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A Study on the Applicability of Agitated Cyanide Leaching and Thiosulphate Leaching for Gold Extraction in Artisanal and Small-Scale Gold Mining

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Abstract: Mercury amalgamation is the method of choice to recover gold in artisanal and small-scale gold mining (ASGM). However, despite the low cost and simplicity of this method, the use of mercury presents serious health and environmental risks, as well as low efficiency in gold extraction. This study investigates the application of cyanide and thiosulphate leaching as alternatives to 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 three ore samples originating from an artisanal mining area in Zimbabwe. The operating conditions ($T = 26\text{ }^{\circ}\text{C}$, solids loading: 30%, particle size: $-300 + 150\text{ }\mu\text{m}$) were selected to mimic as closely as possible the conditions of artisanal mining processes. It was found 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 three ore samples (Sample 1, Sample 2, and Sample 3, respectively), whereas thiosulphate leaching achieved gold extractions of 54.1%, 35.6%, and 38.0% for the three ores, respectively. Both methods outperformed mercury amalgamation, which typically achieves gold recoveries of 30%–50%. Studying the minerology of the ores, using XRF, XRD, QEMSCAN, SEM-EDS, and a diagnostic leach, revealed the presence of sulphide minerals hosting refractory gold which contributed to the low gold extractions observed. Besides achieving higher gold extraction, cyanide leaching proved to be a system that is easier to control compared to thiosulphate leaching, making it much more attractive to artisanal miners.

Keywords: artisanal mining; cyanide; gold; mercury; thiosulphate



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1. Introduction

Artisanal and small-scale gold mining (ASGM) refers to operations that make use of rudimentary techniques to mine and process gold [1]. However, due to modernisation and the visible migration of skilled people into the sector, there are operations that employ basic mechanisation. The artisanal and small-scale mining (ASM) sector, as a whole, represents a source of livelihood for ~43 million people worldwide [2]. Although the majority of miners in the sector are involved in industrial/construction minerals such as sand and aggregates, about 15 million miners process ores that contain precious metals such as gold [3–5].

ASGM provides ~20% of the world's gold supply, and the primary recovery method is mercury (Hg) amalgamation. This method is popular amongst artisanal miners due to its simplicity and low cost [1]. However, the use of Hg presents serious health risks, ranging from severe kidney and nervous system damage to potential death, and environmental risks such as air pollution via amalgam burning and river pollution via tailings disposal. It is estimated that the ASGM sector uses ~1400 t of Hg annually which is virtually never recycled [6]. Hg emissions generated by the ASGM sector alone represent ~37% of all

anthropogenic Hg released into the environment [3]. Furthermore, Hg amalgamation has been viewed as a ‘one size fits all’ technology despite that ASGM, just as other mining sectors, is processing increasingly complex ores [7].

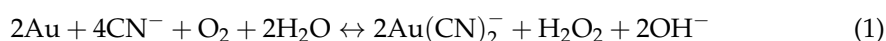
One of the major actions taken against Hg use was the UN Minamata Convention on Mercury, which was signed by 128 countries in 2013. Its main objective is to control and reduce the use of Hg, with the ultimate goal of completely phasing it out by 2030. This otherwise noble objective would be difficult to realise in the absence of viable technologies to replace Hg amalgamation. Furthermore, developing countries striving to phase out the Hg amalgamation technology are facing hurdles in that more under-resourced people are entering the ASGM sector due to high unemployment rates which have been worsened by the COVID-19 pandemic.

Given these concerns, some alternative methods have been proposed over the years, such as the Gemini table, cyanidation, borax smelting, chlorine leaching, and thiosulphate leaching, to name a few [3,8,9]. However, adoption and sustaining of these methods by ASGM are poor due to factors such as complexity of the process, poor understanding, inability to independently run the processes, high capital requirements, etc. On the other hand, despite its perceived benefits to artisanal miners, the Hg amalgamation process has poor gold recoveries which translate to even lower profit margins, thereby contributing to keeping the miners in the so-called poverty trap.

In order to ensure and enhance the 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. This is difficult to achieve, particularly in the ASM sector where many miners face economic hardship, since methods that meet high recovery, environmental, and safety standards are often expensive. However, if such technologies could be developed, they would have a tremendous impact on the overall status and acceptance of the sector which faces serious socio-economic challenges and is heavily criticised due to its safety and environmental impacts. This would ultimately lead to significant economic growth for artisanal miners and contribute to the realisation of the Sustainable Development Goals (SDGs) 1, 3, 6, 8, and 14, which aim to alleviate poverty and promote economic growth, good health, and preservation of the environment.

Cyanidation, a process that follows the redox chemistry described in Equation (1), has the potential to be a sustainable alternative (i.e., a technology that can help reduce socio-economic challenges and that artisanal miners can keep in operation in the long term) to Hg amalgamation. This is due to the fact that it achieves high gold extractions and is a technology that quite a few artisanal miners are familiar with since, in some regions, they employ the technology in vat leaching of amalgamation tailings. While cyanidation is toxic in its own right, methods for its safe disposal, such as natural degradation, the SART (Sulfidization, Acidification, Recycling, and Thickening) process, Caro’s acid, and more, can be put in place [10,11]. Veiga et al. [12] reported on the use of cyanidation in field experiments conducted in North Sulawesi (Indonesia) and Portovelo (Ecuador), whereby high Au extractions of 93.6% (mill leaching, 1 g/L NaCN) and 84% ($d_{80} = 250 \mu\text{m}$, 1 g/L NaCN) were achieved in Indonesia and 94% ($d_{80} = 150 \mu\text{m}$, 5 g/L NaCN) in Ecuador.

The overall dissolution reaction is given in Equation (1), and the chemistry and dynamics of the reaction are well understood.



However, in the context of ASGM, more research needs to be conducted to understand the factors that affect the gold extraction process using cyanide on ores found in ASGM areas. One key factor is pH. In solution, cyanide hydrolyses according to Equation (2):

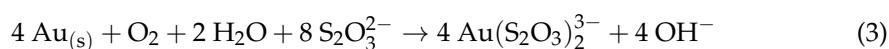


At ambient temperature, the acid ionisation constant (K_a) and $\text{p}K_a$ are 6.2×10^{-10} and 9.31, respectively, which suggests that hydrogen cyanide (HCN) does not readily dissociate

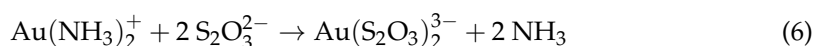
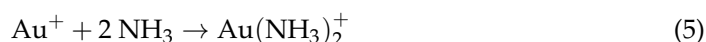
in solution—it is a weak acid. This means that the solution pH must be higher than 9.31 to deprotonate HCN into free cyanide (CN^-), which is the desired cyanide specie in solution for gold complexation. Marsden and House [7] have shown that at a pH of 9.3, about half of the HCN is present as HCN and 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 a 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 volatilise and become a serious health hazard. Further, operating at a pH above 10 minimises the loss of free cyanide, which is necessary for the gold complexation reaction [7,13].

Another promising technology is thiosulphate leaching, which follows the redox chemistry given in Equations (3)–(8) [14]. It has shown good results, as demonstrated in the study conducted by Zhang et al. [15] on colloid gold whereby a gold extraction of 90% was achieved after 1 h of leaching. In addition, thiosulphate presents the advantage of being relatively safe and less toxic compared to cyanide [16]. This is particularly important for ASGM where leakages of chemicals to the environment are more common. However, there is a need for more research on its applicability in the context of ASGM, factoring in its challenges with decomposition in aqueous solutions (Equation (9)) and complex chemistry. The decomposition of thiosulphate leads to challenges with the hindered dissolution of gold due to a build-up of sulphur on the gold surface. It has been extensively shown, however, that Cu(II) plays a key role in facilitating the electron transfer between oxygen and the oxidising mineral, and that NH_3 plays the role of catalysing the reaction involving gold and thiosulphate, thereby reducing hindered dissolution and stabilising Cu(II) in the alkaline environment [15–27].

