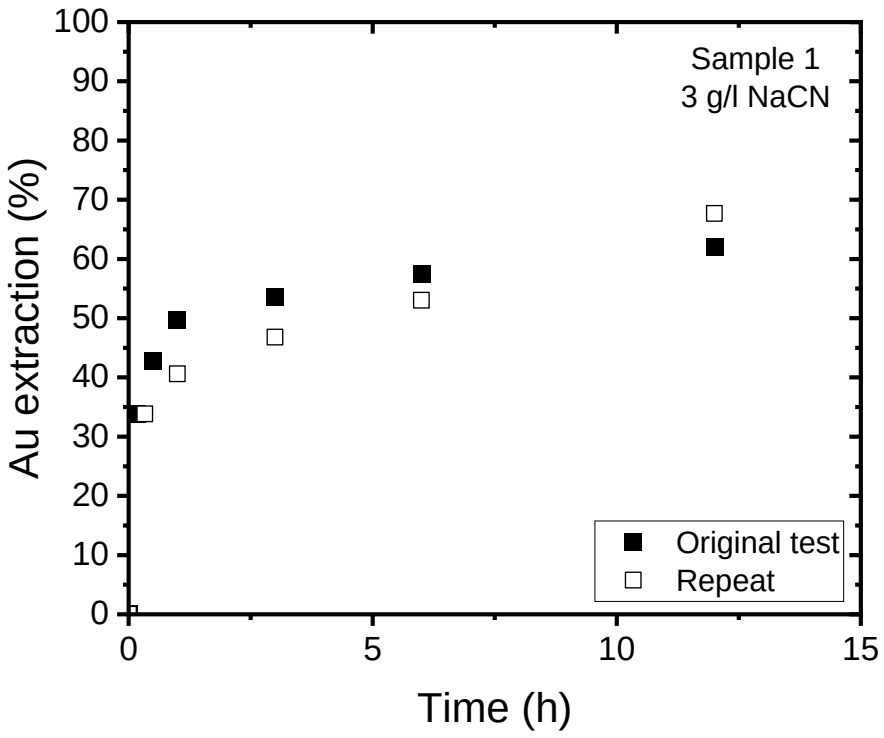

Figure 53: Au extraction reproducibility test for sample 1 (30% solids, -300 +150 µm PSD, 300 rpm, 26°C)

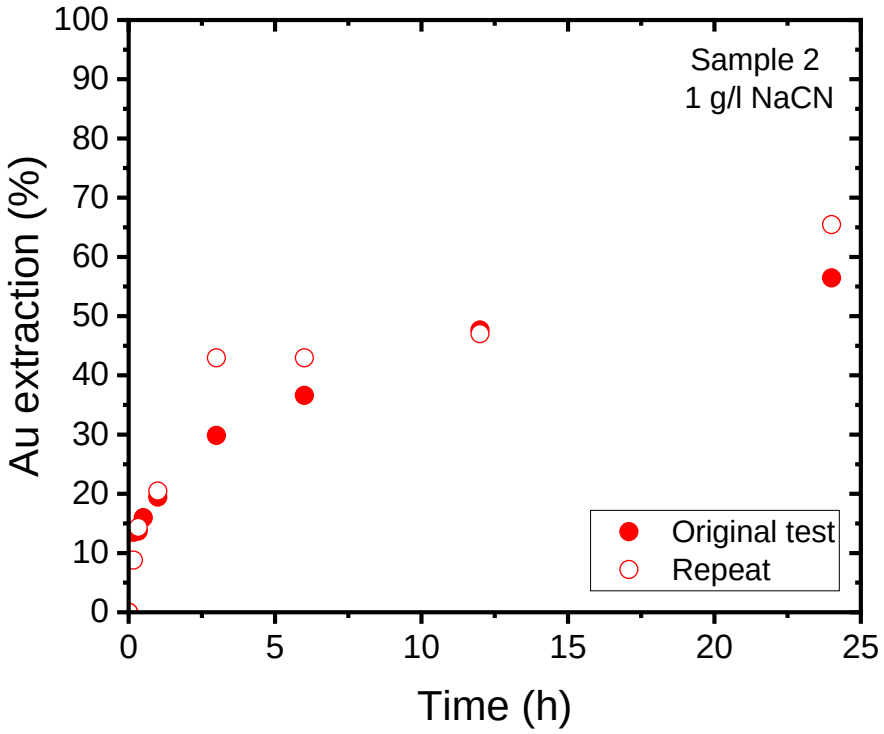

Figure 54: Au extraction reproducibility test for Sample 2 (30% solids, -300 +150 µm PSD, 300 rpm, 26°C)

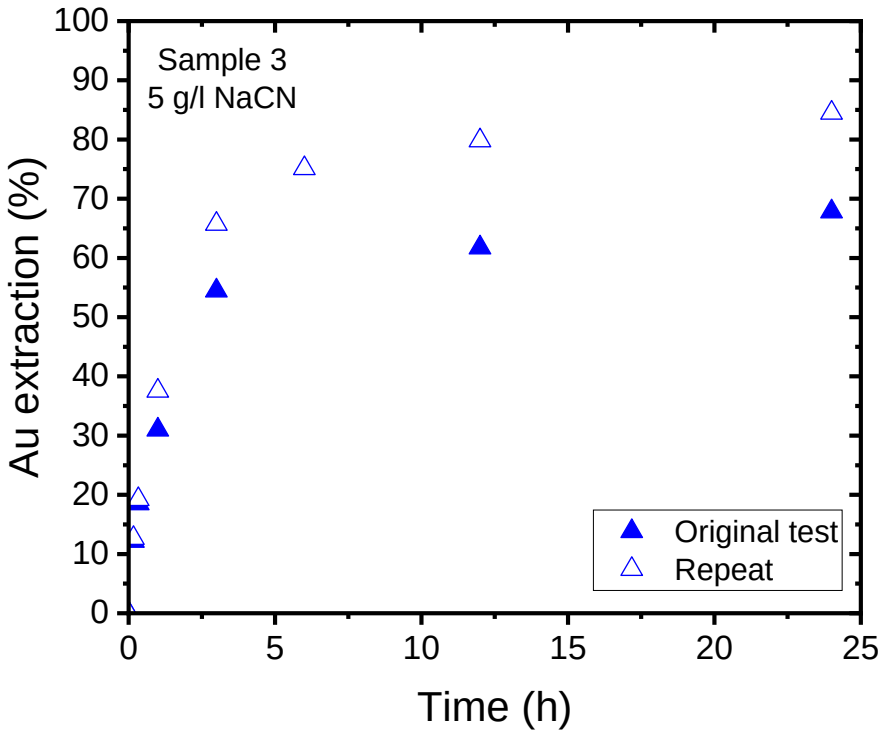

Figure 55: Au extraction reproducibility test for Sample 3 (30% solids, -300 +150 µm PSD, 300 rpm, 26°C)

It can be observed from Figure 53 and Figure 54 that for Sample 1 and Sample 2, repeating the experiments lead to similar extraction behaviours. However, for Sample 3, shown in Figure 55, there seems to be a significant difference with a final extraction of 84.5% after 24 h of leaching for the repeat experiment while the original test reached 67.8% extraction after 24 h. This could be attributed to the fact that the repeat leach samples for Sample 3 were analysed by a different laboratory that may have used different calibrations however, leach samples for all the main leach experiments were analysed by one laboratory to ensure consistency.

Vat leach experiment

Figure 56 shows the Au extraction trends observed for the vat leaching of the 3 ores under study. For sample 1, the final extraction after 12 h of leaching was 47.1%, 35.6% for Sample 2 and 33.6% for Sample 3. Since there was no agitation in the reactors, it is possible that the samples taken for gold analysis were not representative of the entire solution volume. This may have affected the values of gold extraction obtained. However, the samples were taken close to the surface of the solids where the concentration of gold would be higher than at the surface of the supernatant.

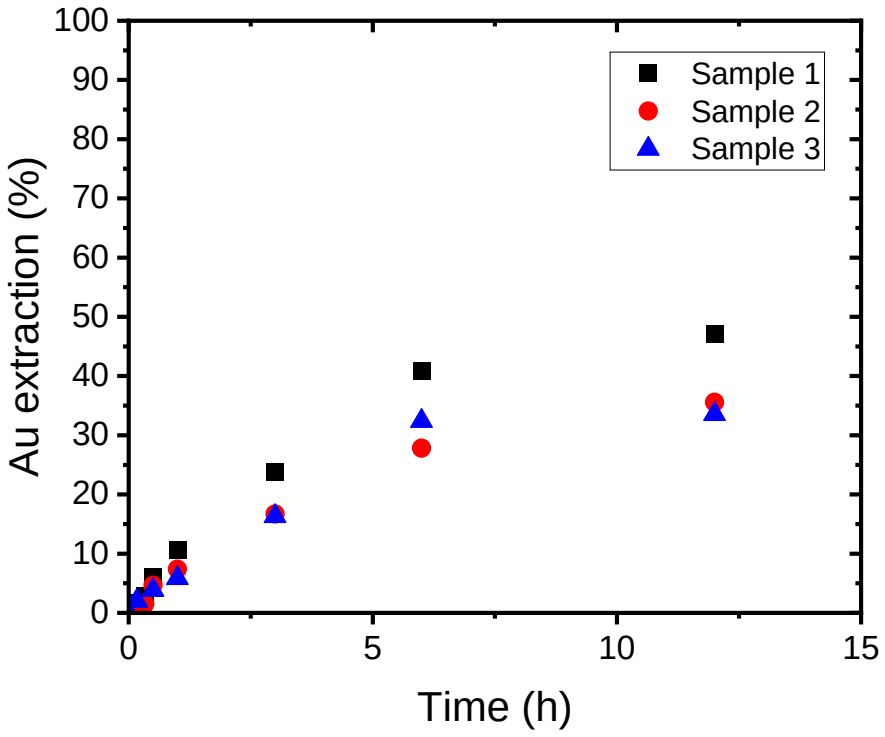

Figure 56: Au extraction for vat leaching of sample 1, Sample 2 and Sample 3 at 5 g/L NaCN (30% solids, -300 +150 µm PSD, 300 rpm, 26°C)

Cu extraction

Due to the relatively low gold extractions observed and the significant Cu content in the ores (96,7 g/t in Sample 1, 128.0 g/t in Sample 2, and 102.0 g/t in Sample 3), determined by ICP-OES (Table 7), it was decided to also quantify Cu extraction. This could give a sense of whether or not cyanide was heavily consumed by secondary metals, leading to less free cyanide being available to leach gold. The findings are shown in Figure 57, Figure 58 and Figure 59. The stoichiometric calculations of cyanide requirement for the Au leaching experiments presented in Appendix A: Stoichiometric calculations of reagent requirement for Au leaching, factored in the dissolution of Cu as well.

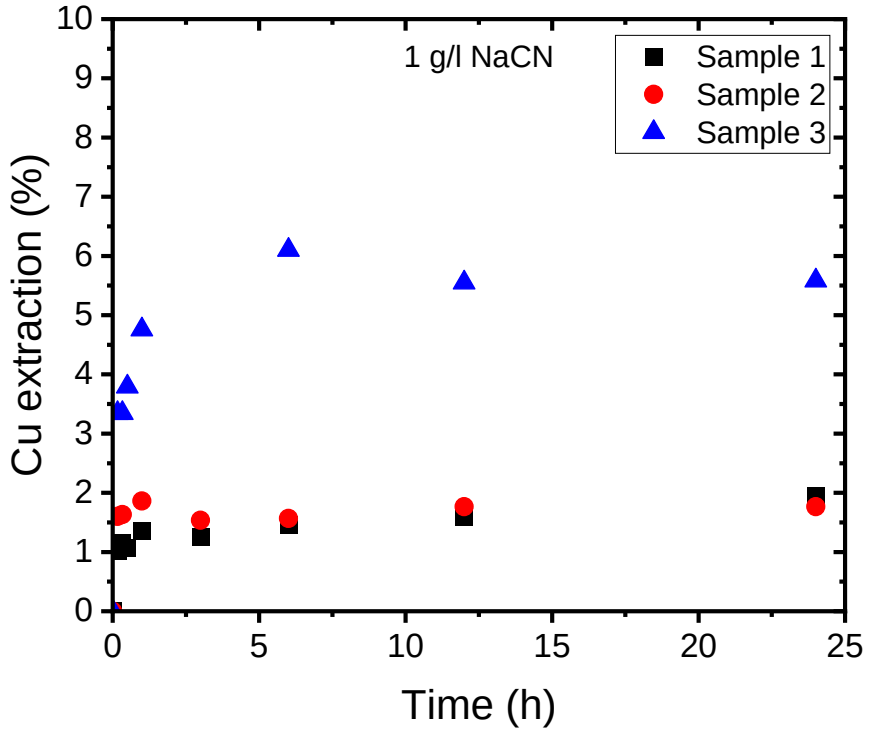

Figure 57: Cu extraction at 1 g/L NaCN (30% solids, -300 +150 µm PSD, 300 rpm, 26°C)

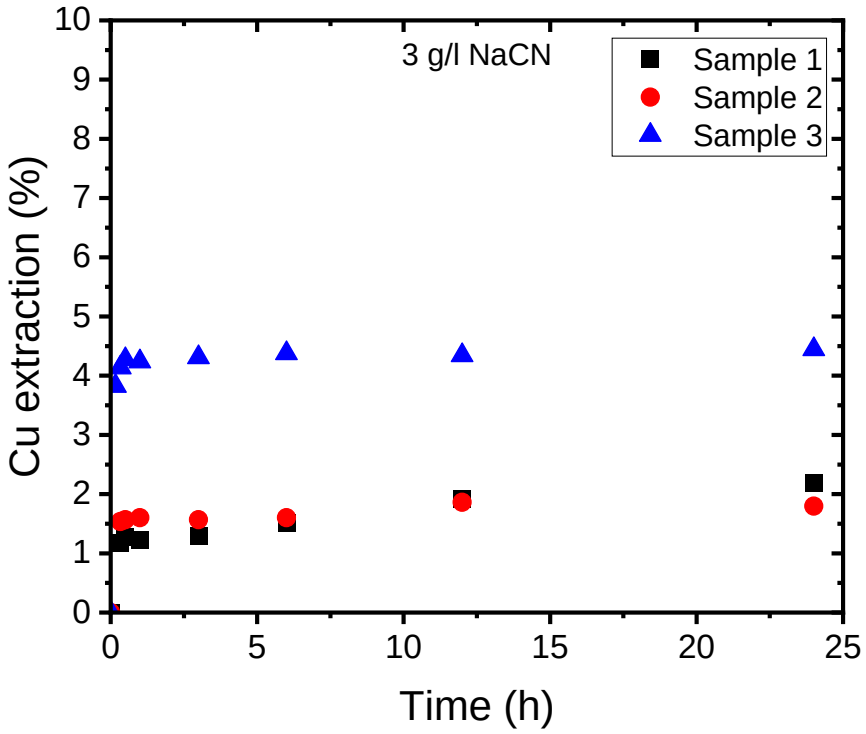

Figure 58: Cu extraction at 3 g/L NaCN (30% solids, -300 +150 µm PSD, 300 rpm, 26°C)

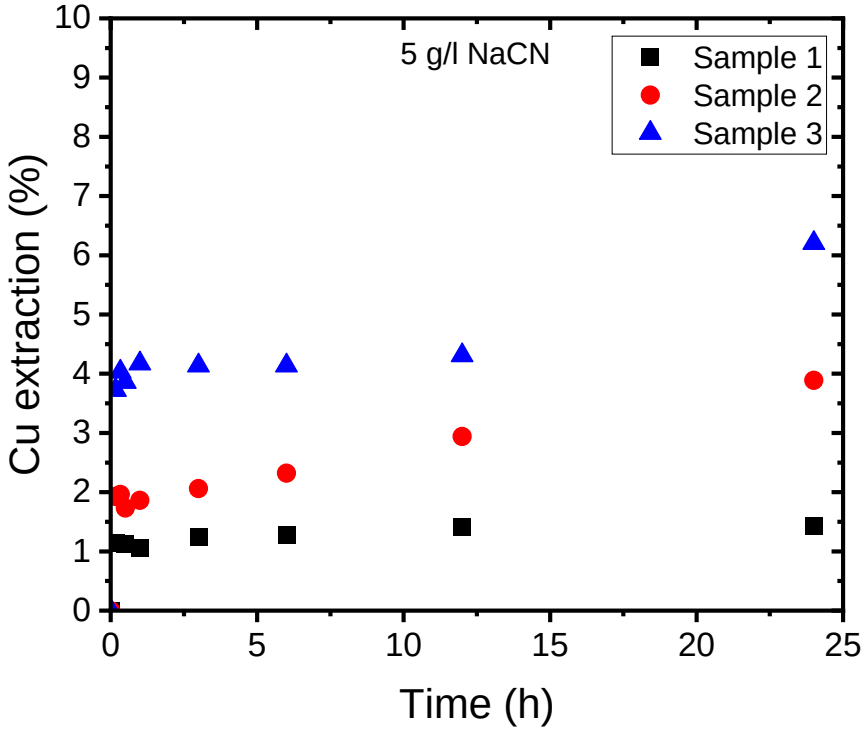

Figure 59: Cu extraction at 5 g/L NaCN (30% solids, -300 +150 µm PSD, 300 rpm, 26°C)

It can be seen on the leaching plots that the Cu extraction is very low across the 3 concentrations of NaCN. At 1 g/L NaCN, Sample 3 achieved the highest extraction at 5.6% while Sample 2 and Sample 1 achieved 1.8% and 1.9% respectively, after 24 h of leaching. At 3 g/L NaCN, Sample 3 reached a Cu extraction of 4.4% while Sample 2 and sample 1 reached 1.8% and 2.1% Cu extraction, respectively. In a similar fashion, at 5 g/L, Sample 3 reached the highest extraction at 6.2% while Sample 1 and Sample 2 reached 3.9% and 1.4% extraction, respectively.

Cyanide consumption

Due to calibration difficulties and the high dilution factor of 20 used to make the 80 mL solution required in the cynoprobe, the consumption of cyanide was only determined for Sample 1 and Sample 3 for the experiments using cyanide solutions at 3 g/L and 5 g/L NaCN, respectively. The cynoprobe was not able to provide accurate readings for the diluted samples obtained from the experiment at 1 g/L NaCN.

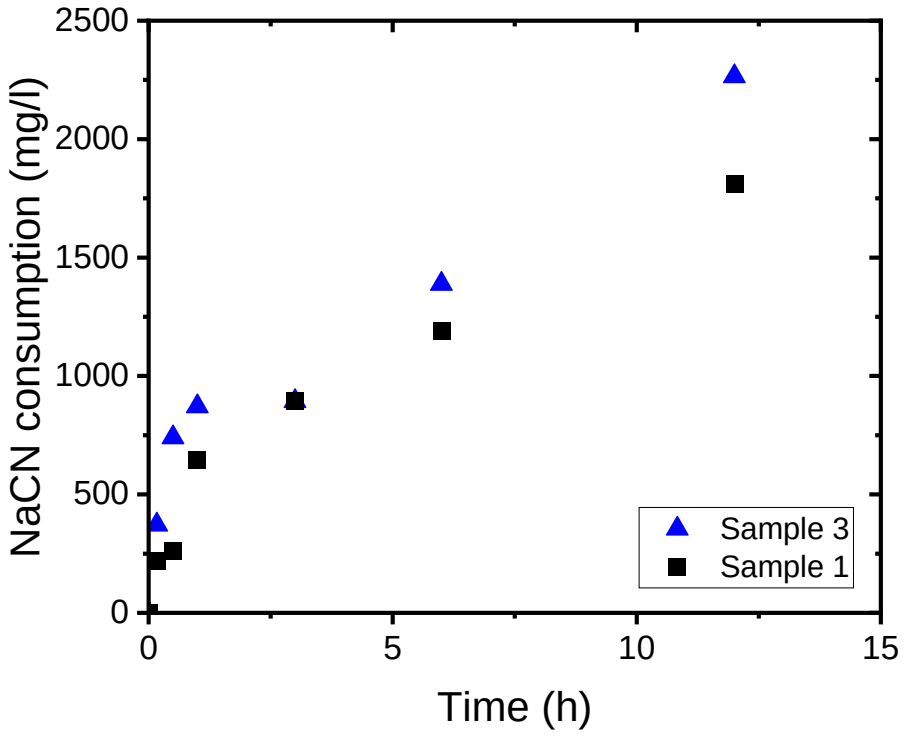

Figure 60: Cyanide consumption for Sample 1 (3 g/L NaCN) and Sample 3 (5 g/L NaCN) (30% solids, -300 +150 µm PSD, 300 rpm, 26°C)

Figure 60 shows that the cyanide consumption rate was higher for Sample 3 which was leached at a higher cyanide concentration compared to Sample 1.

4.2.2. Discussion

4.2.2.1. Effect of PSD

Comparisons of the leaching performance at -150 µm and -300 +150 µm for the 3 ores are presented on Figure 61. It is quite clear from the trends shown that leaching at a finer size significantly improved gold extraction for the 3 ores as well as the kinetics of the process.

As much as milling finer sounds like a simple fix for higher gold extraction, it presents challenges when assessing it through the lens of ASGM. The sector relies significantly on rudimentary and low efficiency gravity concentration methods, such as panning, to concentrate gold to either be directly sold, if the grade is high enough, or fed into a subsequent process such as amalgamation or leaching. Milling too fine makes gravity concentration much harder to achieve efficiently since gold can be lost with gangue minerals. This is something very difficult for miners to compromise on since, even in the case where no gold is wasted at all throughout the entire process, they will most likely only obtain about 30% of it by amalgamation. However, if cyanide leaching becomes a substitute for all other recovery methods, working with smaller sizes would yield high Au recoveries.

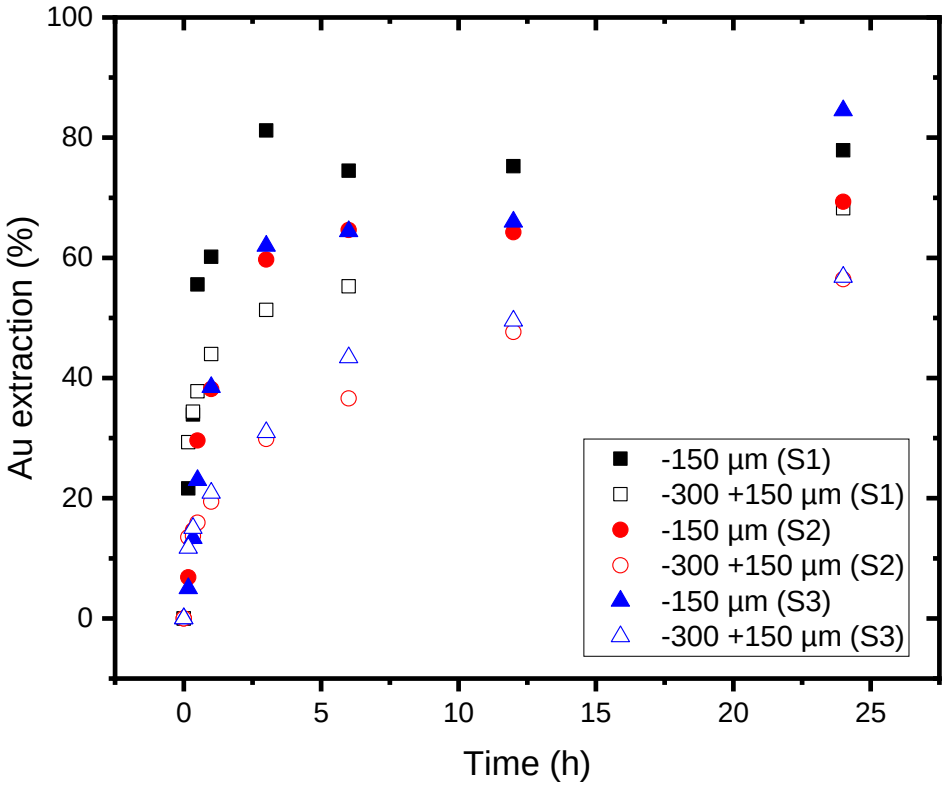

Figure 61: Au leaching at -150 µm vs -300 +150 µm for Sample 1 (S1), Sample 2 (S2) and Sample 3 (S3) (1 g/L NaCN, 30% solids, 300 rpm, 26°C)

4.2.2.2. Reasons for low Au extractions

In trying to understand why the extractions achieved in this current study are lower than what is generally reported for conventional cyanidation experiments, as shown in section 2.5.1.4 (page 38) where gold extractions of 94% (d_{80} = 150 µm, 5 g/L NaCN), 93.6% (mill leaching, 1 g/L NaCN) and 84% (d_{80} = 250 µm, 1 g/L NaCN) were achieved (Veiga et al., 2009), it is important to look at the minerology of the ores. As highlighted in section 4.1, the presence of sulphide minerals, that may host gold, in the 3 ores can be a major reason for the low gold extractions achieved as any gold hosted by these minerals would be locked and difficult to recover by conventional cyanidation. This was confirmed by the diagnostic leach results which showed that, by the action of acids, the gold locked in sulphides could be extracted. In actual fact, Sample 1 which had the lowest proportion of sulphides (Table 14) consistently achieved higher gold extractions at the 3 cyanide concentrations compared to Sample 2 and Sample 3. In addition, sulphides of copper and iron such as pyrite, arsenopyrite, and chalcopyrite, which have been shown to be present in these ores (Figure 41) can consume cyanide by forming cyanide complexes and converting free cyanide ions to cyanate and thiocyanate leading to cyanide losses (Kianinia et al., 2018). Passive aeration, which was used in the leach tests to mimic ASM conditions, could also have impacted the process negatively since not enough oxygen was present.