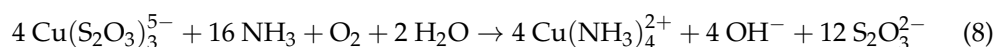
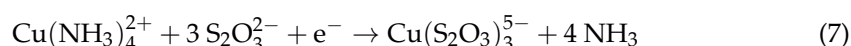
Overall reaction:



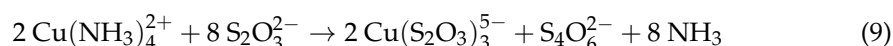
Anodic reactions:



Cathodic reactions:



Side reaction forming thiosulphate degradation products:



1.1. Key Parameters in Cyanide and Thiosulphate Leaching

1.1.1. Oxidant

Gold dissolution in cyanide media is an oxidative dissolution process that is highly dependent on the diffusion rates of oxygen and cyanide. Heath and Rumball [28] have shown that the ratio of $[\text{CN}^-]/[\text{O}_2]$ must vary between 4:1 and 7:1 to prevent the cyanide concentration from being rate limiting. However, the problem with oxygen in leaching systems is its solubility. Oxygen has a low solubility in water of 8.2 mg/L (at 25 °C, 1 atm), which decreases further with increasing temperature and ionic strength. One way to circumvent this problem is by using pressure leaching to increase oxygen dissolution. In thiosulphate systems, the gold leaching reaction is known to be sluggish, and oxygen is not effectively reduced. For this reason, Cu(II) is required to act as a redox mediator by facilitating the electron transfer between the dissolved oxygen and the oxidising mineral [20].

1.1.2. Temperature

In cyanide leaching, increasing temperature has been shown to be beneficial to leaching as it increases the diffusion rates of the reacting species. However, increasing temperature can have a negative impact on oxygen dissolution, as mentioned earlier. Marsden and House [7] have, in fact, shown that temperature is beneficial to the process only up to 85 °C due to the decreased solubility of oxygen. In thiosulphate leaching, however, increasing temperature has been shown to generally have a negative impact. Abbruzzese et al. [17] have shown that temperature increases thiosulphate decomposition and facilitates a thermal reaction between copper and thiosulphate forming cupric sulphide, which causes passivation.

1.2. Motivation for the Study

Given the aforementioned challenges faced by ASGM, the aim of this study is to investigate the applicability of agitated cyanide and thiosulphate leaching as alternatives to Hg amalgamation for the extraction of gold in the ASGM context. The research investigates the gold extractions that can be achieved by both methods and compares them to Hg amalgamation. The effect of reagent concentration, particle size, as well as mineralogy on leaching with both cyanide and thiosulphate are investigated as well.

It is a fact that cyanide and thiosulphate leaching are mature technologies for gold extraction. However, in the context of ASGM, their applicability has not been widely demonstrated experimentally. Cyanidation in ASGM has mostly been applied only in vat leaching of amalgamation tailings, which further pollutes the environment via the dumping of tailings (Hg^- and CN^- -contaminated) in rivers. In addition, given the increasingly complex nature of the ores currently processed in ASGM, it is crucial that technological investigations are conducted using materials sourced from ASGM areas. This study's contribution to the ASGM field consists firstly of demonstrating that the direct agitated leaching of actual ores found in ASGM areas with cyanide and thiosulphate, at ambient conditions, can compete with and even outperform the Hg amalgamation process. Ambient conditions are advantageous given the rudimentary nature of the equipment typically used in the sector. Secondly, ores found in ASM are often not characterised thoroughly enough, leading to poor implementation of theoretically successful technologies. Therefore, in this study, a thorough mineralogical characterisation of the samples used is conducted, using XRF, XRD, QEMSCAN, SEM-EDS, and a diagnostic leach sequence.

2. Materials and Methods

2.1. Materials

In total, 3 gold ore samples (referred to as Sample 1, Sample 2, and Sample 3 throughout the paper) 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. Before being used in the experiments, the samples went through a series of ore preparation steps which include crushing with a jaw crusher, milling with a rod mill, and sieving using three sieves of 300 μm , 212 μm , and 150 μm aperture, and splitting using a rotary splitter. After the ore preparation steps, 1.5 kg of ore in the particle size range of $-300 + 150 \mu\text{m}$ were obtained for each of the 3 ore samples. This particle size range was chosen with the aim to stay consistent with ASGM practices whereby the particle size used in leaching operations is typically below 250 μm [12]. The Au grades of the 3 samples, at $-300 + 150 \mu\text{m}$ PSD, as well as the compositions of other key elements, are shown in Table 1. These grades were used in all calculations for Au extraction.

Table 1. Elemental composition of ore samples.

	Au	Cu	Co	Fe	Ca	Mg
	g/t	g/t	g/t	%	%	%
Sample 1	5.9	128.1	50.9	7.3	1.2	2.4
Sample 2	16.3	102.2	24.1	4.1	7.9	0.8
Sample 3	14.2	96.7	25.6	3.9	4.6	1.3

2.2. Reagents

For cyanide leaching experiments, sodium cyanide (97%) was used. Sodium carbonate (99.5%) and sodium bicarbonate ($\geq 95\%$) were used to ensure that pH is maintained above 9.3 to prevent the formation of hazardous HCN [29]. For thiosulphate leaching experiments, ammonium thiosulphate (98%), copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$: 98.5%), and ammonia (30% in water) were used.

2.3. Apparatus

A total of 3 jacketed batch stirred tank reactors (BSTRs) with a volume of 1 L were used to conduct the leach experiments. A solid in pulp concentration of 30% was chosen to mimic what is typically conducted in ASGM operations [12]. The solution inside the reactors was agitated using mounted mechanical stirrers with impellers rotating at 300 rpm. The same reactors were also used to conduct a vat leach experiment, but with the impellers turned off. The temperature was kept at 26 °C using a water bath for all experiments. This was primarily conducted because ASGM operations are typically conducted at the atmospheric temperature of the day (20–30 °C). However, industrial cyanidation and thiosulphate leaching of gold are also typically conducted at ambient temperature (25–30 °C) [16,17,30].

2.4. Methods

2.4.1. Cyanide Leaching

Leach tests

Cyanide concentration in ASGM is often kept very high (10 g/L or higher) simply because miners believe 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 [12]. The three concentrations selected provide enough excess cyanide to prevent it from being a limiting factor. In industrial applications, cyanide concentration can vary in the range of 0.1–0.5 g/L in dilute systems [31] and, in higher concentrations, of 1–5 g/L [30,32,33]. In some instances, such as the leaching of high-grade Au ores or secondary materials (e.g., jewellery waste), cyanide concentrations can be as high as 12 g/L [34]. The pH was maintained above 10 using a combination of 1 g/L of sodium carbonate and 9.3 g/L of sodium bicarbonate. Table 2 presents a summary of the experimental conditions.