A comparison of the gold extracted by the diagnostic leach (after stage 2 which leached unlocked gold) and the cyanide leach of fresh samples (Figure 49) is shown in Figure 62 alongside the head grades of the 3 samples. The cyanide leach of fresh samples at 5 g/L NaCN extracted free milling gold while the diagnostic leach was able to extract gold locked in sulphides by the successive action of aggressive acid and cyanide leach stages. In fact, when the total gold amounts extracted by both leach methods are added, the values obtained are similar to the head grades of the samples. This, once again, shows that cyanidation had reached a mineralogical barrier, preventing it from extracting more gold, which the diagnostic leach on the other hand was able to overcome.

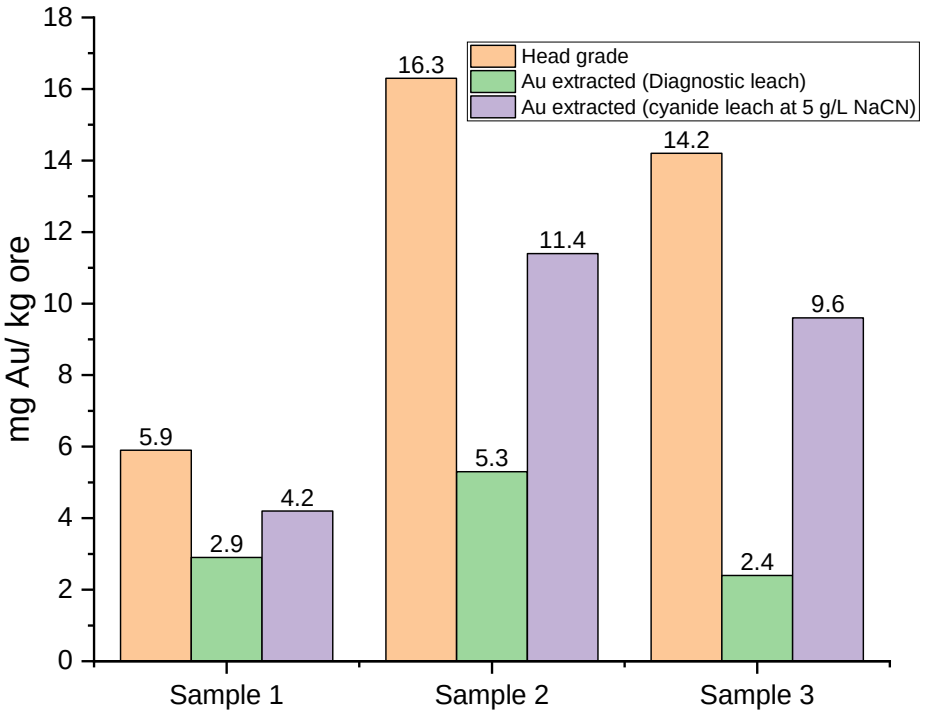

Figure 62: Comparison of total Au extracted by diagnostic leach and cyanide leach

4.2.2.3. Agitated leach vs vat leach

Figure 63, Figure 64 and Figure 65 show a comparison of the Au extractions achieved by agitated leaching with those achieved by vat leaching. For all 3 ores under study, agitated leaching significantly outperformed vat leaching. Within the first hour of agitated leaching, the extractions achieved for the 3 ores were already higher than those achieved by vat leaching after 12 h. For Sample 1, the final extractions achieved with agitated leaching and vat leaching are 68.2% and 47.1%, respectively. For Sample 2, final extractions were 68.7% and 35.6%, respectively. Finally, for Sample 3, final extractions were 61.7% and 33.6%, respectively.

It is evident from these findings, as previously mentioned in section 2.5.1.3 (page 38), that agitation increases extraction by homogenising the solution and reducing the diffusion layer thickness between the lixiviant and the gold particles. This could also relate to CN^- consumption in the pores and the time it takes for more to diffuse in from the supernatant. However, the solids loading was kept the same for both agitated and vat leaching (30% solids), meaning that it is unlikely that a reagent limitation occurred in vat leaching.

As much as vat leaching is widely applied in ASGM, there is a potential for miners to make quicker returns with agitated leaching.

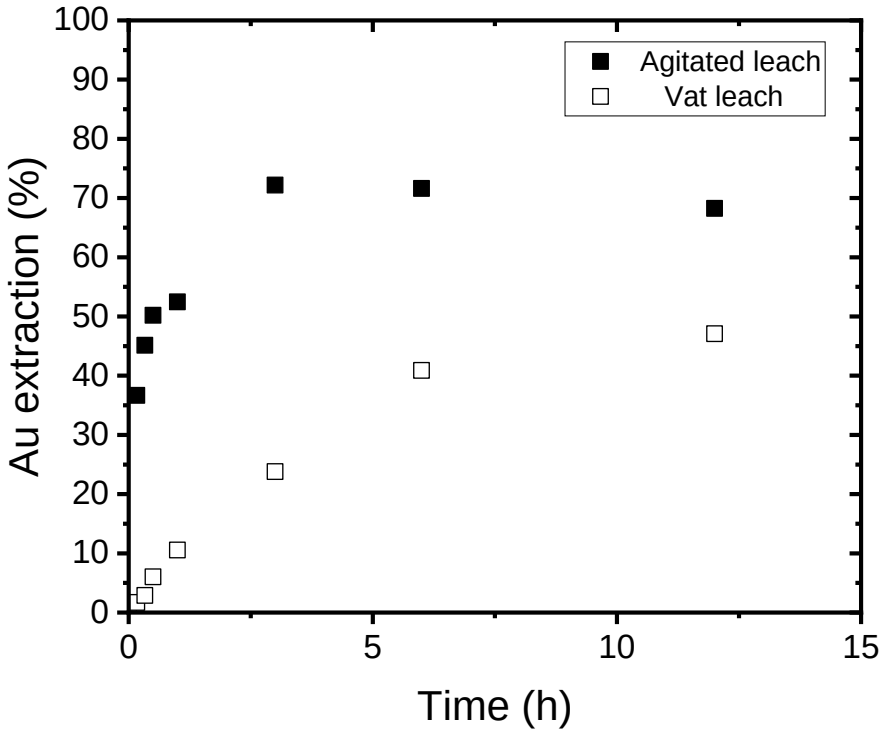

Figure 63: Comparison of Au extraction between agitated cyanide leach and vat cyanide leach for Sample 1 (30% solids, -300 + 150 µm PSD, 26°C)

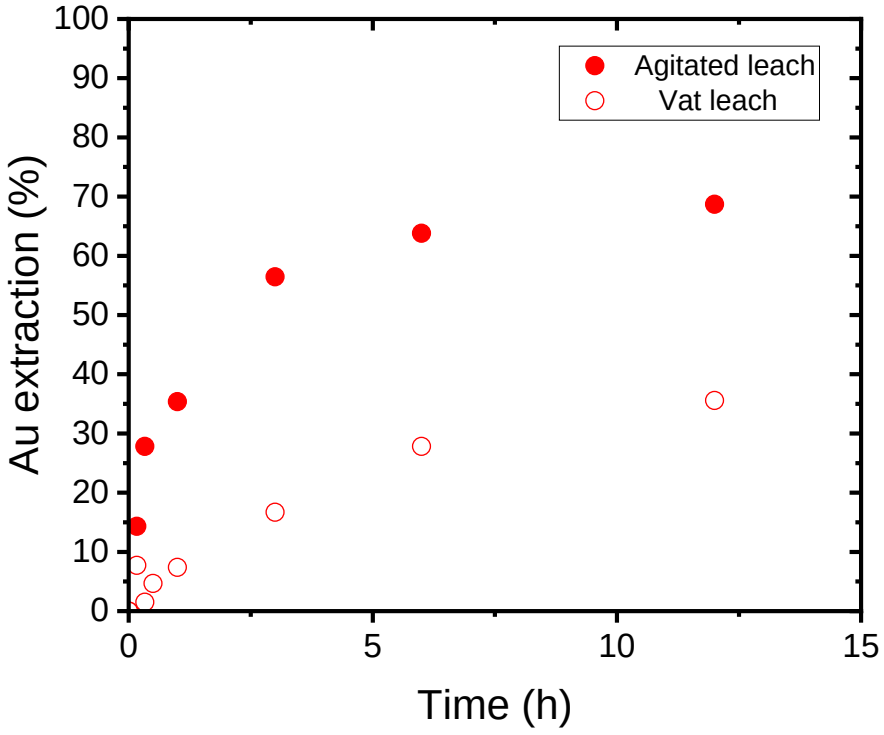

Figure 64: Comparison of Au extraction between agitated cyanide leach and vat cyanide leach for Sample 2 (30% solids, -300 + 150 µm PSD, 26°C)

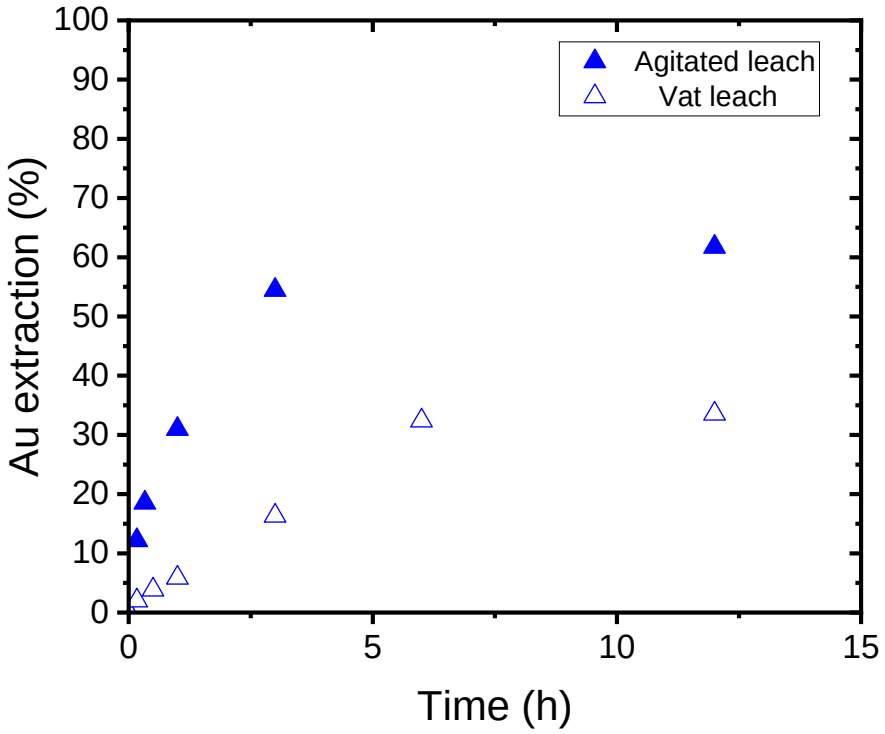

Figure 65: Comparison of Au extraction between agitated cyanide leach and vat cyanide leach for Sample 3 (30% solids, -300 + 150 µm PSD, 26°C)

4.3. Thiosulphate leaching

4.3.1. Results

4.3.1.1. Effect of $(NH_4)_2S_2O_3$ concentration

Figure 66, Figure 67 and Figure 68 show the effect of varying thiosulphate concentration on Sample 1, Sample 2, and Sample 3, respectively, while maintaining the NH_3 and Cu concentration at 0.5 M and 1 mM, respectively. The general observation is that Au extractions are low in the thiosulphate system. However, across the 3 ores, increasing the thiosulphate concentration from 0.1 M to 0.5 M did result in an increase in gold extraction. For Sample 1, final extraction increased from 41.7% to 54.1%, for Sample 2, extraction increased from 27.0% to 35.6% after 24 h of leaching while Sample 3 experienced a more modest increase from 36.1% to 38.0%.