Table 2. 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 ingress from an open reactor
Mass of ore used	100 g in each reactor
Solids in pulp ratio	30% (100 g of ore in 333 mL solution)

Vat leach test

Since cyanide vat leaching is a common practice in ASGM, it was decided to conduct an experiment imitating 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 ($-300 + 150 \mu\text{m}$ PSD, 30% solids, 26°C) used for the agitated leach tests were applied. This test was conducted at a cyanide concentration of 5 g/L for the 3 ores under study.

2.4.2. Thiosulphate Leaching

In this set of experiments, the Cu(II) concentration, $(\text{NH}_4)_2\text{S}_2\text{O}_3$ concentration, and NH_3 concentration were varied. The particle size was kept at $-300 + 150 \mu\text{m}$. Table 3 presents a summary of the experimental conditions. These experiments were performed on the original untreated ore samples.

Table 3. Thiosulphate leaching experiment conditions.

Parameters	Specifications
Reagent concentration	0.1 M and 0.5 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$, 0.5 M and 1 M NH_3
Temperature	26°C
Particle size	$-300 + 150 \mu\text{m}$
pH	10–11
Oxidant/catalyst	1 mM and 10 mM CuSO_4
Mass of ore used	100 g in each reactor
Solids in pulp ratio	30% (100 g of ore in 333 mL solution)

2.4.3. Analysis Techniques

Fire assaying was used to determine the Au grade of the 3 ore samples. X-ray fluorescence (XRF) analysis was used on the 3 ores to measure the composition of major and trace elements. X-ray diffraction (XRD) was used to qualitatively and quantitatively identify mineral structures within the ores. QEMSCAN was used to quantify minerals and elements within the ores using 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 [35,36].

For the analysis of leach samples, an Agilent 4200 MP-AES was used to determine the concentrations of Au. Diagnostic leaching was used, as an analytical tool, to make an assessment of the mode of occurrence of gold within the ores and provide some information on the extent of its refractoriness [37]. The sequence of the diagnostic leach tests is presented in Table 4. 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 to collect the tailings which will then go through a series of increasingly aggressive leach tests, as listed in Table 4. The diagnostic leach study was conducted 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 run for 24 h. The high concentration of cyanide was purposely chosen to ensure that each cyanide leach stage leaches all the available gold before any subsequent acid leach.

Table 4. Diagnostic leach sequence.

Stage	Treatment Method
1	Gravity concentration by panning
2	Cyanide leach of tailings (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. Results and Discussion

3.1. Ore Characterisation

The XRD and QEMSCAN bulk mineralogy data are shown in Table 5 and were in accordance with XRF data. The data showed that the three ores are predominantly made of quartz, feldspar, chlorite, mica, calcite, and Fe-Ti oxides. It must be noted that the XRF results indicated quite high loss on ignition percentages (LOI%) for the three ores: 5.4%, 10.8%, and 7.6% for Sample 1, Sample 2, and Sample 3, respectively. As much as the LOI% predominantly accounts for water in the ore, it also accounts for the organic matter content of a sample. A high carbon content in an ore can cause Au reabsorption during leaching in what is known as preg-robbing.

Table 5. 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

By manual search on SEM-EDS, gold was visually examined in the three ores (Figures 1–3). This indicates that some of the gold particles exist in their native form as free gold and can therefore be extracted effectively by leaching and gravity separation. The gold particles in Figures 1–3 had a long diameter of 4 μm , 5 μm , and >1 μm , respectively.

Evidence of the presence of sulphide minerals (pyrite and arsenopyrite) in Sample 1 and Sample 3 was found, as shown in Figure 4. 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.

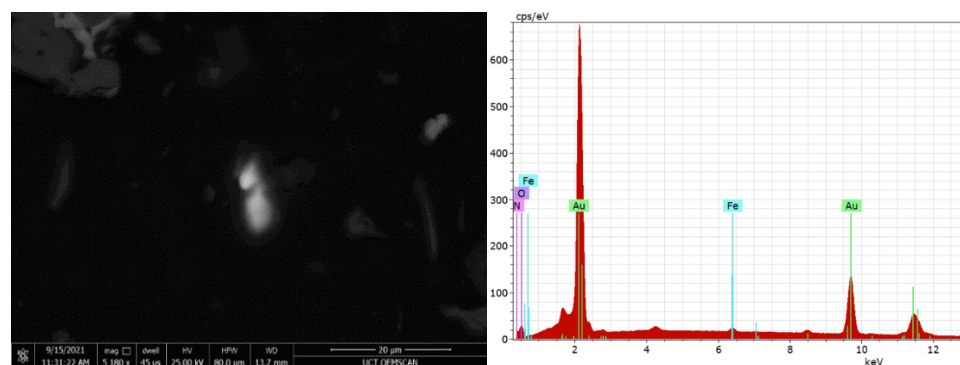


Figure 1. SEM-EDS image of gold particle in Sample 1.

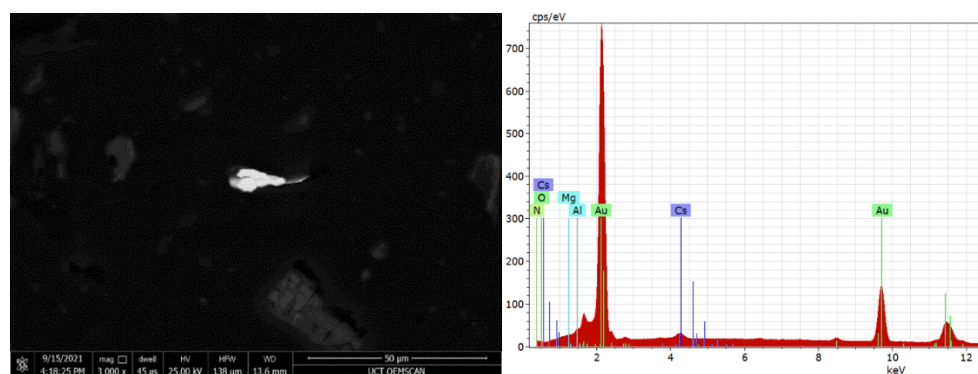


Figure 2. SEM-EDS image of gold particle in Sample 2.

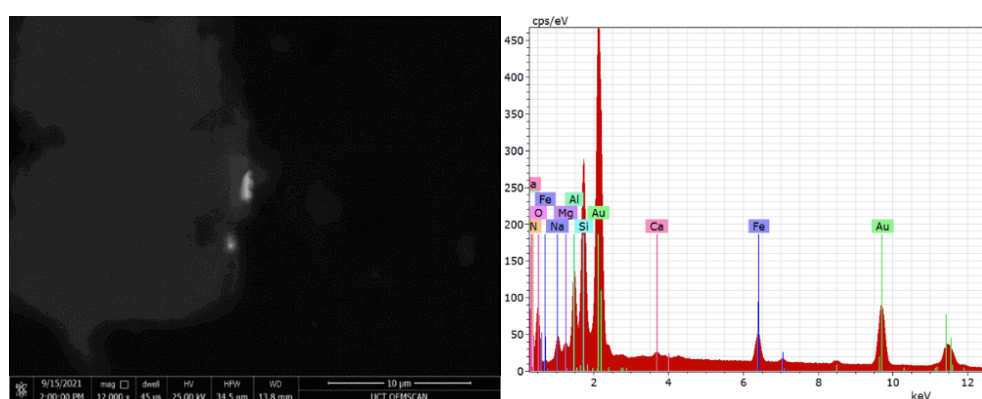


Figure 3. SEM-EDS image of gold particle in chlorite boundary in Sample 3.