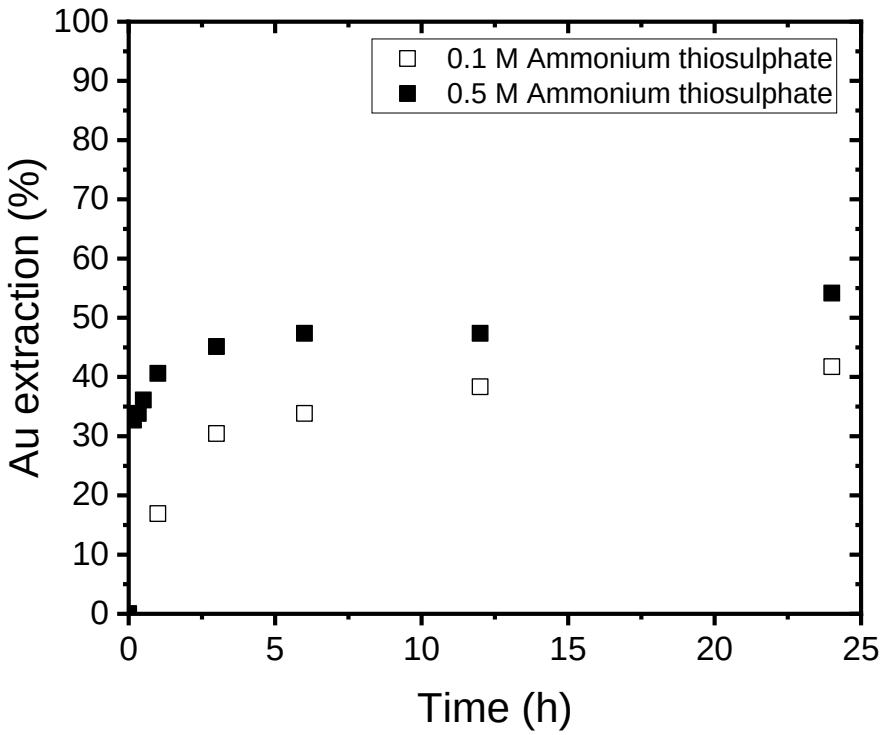

Figure 66: Effect of varying thiosulphate concentration on gold extraction for Sample 1 at 0.5 M NH_3 and 1 mM Cu (30% solids, -300 + 150 µm PSD, 26°C)

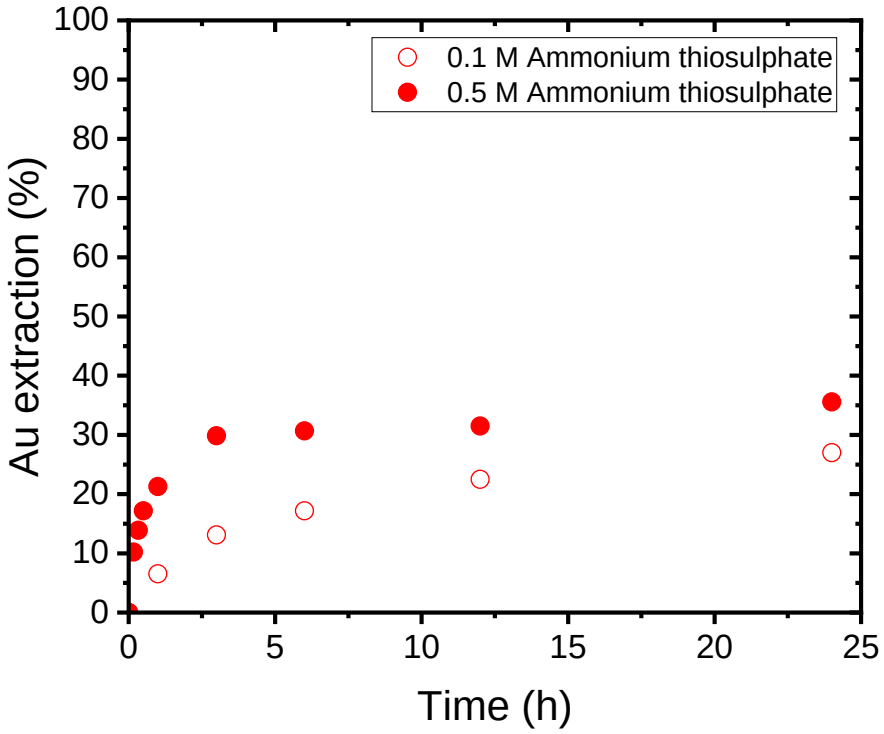

Figure 67: Effect of varying thiosulphate concentration on gold extraction for Sample 2 at 0.5 M NH_3 and 1 mM Cu (30% solids, -300 + 150 µm PSD, 26°C)

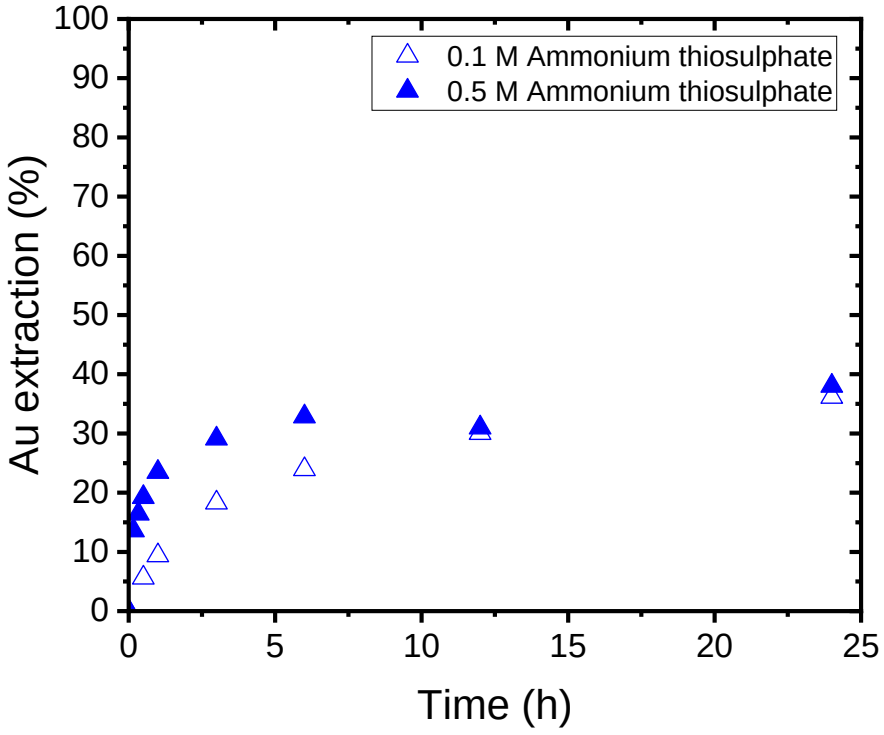

Figure 68: Effect of varying thiosulphate concentration on gold extraction for Sample 3 at 0.5 M NH_3 and 1 mM Cu (30% solids, -300 + 150 µm PSD, 26°C)

4.3.1.2. *Effect of background copper concentration*

Increasing Cu(II) concentration from 0 mM to 1 mM at 0.5 M $(NH_4)_2S_2O_3$ and 0.5 M NH_3

Figure 69 shows the impact of the presence of Cu(II) on gold extraction for Sample 1, Sample 2, and Sample 3, respectively. Across the 3 ores, the presence of Cu(II) had a positive impact on extraction when compared to a system with no Cu(II) present. For Sample 1, final extraction with no Cu(II) present was 38.4%, while the presence of 1 mM Cu(II) resulted in a higher extraction of 54.1%. For Sample 2, gold extraction increased from 17.2% to 35.6% after adding Cu(II) and for Sample 3, gold extraction increased from 26.3% to 38.0%, after 24 h of leaching.

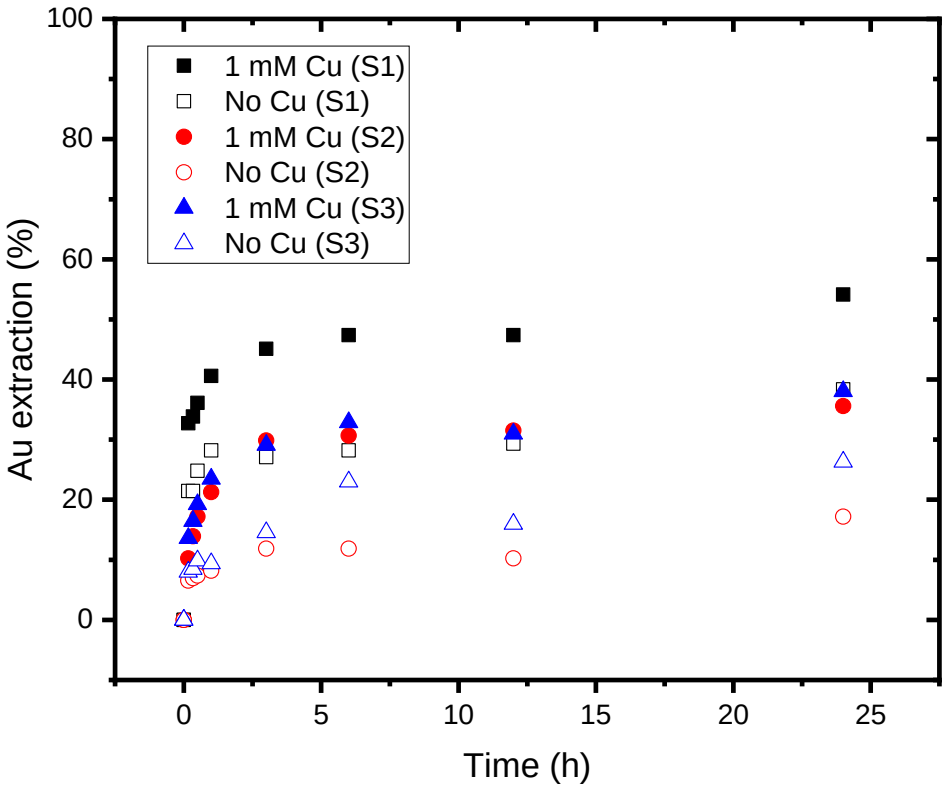

Figure 69: Effect of Cu(II) presence on gold extraction for Sample 1 (S1), Sample 2 (S2) and Sample 3 (S3) at 0.5 M $(NH_4)_2S_2O_3$ and 0.5 M NH_3 (30% solids, -300 + 150 µm PSD, 26°C)

Increasing Cu(II) concentration from 1 mM to 10 mM at 0.1 M $(NH_4)_2S_2O_3$ and 0.5 M NH_3

Figure 70 shows what effect varying the concentration of Cu(II) from 1 mM to 10 mM had on gold extraction. The 3 ores all responded negatively to the increased Cu(II) concentration as shown by the poor extractions achieved. For Sample 1 and Sample 2, at 10 mM Cu(II), extraction dropped dramatically after 3 h of leaching. In the case of Sample 1, gold extraction peaked at 57.5% at the 3 h mark then fell to almost 0% and, similarly for Sample 2, extraction reached a peak of 10.2% after 3 h then dropped to almost 0% extraction as well, after 24 h of leaching. For Sample 3, the first observation is the significant drop in extraction at 10 mM Cu(II) compared to the same process at 1 mM Cu(II). Secondly, in a manner similar to Sample 1 and Sample 2, gold extraction at 10 mM Cu(II) decreased from a peak of 9.9% to 5.2%.

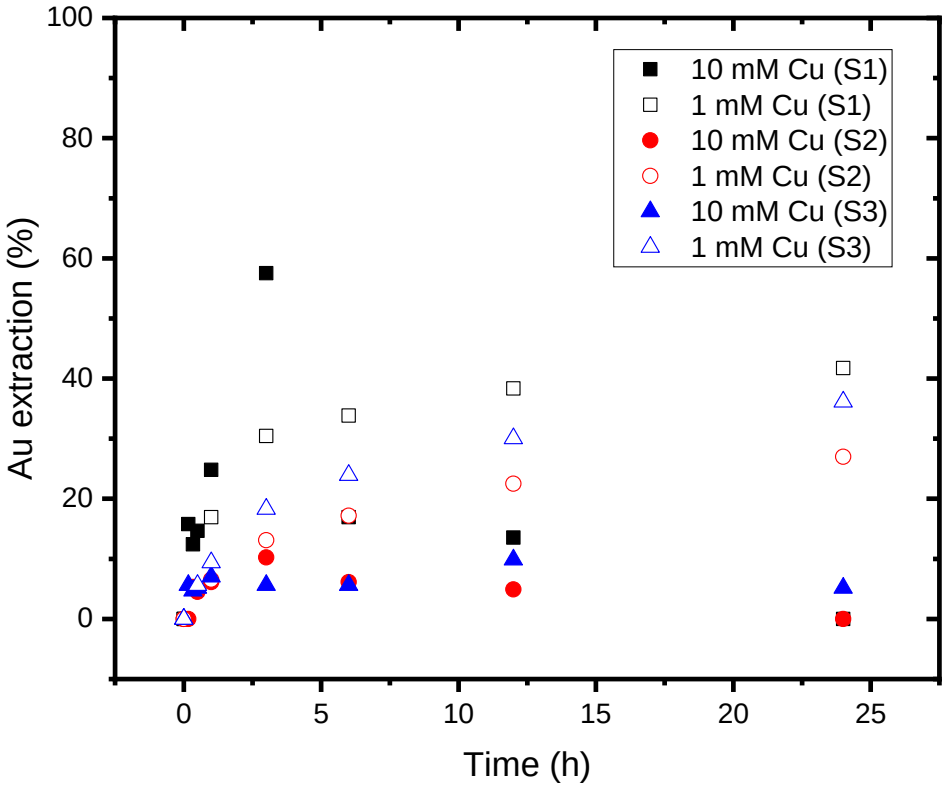

Figure 70: Effect of varying Cu (II) concentration on gold extraction for Sample 1 (S1), Sample 2 (S2) and Sample 3 (S3) at 0.1 M $(NH_4)_2S_2O_3$ and 0.5 M NH_3 (30% solids, -300 + 150 µm PSD, 26°C)

4.3.1.3. *Effect of NH_3 concentration*

Figure 71, Figure 72 and Figure 73 show the effect of increasing the concentration of NH_3 from 0.5 M to 1 M on gold extraction, for each ore. Overall, increasing the concentration did not have a significant impact on the leaching process. For Sample 1, the extraction trends did not change, with the final extraction at both concentrations of NH_3 reaching 54.1% after 24 h. For Sample 2, increasing the concentration of NH_3 resulted in a decrease in gold extraction, from 35.6% at 0.5 M NH_3 to 29.9% at 1 M NH_3. In a similar way, the gold extraction for Sample 3 dropped from 38.0% at 0.5 M NH_3 to 32.9% at 1 M NH_3.