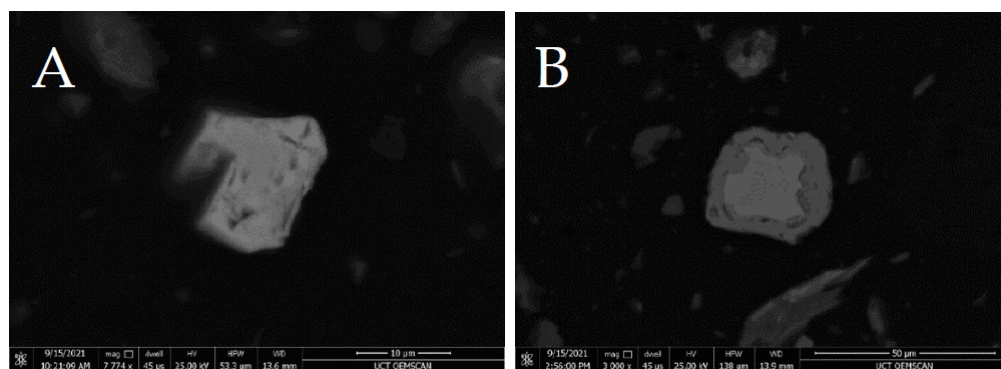


Figure 4. (A) Arsenopyrite in Sample 1. (B) Pyrite surrounded by iron oxide layer in Sample 3.

The diagnostic leach tests were conducted following the procedure presented in Table 4. In stage 2, the first cyanide leach test after panning (Figure 5A) 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, there was further extraction of gold 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 conducted 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 hosted by sulphides such as pyrrhotite. The HCl leach also extracted As, especially in Sample 2, as well as Cu and Fe. In stage 4, the second cyanide leach test (Figure 5B) 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 further leached by cyanide in stage 4.

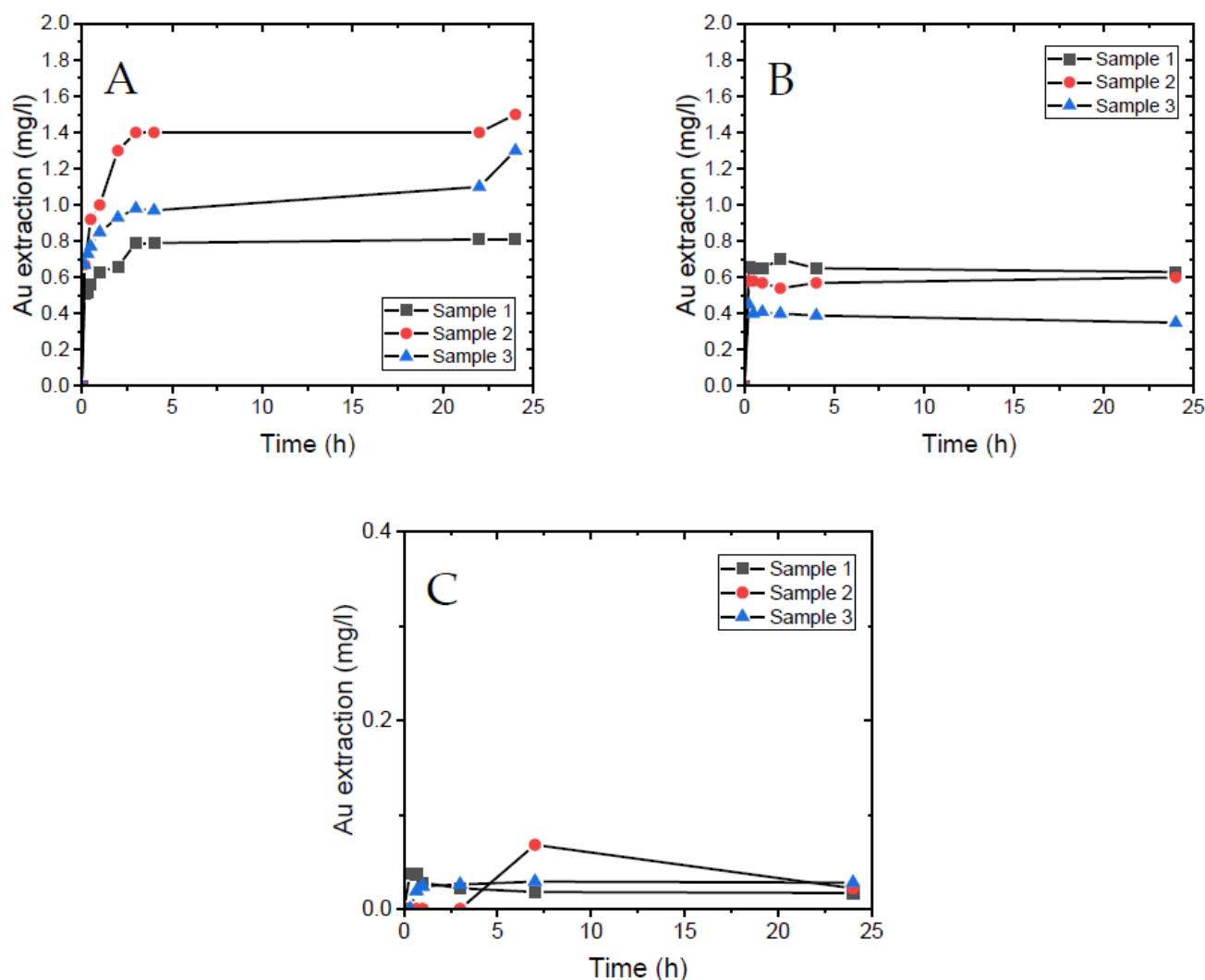


Figure 5. Cyanide leaching using 20 g/L NaCN (A) stage 2, (B) stage 4, and (C) stage 6.

H₂SO₄ 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 5B) to those of stage 6 (Figure 5C). In stage 4, the gold extractions for the three 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 H₂SO₄ in stage 5 further unlocked some gold which was then recovered by cyanidation in stage 6 (Figure 5C). 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. The drop in extraction for Sample 2 in Figure 5C could be due to carbonaceous matter reabsorbing some of the Au, as XRF data showed high LOI% (10.8%) for Sample 2. No more gold was recovered in the remaining tests, indicating that the ores had been spent and the maximum amount of gold was recovered.

Figure 6 shows the cumulative total Au extracted in each of the stages for which Au concentration could be measured, for all three 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.

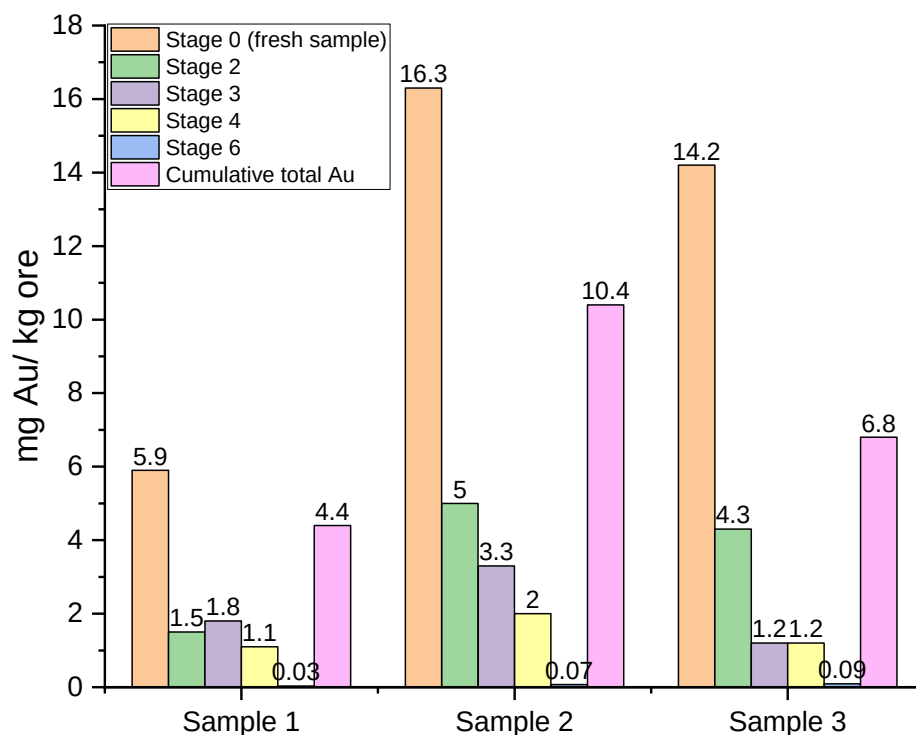


Figure 6. Au extraction in each stage for each sample.