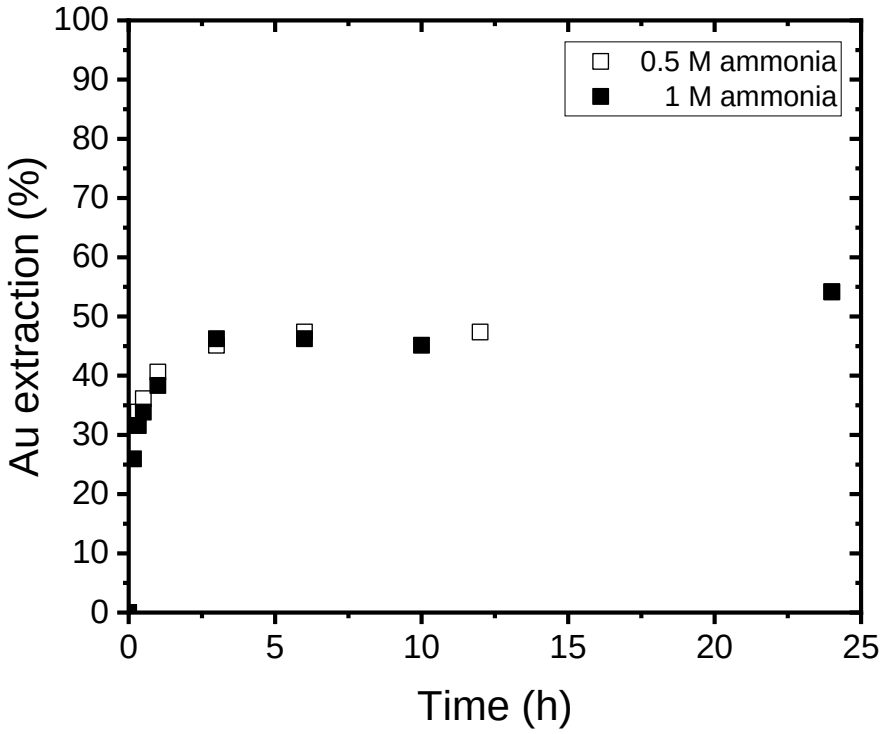

Figure 71: Effect of varying NH_3 concentration on gold extraction for Sample 1 at 0.5 M $(NH_4)_2S_2O_3$ and 1 mM Cu (30% solids, -300 + 150 µm PSD, 26°C)

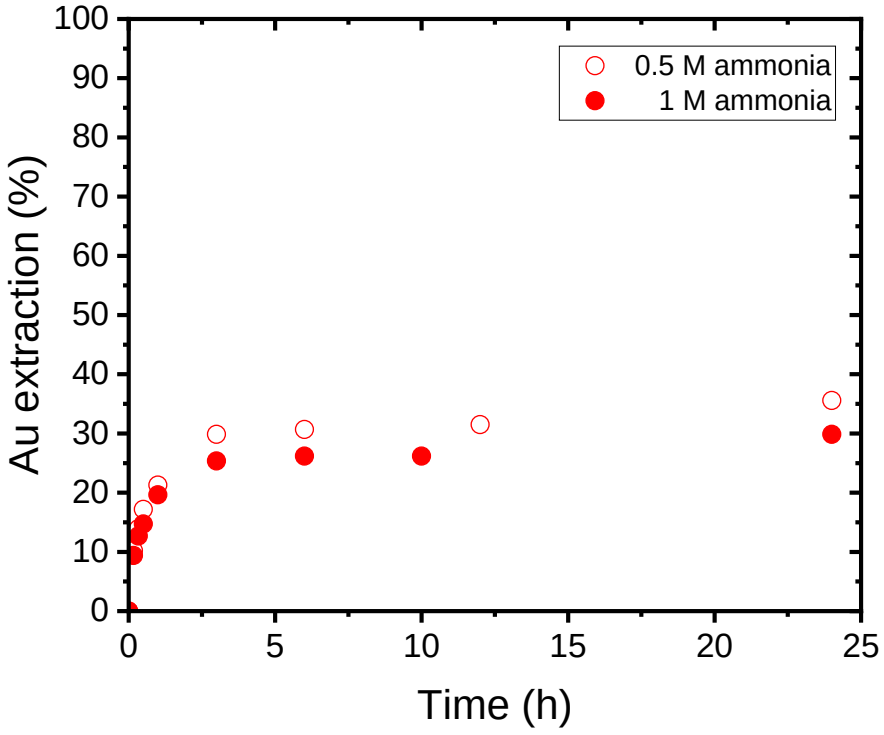

Figure 72: Effect of varying NH_3 concentration on gold extraction for Sample 2 at 0.5 M $(NH_4)_2S_2O_3$ and 1 mM Cu (30% solids, -300 + 150 µm PSD, 26°C)

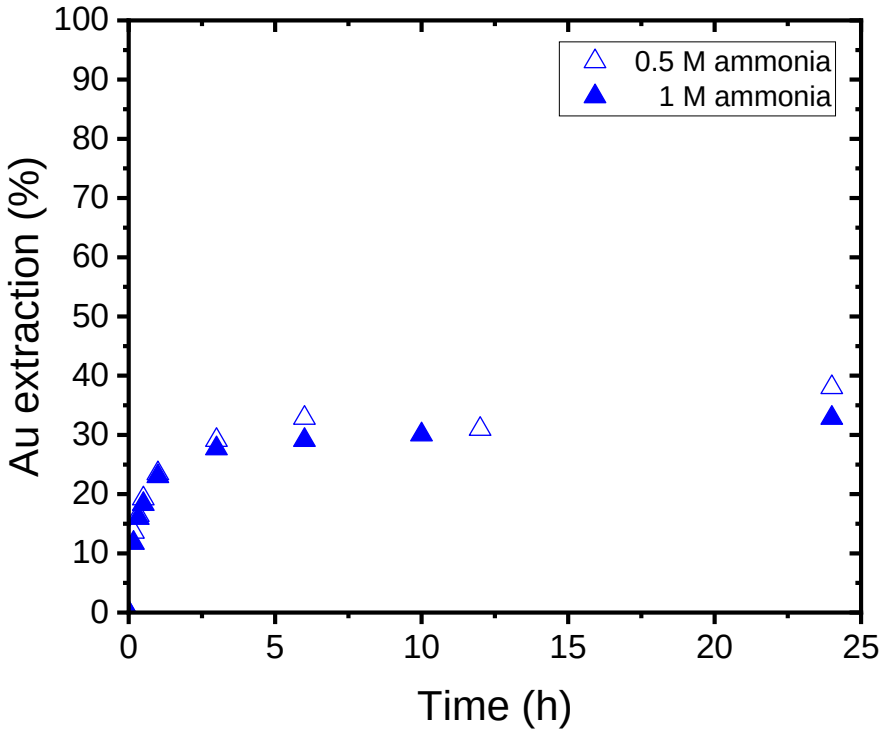

Figure 73: Effect of varying NH_3 concentration on gold extraction for Sample 3 at 0.5 M $(NH_4)_2S_2O_3$ and 1 mM Cu (30% solids, -300 + 150 µm PSD, 26°C)

4.3.2. Discussion

The aim of the thiosulphate leaching experiments was to determine the extent to which gold ores, typically encountered in ASGM, respond to thiosulphate leaching. A discussion of the findings of the experiments is presented in this section.

4.3.2.1. Effect of $(NH_4)_2S_2O_3$ concentration

The trends observed from the results presented above were generally in accordance with literature, in particular, with the work conducted by Rath et al. (2003) who investigated the effect of $(NH_4)_2S_2O_3$, NH_3 and Cu(II) concentration on the leaching of two gold ores, Akeshi and Hishikari, with gold grades of 10.5 g/t and 31 g/t, respectively. The study found that, for Akeshi, the gold extraction increased with decreasing concentration of $(NH_4)_2S_2O_3$. However, for Hishikari, gold extraction increased with an increase in $(NH_4)_2S_2O_3$ concentration from 0.1 to 0.5 M and then decreased as the $(NH_4)_2S_2O_3$ concentration was increased above 0.5 M.

The findings of this study are in accordance with the behaviour observed with Hishikari, whereby, it was also found that increasing the concentration of $(NH_4)_2S_2O_3$ from 0.1 M to 0.5 M, for the 3 ore types, resulted in an increase in gold extraction, as shown in Figure 66, Figure 67 and Figure 68. However, they showed the opposite trend when compared to Akeshi ore. Another key observation that can be made is that, overall, the extractions achieved with these two ores, Akeshi and Hishikari, are low despite their high grade. This behaviour was observed in the case of the 3 ores under study, as well. It is important to note that the experiments on Akeshi and Hishikari ores were run for only 5 h and the study did not provide a detailed minerology or an indication of whether or not some gangue minerals in the ore could have been consumers of the reagent. In this current study, the experiments were ran for 24 h, however, the extractions achieved with the 3 ores after 5 h were already close to those achieved after 24 h.

These findings are further supported by a study conducted by Bae et al. (2020) that also investigated the effect of $(NH_4)_2S_2O_3$, NH_3 and Cu(II) concentrations on the leaching of a gold ore. This ore had a much higher gold and copper content (84 g/t and 0.38 wt.%, respectively) compared to the 3 ores under study. It was found that increasing the $(NH_4)_2S_2O_3$ concentration from 0.05 M to 0.5 M increased gold extraction, reaching an impressive 99% extraction at 0.5 M. It should be highlighted that despite the fact that Sample 1, Sample 2 and Sample 3 responded similarly to the increase in $(NH_4)_2S_2O_3$ concentration, the magnitude of the increase in gold extraction was not similar to what Bae et al. (2020) observed. In their case, extraction increased from 30% to 99% as the $(NH_4)_2S_2O_3$ concentration was increased from 0.1 M to 0.5 M while for Sample 1, Sample 2 and Sample 3, extraction only increased by a maximum of 10%. This must be attributed to the fact that the experiment conducted by Bae et al. (2020) was done at a much finer grind size (45.3 µm) and a lower solids loading (20%) which significantly improved leaching. The leach study conducted by Bae et al. (2020) was terminated after 4 h, and the authors did not provide a detailed minerology indicating whether or not thiosulphate was heavily consumed by gangue species which could have led to it being completely consumed within 4 h of leaching.

It seems that a suitable $(NH_4)_2S_2O_3$ concentration should be below 1 M although it appears that the effect of $(NH_4)_2S_2O_3$ concentration varies from one ore to the next based on the concentrations of base metals. In the particular case of Cu, a high concentration can cause an increase in thiosulphate consumption and Cu will catalyse the thiosulphate oxidation reaction. In addition, Rath et al. (2003) suggest that, since the role of NH_3 is to preferentially absorb onto gold and subsequently substitute with thiosulphate, a high concentration of $(NH_4)_2S_2O_3$ could cause a challenge for NH_3 to absorb onto gold, leading to passivation due to thiosulphate decomposition on the gold surface and, as a result, poor gold dissolution.

4.3.2.2. Effect of Cu(II) concentration

When looking at the effect of Cu(II) in the study conducted by Rath et al. (2003), it was shown that increasing the concentration of Cu(II) from 0 to 0.01 M (= 10 mM) resulted in an increase in gold extraction. This was observed for the two ores. In a similar way, Sample 1, Sample 2, and Sample 3 showed an increase in extraction when Cu(II) was introduced at 1 mM, as shown in Figure 69. However, increasing the Cu(II) concentration from 1 to 10 mM resulted in a dramatic decrease in gold extraction across the 3 ores, as shown in Figure 70. This behaviour contradicts the findings of Rath et al. (2003) as well as those of Bae et al. (2020) who also found that increasing the Cu(II) concentration from 0.05 M to 0.25 M improved gold extraction. Abbruzzese et al. (1995) who investigated $(NH_4)_2S_2O_3$ leaching of a gold ore (grade: 51.6 g/t) also found that increasing the concentration of Cu(II) leads to an increase in gold extraction. Concentrations up to 0.1 M were tested and found to benefit the leaching, achieving extractions of ~80%, although this contradicts the theory presented earlier that high Cu(II) can destroy $S_2O_3^{2-}$ and result in CuS precipitation.

4.3.2.3. Effect of NH_3 concentration

Rath et al. (2003) observed that increasing the NH_3 concentration from 1 M to 3 M resulted in a decrease in gold extraction for the two ores studied. This supports the findings of the experiments conducted on Sample 2 and Sample 3, whereby it was found that increasing the concentration of NH_3 from 0.5 M to 1 M caused a decrease in gold extraction. In the case of Sample 1, the concentration increase did not affect the leaching process.

Increasing NH_3 concentration eventually ends up negatively impacting the leaching process as when the NH_3 concentration is increased, the pH is increased as well, therefore the area of stability of $Cu(NH_3)_4^{2+}$ is reduced while the area of stability of unwanted solid Cu species is increased. Since Cu(II) is prevented to play its catalytic role by existing in the form of $Cu(NH_3)_4^{2+}$, the gold extraction decreases as a result. This was highlighted in the study conducted by Tozawa et al. (1976) whereby the stability window of $Cu(NH_3)_4^{2+}$ was shown to increase with decreasing ammonia concentration (Figure 74).

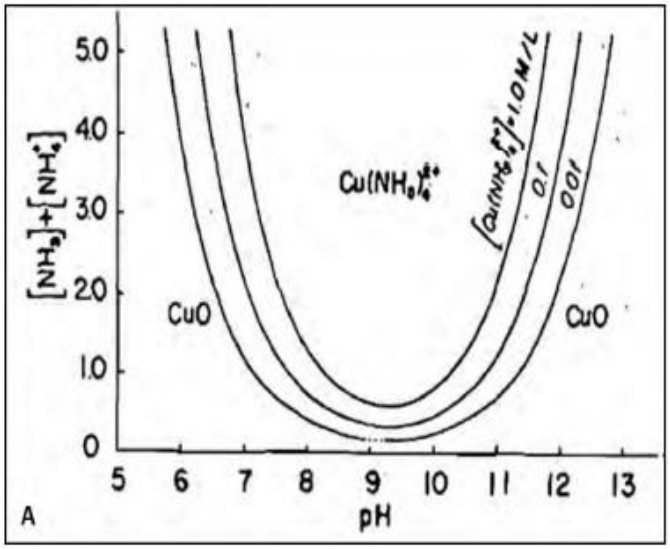

Figure 74: stability regions of $Cu(NH_3)_4^{2+}$ (Tozawa et al., 1976)

4.4. Comparison of technologies investigated

Figure 75, Figure 76 and Figure 77 show comparisons of gold extractions achieved by cyanide leaching and thiosulphate leaching for each ore. For each technology, the leaching results displaying the best gold extraction were selected for the comparison. For cyanide leaching, the results of the experiment conducted at 5 g/L NaCN, 30% solids and 26 °C were selected, while for thiosulphate leaching, the results at 0.5 M $(NH_4)_2S_2O_3$, 0.5 M NH_3, 1 mM Cu(II) and 26 °C were selected. The trends presented show clearly that cyanidation outperformed thiosulphate leaching by a large margin.

The amalgamation results, provided in Appendix C: Field work summary report, revealed that 100.7 g of gold were recovered. This represents an estimated recovery of approximately 34% (3 t of ore processed with a grade of ~100 g/t) which is in accordance with typical gold recoveries reported for Hg amalgamation (Veiga et al., 2009). Gold recovery post-leaching, either by activated carbon or ion exchange resins followed by elution with zinc cementation or electrowinning, is highly efficient. This is the case especially if the gold purification steps are run in a circuit, meaning that gold will not be lost. Therefore, the gold recoveries, based on the extractions achieved by the cyanide leach experiments, will be much higher than the recovery achieved with Hg amalgamation (34%). As much as the extractions achieved with thiosulphate leaching were lower in comparison to cyanide leaching, thiosulphate leaching has the potential to outperform Hg amalgamation as well, depending on the ore type, since Sample 1 achieved a maximum Au extraction of 54%.

In ASGM, Hg amalgamation is often conducted in conjunction with vat leaching of tailings using cyanide. This study found that agitated cyanide leaching outperformed vat leaching (Figure 63, Figure 64 and Figure 65, page 85) and it must be noted that these vat leach tests were conducted on fresh samples and not amalgamation tailings. As much as the samples showed little free gold after panning and amalgamation, the gold extraction could have been even lower with tailings since the ores would have had already been treated with mercury. This shows that agitated cyanide leaching can potentially achieve better gold recoveries than the combination of amalgamation and vat leaching of tailings. In addition, the use of cyanide alone prevents the emission of not only mercury but also the highly toxic mercury cyanide which is formed during cyanide vat leaching of mercury-contaminated tailings. It must be acknowledged that achieving agitation will be a challenge to diggers who make use of rudimentary processing methods. However, for the more equipped small-scale operations, investing in agitated leaching is a decision that can be made based on evaluating the revenue that can be generated by adopting the method.

Another important factor is time. With vat leaching, artisanal miners typically let the vats sit for 3-7 days. This is a major disadvantage when compared to agitated cyanide leaching whereby the extractions reported were obtained after 24 h. As much as amalgamation can yield gold in a matter of hours, its much lower gold recovery and use in combination with vat leach do not perform as well as cyanide leaching, overall. However, one key consideration specific to the ASGM context is that artisanal miners trust mercury amalgamation because they can visually inspect the process in which gold, in its solid state, gets upgraded by gravity concentration and

collected as sponge gold. They can then weigh the sponge gold obtained and ensure transparent splitting of revenue based on the agreed revenue structure of their operation. On the other hand, leaching consists of dissolving gold into aqueous solutions, making it invisible to the naked eye, and is purely based on a scientific understanding of the mechanisms that govern the extraction process. As much as the gold leached from the vats will eventually be visible in the end after cementation, miners do not trust and understand gold being in solution. This lack of trust and familiarity with the technology can be a major challenge in its acceptance. Therefore, from an implementation point of view, time and resources would need to be invested, in the form of training programs for example, to create trust for such methods as much as they have been shown to outperform amalgamation.

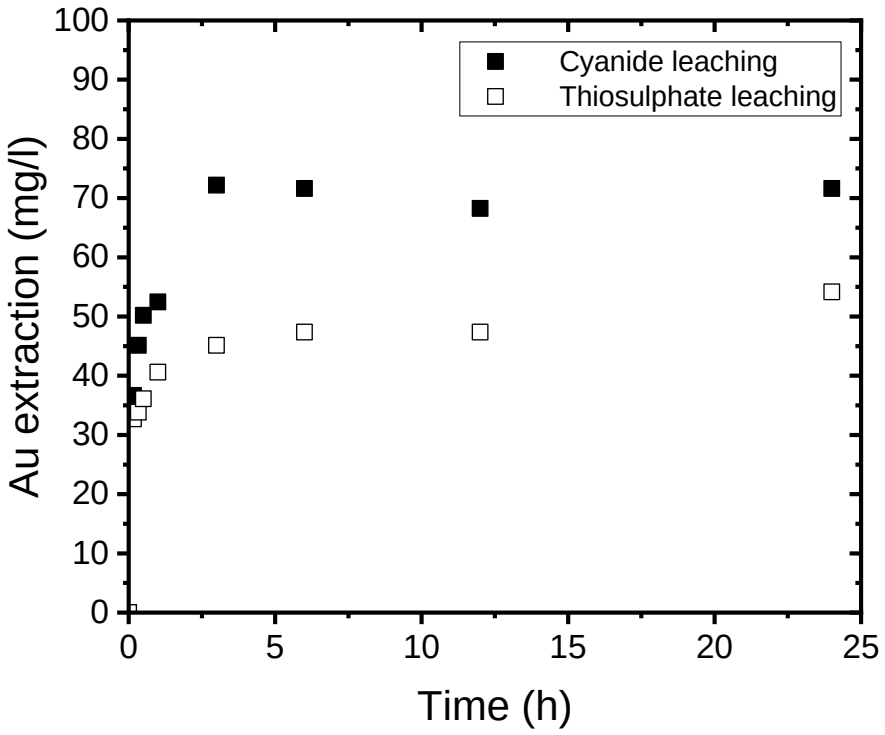

Figure 75: Agitated cyanide leaching (5 g/L NaCN) vs thiosulphate leaching (0.5 M $(NH_4)_2S_2O_3$, 0.5 M NH_3 and 1 mM Cu(II)) for Sample 1 at 30% solids, -300 + 150 µm PSD and 26°C

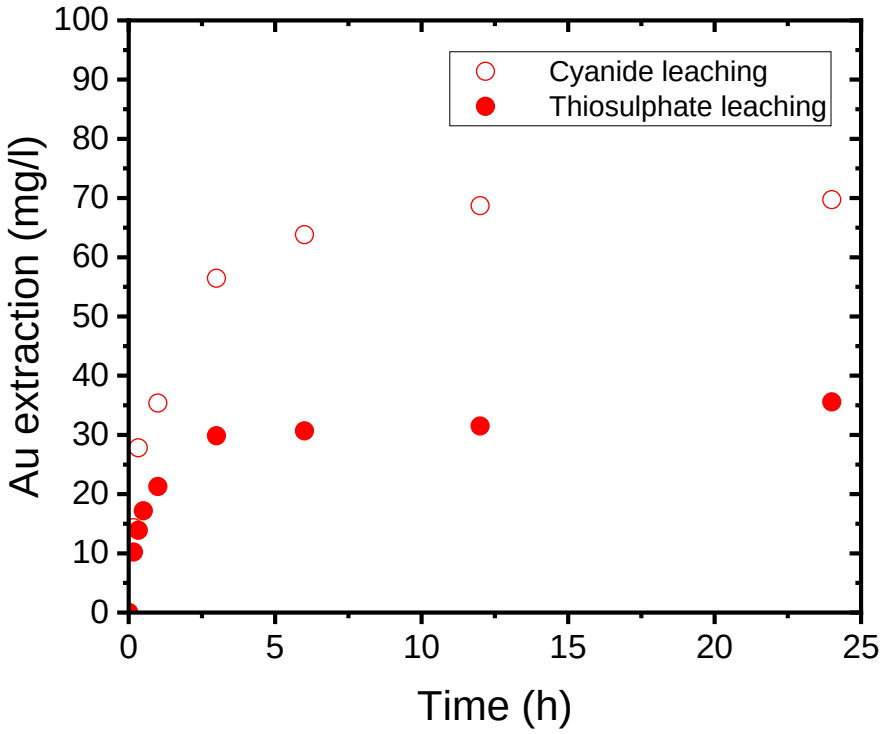

Figure 76: Agitated cyanide leaching (5 g/L NaCN) vs thiosulphate leaching (0.5 M $(NH_4)_2S_2O_3$, 0.5 M NH_3 and 1 mM Cu(II)) for Sample 2 at 30% solids, -300 + 150 µm PSD and 26°C

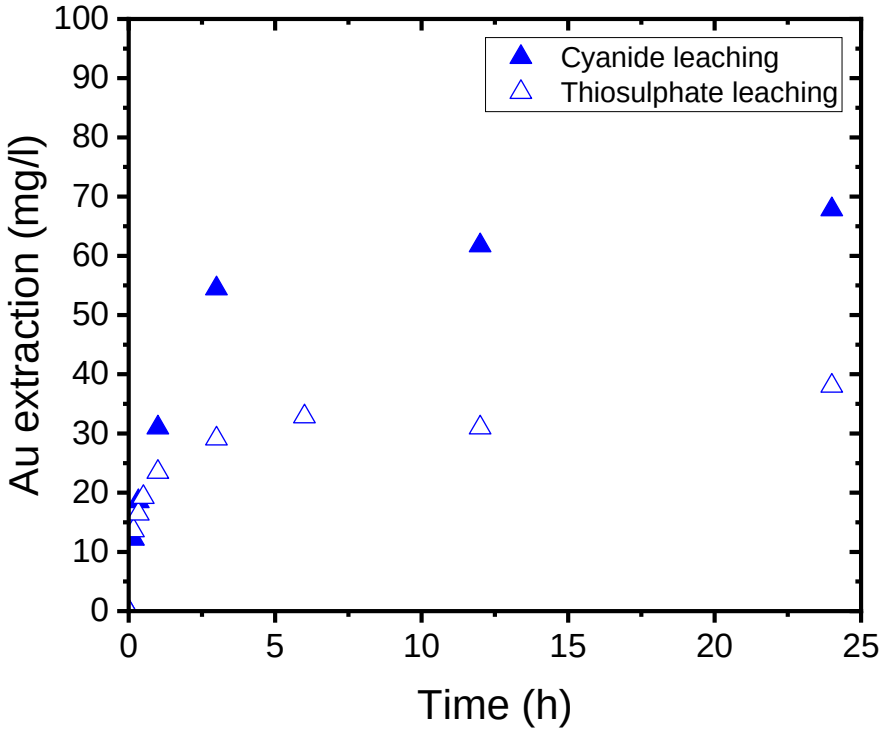

Figure 77: Agitated cyanide leaching (5 g/L NaCN) vs thiosulphate leaching (0.5 M $(NH_4)_2S_2O_3$, 0.5 M NH_3 and 1 mM Cu(II)) for Sample 3 at 30% solids, -300 + 150 µm PSD and 26°C

5. Conclusions and recommendations

The overarching theme of this study was to assess the efficacy of two alternative gold extraction technologies to Hg amalgamation, namely cyanide leaching and thiosulphate leaching, in the ASGM context.