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.

3.2. Cyanide Leaching

3.2.1. Au Extraction

The plots in Figures 7–9 show the Au extractions achieved by the three ore samples under study at 1 g/L, 3 g/L, and 5 g/L NaCN, respectively.

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 should be noted that for Sample 1, at 3 g/L NaCN, gold extraction data were plotted only up to 12 h of leach time, as the leach sample at the 24 h mark was lost. 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 h of leaching. Sample 2 and Sample 3 (the higher-grade ores) showed similar initial kinetics at the three cyanide concentrations.

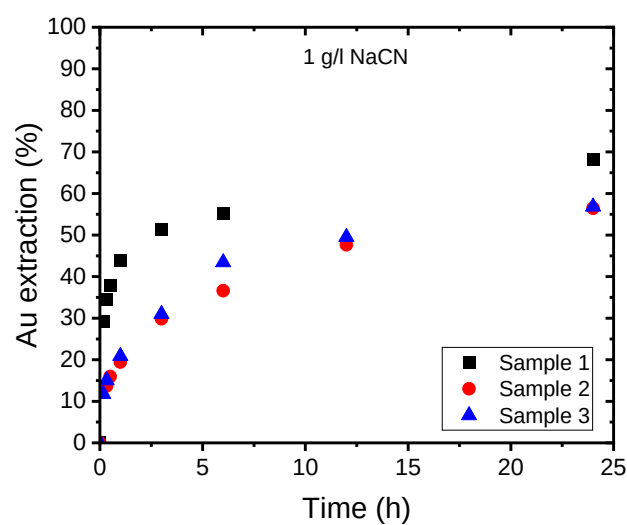


Figure 7. Au extraction at 1 g/L NaCN (30% solids, $-300 + 150 \mu\text{m}$ PSD, 300 rpm, 26 °C).

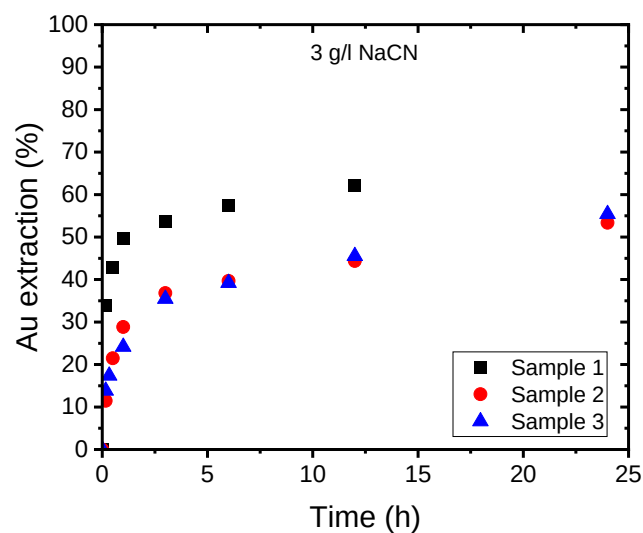


Figure 8. Au extraction at 3 g/L NaCN (30% solids, $-300 + 150 \mu\text{m}$ PSD, 300 rpm, 26 °C).

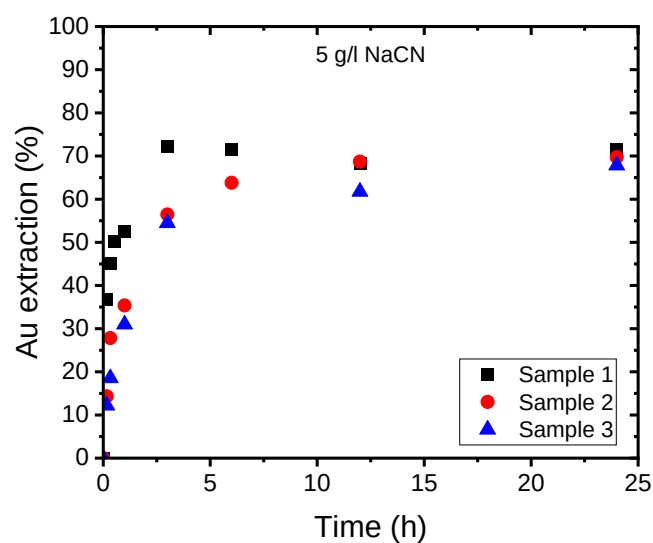


Figure 9. Au extraction at 5 g/L NaCN (30% solids, $-300 + 150 \mu\text{m}$ PSD, 300 rpm, 26 °C).

3.2.2. Reasons for Low Au Extractions

The presence, in the three ores, of sulphide minerals that host gold can be a major reason for the low gold extractions achieved, since any gold hosted by these minerals would be locked and difficult to recover by conventional cyanidation. This was in fact confirmed by the diagnostic leach results which showed that, by the action of acids, the gold locked in sulphides could be extracted. In addition, sulphides of copper and iron such as pyrite, arsenopyrite, and chalcopyrite, which have been shown to be present in these ores (Figure 4), can consume cyanide by forming cyanide complexes and converting free cyanide ions to cyanate and thiocyanate, leading to cyanide losses [38]. This cyanide consumption could be a reason, as well, for the leaching only improving at the higher cyanide concentration of 5 g/L as opposed to the experiment at 3 g/L NaCN, whereby Au extraction did not improve from the 1 g/L NaCN experiment. 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 9) is shown in Figure 10 alongside the head grades of the three 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 within 20% of the respective head grades of the samples. This, once again, shows that direct cyanidation had reached a mineralogical barrier, preventing it from extracting more gold, which the diagnostic leach on the other hand was able to overcome.

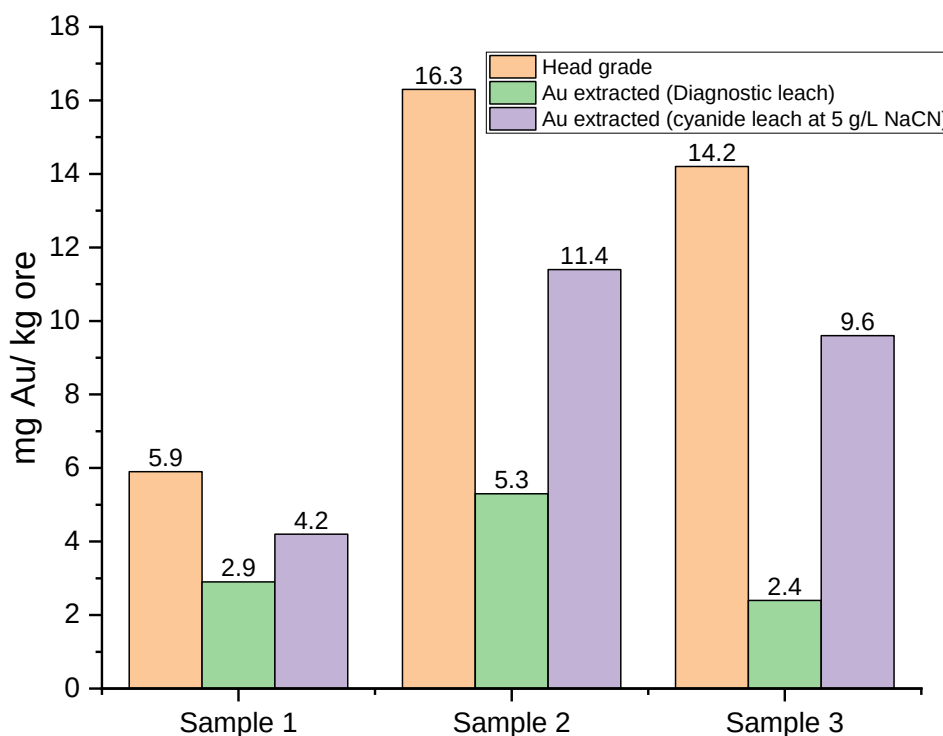


Figure 10. Comparison of total Au extracted by diagnostic leach and cyanide leach.

3.2.3. Effect of PSD

Leaching at a finer PSD significantly improved Au extractions and kinetics at $-150\ \mu\text{m}$ compared to $-300 + 150\ \mu\text{m}$ for the three ores (Figure 11). This is due to the higher liberation achieved by milling finer. However, this liberation is obtained from locked-in free gold, but not from the sulphides, as shown by the diagnostic leach results. As much as milling

finer sounds like a simple fix to achieve 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 since gold is more easily 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 30%–50% of it by amalgamation [12]. However, if cyanide leaching becomes a substitute for all other recovery methods, working with smaller sizes would yield high Au recoveries.

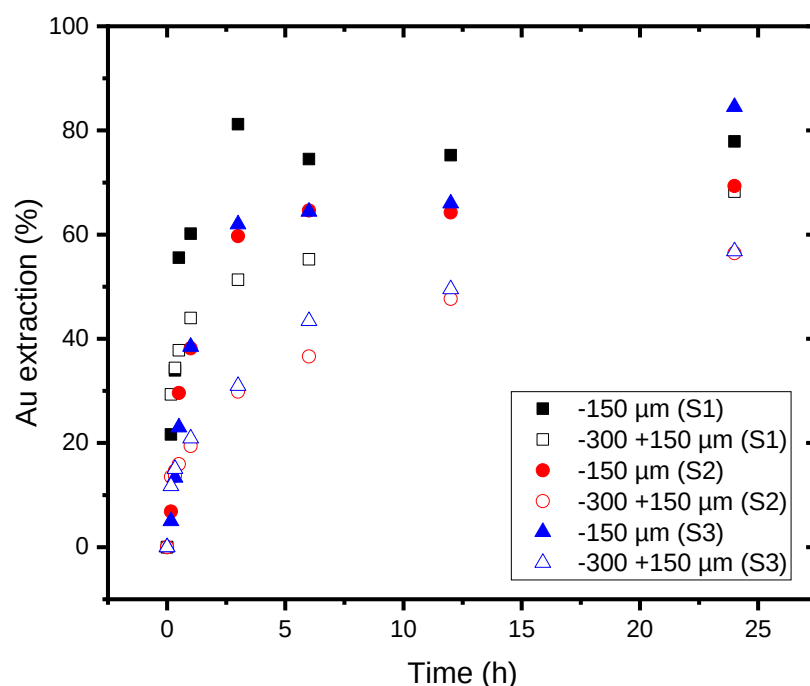


Figure 11. Au leaching at $-150\ \mu\text{m}$ vs. $-300 + 150\ \mu\text{m}$ for Sample 1 (S1), Sample 2 (S2), and Sample 3 (S3) (1 g/L NaCN, 30% solids, 300 rpm, 26 °C).

3.2.4. Agitated Leach vs. Vat Leach

For all three ores under study, agitated leaching significantly outperformed vat leaching (Figure 12). Within the first hour of agitated leaching, the extractions achieved for the three ores were already higher than those achieved by vat leaching after 12 h, i.e., 68.2% for agitated leaching and 47.1% for vat leaching for Sample 1. Similarly, Samples 2 and 3 achieved 68.7% and 35.6%, and 61.7% and 33.6%, for agitated and vat leach, respectively. The higher extraction achieved with agitated leaching is likely due to better mixing of the solution and a reduction of the diffusion layer thickness between the lixiviant and the gold particles, as well as a higher degree of air ingress into the solution, which is severely limited in vat leaching. Given that vat leaching is widely applied in ASGM, there is potential for miners to make better returns by introducing a degree of agitation during leaching or at least some form of solution circulation to ensure re-aeration of the solution.

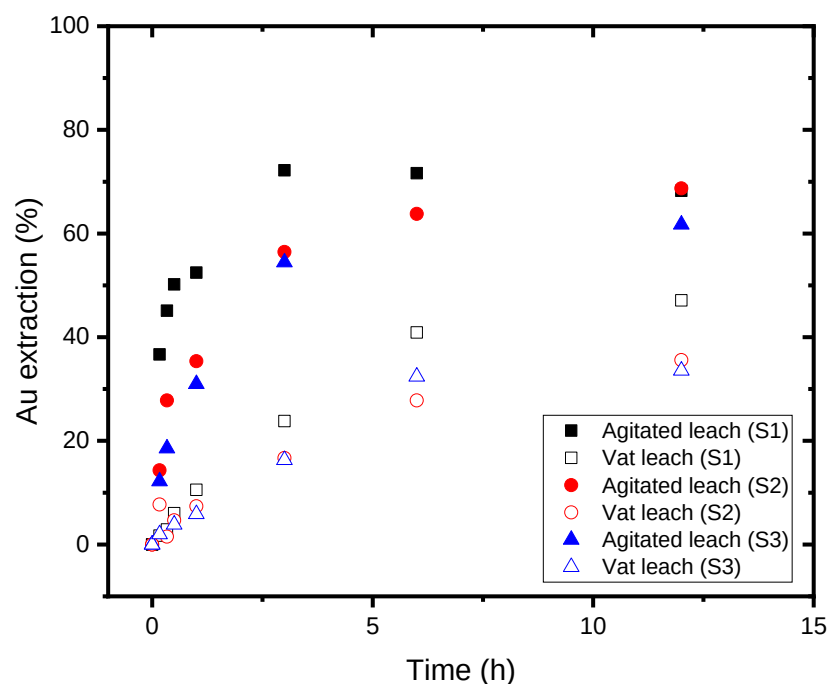


Figure 12. Comparison of Au extraction between agitated cyanide leach and vat cyanide leach for Sample 1 (S1), Sample 2 (S2), and Sample 3 (S3) (30% solids, $-300 + 150 \mu\text{m}$ PSD, 26°C).

3.3. Thiosulphate Leaching

3.3.1. Effect of $(\text{NH}_4)_2\text{S}_2\text{O}_3$ Concentration

Figures 13–15 show the effect of varying thiosulphate concentrations on the three ore samples 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 three ores, increasing the thiosulphate concentration from 0.1 M to 0.5 M resulted 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%.