Firstly, based on the findings of this study, it can be confidently concluded that cyanide leaching is the better performing technology compared to thiosulphate leaching. For the 3 ores studied, Sample 1, Sample 2, and Sample 3, the highest Au extraction achieved by cyanidation were 71.6%, 69.7% and 67.8% respectively, while thiosulphate leaching achieved 54.1%, 35.6% and 38.0% Au extraction, respectively. The leaching experiments showed relatively low Au extractions compared to literature data. In an attempt to understand this behaviour, ore characterisation using a combination of XRF, XRD, QUEMSCAN, SEM-EDS and diagnostic leach was conducted on the 3 ores and revealed the presence of sulphide minerals such as pyrite and arsenopyrite. The presence of these sulphide minerals that host gold as ultrafine solid solutions, making it difficult to leach, was found to be a major reason behind the low Au extractions observed. The diagnostic leach, in particular, was able to quantitatively show that the cyanide leach of fresh samples had reached a mineralogical barrier that the series of aggressive leach stages of the diagnostic leach was able to break, in order to recover more gold. Besides the superiority in performance, this study found that cyanidation is easier to control compared to thiosulphate leaching which showed to have a complex chemistry involving many species and potential side reactions.

Secondly, cyanide leaching outperformed Hg amalgamation which only achieved 34% gold recovery from the field experiment, and although thiosulphate leaching could not compete with cyanide leaching, it still showed the potential to outperform Hg amalgamation.

Thirdly, milling finer, at a particle size of -150 µm, proved to yield better Au extractions of 77.9%, 69.3%, and 84.5% with cyanidation for Sample 1, Sample 2 and Sample 3, respectively, while at +300 -150 µm, the Au extractions achieved were 68.2%, 56.4% and 56.8%, respectively.

For ASGM, these results prove that agitated cyanide leaching can be advocated as an alternative method for Hg amalgamation as a whole and not as an additional step to recover Au that follows amalgamation, as it is done in many operations. Not only does cyanidation achieve higher gold extractions, but it is also a technology that many artisanal miners already know of and have shown the technical ability to use in vat leaching. This existing familiarity with the technology overcomes, by itself, a major barrier in the acceptance of methods that challenge Hg amalgamation, as artisanal miners are mostly resistant to technologies that deviate from their existing methods without clear incentive. This reluctance can stem from a simple lack of trust or a fear of being defrauded. Additionally, the fact that cyanidation is less sensitive and, therefore, easier to control compared to thiosulphate leaching means that it would be easier to train miners on reagent proportions with cyanidation, even in the absence of equipment such as scales and volumetric flasks.

A key finding of relevance to the ASGM context of this study is that there was a lack of uniformity in the way the 3 ores responded to leaching with both cyanide and thiosulphate. This highlights that, in the quest to assist ASGM and ASM in general, and make the sector more sustainable for mining communities, there is a serious need to assist miners in conducting mineralogical studies on the deposits they mine from. With this assistance, they will be able to optimise their processes, make use of methods that best fit their ores and not settle for poor recoveries simply by lack of information. For example, the 3 ores (Sample 1, Sample 2, and Sample 3) were determined to have a significant Cu content which could hinder the selective leaching of Au. Having such information beforehand could help in developing a better extraction strategy for Au and create the possibility of extracting Cu alongside Au or at a later stage. However, what is observed in practice is that artisanal miners simply settle for recoveries of 30-50% and either dump their tailings leading to pollution or leave their mineral-rich tailings to processing centres that end up making more profit than them.

Finally, to prevent the redundancy of replacing a toxic chemistry with another toxic chemistry, it is key that cyanide management controls for effluent streams, taking into account dissolved metals, are implemented, as well as cyanide recycling where possible. It must, however, be acknowledged that in this proposition of cyanide as a long-term substitute for Hg, it may not be a solution that fits all ASGM operations. Each artisanal mine has its own reality and faces its own challenges which will dictate how well the uptake of this technology, or any other technology, will be. It is also important to keep in mind that any solution or process that has the potential to benefit the ASGM sector in the long term can only do so if artisanal miners themselves are actively involved every step of the way. This will ensure that they develop a sense of ownership of it and incentivise them to maintain good practices in their operations, for themselves and their communities.

Recommendations

For future work, the following recommendations are suggested:

- Conduct further leaching experiments using both cyanide and thiosulphate, however, this time using gravity concentrated ore samples and compare the results to those of the current study.
- Conduct field experiments using the findings of this study to have a better sense of the applicability of the gold extraction technologies investigated and the challenges and opportunities that may exist in upscaling. Such field studies could also investigate how to operate agitated tank leach at appropriate scale in ASGM operations.
- Investigate other extraction technologies that have shown promising results, such as urea leaching and chlorine leaching and compare them to the technologies investigated in this study.
- Study processes that recover gold post-leaching such as carbon in leach (CIL), carbon in pulp (CIP) and the Merrill-Crowe process, to name a few. As much as it is important to study the mechanisms in which various lixiviants dissolve gold, it is equally relevant to have an indication of how much gold artisanal miners can actually have on hand.

- Given the concerning health and environmental risks that emanate from the cyanidation of Hg contaminated tailings, conduct further studies on the extent of toxicity of mercury cyanide in rivers and the mechanisms by which it bioaccumulates in marine ecosystems.
- Develop simple diagnostic tool kits for miners in place of sending samples to laboratories for mineralogical analysis.
- Invest time and effort via seminars or field studies to bridge the gap that exists between scientists and artisanal miners. This gap contributes greatly to artisanal miners' reluctance to adopt new processing methods that scientists come up with. Scientists would also benefit greatly from such interactions by coming away with a deeper understanding of the methods and tools artisanal miners employ as well as the socio-economics of ASM.

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7. Appendices

Appendix A: Stoichiometric calculations of reagent requirement for Au leaching

Sodium cyanide (NaCN)

$$2Au + 4CN^- + O_2 + 2H_2O \leftrightarrow 2Au(CN)_2^- + H_2O_2 + 2OH^-$$

Stoichiometrically, 1 mole of Au requires 2 moles of CN^-

It was determined, by fire assay, that the gold grade for Sample 2 is 16.3 g/t.

Amount of gold in 100 g of Sample 2 as placed in reactor:

$$1\ t\ of\ Sample\ 2\ \rightarrow 16.3\ g\ Au$$

$$100\ g\ of\ Sample\ 2\ \rightarrow \frac{16.3\ g\ \times 100}{1\ 000\ 000} = 0.00163\ g\ Au$$

In moles: $$0.00163\ g\ \times \frac{mol}{196.967\ g} = 8.28\ \times 10^{-6}\ moles$$

Moles of CN^- required to completely react with Au:

$$8.28\ \times 10^{-6}\ moles\ Au\ \times \frac{4\ moles\ CN^-}{2\ moles\ Au} = 16.56\ \times 10^{-6}\ moles\ of\ CN^-$$

Assuming the NaCN concentration is 1 g/L (which is the lowest of the 3 concentrations used for cyanide leach experiments)

$$1\frac{g}{L}NaCN\ \rightarrow 1\frac{g}{L} \times \frac{mol}{49.0072\ g} = 0.020405\frac{mol}{L}$$

$$[CN^-] = 0.020405\frac{mol}{L} \times \frac{26.02\ (MM\ CN^-)}{49.0072\ (MM\ NaCN)} = 0.010834\frac{mol}{L}$$

Each reactor contained 333.3 mL of NaCN solution, therefore:

$$In\ 333.3\ mL\ solution\ \rightarrow \frac{0.010834\ mol\ \times 333.3}{1000} = 0.00361\ moles\ of\ CN^-$$
$$= 3.61\ \times 10^{-3}\ moles\ CN^-$$

$$3.61\ \times 10^{-3}\ moles \gg\ 16.56\ \times 10^{-6}\ moles\ (CN^-\ required\ stoichiometrically)$$

Therefore, at a concentration of 1 g/L, CN^- is present in excess.

Given the fact that Cu, which was found in significant amount in the 3 ores (highest grade: 102 g/t for Sample 2), can be readily dissolved by cyanide and compete with Au, it is important to know if at 1 g/L NaCN there is still sufficient CN^- to drive the Au leaching reaction, assuming that all the Cu gets dissolved as well. Bas et al. (2015) have reported that 1% of reactive Cu in an ore can consume ~ 30kg of NaCN per tonne of ore.

Using this Cu consumption,

$$1\ \%\ Cu\ \rightarrow \frac{30\ kg\ NaCN}{1\ t\ ore}$$

$$1\ \%\ Cu\ \rightarrow \frac{3\ g\ NaCN}{100\ g\ ore\ (as\ placed\ in\ reactor)}$$

The Cu content in sample 2 is 102 ppm which is corresponds to 0.0102 % Cu

$$0.0102\ \%\ Cu\ \rightarrow \frac{0.0102\ \times 3\ g\ NaCN}{100\ g\ ore} = \frac{0.0306\ g\ NaCN}{100\ g\ ore}$$

Since 100 g of ore is placed in the BSTR and that the volume is 333 mL, this mass of NaCN is what will be contained in the 333 mL of solution.

$$moles\ of\ NaCN\ in\ 333\ ml = 0.0306\ g\ \times \frac{1\ mol}{49.0072\ g} = 6.24\ \times 10^{-4}\ mol$$

$$moles\ of\ CN^- = 6.24\ \times 10^{-4} mol\ \times \frac{26.02\ (MM\ CN^-)}{49.0072\ (MM\ NaCN)} = 3.3\ \times 10^{-4}\ mol$$

It was found above that 1 g/L NaCN in 333 mL of solution corresponds to 3.61 x 10^{-3} mol of CN^-

This means that at 1 g/L NaCN, there is sufficient CN^- since,

$$3.61\ \times 10^{-3}\ moles\ CN^-\ \gg 3.3\ \times 10^{-4}\ mol\ (CN^- required\ to\ leach\ Cu) +\ 16.56\ \times 10^{-6}\ moles\ (CN^-\ required\ to\ leach\ Au)$$

Ammonium thiosulphate $(NH_4)_2S_2O_3$

$$4\,Au_{(s)} + O_2 + 2\,H_2O + 8\,S_2O_3^{2-} \rightarrow 4\,Au(S_2O_3)_2^{3-} + 4\,OH^-$$

Stoichiometrically, 1 mole of Au requires 2 moles of $S_2O_3^{2-}$

It was determined, by fire assay, that the gold grade for Sample 2 is 16.3 g/t.

Amount of gold in 100 g of Sample 2 as placed in reactor:

$$1\ tonnes\ of\ Sample\ 2\ \rightarrow 16.3\ g\ Au$$

$$100\ g\ of\ Sample\ 2\ \rightarrow \frac{16.3\ g\ \times 100}{1\ 000\ 000} = 0.00163\ g\ Au$$

In moles: $$0.00163\ g\ \times \frac{mol}{196.967\ g} = 8.28\ \times 10^{-6}\ moles$$

Moles of $S_2O_3^{2-}$ required to completely react with Au:

$$8.28\ \times 10^{-6}\ moles\ Au\ \times \frac{8\ moles\ S_2O_3^{2-}}{4\ moles\ Au} = 16.56\ \times 10^{-6}\ moles\ of\ S_2O_3^{2-}$$

Assuming the $(NH_4)_2S_2O_3$ concentration is 0.1 M (which is the lowest of the 2 concentrations used for thiosulphate leach experiments), $[S_2O_3^{2-}]$:

$$[S_2O_3^{2-}] = 0.1\frac{mol}{L} \times \frac{112.1282\ (MM\ S_2O_3^{2-})}{148.2051\ (MM\ (NH_4)_2S_2O_3)} = 0.07566\frac{mol}{L}$$

Each reactor contained 333.3 mL of $(NH_4)_2S_2O_3$ solution, therefore:

$$In\ 333.3\ mL\ solution\ \rightarrow \frac{0.07566\ mol\ \times 333.3}{1000} = 0.0252\ moles\ of\ S_2O_3^{2-}$$
$$= 2.52\ \times 10^{-2}\ moles\ S_2O_3^{2-}$$

$$2.52\ \times 10^{-2}\ moles\ \gg\ 16.56\ \times 10^{-6}\ moles\ (S_2O_3^{2-}\ required\ stoichiometrically)$$

Therefore, at a concentration of 0.1 M, $S_2O_3^{2-}$ is present in excess.