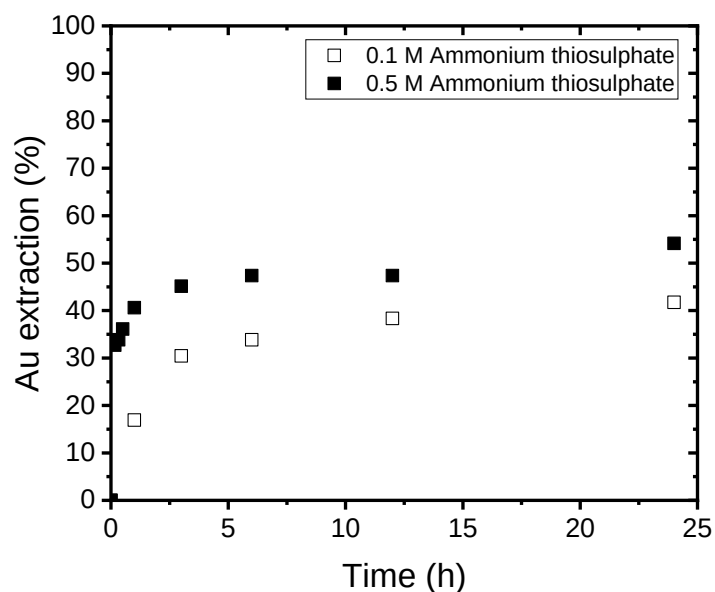


Figure 13. Effect of varying thiosulphate concentrations on gold extraction for Sample 1 at 0.5 M NH_3 and 1 mM Cu (30% solids, $-300 + 150 \mu\text{m}$ PSD, 26°C).

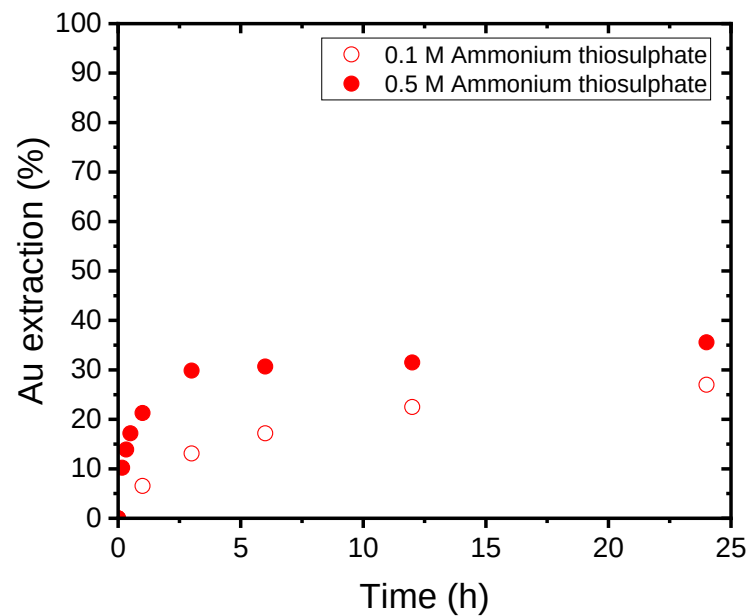


Figure 14. Effect of varying thiosulphate concentrations on gold extraction for Sample 2 at 0.5 M NH_3 and 1 mM Cu (30% solids, $-300 + 150 \mu\text{m}$ PSD, 26°C).

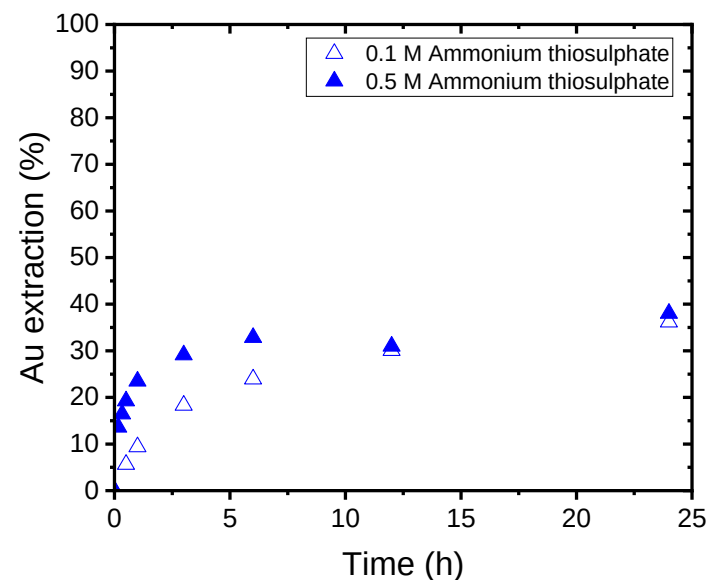


Figure 15. Effect of varying thiosulphate concentrations on gold extraction for Sample 3 at 0.5 M NH_3 and 1 mM Cu (30% solids, $-300 + 150 \mu\text{m}$ PSD, 26°C).

The trends observed from the results presented were generally in accordance with the literature, in particular, with the work conducted by Rath et al. [24] who investigated the effect of $(\text{NH}_4)_2\text{S}_2\text{O}_3$, NH_3 and Cu(II) concentration on the leaching of two gold ores (Akeshi and Hishikari). For Hishikari ore, it was found that the gold extraction increased with an increase in $(\text{NH}_4)_2\text{S}_2\text{O}_3$ concentration from 0.1 to 0.5 M and then decreased as the $(\text{NH}_4)_2\text{S}_2\text{O}_3$ concentration was increased above 0.5 M. This behaviour is in accordance with the findings of this study, whereby it was also found that increasing the concentration of $(\text{NH}_4)_2\text{S}_2\text{O}_3$, from 0.1 M to 0.5 M for the three ore types resulted in an increase in gold extraction, as shown in Figures 13–15. So, the extractions achieved with the ores investigated by Rath et al. [24] are relatively low despite their high grade, which is a behaviour that was observed in the case of the three ores under study as well. It is

important to note that the experiments on the Akeshi and Hishikari ores were run for only 5 h, and the study did not provide detailed mineralogy 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 run for 24 h; however, the extractions achieved with the three 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. [39] that also investigated the effect of $(\text{NH}_4)_2\text{S}_2\text{O}_3$, NH_3 , and Cu(II) concentrations on the leaching of gold ores. This ore had a much higher Au and Cu content (84 g/t and 0.38 wt.%, respectively) compared to the three ores under study. It was found that increasing the $(\text{NH}_4)_2\text{S}_2\text{O}_3$ concentration from 0.05 M to 0.5 M increased gold extraction, reaching an impressive 99% extraction at 0.5 M. This extraction was however much faster than what this study achieved. This must be attributed to the fact that the experiment conducted by Bae et al. [39] was conducted at a much finer grind size (45.3 μm) and a much lower solids loading (20%), which significantly improved leaching.

3.3.2. Effect of Background Copper Concentration

Figure 16 shows the impact of the presence of Cu(II) on gold extraction at 0.5 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$ and 0.5 M NH_3 for Sample 1, Sample 2, and Sample 3, respectively. Across the three 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, the final extraction without Cu(II) 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.