Appendix B: Gold distribution

Table 16: Gold distribution within the 3 ores

Ore deposit	Grade (g/t)	Size range (µm)	mass fraction (%)	Au content	Au % distribution
Sample 1	4.7	+300	16.66	0.78	14.53
	5.9	+150 -300	62.63	3.70	68.56
	4.4	-150	20.71	0.91	16.91
	Sum of all fractions		100	5.39	100
Sample 2	22.4	+300	16.23	3.64	19.54
	16.3	+150 -300	58.09	9.47	50.91
	21.4	-150	25.68	5.50	29.54
	Sum of all fractions		100	18.60	100
Sample 3	11.4	+300	32.20	3.67	27.00
	14.2	+150 -300	53.67	7.62	56.05
	16.3	-150	14.13	2.30	16.94
	Sum of all fractions		100	13.60	100

$$Mass\ fraction\ (\%) = \frac{mass\ of\ ore\ in\ each\ size\ range}{total\ mass\ of\ ore\ in\ all\ size\ ranges}$$

$$Au\ content = mass\ fraction\ (\%)\ \times Grade\ of\ each\ size\ range\ \left(\frac{g}{t}\right)$$

$$Au\ \%\ distribution = \frac{Au\ content\ of\ each\ size\ range}{Au\ content\ of\ all\ size\ ranges} \times 100$$

Appendix C: Field work summary report

The field experiment was conducted in Zimbabwe, in the Kensington area, which is the same geographical area where Sample 3 was sourced from. 3 t of ore were mined at a depth of 15 m. The gold grade was not determined by fire assay but was instead estimated to be ~100 g/t by the miners, based on their experience in processing ores in this particular area. It must, however, be acknowledged that this estimate seems quite high and was not confirmed by fire assay. The ore was milled using a hammer mill to a size range similar to the size range of the 3 ores used in this study (-300 +150 µm). The mill was connected to a sluice which collected the concentrate (Figure 78). This concentrate was then panned with mercury to initiate amalgamation (Figure 79a). After the amalgam was formed and collected, it was roasted on a burning wood log for approximately 2 min, after which the gold sponge was recovered (Figure 79b). From the 3 t of ore processed, 143.86 g of sponge gold was recovered. Accounting for the fact that ~30% of sponge gold is mercury (this value is specific to this artisanal mine and was provided by the miners at this particular operation), the final Au recovery was approximately 100.7 g. This recovery will be used as benchmark for comparison with the cyanidation and thiosulphate leaching results.

Figure 78: Hammer mill connected to sluice

a) 

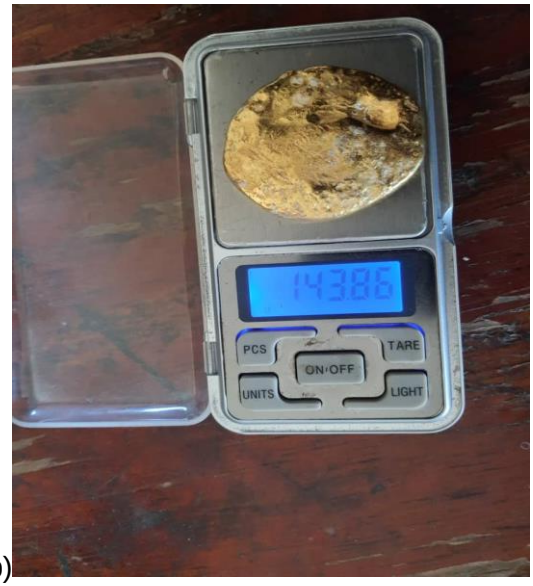
b) 

Figure 79: a) concentrate panned with mercury b) gold sponge obtained after amalgam burning

Appendix D: Material Safety Data Sheets (MSDS)

Sodium Cyanide (NaCN)

ScienceLab.com
Chemicals & Laboratory Equipment

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.

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

Ammonia (NH_3)

Safety Data Sheet
according to 29CFR1910/1200 and GHS Rev. 3

Effective date : 12.31.2014 Page 1 of 7

Ammonia

SECTION 1 : Identification of the substance/mixture and of the supplier

Product name : **Ammonia**

Manufacturer/Supplier Trade name:

Manufacturer/Supplier Article number: **S25164**

Recommended uses of the product and uses restrictions on use:

Manufacturer Details:

AquaPhoenix Scientific
9 Barnhart Drive, Hanover, PA 17331

Supplier Details:

Fisher Science Education
15 Jet View Drive, Rochester, NY 14624

Emergency telephone number:

Fisher Science Education Emergency Telephone No.: 800-535-5053

SECTION 2 : Hazards identification

Classification of the substance or mixture:

Corrosive
Skin corrosion, category 1B

Environmentally Damaging
Acute hazards to the aquatic environment, category 1

Irritant
Specific target organ toxicity following single exposure, category 3

STOT SE 3
AcAq Tox 1
Skin Corr. 1B

Signal word :Danger

Hazard statements:
Causes severe skin burns and eye damage
May cause respiratory irritation
Very toxic to aquatic life

Precautionary statements:
If medical advice is needed, have product container or label at hand
Keep out of reach of children
Read label before use
Do not breathe dust/fume/gas/mist/vapours/spray
Avoid release to the environment
Wear protective gloves/protective clothing/eye protection/face protection
Use personal protective equipment as required

Ammonium thiosulphate ($(NH_4)_2S_2O_3$)

MARTIN RESOURCES

SAFETY DATA SHEET

SECTION 1) CHEMICAL PRODUCT AND SUPPLIER'S IDENTIFICATION

Product ID:	Ammonium Thiosulfate		
Product Name:	Ammonium Thiosulfate		
Revision Date:	Jul 13, 2015	**Date Printed:**	Sep 29, 2015
Version:	2.0	**Supersedes Date:**	Jun 05, 2015
Manufacturer's Name:	Martin Operating Partnership, L.P.		
Address:	P.O. Box 191, Kilgore, TX, US, 75663		
Emergency Phone:	CHEMTREC (800) 424-9300		
Information Phone:	800-231-4595		
Fax:			

Product/Recommended Uses: Industrial uses

SECTION 2) HAZARDS IDENTIFICATION

Classification:

Acute toxicity, Oral - Category 4

Pictograms:

Signal Word:

Warning

Hazardous Statements - Health:

Harmful if swallowed

Precautionary Statements - General:

If medical advice is needed, have product container or label at hand.

Keep out of reach of children.

Read label before use.

Precautionary Statements - Prevention:

Wash with soap and water thoroughly after handling.

Do not eat, drink or smoke when using this product.

Precautionary Statements - Response:

IF SWALLOWED: Call a POISON CENTER/doctor if you feel unwell.

Rinse mouth.

Precautionary Statements - Storage:

No precautionary statement available.

Precautionary Statements - Disposal:

Dispose of contents/container to disposal recycling center. Under RCRA it is the responsibility of the user of the product to determine at the time of disposal whether the product meets RCRA criteria for hazardous waste. Waste management should be in full compliance with federal, state and local laws.

Appendix E: 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		Archippe Ngwey Manzila
Department		Chemical Engineering
Preferred email address of applicant:		mnzarc001@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.	
	Name of Supervisor (if supervised):	Jochen Petersen Thandazile Moyo
If this is a researchcontract, indicate the source of funding/sponsorship		
Project Title		A study of alternative methods for gold extraction from alluvial deposits

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

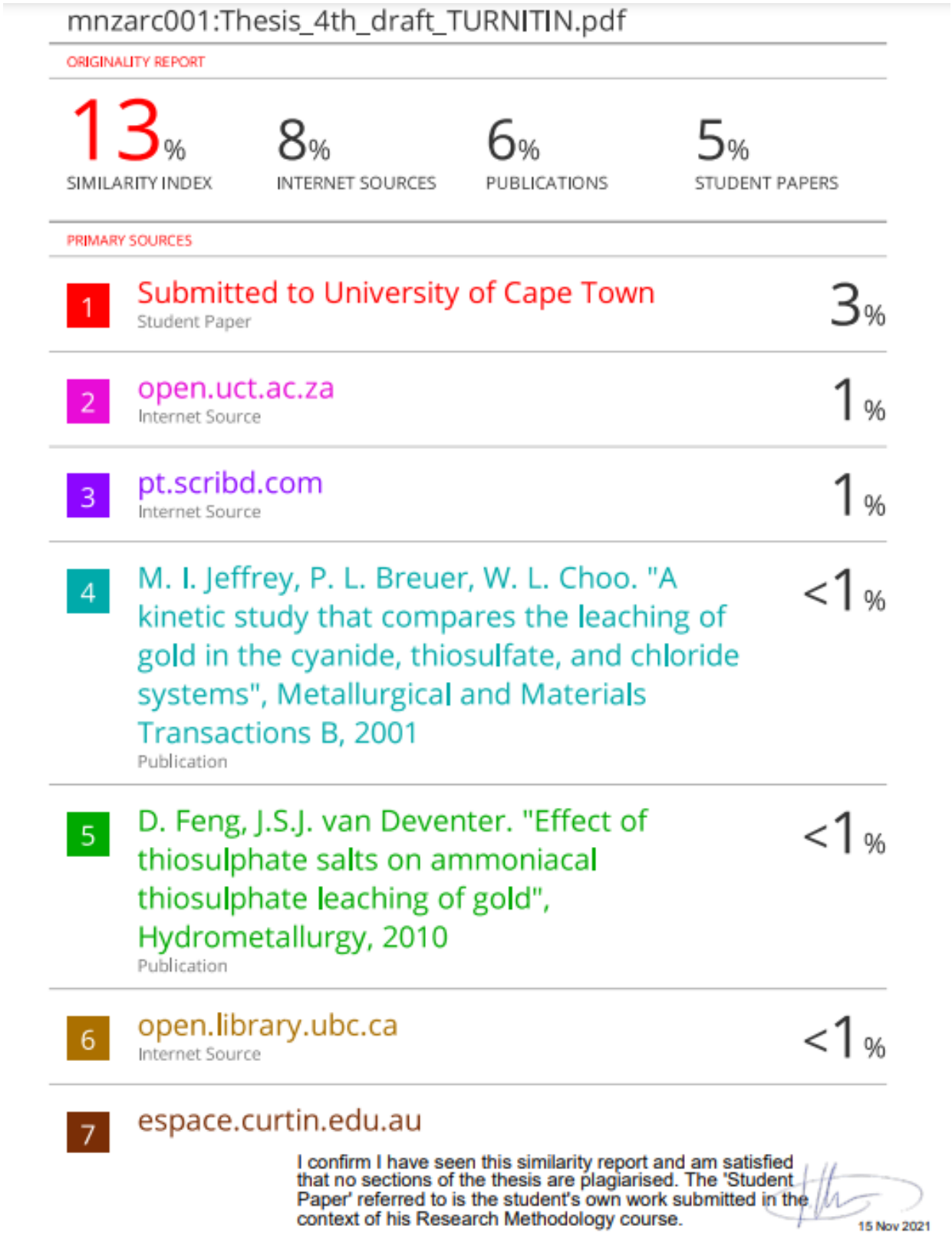
- there is no apparent legal objection to the nature or the method of research; and
- the research will not compromise staff or students or the other responsibilities of the University;
- the stated objective will be achieved, and the findings will have a high degree of validity;
- limitations and alternative 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	Archippe Ngwey Manzila	Signed by candidate	21/01/2020
SUPPORTED BY	**Full name**	**Signature**	**Date**
Supervisor (where applicable)	Thandazile Moyo		21/01/2020

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).	Prof H von Blottnitz		19/02/2020
Chair: Faculty EIR Committee For applicants other than undergraduate students who have answered YES to any of the questions in Section 1.			

Page 1 of 1

Appendix F: Similarity report



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ORIGINALITY REPORT

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7	espace.curtin.edu.au	

I confirm I have seen this similarity report and am satisfied that no sections of the thesis are plagiarised. The 'Student Paper' referred to is the student's own work submitted in the context of his Research Methodology course.

15 Nov 2021