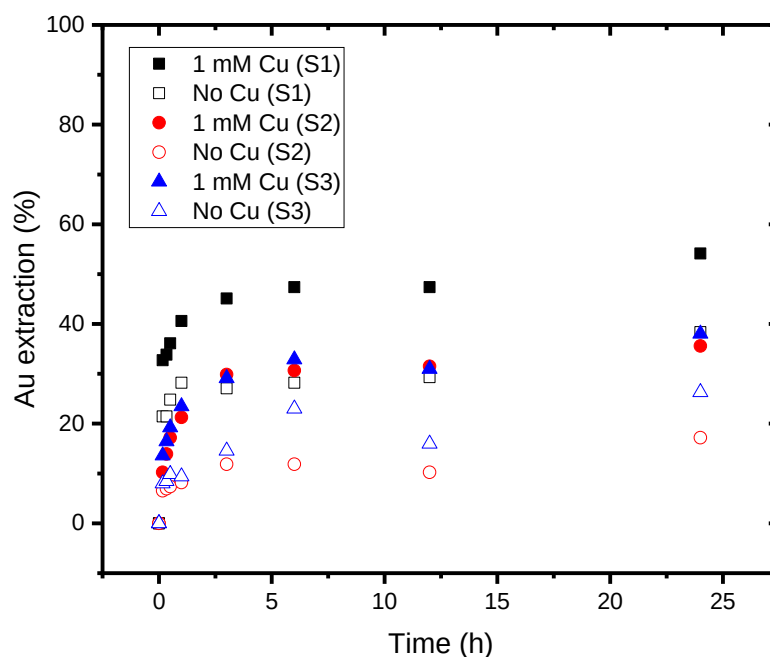


Figure 16. Effect of Cu(II) presence on gold extraction for Sample 1 (S1), Sample 2 (S2), and Sample 3 (S3) at 0.5 M $(\text{NH}_4)_2\text{S}_2\text{O}_3$ and 0.5 M NH_3 (30% solids, $-300 + 150 \mu\text{m}$ PSD, 26°C).

When looking at the effect of Cu(II) in the study conducted by Rath et al. [24], 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 16. Increasing Cu(II) concentration further may result in much reduced Au extraction, due to enhanced thiosulphate decomposition and consumption via conversion to tetrathionate [40].

3.3.3. Effect of NH₃ Concentration

Figure 17 shows the effect of increasing the concentration of NH₃ 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 NH₃ reaching 54.1% after 24 h (both final extraction data points coincide in Figure 17). For Sample 2, increasing the concentration of NH₃ resulted in a decrease in gold extraction, from 35.6% at 0.5 M NH₃ to 29.9% at 1 M NH₃. In a similar way, the gold extraction for Sample 3 dropped from 38.0% at 0.5 M NH₃ to 32.9% at 1 M NH₃.

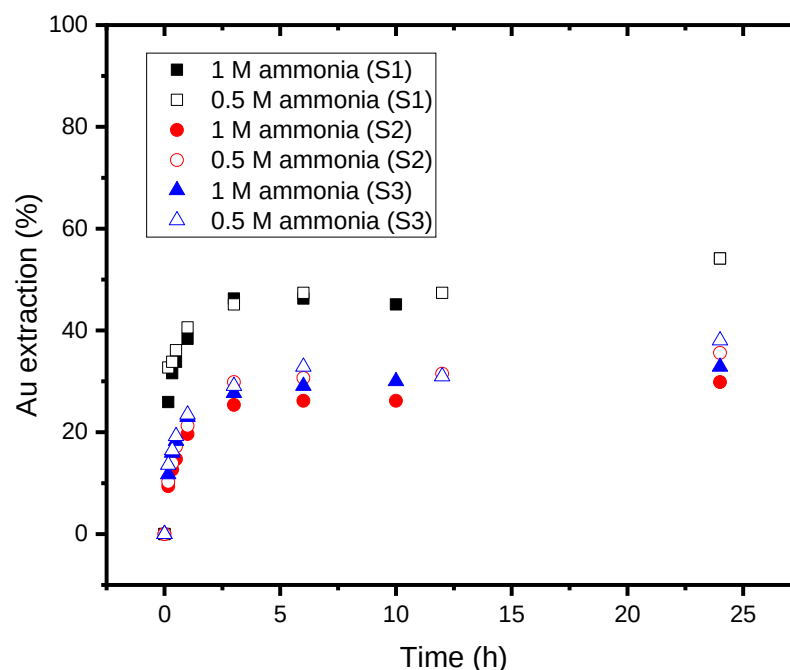
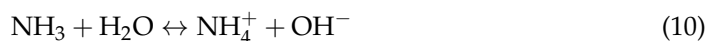


Figure 17. Effect of varying NH₃ concentrations on gold extraction for Sample 1 (S1), Sample 2 (S2), and Sample 3 (S3) at 0.5 M (NH₄)₂S₂O₃ and 1 mM Cu (30% solids, −300 + 150 μm PSD, 26 °C).

Rath et al. [24] observed that increasing the NH₃ concentration from 1 M to 3 M resulted in a decrease in gold extraction for the two ores studied. This supports the findings made on Samples 2 and 3 in this study. Increasing NH₃ concentration eventually ends up negatively impacting the leaching process as, when the NH₃ concentration is increased, the pH is increased as well. This increase in pH, as more NH₃ is present, is due to the dissociation of NH₃ in the solution (Equation (10)).



Cu(NH₃)₄²⁺, which is the form in which Cu(II) is able to play its catalytic role in the Au extraction process, is only stable in the pH range 8–11 [41], and an increase in pH beyond this range will result in the formation of unwanted solid Cu species. Therefore, by increasing the NH₃ concentration from 0.5 M to 1 M in the current study, less Cu(NH₃)₄²⁺ was present to catalyse the reaction leading to a decrease in gold extraction. This was highlighted in the study conducted by Tozawa et al. [42], whereby the stability window of Cu(NH₃)₄²⁺ was shown to widen with decreasing NH₃ concentration.

4. Conclusions

From the results obtained, agitated cyanide leaching was found to be the easier to control and better performing technology compared to thiosulphate leaching, which showed to have a complex chemistry that would make its uptake in ASGM difficult. For the

three ores studied, Sample 1, Sample 2, and Sample 3, the highest Au extractions 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. Despite the relatively low Au extractions, agitated cyanide leaching outperforms Hg amalgamation, which typically only achieves 30%–50% gold recovery. Thiosulphate leaching performed significantly poorer than cyanide leaching; however, it still showed the potential to outperform Hg amalgamation. The ore characterisation using a combination of XRF, XRD, QEMSCAN, and SEM-EDS revealed the presence of sulphide minerals such as pyrite and arsenopyrite, which host gold as ultrafine solid solutions, making it difficult to leach. This was identified as 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. The series of more aggressive leach stages of the diagnostic leach was able to break this barrier in order to recover more gold. The ore characterisation results are of high value to ASGM in that they show that ores found in ASGM areas can vary significantly in mineralogy and are not as easily exploitable as often described. This introduces a clear need to assist artisanal miners in conducting mineralogical studies on their ores so they can adjust their methods accordingly and not settle for poor recoveries simply by lack of knowledge.

Agitated cyanide leaching outperformed Hg amalgamation and vat leaching of tailings when run sequentially. This proves that agitated cyanide leaching can confidently be advocated as an alternative for the entire Hg amalgamation process and not only as an additional step after amalgamation. It must be acknowledged that achieving agitation will be a challenge for informal diggers. However, for better 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. If agitation cannot be achieved, ensuring at least some degree of solution circulation to re-aerate the system should still improve leaching.

Cyanide leaching has the potential to become the Au extraction technology of choice in ASGM and completely replace Hg amalgamation. However, to prevent the redundancy of replacing one toxic chemistry with another, 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 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, quite often nontechnical, which will dictate how good 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. 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.

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